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Synthesis, Crystallization, and Optical Properties of YAG:Cr³⁺ Aerogels

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ABSTRACT

In this thesis, YAG:Cr³⁺ was prepared in aerogel form using a sol–gel route followed by supercritical CO₂ drying and annealing at 1000 °C. The aim was to determine whether the thermometric response of Cr³⁺ is preserved when YAG is prepared as a nanocrystalline, highly porous material, and whether different temperature-dependent spectral features can be used for thermometry over a broad temperature range.

XRPD, SEM and TEM measurements confirmed the formation of cubic YAG with a lattice parameter of 12.065 Å and a mean crystallite size of about 29 nm. The structural and spectroscopic results are consistent with Cr³⁺ occupying the octahedral Al³⁺ sites of the YAG lattice. Temperature-dependent photoluminescence spectra were collected from –150 to 600 °C and analyzed using a nine-Gaussian fitting model. This fitting separated the R₁ zero-phonon line, the anti-Stokes and Stokes phonon sidebands, and the broad ⁴T₂ emission.

Ratiometric optical thermometry in YAG:Cr³⁺ is based on the thermal coupling between the ²E and ⁴T₂ excited states of Cr³⁺. In single-crystal and ceramic YAG:Cr³⁺, the energy separation between these energy states is commonly reported to be close to 1000 cm^{–1}. At higher temperatures, the ratio between the ⁴T₂ and ²E emission areas was used as the thermometric parameter. For the 1 mol% Cr³⁺ sample, the Boltzmann fit between 293 to 453 K (20 and 180 °C) gave an energy separation of $\Delta E = 890 \pm 10$ cm^{–1}, with $R^2 = 0.999$. Using the perturbation model that consider the electron-phonon coupling and the ⁴T₂–²E interaction, an independent analysis of the temperature-dependent lifetime at four emission wavelengths gave an average value of $\Delta E = 917 \pm 10$ cm^{–1}. The two values well agree within the errors, showing that the steady-state and lifetime measurements describe the same thermal coupling between the ²E and ⁴T₂ states. Both values are somewhat lower than the approximately 1000 cm^{–1} commonly reported for single-crystal YAG:Cr³⁺. This difference may be related to the nanocrystalline nature of the aerogel-derived material, including variations in the local Cr³⁺ environment and the contribution of Cr³⁺ ions located close to particle surfaces.

At low temperature, the ⁴T₂ emission becomes too weak for reliable use of the ⁴T₂/²E ratio. In this region, the anti-Stokes and Stokes phonon sidebands of the ²E → ⁴A₂ transition provide an alternative temperature-dependent parameter. The ratio between the integrated anti-Stokes and Stokes sidebands was obtained from the same nine-Gaussian fits. A fit between –150 and +210 °C gave an effective phonon energy of $\hbar\omega_{\text{eff}} = 296 \pm 6$ cm^{–1}, with $R^2 = 0.9962$. This value falls within the range of phonon energies involved in the vibronic coupling of Cr³⁺ in YAG. Since several Stokes and anti-Stokes components are included in the ratio, the fitted value should be considered an effective phonon energy rather than the energy of a single lattice vibration.

The two ratiometric methods therefore cover different temperature regions. The Stokes/anti-Stokes sideband ratio operates from approximately 123 to 483 K, while the ⁴T₂/²E ratio gives a reliable calibration from approximately 293 to 453 K. The maximum relative sensitivity of the low-temperature method is 2.81% K^{–1} at –150 °C, while the high-temperature ⁴T₂/²E method reaches 1.39% K^{–1} at 30 °C.

The effect of Cr³⁺ concentration was also studied using 0.5, 1 and 2 mol% samples. Among the three compositions, the 1 mol% sample gave the most precise determination of the ²E–⁴T₂ energy

separation and the most reliable thermometric response. Measurements on powder and monolith forms showed similar spectral features, indicating that the local Cr^{3+} environment is not significantly changed by grinding. The powder form, however, is more convenient for temperature calibration because thermal equilibration is faster and optical effects associated with the thicker monolith are reduced.

Overall, the results show that the characteristic Cr^{3+} thermometric behavior of YAG is preserved when the material is prepared as a nanocrystalline aerogel. The same sample can be used with two different temperature-dependent mechanisms: phonon-sideband thermometry at low temperature and ${}^2\text{E}-{}^4\text{T}_2$ Boltzmann thermometry at higher temperature. At the same time, the material retains the low density, high surface area and open porosity associated with the aerogel structure. This combination makes aerogel-derived YAG: Cr^{3+} an interesting form of a well-established luminescent thermometer, particularly for applications where temperature sensing is required together with accessible porosity or a large internal surface area.

Declaration on the use of Artificial Intelligence tools

In preparing this thesis, generative AI tools were used as follows. Claude (Anthropic) / ChatGPT (OpenAI)] during the writing phase to revise and refine the language of the text, improving clarity, grammar and coherence. It was not used to generate scientific content, data, results or interpretations. FigureLabs and BioRender were used to produce illustrative schematic figures (e.g. Figure 1.1 and 1.15), as indicated in the respective captions. All AI-assisted text and images were critically reviewed by the author, who verified their accuracy, quality and reliability and takes full responsibility for the content of this thesis.

1. INTRODUCTION

1.1 Aerogels: definition and fundamental properties

Aerogels are three-dimensional solid materials well known for their remarkable properties, including an open porous network, extremely low density, and very high specific surface area. Producers typically use specific synthesis routes for aerogels, with the most critical step being the preservation of the gel structure against collapse. By carefully removing the liquid phase from the wet gel while maintaining the interconnected solid skeleton, this process achieves a final material that can contain up to 90% air. Scientists consider aerogels to be among the lightest solid materials because of their unusual structure. They are often called "solid air." Because they have a low density, sufficient pores, and a network that goes through them all the time, they have physical and chemical properties that are very different from those of dense bulk materials. This leads to more applications for aerogels compared to dense materials [1,2].

There is still not a unique definition of the term aerogel, even though this word is widely used in literature. Mostly in literature, aerogels are described by their method of preparation, it is described as a gel network undergoing a drying method that guarantees the preservation of the original framework and minimizes capillary stress. Recently, numerous researchers emphasized the importance of understanding aerogel as a form of geometrical matter, as a highly porous solid 3D network in which the dispersed phase is gaseous and the solid phase forms a continuous, nanostructured network [1]. This important view is helping to study aerogels as a material that is not restricted to a single chemical composition or a single synthesis method but represents a structural class of materials whose properties arise from their hierarchical porosity and large internal interface.

The porous structure gives aerogels new and amazing features and properties. Their porosity is often 90% or more filled with air, which makes them very light and makes them not conduct heat well at all. In the meantime, their large specific surface area and easy-to-reach pore network make them very useful for adsorption, catalysis, surface fractionalization, and mass transport processes[1-3]. Aerogels may also be optically transparent, have a low acoustic velocity, be highly compressible, or have better transport properties, depending on their composition and microstructure. In functional systems, the porous framework can also help reveal active sites, make it easier for guest species to diffuse, and make pleasant paths for light or charge transfer[2,4].

A wide range of building blocks, including silica, metal oxides, chalcogenides, carbons, polymers, and hybrid organic–inorganic components, allows for aerogel synthesis. This broad ability to compose different precursors has significantly expanded their range of applications beyond traditional thermal insulation. Researchers have recently shown growing interest in aerogels, focusing on their applications in sensing, photocatalysis, energy conversion and storage, environmental remediation, and optics [4]. This progress has shifted the application field from classical lightweight insulators to advanced functional materials with controllable structural and physicochemical properties across multiple length scales.

Before discussing more specialized subclasses such as nanoparticle-based aerogels, functional luminescent aerogels, and transition-metal-doped oxide aerogels, Understanding the general definition and fundamental characteristics of aerogels is essential. In the present thesis, these general features are particularly important because the porous architecture of aerogels not only influences their structural stability during processing but also plays a key role in determining phase evolution, surface accessibility, and ultimately optical performance in Cr³⁺-doped YAG-based systems.

1.2 Epoxide-assisted sol–gel synthesis and formation of metal-oxide aerogels

Sol–gel processing is widely used for the preparation of oxide aerogels because the three-dimensional porous network can be formed directly from molecular precursors in solution, without requiring pre-formed nanoparticles or high-temperature treatment during gel formation. Metal alkoxides, M(OR)_n, are commonly used as precursors and undergo hydrolysis and condensation reactions, usually under acidic or basic conditions. Their reaction rates can be controlled by adjusting the synthesis conditions, making them suitable for the preparation of homogeneous oxide gels. However, many transition-metal and rare-earth alkoxides are highly sensitive to moisture, relatively expensive, and often require careful handling under anhydrous conditions, which can limit their practical use [1].

Inorganic metal salts, such as chlorides and nitrates, provide a simpler and less expensive alternative. They are generally stable under ambient conditions and can be dissolved directly in water or alcohol–water mixtures. However, gelation from metal salts requires careful control of the solution chemistry. Acidic solutions containing trivalent metal ions, such as Al³⁺, Y³⁺, or Fe³⁺, can remain stable because hydrolysis and condensation are suppressed at low pH. Formation of an extended oxide network therefore requires a controlled increase in pH to promote hydrolysis and subsequent condensation of the metal species.

The epoxide-assisted sol–gel route was developed as a way to control the increase in pH during the gelation of metal-salt solutions. Early work by Itoh and co-workers was later extended by Gash *et al.* to the preparation of metal-oxide gels [5, 6]. In this method, an organic epoxide, most commonly propylene oxide (PO), is added to an acidic aqueous or hydro-alcoholic solution containing the metal salts. Under acidic conditions, the epoxide is protonated and undergoes ring opening, gradually consuming H⁺ from the solution. As a result, the pH increases progressively rather than changing abruptly throughout the solution.

This gradual increase in pH promotes the hydrolysis of the hydrated metal ions and the formation of metal–hydroxyl species. These species subsequently react through ololation and oxolation reactions, forming M–OH–M and M–O–M bridges between neighboring metal centers. As these reactions continue, the initially separated metal species become interconnected, eventually forming a continuous three-dimensional inorganic network. The liquid sol is therefore converted into a wet gel, which can subsequently be aged, solvent-exchanged, and dried to obtain the corresponding oxide aerogel.

An important advantage of the epoxide-assisted route is the gradual and relatively uniform increase in pH during gelation. When a conventional base, such as NaOH or NH₄OH, is added

directly to a metal-salt solution, the pH can increase rapidly around the point of addition. This may cause local precipitation of metal hydroxides before a continuous gel network can develop. In the epoxide-assisted method, the progressive consumption of H^+ provides a more controlled increase in pH throughout the solution, allowing hydrolysis and condensation to occur more uniformly. This favors the formation of a homogeneous and interconnected wet-gel network rather than separate precipitated particles.

This control is particularly important in multicomponent oxide systems, where the different metal ions may not hydrolyze at the same rate or under the same conditions. This is relevant to the Y–Al–O system used in the present work, since Y^{3+} and Al^{3+} show different hydrolysis behavior. A rapid increase in pH can therefore promote preferential hydrolysis or precipitation of one component, leading to compositional inhomogeneity in the precursor gel. A gradual increase in pH reduces this problem and favors a more uniform distribution of the metal species within the gel network. Such homogeneity is important for the subsequent thermal treatment, during which the amorphous Y–Al–O network is progressively converted into crystalline YAG.

The epoxide-assisted sol–gel method has been applied to the preparation of several metal-oxide aerogels, including Al_2O_3 , Y_2O_3 , Fe_2O_3 , and TiO_2 [7]. The method has also been extended to mixed Y–Al oxide systems. Hu *et al.* [ref, Hu 2022] prepared monolithic yttria–alumina aerogels from an ethanol–water solution containing $YCl_3 \cdot 6H_2O$ and $AlCl_3 \cdot 6H_2O$, using propylene oxide as the gelation agent[8]. The resulting aerogel had a bulk density of 0.203 g cm^{-3} , a specific surface area of $455.6 \text{ m}^2 \text{ g}^{-1}$, and an average pore width of approximately 33 nm. These results show that the epoxide-assisted route can produce monolithic Y–Al oxide aerogels with a highly porous structure after drying.

The same approach has also been used for luminescent Y–Al–O systems. Metzkow *et al.*[9] prepared lanthanide-doped alumina and YAG aerogels containing Tb^{3+} and Eu^{3+} , showing that luminescent dopant ions can be introduced during the preparation of the oxide gel. This is particularly relevant to the present work, in which the epoxide-assisted sol–gel route was used to prepare a Y–Al–Cr precursor gel. After drying and subsequent heat treatment, the initially amorphous oxide network is converted toward crystalline YAG, while Cr^{3+} is incorporated into the developing YAG structure.

Following gelation and aging, the wet gel is placed in a solvent bath, typically ethanol, to remove residual reactants and replace the liquid remaining within the pores. The solvent is then exchanged with liquid CO_2 , which is subsequently brought above its critical temperature and pressure. Under these conditions, CO_2 can be removed without crossing a liquid–gas phase boundary, thereby avoiding the capillary stresses that would otherwise cause shrinkage or collapse of the porous gel network during conventional drying. This process allows the wet gel to be converted into a dry aerogel while preserving much of its porous structure.

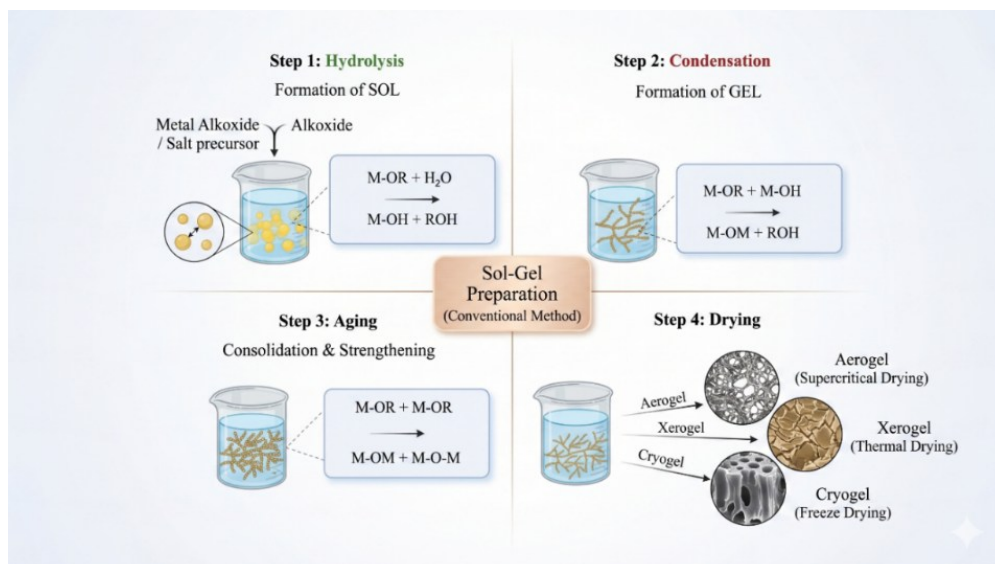


Figure 1.1: Main steps of the sol-gel process, including hydrolysis, condensation, aging, and drying. Created in BioRender: Khalaji, M. (2026).

1.3 Functional and luminescent aerogels



Figure 1.2: Photograph illustrating the excellent thermal-insulation properties of an aerogel

Until the last two decades, aerogels applications were mainly limited to ultralight thermal insulators. Recently, the scientific interest has been focused on designing porous materials where the porosity is something more than simply a reduction of density. By combining luminescent systems and aerogels, we can take advantage of the properties of both materials like, low density, high specific surface area, optical accessibility, and a large internal interface with the possibility of controlled light absorption and emission. This combination is attractive for applications such as optical sensing, bioimaging, photocatalysis and radiation detection.

Generally, luminescence can be defined as light emission that follows a non-thermal excitation process. For inorganic functional materials, one of the most relevant cases is photoluminescence, where emission happened by populating excited states with absorbed photon and then radiative relaxation. In porous materials, the presence of an emitting center is not the only necessary factor for controlling the final optical response, but also local chemical environment, defect density, interparticle coupling, and accessibility of the porous framework could also play an important role. For this reason, aerogels provide an especially interesting platform: they can host luminescent ions, nanocrystals, or molecular emitters while still offering continuous and highly accessible three-dimensional architecture.

There are several methods to design luminescent aerogels. One strategy is to introduce preformed luminescent nanoparticles, such as incorporating a semiconductor, quantum dots or nanocrystals, into a porous scaffold. Doping the aerogel matrix itself with optically active ions, especially lanthanides or transition metals is the second method. A third route is to build hybrid systems in which the emitting center is a molecular complex, a carbon-based fluorophore, or a multicomponent supramolecular assembly. These different approaches do not only produce different colors of emission; they also lead to different physical mechanisms, ranging from quantum confinement and interparticle charge transport to crystal-field-controlled d–d transitions and shielded f–f transitions.

Luminescence is the emission of light by a material after excitation by a non-thermal energy source. Unlike black-body radiation, which arises from the temperature of a body and gives a continuous thermal spectrum, luminescence is not governed primarily by heat. Instead, it results from the creation of excited electronic states followed by radiative relaxation, and it is therefore characterized by a definite emission lifetime. In this broad sense, the emitted light may fall in the ultraviolet, visible, or near-infrared region, depending on the nature of the emitting center and its local environment [10,11,12].

Several forms of luminescence can be distinguished according to the source of excitation, including photoluminescence, chemiluminescence, radioluminescence, electroluminescence, mechanoluminescence, and piezoluminescence. Among these, photoluminescence is the most relevant for the present work and, more generally, for the optical study of doped inorganic solids. In photoluminescence, photons are absorbed by the material, promoting electrons to excited states; after a sequence of relaxation processes, part of this energy is released again as light. Because of this sequence, the emitted radiation reflects not only the energy structure of the luminescent center itself, but also the interactions between that center and the surrounding host lattice [12].

A simple way to describe photoluminescence is through the Jablonski diagram (Figure 1.3), in which excitation is followed by rapid non-radiative processes such as vibrational relaxation and internal conversion before radiative emission takes place. In many materials, emission occurs from the lowest excited state reached after relaxation. When the transition takes place without a change in multiplicity, the process is generally described as fluorescence; when it involves a change in multiplicity, it is referred to as phosphorescence. In real solids, however, the final spectral shape and intensity depend on more than the emitting transition alone. They are also influenced by electron–phonon coupling, structural disorder, defect states, and the efficiency of competing non-radiative processes.

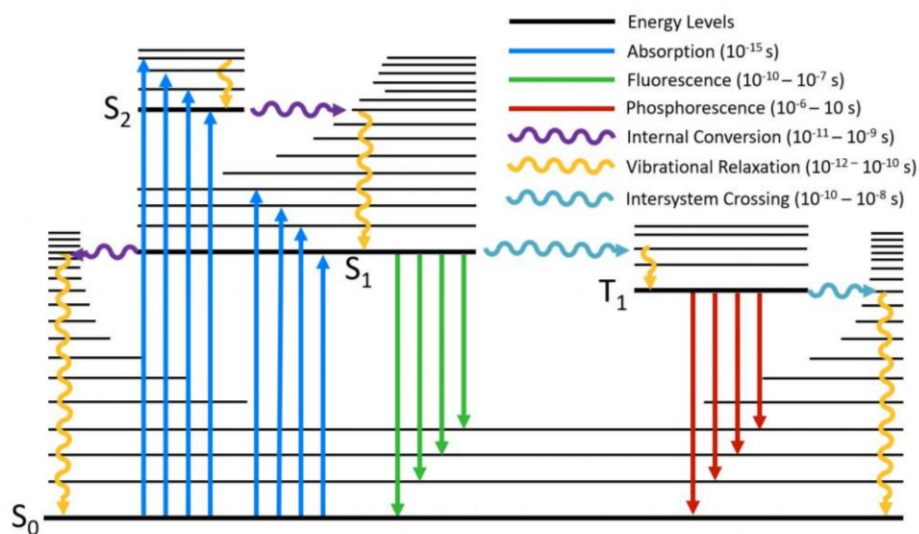


Figure 1.3: Jablonski diagram showing the main radiative and non-radiative processes involved in photoluminescence.

In doped inorganic materials, localized emitting centers are mostly the origin of luminescence, often the localized emitting center embedded in the host matrix called activator. These centers can be excited in different ways: by direct absorption at the activator, by absorption in the host followed by energy transfer, or by sensitized excitation through a second ion or defect acting as an energy donor. Once excitation has been created, migration and redistribution of energy between neighboring centers may also occur through processes such as energy transfer, cross-relaxation, or energy migration. As a result, the optical response of a luminescent solid is controlled not only by the intrinsic electronic structure of the activator, but also by the crystal chemistry of the host, the local symmetry around the emitting ion, and the presence of defects or secondary sensitizing species. These points are especially important in porous functional materials, where the local environment may differ significantly from that of dense bulk solids.

For this reason, luminescence in aerogel-based materials cannot be understood only in terms of the emitting ion or nanoparticle itself. The porous framework, the connectivity between building blocks, the density of surface groups and defects, and the degree of crystallinity after heat treatment may all influence the balance between radiative and non-radiative pathways. This is why aerogels are not merely passive supports for luminescent centers, but active structural environments that can modify intensity, spectral shape, lifetime, and thermal stability of the emitted light.

1.3.1 Quantum-dot-based luminescent aerogels

Quantum-dot-based aerogels form one of the most developed classes of luminescent aerogels. Their main advantage lies in the fact that the size-dependent optical properties of semiconductor nanocrystals can be carried from a colloidal dispersion into a macroscopic, self-supporting porous body. In other words, the aerogel network provides mechanical integrity and high porosity, while the quantum dots remain the active optical units.

Among metal chalcogenide systems, CdSe-, CdS-, and PbS-based nanocrystal aerogels are among the most studied examples. Song et al. showed that silica-nanobelt aerogels loaded with CdSe/CdS/ZnS core-shell quantum dots can retain the luminescent properties of the dispersed nanocrystals after freeze-drying, which is important because it demonstrates that a porous monolith can be prepared without destroying the optical behavior of the quantum dots [13]. In a related direction, Rusch et al. investigated CdSe/CdS dot/rod aerogel networks showing that the optical response is strongly influenced by network formation, temperature, and the ratio between different nanocrystal building blocks [14]. This is particularly interesting because it means that color tuning can be achieved not only by changing the composition of a single emitter, but also by controlling how different building blocks are combined inside the same porous network.

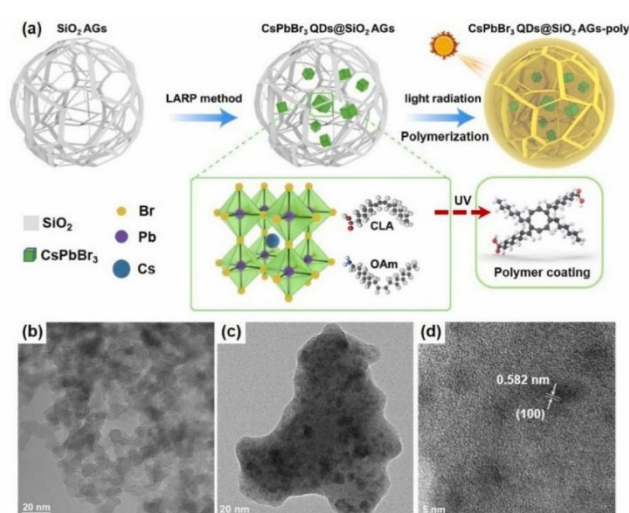


Figure 1.4: Example of a perovskite quantum-dot/silica aerogel composite used to improve the stability of luminescent nanocrystals [19].

Near-infrared quantum-dot aerogels have also been investigated. Pluta *et al.* reported three-dimensional networks based on PbS and PbS/CdS quantum dots, showing that their optical properties depend strongly on the surface chemistry and on the presence of a protective shell [15]. The initial PbS quantum dots showed photoluminescence centered at **1215 nm**, whereas after network formation the emission shifted to **1476 nm** for the PbS-MUA aerogel and to approximately **1378 nm** for the PbS-MPA aerogel. In contrast, the PbS/CdS core/shell quantum dots showed a much smaller shift, from **1087 nm** to **1118 nm** after aerogel formation. The CdS shell therefore helps to preserve the optical

properties of the PbS core, while the stronger interactions and partial coalescence between PbS particles produce larger spectral shifts and changes in the photoluminescence lifetime. These results show that the formation of the aerogel network can directly modify the photophysical behavior of the nanocrystals. A second major subgroup is based on metal halide perovskite quantum dots. These materials are well known for their high photoluminescence efficiency, narrow emission bands, and easily tunable colors, but they also suffer from poor chemical and thermal stability. For this reason, encapsulation in silica aerogels has become a practical strategy. You et al. encapsulated $\text{CH}_3\text{NH}_3\text{PbBr}_3$ quantum dots in superhydrophobic silica aerogels and showed that the porous hydrophobic matrix could protect the quantum dots from water while preserving fluorescence, allowing reversible SO_2 sensing [16]. Later work extended this idea to more robust all-inorganic systems. Zhao et al. prepared ligand-free CsPbBr_3 quantum dots in silica-aerogel composites for display and white-LED applications [17], while He et al. combined Ca^{2+} doping with superhydrophobic silica aerogel encapsulation to improve both photoluminescence efficiency and stability in CsPbBr_3 - and $\text{CsPbBr}_3\text{I}_2$ -based composites [18] (Figure 1.4). Xiong et al. further showed that hydrophobic silica aerogels, together with a polymer shell formed around the perovskite quantum dots, can

strongly improve water stability and maintain high quantum yield, which is especially relevant for lighting devices [19]. Altogether, these studies make it clear that aerogel encapsulation is not only a packaging step; it is often the key condition that makes perovskite quantum dots usable in practical optical devices.

1.3.2 Lanthanide-doped luminescent aerogels

Lanthanide-doped aerogels represent a different design philosophy. In these systems, the main luminescent center is usually a trivalent rare-earth ion, such as Eu^{3+} , Tb^{3+} , or Ce^{3+} , introduced into an oxide or hybrid aerogel matrix. Compared with quantum dots, lanthanide ions generally provide sharper emission bands, better color purity, and longer excited-state lifetimes. Their emission is less sensitive to particle size, but highly dependent on local symmetry, defect concentration, and the efficiency of energy transfer from the host.

A good example is the recent work of Metzkow et al. on Eu^{3+} - and Tb^{3+} -doped alumina and YAG aerogels [9]. In that study, luminescence can be probed only after sufficient heat treatment, when residual organics were removed and crystallinity increased. This point is important for oxide aerogels: the porous network alone is not enough to guarantee good emission, because the optical performance depends strongly on how the local environment of the dopant evolves during calcination. The same trend appears in $\text{La}_2\text{O}_3:\text{Eu}^{3+}$ aerogels reported by García Ramírez et al., where the red emission became more pronounced after thermal treatment and improved structural order [20].

Another important line of work concerns sensitization and host engineering. Cao et al. showed that in Al_2O_3 aerogels, Gd^{3+} can act as a sensitizer for Tb^{3+} , enhancing the green emission through $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$ energy transfer [21]. Xu et al. reported Eu^{3+} -doped ZnAl_2O_4 -based ceramic aerogels with improved thermal stability, and this is especially relevant for optical devices operating under significant thermal load [22]. In a somewhat different approach, Odziomek et al. prepared highly transparent silica aerogels loaded with YAG:Ce nanocrystals (Figure 1.5), combining the porous silica framework with the efficient luminescence and scintillation response of the embedded nanocrystals [23]. This shows that lanthanide-based luminescent aerogels do not need to be limited to direct ionic doping of the matrix; they can also be built as nanocrystal–aerogel composites.

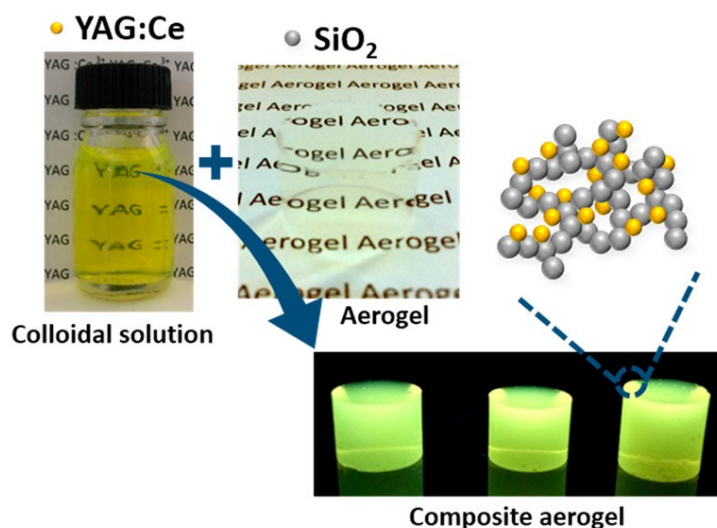


Figure 1.5: Schematic preparation and luminescence of a YAG:Ce nanocrystal-silica aerogel composite [23].

Overall, lanthanide-doped aerogels are particularly attractive where narrow emission lines, stable color output, and long-term optical robustness are needed. At the same time, the literature shows that their performance depends strongly on the phase evolution of the host matrix and on the way the lanthanide ions are incorporated into the porous structure.

1.3.3 Transition-metal-doped luminescent aerogels

Transition-metal-doped aerogels are especially interesting because their optical behavior is much more sensitive to local coordination and crystal field than that of lanthanide-doped systems. This sensitivity can be a disadvantage when structural disorder is too high, but it also creates opportunities for optical sensing, thermometry, and persistent luminescence.

A representative example is the $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ aerogel reported by Zhang et al. [24]. In that work, the aerogel was obtained as a porous, dendritic structure with homogeneous elemental distribution. After calcination, the material crystallized and developed clear Cr^{3+} emission as well as long afterglow behavior. This example is especially relevant to the present thesis because it shows that a Cr^{3+} -activated gallate host can be prepared in aerogel form while still retaining both luminescent and porous characteristics. It also illustrates a point that is central for many transition-metal aerogels: heat treatment is not simply a densification step, but a structural activation step for the optical centers.

A broader materials-design approach was demonstrated by Villarreal et al., who prepared color-tunable aerogels from luminescent nanofiber precursors containing $\text{Mn}:\text{Zn}_2\text{GeO}_4$ nanorods and $\text{Cr}:\text{ZnGa}_2\text{O}_4$ nanoparticles [25]. By varying the relative amount of the green- and red-emitting fillers, they obtained aerogels and sponge-like structures with tunable emission color. This result is significant because it shows that aerogel processing can be used not only to preserve luminescence, but also to engineer composite optical responses at the macroscopic level.

Compared with lanthanide systems, transition-metal luminescence is often more strongly coupled to the host lattice. Because of that, transition-metal-doped aerogels can be particularly

sensitive to structural disorder, site distortion, and phase transformation. In practical terms, this means that they are promising for responsive optical materials, but their synthesis and thermal treatment must be controlled more carefully if reproducible emission properties is desired.

1.3.4 Other hybrid luminescent aerogels

Besides inorganic ion-doped systems, a growing number of hybrid luminescent aerogels have been reported. These systems use molecular emitters, carbon dots, or mixed organic–inorganic assemblies to introduce optical functionality into a porous framework.

Yorov et al. prepared alumina aerogels modified with tris(8-hydroxyquinolino)aluminum (AlQ_3), obtaining highly porous monolithic aerogels with bright UV-excited green luminescence [26]. Carbon-dot-based systems provide another important branch (Figure 1.6) Yuan et al. designed a fluorescent aerogel from carboxymethylated cellulose nanofibrils and carbon dots for Cr(VI) adsorption and sensing [27], while Wu et al. reported chemically crosslinked nanocellulose–carbon-dot aerogels as optical sensors [28]. These materials are interesting because the luminescent function is directly tied to environmental response. In such cases, the open porosity of the aerogel is not just a structural property; it becomes part of the sensing mechanism by allowing rapid access of analytes to the emitting centers.

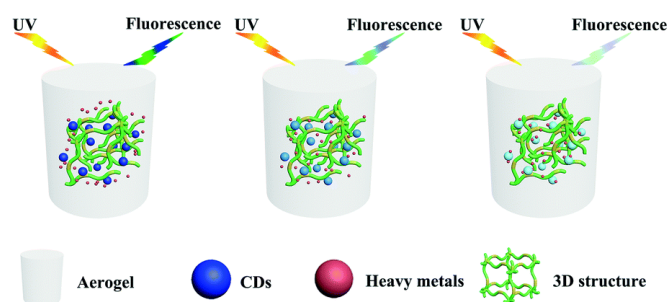


Figure 1.6: Schematic representation of a carbon-dot-containing aerogel used for fluorescence sensing. [27]

Taken together, these studies show that the field of luminescent aerogels is broader than oxide phosphors alone. It includes nanoparticle networks, ion-doped oxide aerogels, nanocrystal-loaded scaffolds, and hybrid soft-matter systems. What unites them is the attempt to preserve luminescent function within a highly porous three-dimensional framework. This point is particularly relevant for the present work, where the challenge is to combine porosity, monolithic form, phase evolution, and optical activity in a Cr^{3+} -doped YAG-related aerogel system.

1.4 Host selection: YAG aerogel and phase evolution

Yttrium aluminum garnet (YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$) is one of the best-known oxide hosts in optical materials, in particular when doped with Ce^{3+} to obtain a yellow emitting phosphor worldwide used in phosphor-converted white LED. It has been used extensively in single-crystal and ceramic form for solid-state lasers, passive Q-switches, scintillators, and other photonic applications because of its high chemical stability, good mechanical strength, and ability to

accommodate optically active ions without severe degradation of the host lattice [29]. In particular, YAG-based materials are widely employed in laser technology, and Cr-doped YAG has been studied for a long time as both a laser-related material and as a temperature-sensitive luminescent system [30].

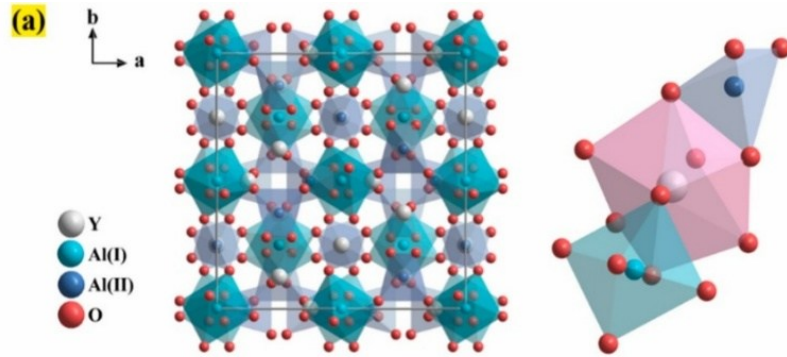


Figure 1.7: Crystal structure of yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$), showing the dodecahedral Y^{3+} sites and the tetrahedral and octahedral Al^{3+} sites in the garnet framework.

From a structural point of view, YAG is a cubic garnet with space group $Ia\bar{3}d$. Its structure contains dodecahedral sites occupied by Y^{3+} , tetrahedral sites occupied by part of the Al^{3+} ions, and octahedral sites occupied by the remaining Al^{3+} ions. This mixed cation framework is especially important for luminescent applications because it provides crystallographically defined sites for dopants and makes it possible to relate spectroscopic behavior to local coordination. In nanocrystalline YAG, the same garnet framework is preserved, even though particle size, disorder, and synthesis route may still influence the final optical response [31].

The choice of YAG as host in the present work is closely related to the aerogel route. In a conventional dense ceramic, the host is usually treated as an already established crystalline matrix. In an aerogel-derived material, however, the starting point is a porous and largely amorphous Y–Al–O network that gradually transforms into crystalline garnet during calcination. This is one of the main advantages of the aerogel approach: it allows the structural evolution of the host to be followed step by step, while preserving a monolithic form during the early stages of processing. In this way, the host is not simply selected as a final composition, but as a system whose crystallization pathway can be studied together with the evolution of porosity, shrinkage, and optical properties [32].

Table 1.1. Phase evolution pathway from amorphous Y–Al–O precursor to crystalline YAG.

stage	phase	Formula	Structure	Space group	explanation
1	Amorphous Y–Al–O gel/aerogel	—	no long-range order	—	untreated / low temperature
2	YAH	YAlO ₃	hexagonal metastable	P6 ₃ /mmc	intermediate phase often appears around ~800–950 °C
3	YAP	YAlO ₃	orthorhombic perovskite	Pnma	more stable YAlO ₃ polymorph
4	YAM	Y ₄ Al ₂ O ₉	monoclinic	P2 ₁ /c	Y-rich intermediate / secondary phase
5	YAG	Y ₃ Al ₅ O ₁₂	cubic garnet	Ia-3d	final desired garnet phase

The phase evolution of YAG produced by wet-chemical methods is known to depend strongly on synthesis conditions. Wang et al. showed that in gel-combustion-derived YAG powders an amorphous precursor remains stable below about 800 °C, after which a hexagonal YAH intermediate appears; on further heating, YAG begins to form and eventually becomes the dominant phase, with complete conversion to single-phase YAG around 925 °C under their conditions. Their work also showed that the precise pathway depends on atmosphere and kinetics, so the presence of YAH should be regarded as a genuine transient stage in garnet formation rather than simply as a synthesis defect [32].

A similar conclusion is found in the broader sol–gel literature. Sharma et al., working on sol–gel-derived YAG:Eu³⁺, reported that prepared material was initially amorphous and that clear cubic YAG diffraction peaks developed only after higher-temperature annealing, in their case between about 900 and 1200 °C. They also observed crystallite growth and improved luminescence with increasing annealing temperature, which they attributed to better crystallinity and reduced non-radiative losses. Although that study involved Eu³⁺ instead of Cr³⁺ its structural investigation is directly relevant here: YAG obtained by wet-chemical routes does not immediately behave as an optically mature host, but reaches that stage only after sufficient thermal treatment [33].

An important point is that YAG is highly sensitive to subtle deviations in composition and microstructure. Kravtsov et al. showed that even small stoichiometric changes in chemically derived YAG:Cr ceramics can affect the lattice parameter, optical transmission, R-line broadening, and excited-state lifetime. This is particularly relevant for aerogel-derived

materials, since wet-chemical synthesis can introduce slight compositional deviations, local heterogeneity, or defect-rich intermediate states. In other words, YAG is not only a suitable host for luminescent ions, but also a demanding one: its final optical quality depends strongly on how well the phase evolution and densification processes are controlled [29].

For these reasons, YAG is an appropriate host for the present thesis. It is a structurally well-defined garnet, widely used in optical materials, able to accommodate luminescent dopants, and sufficiently sensitive to synthesis history that the link between aerogel processing and final optical response becomes meaningful. Discussing YAG first as the host matrix also provides the necessary basis for the next section, where the behavior of Cr^{3+} will be considered within that evolving crystal environment.

1.5 Dopant selection: crystal-field behavior, and thermometric potential of Cr^{3+} -activated phosphors

Electronic configuration	Transition metal ions									
$3d^0$	Ti^{4+}	V^{5+}	Cr^{6+}	Mn^{7+}						
$3d^1$	Ti^{3+}	V^{4+}	Cr^{5+}	Mn^{6+}						
$3d^2$	Ti^{2+}	V^{3+}	Cr^{4+}	Mn^{5+}						
$3d^3$		V^{2+}	Cr^{3+}	Mn^{4+}						
$3d^4$			Cr^{2+}	Mn^{3+}						
$3d^5$			Cr^{+}	Mn^{2+}						
$3d^6$				Mn^{+}		Fe^{2+}				
$3d^7$							Co^{3+}			
$3d^8$							Co^{2+}		Ni^{3+}	
$3d^9$							Co^{+}		Ni^{2+}	
$3d^{10}$									Cu^{+}	Cu^{2+}

Figure 1.8: Transition Metal in Periodic Table[34].

why Cr^{3+} is so useful here: it is not only a light-emitting center, but also a sensitive probe of the structural environment created during the formation of YAG aerogel.[34]

Cr^{3+} is a $3d^3$ ion and, in oxide materials, it most often occupies octahedral sites. In that environment, its luminescence originates from electronic transitions within the split $3d$ manifold. Because the $3d$ orbital is a valence orbital, the energy configuration of the excited state is not identical to that of the ground state. Consequently, in a configurational-coordinate picture the excited-state parabola can be displaced with respect to the ground-state parabola, and the amount of this displacement depends on the excited state nature and local environment. This is why transition-metal luminescence is particularly sensitive to lattice vibrations, site symmetry, bond length, and electron–phonon coupling. In practical terms, the

The choice of Cr^{3+} ion as dopant is central for the present work because its optical response is strongly tied to the local structure of the host. In transition-metal ions, the outer $3d$ orbitals are directly involved in bonding and are therefore much more sensitive to the surrounding ligands than the shielded $4f$ orbitals of lanthanides. For this reason, the luminescence of transition-metal ions is usually governed by d–d electronic transitions, and their spectroscopic behavior depends strongly on coordination geometry, metal–ligand distance, covalency, and local distortion. This is exactly

same Cr^{3+} ion can show very different optical behavior in different hosts, even when the overall chemical composition changes only slightly.

This sensitivity is an advantage for our work. In a dense, fully crystallized ceramic, Cr^{3+} is usually discussed in terms of a relatively well-defined local environment. In an aerogel-derived material, by contrast, the host evolves gradually from an amorphous porous network to a more ordered crystalline phase. Before full crystallization, Cr^{3+} may experience local disorder, intermediate phases, surface-related defects, or incomplete incorporation into the final lattice. During calcination, the optical response of Cr^{3+} can therefore track the structural development of the host. This is one of the main reasons why Cr^{3+} is an appropriate dopant for YAG aerogel: the same ion provides both luminescence and structural information. The optical behavior of Cr^{3+} is not intrinsic to the free ion — it is determined almost entirely by the electrostatic environment imposed by the surrounding ligands. Understanding that environment requires understanding the crystal-field framework

Crystal field theory is one of the simplest models for explaining the structures and properties of transition metal complexes. The theory is based on the electrostatics of the metal-ligand interaction, and so its results are only approximate in cases where the metal-ligand bond is substantially covalent. But because the model makes effective use of molecular symmetry, it can be surprisingly accurate in describing the magnetism, colors, structure, and relative stability of metal complexes.

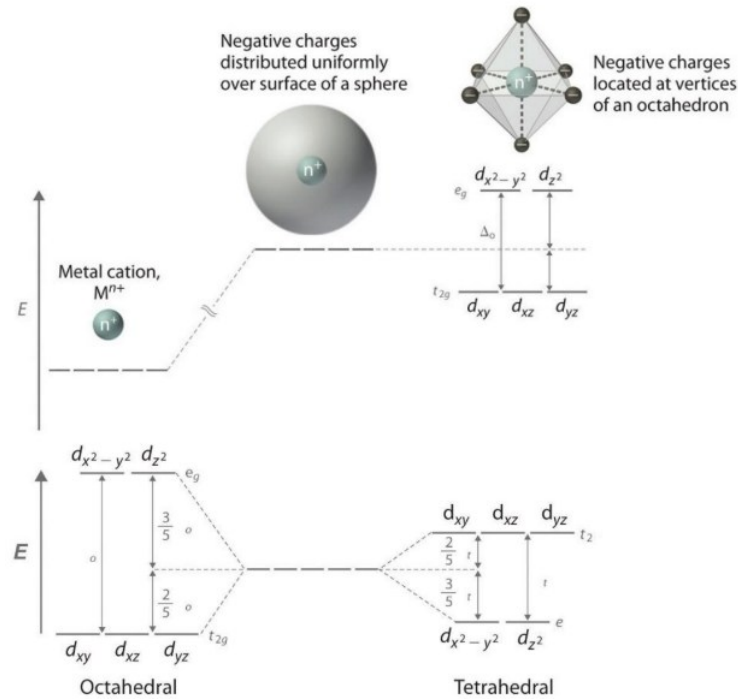


Figure 1.9: Position of transition-metal ions in the periodic table and representative 3d electron configurations[34].

The behavior of Cr^{3+} in an octahedral site is commonly described by crystal-field theory and the Tanabe–Sugano diagram for a d^3 ion. In this framework, the ground state is $^4A_2$, while the most important excited states are $^4T_2$, $^4T_1$, and ^2E . The broad absorption bands of Cr^{3+} are usually assigned to the spin-allowed $^4A_2 \rightarrow ^4T_2$ and $^4A_2 \rightarrow ^4T_1$ transitions. Emission may then occur either from the spin-forbidden $^2E \rightarrow ^4A_2$ transition, which gives sharp *R*-lines, or from the spin-allowed $^4T_2 \rightarrow ^4A_2$

transition, which gives a broad band. The balance between these two emission channels is one of the defining features of Cr^{3+} spectroscopy.

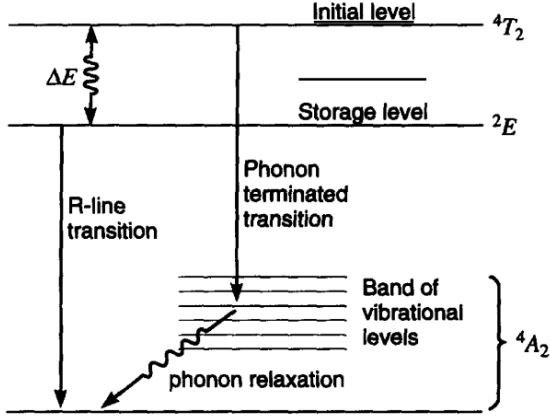


Figure 1.10: The two level model for the Cr^{3+} fluorescence in a high crystal field [35].

A key point is that the ${}^2\text{E}$ level is much less sensitive to crystal-field strength than the ${}^4\text{T}_2$ level. As the host changes, the ${}^4\text{T}_2$ level moves substantially, while the ${}^2\text{E}$ level moves only weakly. This produces the familiar weak-, intermediate-, and strong-field regimes. In weak crystal fields, ${}^4\text{T}_2$ lies lower and the emission is dominated by a broad ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ band. In strong crystal fields, ${}^2\text{E}$ becomes the lowest excited state and the emission is dominated by narrow ${}^2\text{E} \rightarrow {}^4\text{A}_2$ R-lines. In intermediate crystal fields, both states contribute, and both sharp-line and broadband emission can appear in the same spectrum [35].

This intermediate regime is especially important for optical thermometry because a thermally driven population redistribution between ${}^2\text{E}$ and ${}^4\text{T}_2$ becomes possible.

The electronic levels of octahedral Cr^{3+} are commonly discussed using the Tanabe–Sugano diagram for a d^3 ion [36,37]. This diagram represents the relative energies of the Cr^{3+} excited states as a function of the crystal-field strength normalized by the Racah parameter (B) [38]. In this approach, the most useful parameter for comparing different host lattices is the ratio:

$$\frac{10Dq}{B} \quad (1)$$

where $10Dq$ is the octahedral crystal-field splitting and B describes the interelectronic repulsion between 3d electrons [39].

The $10Dq$ parameter corresponds to the energy separation between the t_{2g} and e_g orbital sets in an octahedral field. Experimentally, $10Dq$ is often estimated from the energy of the spin-allowed ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ absorption band, because this transition corresponds approximately to promotion of an electron within the crystal-field-split 3d levels [36,37]. A larger $10Dq$ value indicates a stronger crystal field, while a smaller value indicates a weaker field [40]. The Racah parameters B and C describe electron–electron repulsion inside the 3d shell of Cr^{3+} [39]. These parameters are not fixed constants, because they are affected by the host lattice and by the covalent character of the Cr–O bond. When the Cr–O bond has stronger covalent character, the effective repulsion between 3d electrons is reduced, and the Racah parameters decrease

compared with the free-ion values. For this reason, $\frac{10Dq}{B}$ does not depend only on the geometrical crystal field but also reflects the chemical environment around Cr^{3+} [38,39].

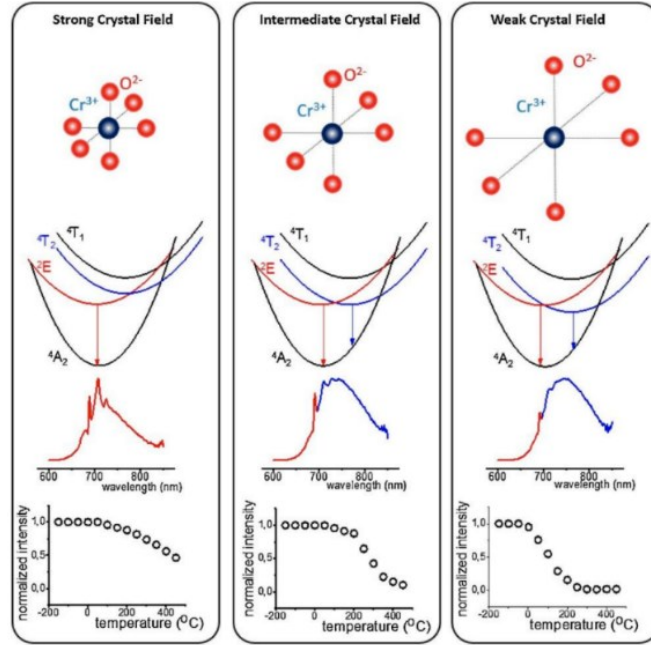


Figure 1.11: Schematic comparison of Cr^{3+} emission behavior in strong, intermediate, and weak crystal fields [41]

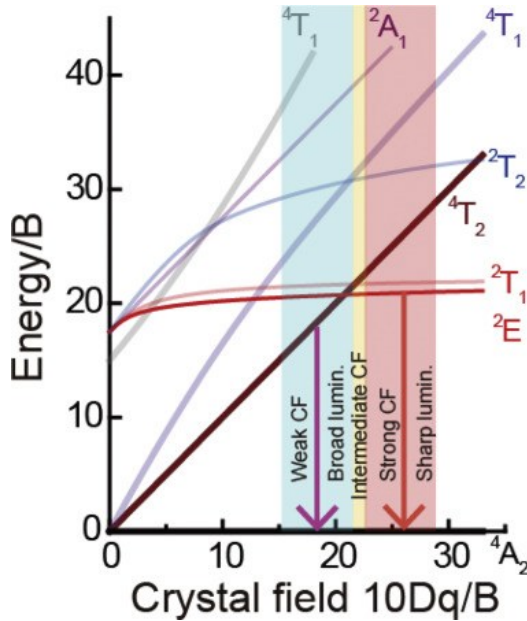


Figure 1.12: Tanabe-Sugano diagram for a d^3 ion, showing the dependence of excited-state energies on crystal-field strength [43]

In the Tanabe-Sugano description, the ${}^2\text{E}$ level changes only weakly with increasing crystal-field strength, whereas the ${}^4\text{T}_2$ level shifts more strongly. This difference is central for Cr^{3+} luminescence because it determines which excited state becomes the lowest emitting level. In a weak crystal field, ${}^4\text{T}_2$ lies below ${}^2\text{E}$, so the emission is usually broad and originates from ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$. In a strong crystal field, ${}^2\text{E}$ lies below ${}^4\text{T}_2$, and the emission is dominated by the sharper ${}^2\text{E} \rightarrow {}^4\text{A}_2$ transition. Near the intermediate-field region, the two excited states are close enough that both may contribute to the emission, especially when temperature increases [37, 39, 41, 43]

For $\text{YAG}:\text{Cr}^{3+}$, the crystal field is strong enough that the ${}^2\text{E}$ state is the principal emitting state at room temperature. However, the ${}^4\text{T}_2$ level is not very far above it, which explains why thermal effects are observed in the emission and lifetime behavior. The reported separation of approximately 1000 cm^{-1} between ${}^2\text{E}$ and ${}^4\text{T}_2$ places $\text{YAG}:\text{Cr}^{3+}$ in a useful region for temperature-dependent luminescence analysis [36,41].

The Tanabe–Sugano model is useful for organizing the electronic structure of Cr^{3+} , but it should not be treated as a complete description of real YAG:Cr^{3+} samples. Real materials may show line broadening, peak shifts, and lifetime changes because of electron–phonon coupling, strain, stoichiometric deviation, particle size, or local disorder [39,42,43]. This limitation is important for the present aerogel-derived samples, because their spectra must be interpreted by considering both the ideal Cr^{3+} energy-level scheme and the structural quality of the calcined YAG host.

The connection between structure and crystal-field behavior has also been emphasized in Cr^{3+} thermometry studies outside YAG. Back et al. showed that different Ga_2O_3 polymorphs doped with Cr^{3+} can display different thermometric behavior because the local ligand field changes with the host structure [38]. This result is useful for the present thesis because it shows that Cr^{3+} thermometry is not controlled only by the dopant ion; it also depends on the crystal structure that surrounds it. Therefore, in aerogel-derived YAG:Cr^{3+} , the thermal response of Cr^{3+} should be discussed together with phase formation and local structural order.

The optical behavior of Cr^{3+} is controlled not only by the formal site symmetry, but also by more detailed chemical factors. The papers on Ga_2O_3 polymorphs emphasize that the relative energies of the ${}^4\text{T}_2$ and ${}^2\text{E}$ states are simultaneously affected by bond length, covalency, and the ionic radius of the substitutional site, and that these factors are reflected spectroscopically in Dq , B , and C . They also show a useful design rule: for a broad family of Cr^{3+} -based Boltzmann thermometers, the ${}^4\text{T}_2$ – ${}^2\text{E}$ energy gap follows a roughly linear trend with crystal-field strength Dq . This means that the temperature range and sensitivity of a Cr^{3+} thermometer can, at least approximately, be anticipated from structural information [38].

1.6 Temperature-dependent emission and Cr^{3+} -based Boltzmann thermometry

Thermometry is the measurement of temperature through physical property that changes reproducibly with temperature. In conventional thermometers, this property may be volume, electrical resistance, or voltage. In luminescence thermometry, temperature is determined from changes in an optical signal emitted by a luminescent material. Temperature can affect several luminescence parameters, including emission intensity, intensity ratio, peak position, bandwidth, spectral shape, and luminescence lifetime. Because the signal can be collected remotely, luminescence thermometry provides a remote method for measuring local temperature, including in small, moving, or otherwise inaccessible systems [45].

Ratiometric luminescence thermometry determines temperature from the ratio of two emission signals rather than from the absolute intensity of a single emission band. The luminescence intensity ratio, LIR , is generally defined as:

$$LIR = \frac{I_2}{I_1} \quad (2)$$

where I_2 and I_1 are the integrated intensities of two selected emission bands. Absolute luminescence intensity can change because of variations in excitation power, sample quantity, dopant concentration, optical alignment, collection geometry, or detector response. When both emission signals are recorded under the same experimental conditions, many of these common effects are partially cancelled in their ratio. Ratiometric thermometry is therefore considered self-referenced and is generally more reliable than thermometry based on a single emission intensity [38], [45], [46]. However, wavelength-dependent detector sensitivity, optical absorption, and spectral overlap must still be considered during calibration.

Ratiometric thermometry may be empirical, in which the intensity ratio is calibrated directly against temperature, or it may be based on a physical model. Boltzmann thermometry is a physically based ratiometric method that uses two excited states whose populations are redistributed by thermal energy. When the population-transfer rate between the two states is sufficiently fast compared with their radiative decay rates, the states approach thermal equilibrium and their relative populations follow the Boltzmann distribution:

$$\frac{N_2}{N_1} = \frac{g_2}{g_1} \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (3)$$

where N_2 and N_1 are the populations of the higher- and lower-energy excited states, g_2 and g_1 are their degeneracies, $\Delta E = E_2 - E_1$ is the energy separation between them, k_B is the Boltzmann constant, and T is the absolute temperature. As temperature increases, a larger fraction of the excited ions occupies the higher-energy state.

The emission intensity from each state is proportional to its population and radiative transition probability. The corresponding intensity ratio can therefore be expressed as

$$LIR = \frac{I_2}{I_1} = A \exp\left(-\frac{\Delta E}{k_B T}\right) \quad (4)$$

where A is a temperature-independent prefactor that includes the degeneracies, radiative transition probabilities, emission energies, and instrumental response associated with the two emission bands [45]. Taking the natural logarithm gives

$$\ln(LIR) = \ln A - \frac{\Delta E}{k_B T} \quad (5)$$

Therefore, a plot of $\ln(LIR)$ against $\frac{1}{T}$ should be linear when the two states follow Boltzmann equilibrium. The slope is equal to $-\frac{\Delta E}{k_B}$, while the intercept gives $\ln A$.

For Cr^{3+} , Boltzmann thermometry commonly uses the temperature-dependent relationship between the ${}^2\text{E}$ and ${}^4\text{T}_2$ excited states. Cr^{3+} has a $3d^3$ electronic configuration, and the relative energies of these states depend strongly on the crystal field produced by the surrounding

ligands. The ${}^2E \rightarrow {}^4A_2$ transition produces the sharp the so-called *R*-line emission, whereas the ${}^4T_2 \rightarrow {}^4A_2$ transition produces a broad emission band because of its stronger coupling with lattice vibrations. In a sufficiently strong crystal field, as in YAG:Cr³⁺, ${}^2E$ lies below ${}^4T_2$ and is the main emitting state at low or moderate temperatures. As the temperature increases, phonons provide sufficient energy to transfer part of the population from ${}^2E$ to the higher-lying ${}^4T_2$ state. The broad ${}^4T_2 \rightarrow {}^4A_2$ mission consequently increases relative to the sharp ${}^2E \rightarrow {}^4A_2$ emission. For Cr³⁺ thermometry, the thermometric parameter may therefore be defined as:

$$LIR_{TE} = \frac{I({}^4T_2 \rightarrow {}^4A_2)}{I({}^2E \rightarrow {}^4A_2)} = A \exp\left(-\frac{\Delta E_{TE}}{k_B T}\right) \quad (6)$$

where

$$\Delta E_{TE} = E({}^4T_2) - E({}^2E) \quad (7)$$

In YAG:Cr³⁺, the ${}^4T_2$ state has been reported to lie approximately 1000 cm⁻¹ above ${}^2E$, although the experimentally fitted value can vary with the sample and measurement method [36,46]. This relatively small separation allows thermal population of ${}^4T_2$ within an experimentally accessible temperature range. Because the spin-allowed ${}^4T_2 \rightarrow {}^4A_2$ transition has a faster radiative rate than the spin-forbidden ${}^2E \rightarrow {}^4A_2$ transition, thermal population of ${}^4T_2$ also causes the effective luminescence lifetime to decrease with increasing temperature.

The performance of a luminescent thermometer is commonly evaluated using absolute sensitivity, relative sensitivity, and thermal resolution. The absolute sensitivity is defined as

$$S_a = \left| \frac{\partial LIR}{\partial T} \right| \quad (8)$$

while the relative sensitivity is

$$S_r = \frac{1}{LIR} \left| \frac{\partial LIR}{\partial T} \right| \quad (9)$$

For an ideal Boltzmann relationship,

$$S_a = LIR \frac{\Delta E}{k_B T^2} \quad (10)$$

and

$$S_r = \frac{\Delta E}{k_B T^2} \quad (11)$$

Relative sensitivity is normally reported as a percentage:

$$S_r(\% \text{ K}^{-1}) = 100 \frac{\Delta E}{k_B T^2} \quad (12)$$

Absolute sensitivity describes the actual change in the measured intensity ratio per kelvin, whereas relative sensitivity is a figure of merit allowing comparison between different thermometers independently of the numerical magnitude of their LIR values. The temperature uncertainty, also called thermal resolution, can be estimated from

$$\delta T = \frac{\delta LIR}{S_a} = \frac{1}{S_r} \frac{\delta LIR}{LIR} \quad (13)$$

where δLIR is the experimental uncertainty in the intensity ratio. A small value of δT indicates that small temperature differences can be resolved [37,45].

Although the ${}^4T_2 \rightarrow {}^4A_2$ intensity ratio is frequently fitted using the Boltzmann equation, Cr^{3+} crossover thermometers do not always behave as ideal Boltzmann systems. At low temperatures, phonon-assisted transfer between ${}^2E$ and ${}^4T_2$ may be too slow to establish complete thermal equilibrium. At high temperatures, nonradiative quenching, electron-phonon coupling, spectral broadening, and overlap between the sharp and broad emissions may also cause deviations from the ideal model. For this reason, Cr^{3+} thermometers based on the ${}^2E \rightarrow {}^4A_2$ crossover are often described as pseudo-Boltzmann thermometers, and the valid temperature range should be determined experimentally from the linear region of the $\ln(LIR)$ versus $1/T$ plot [33,37, 38].

1.7. Thermometry applications

Cr^{3+} -based luminescence thermometry is useful when direct contact with the sample is difficult or when a conventional thermometer may disturb the system. Temperature is measured from changes in the emitted light, such as the luminescence intensity ratio, spectral position, broadening or lifetime. Since the signal can be collected remotely, this method can be used for small objects, moving parts, biological samples, catalytic systems, and environments exposed to strong radiation, electromagnetic fields or harsh environments [45].

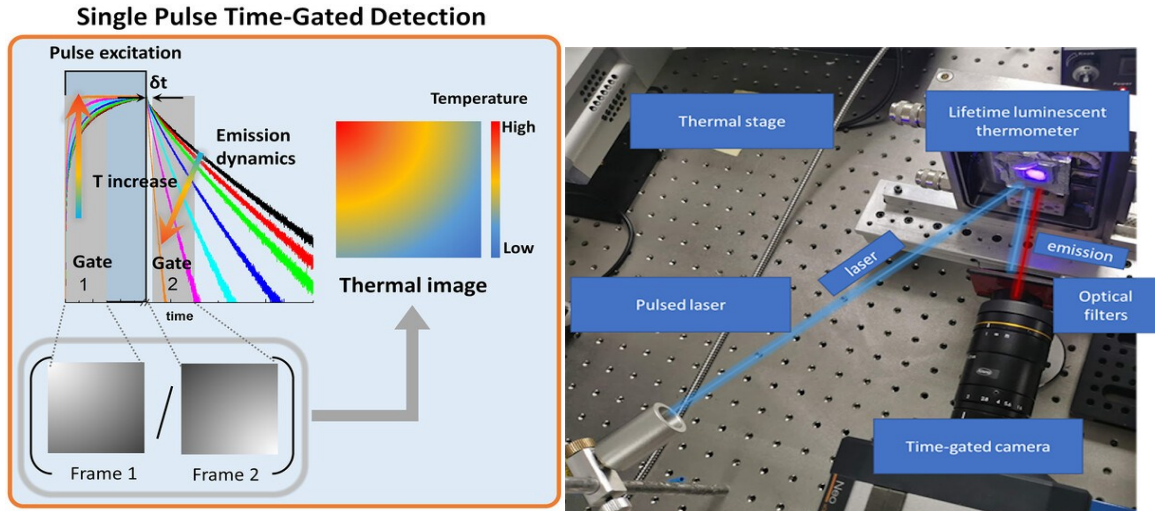


Figure 1.13; Principle and experimental arrangement of time-gated luminescence thermometry [48].

One important application is real-time thermal imaging. Avram et al. used $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ to produce two-dimensional temperature maps [48]. The luminescence lifetime decreased from about 9 ms at 303 K to nearly 1 ms at 533 K. Instead of recording and fitting the complete decay curve at every point, the emission was collected in two time windows after a single excitation pulse. The ratio between the signals recorded in the two gates was used as the temperature-dependent parameter:

$$\text{LIR}_G = \frac{I_{\text{Gate 1}}}{I_{\text{Gate 2}}}$$

where

$$I_{\text{Gate 1}} = \int_{t_1}^{t_2} I(t) dt$$

and

$$I_{\text{Gate 2}} = \int_{t_3}^{t_4} I(t) dt.$$

After calibration, this ratio was calculated for each camera pixel and converted into temperature, allowing the authors to obtain spatial thermal images. Because only two gated images were needed, the method was faster than conventional lifetime fitting and was suitable for real-time measurements

Cr^{3+} luminescence thermometry has also been used to monitor temperature during catalytic reactions. Back et al. used $\beta\text{-Ga}_2\text{O}_3:\text{Cr}^{3+}$ as both a catalyst-support material and an optical thermometer during the hydrogenation of ethylene over Pt particles. The temperature was

obtained from the ratio between the broad ${}^4T_2 \rightarrow {}^4A_2$ emission and the sharp ${}^2E \rightarrow {}^4A_2$ emission. The luminescence measurements followed the temperature changes during the reaction and were compared with thermocouple and radiation-thermometer readings. This application is important because it allows the temperature close to the catalyst particles to be measured in a more reliable way than conventionally done by means of a thermocouple or infrared camera [38].

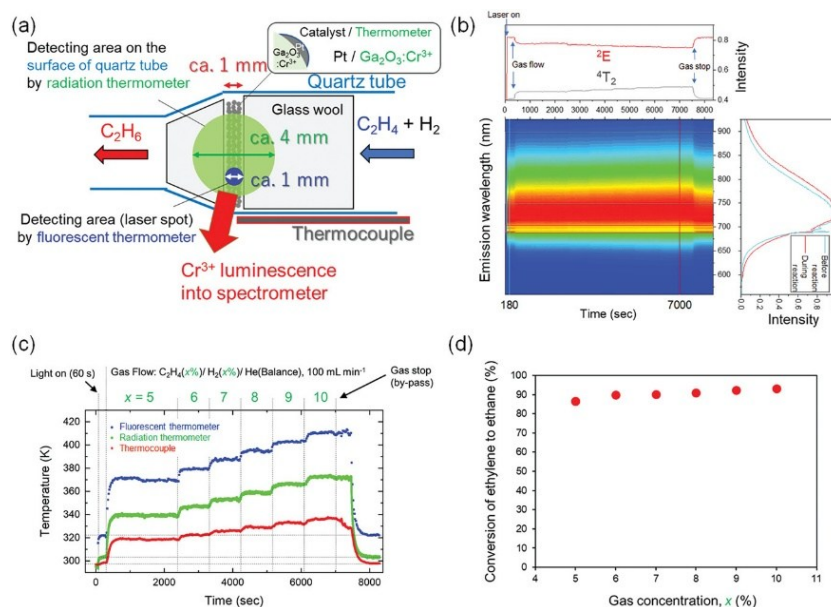


Figure 1.14: Example of Cr³⁺ luminescence thermometry applied to temperature monitoring during a catalytic reaction [38].

Another application is cryogenic thermometry. Mykhaylyk et al. investigated Cr³⁺-doped Al₂O₃, Ga₂O₃, YAG, and YAlO₃ over a temperature range of about 5–300 K. Different luminescence parameters were used in different temperature regions, including the intensity ratio of the Cr³⁺ R lines, their spectral shift, and the luminescence lifetime. Ga₂O₃:Cr³⁺ showed good temperature resolution over a wide range. This type of non-contact measurement is useful at low temperatures because electrical sensors may cause heat transfer or may not remain in good thermal contact with the sample [49]. Back et al. proposed the engineering of the ΔE_{T-E} to achieve ultranarrow energy gap between the ${}^4T_2$ and ${}^2E$ states in CaHfO₃:Cr³⁺ perovskite and take advantage of the thermal equilibrium between them already at low temperatures[46]

Cr³⁺-based thermometers can also be used in high-radiation environments. In synchrotron experiments, for example, X-ray beams may heat cryogenic biological samples. A Cr³⁺ luminescent probe can be placed close to the sample and used to measure this local heating without electrical wiring. This helps confirm that the sample remains below the temperature at which ice crystallization and radiation damage become more serious [49].

A further application is the combination of optical heating and temperature sensing in the same material. Elzbieciak-Piecka and Marciniak studied YAl₃(BO₃)₄:Cr³⁺, where Cr³⁺ absorbs laser radiation and converts part of the absorbed energy into heat. At the same time, the temperature can be followed from the relative intensities of the ${}^2E \rightarrow {}^4A_2$ and ${}^4T_2 \rightarrow {}^4A_2$ emissions. This makes it possible to heat a sample and measure its temperature using the same luminescent

material. Such a system may be useful in photothermal treatment, where the temperature must be controlled carefully to avoid insufficient or excessive heating [50].

Cr³⁺-doped materials have also been considered for biological temperature sensing. Marciniak et al. studied YAG:Cr³⁺,Nd³⁺ nanocrystals designed to operate in the near-infrared range, where light can penetrate biological tissue more effectively than visible light. In this system, the temperature-dependent Cr³⁺ emission was combined with Nd³⁺ emission to create several intensity ratios. This approach extended the useful temperature range and provided good sensitivity near physiological temperatures, making the material relevant for temperature monitoring during optical heating or hyperthermia [31].

More generally, luminescent thermometers can be applied to microelectronic devices, microheaters, microfluidic channels, and other small systems where local temperature gradients are difficult to measure with thermocouples. The sensing particles may be deposited as a thin layer on a surface, dispersed in a liquid, or incorporated into a component. A camera can then record the luminescence and produce a temperature map after calibration. Unlike infrared thermography, this method is less dependent on the surface emissivity of the measured object [45].

These studies show that Cr³⁺-based luminescence thermometry can be used for thermal imaging, catalytic-reaction monitoring, cryogenic measurements, optical heating, biological sensing, and temperature mapping of small devices. Cr³⁺ is particularly useful because temperature affects both the population of its ²E and ⁴T₂ states and the luminescence lifetime. However, its thermometric behavior depends strongly on the host material. Phase purity, crystal structure, local disorder, particle size, and electron–phonon coupling can all influence the emission and temperature response. For aerogel-derived YAG:Cr³⁺, possible applications include remote temperature sensing, high-temperature monitoring, and optical thermal mapping in places where contact thermometers are unsuitable.

1.8 Aim of the thesis

Building on the theoretical background presented in this chapter, this work has two main objectives.

The first objective is to prepare YAG:Cr³⁺ in the form of a nanocrystalline aerogel. Aerogels are highly porous three-dimensional materials obtained by sol–gel processing followed by supercritical drying. In this work, the aerogel route is used to produce YAG:Cr³⁺ as a porous network of nanometric crystallites rather than as a dense ceramic or single crystal. The main aim is to determine whether this preparation method can produce phase-pure crystalline YAG:Cr³⁺ while preserving the porous structure of the aerogel and maintaining the local environment required for Cr³⁺ luminescence. To the best of our knowledge, YAG:Cr³⁺ in aerogel form has not been previously reported.

The second objective is to study the optical and thermometric properties of the aerogel-derived YAG:Cr³⁺. Particular attention is given to the thermal coupling between the ²E and ⁴T₂ excited

states, which is responsible for the temperature-dependent luminescence of Cr^{3+} in YAG. The behavior of the material is examined using three approaches: the luminescence intensity ratio between the ${}^4\text{T}_2$ broadband and the ${}^2\text{E}$ -related emission, the ratio between the Stokes and anti-Stokes phonon sidebands, and the temperature dependence of the Cr^{3+} lifetime. Moreover, the potential of the material as optical thermometer was addressed considering the relative and absolute thermal sensitivities, S_r and S_a .

The emission spectra are separated using a nine-Gaussian fitting model in order to follow the ${}^2\text{E}$ and ${}^4\text{T}_2$ contributions independently with temperature. The energy separation ΔE obtained from the *LIR* analysis is compared with the value obtained from the lifetime measurements and with values reported for single-crystal $\text{YAG}:\text{Cr}^{3+}$. This comparison is used to determine whether the nanocrystalline aerogel structure changes the thermal behavior of Cr^{3+} compared with conventional YAG materials.

The effect of Cr^{3+} concentration is also studied using samples containing 0.5, 1, and 2 mol% Cr^{3+} . The aim is to determine which concentration gives the most suitable combination of emission intensity, fitting quality, and thermal sensitivity. In addition, the temperature-dependent emission of the 1 mol% sample is compared in powder and monolith form to examine whether the macroscopic form of the material affects the measured thermometric response.

Overall, this work investigates whether $\text{YAG}:\text{Cr}^{3+}$ can retain its known temperature-dependent luminescence when prepared as a porous nanocrystalline aerogel. The results are used to relate the structural properties of the aerogel to its optical and thermometric behavior and to evaluate the possible use of this material as a porous luminescent thermometer to be employed in the future as thermometer and support for catalytic reactions.

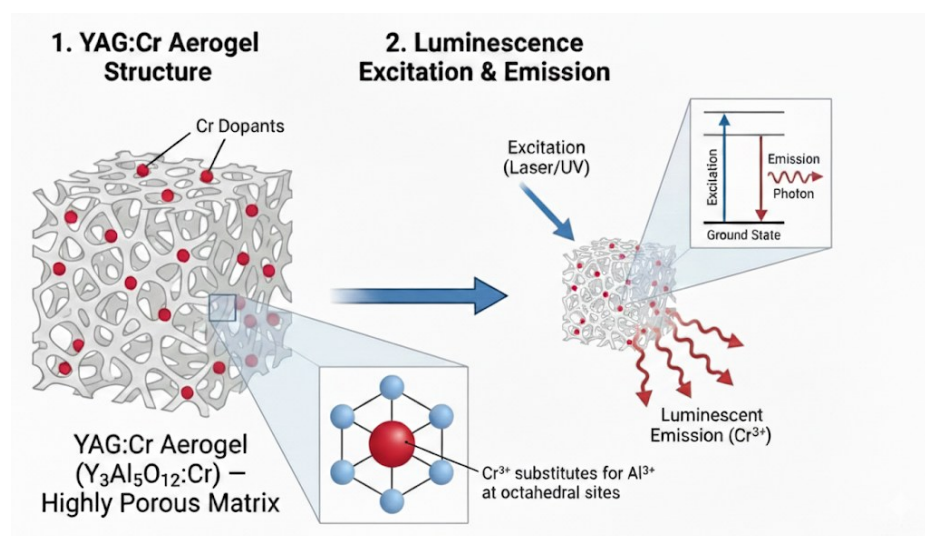


Figure 1.15: The schematic illustrates the structure of the $\text{YAG}:\text{Cr}^{3+}$ aerogel and the origin of its luminescence. Cr^{3+} ions are incorporated into the YAG lattice by replacing Al^{3+} at octahedral sites within the porous nanocrystalline network. Upon excitation, the Cr^{3+} ions are promoted to excited states and relax radiatively to the ground state, giving rise to the characteristic red/near-infrared emission (${}^2\text{E}/{}^4\text{T}_2 \rightarrow {}^4\text{A}_2$). (Image generated with FigureLabs, 2026)

2. EXPERIMENTAL METHODS

Cr³⁺-doped yttrium aluminum garnet (YAG) aerogels were prepared by an epoxide-assisted sol-gel route, followed by solvent exchange, supercritical carbon dioxide drying, and thermal treatment. The synthesis was designed to obtain nominal compositions of Y₃Al_{5-x}Cr_xO₁₂, in which Cr³⁺ replaces a fraction of the Al³⁺ ions.

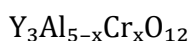
2.1. Materials

The reagents used for the preparation of the aerogels are listed in Table 2.1. All commercial reagents were supplied by Sigma-Aldrich with a stated purity of 99% and were used as received. Milli-Q water was obtained from the laboratory purification system.

Table 2.1. Reagents used for the synthesis and supercritical drying of YAG:Cr³⁺ aerogels.

Reagent	Chemical formula	Purity	Supplier
Aluminum chloride hexahydrate	AlCl ₃ ·6H ₂ O	99%	Sigma-Aldrich
Yttrium chloride hexahydrate	YCl ₃ ·6H ₂ O	99%	Sigma-Aldrich
Chromium(III) nitrate nonahydrate	Cr(NO ₃) ₃ ·9H ₂ O	99%	Sigma-Aldrich
Ethanol	C ₂ H ₅ OH	99%	Sigma-Aldrich
Acetone	C ₃ H ₆ O	99%	Sigma-Aldrich
Propylene oxide	C ₃ H ₆ O	99%	Sigma-Aldrich
Water	H ₂ O	Milli-Q grade	Laboratory purification system
Carbon dioxide	CO ₂	99%	Sigma-Aldrich

The nominal composition of the Cr³⁺-doped garnet was written as:



The chromium content was defined relative to the five Al sites in YAG. The corresponding values of x and the nominal compositions are given in Table 2.2. Since Cr³⁺ and Al³⁺ have the same formal charge, substitution does not require charge compensation in the ideal composition.

Table 2.2. Nominal compositions and sample nomenclature.

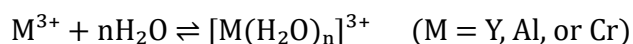
Nominal Cr content	x	Nominal composition	Example sample label
0.5%	0.025	Y ₃ Al _{4.975} Cr _{0.025} O ₁₂	YAG:Cr 0.5%-1000 °C
1.0%	0.050	Y ₃ Al _{4.95} Cr _{0.05} O ₁₂	YAG:Cr 1%-1000 °C
2.0%	0.100	Y ₃ Al _{4.90} Cr _{0.10} O ₁₂	YAG:Cr 2%-1000 °C

2.2. Cr³⁺-doped YAG aerogels Synthesis

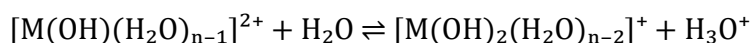
Stoichiometric amounts of aluminum chloride hexahydrate, yttrium chloride hexahydrate, and chromium(III) nitrate nonahydrate were used to obtain the selected nominal composition. The metal salt precursors were dissolved in ethanol under continuous stirring. Milli-Q water was added while it reached 0 °C in ice tube before adding to the mixed precursor solution. The low temperature limited rapid local hydrolysis and precipitation.

Propylene oxide was added slowly by syringe while the solution was stirred continuously. The epoxide consumed protons generated during hydrolysis and produced a gradual increase in pH. This promoted homogeneous hydrolysis and condensation of the Y³⁺, Al³⁺, and Cr³⁺ species. The resulting sol was transferred into cylindrical molds, including open syringes, and left undisturbed until gelation. The gels were aged in the molds for 24 h before removal. The wet-gel synthesis involved aquation, hydrolysis, epoxide ring opening, and condensation. The equations below are simplified reaction schemes. The wet gel consisted of a mixed amorphous Y-Al-Cr hydroxo/oxo network rather than a physical mixture of isolated Y(OH)₃, Al(OH)₃, and Cr(OH)₃ precipitates.

After dissolution, the trivalent metal ions are present as solvated aqua or mixed aqua-ethanol complexes. Their aquation can be written in general form as:

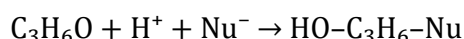


Polarization of coordinated water permits stepwise hydrolysis:



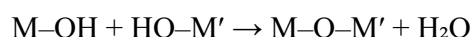
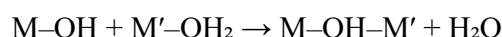
Hydrolysis releases protons. If the pH increases too rapidly or non-uniformly, localized precipitation can occur. The role of propylene oxide is to remove protons gradually throughout the solution.

Propylene oxide is protonated in the acidic precursor solution. Nucleophilic attack then opens the strained epoxide ring and consumes the proton. The net process can be written as:



Nu⁻ denotes an anion present in the precursor solution. Chloride ions supplied by AlCl₃·6H₂O and YCl₃·6H₂O are expected to contribute to ring opening. The equation is a general reaction scheme because the exact distribution of ring-opened organic products was not measured.

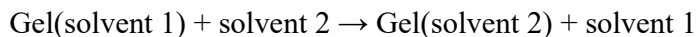
As the degree of hydrolysis increases, hydroxo-containing species condense through olation and oxolation. Representative reactions are:



M and M' may be Y, Al, or Cr. Repeated condensation forms Y-O-Al, Al-O-Al, Y-O-Y, Al-O-Cr, and Y-O-Cr linkages. Gelation occurs when the connected hydroxo/oxo network extends through the whole liquid volume.

After 24 h of aging, the gels were removed carefully from the molds and immersed in ethanol for three days. The ethanol was replaced every 24 h. The gels were then transferred to acetone

for a further three days, with daily solvent replacement. Solvent exchange removed soluble reaction products and residual precursor species and replaced the pore liquid with acetone before CO₂ extraction.



This equation describes physical solvent exchange rather than formation of a new inorganic compound.

2.3 Supercritical CO₂ drying

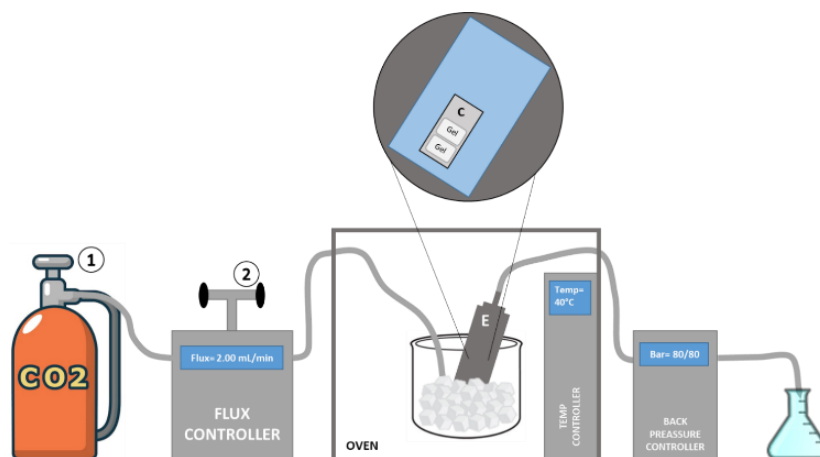


Figure 2.1: super critical drying system sketch.

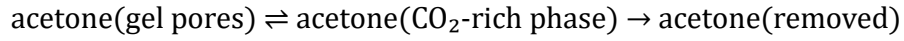
A maximum of two acetone-filled gels were processed in each drying cycle. The gels were placed in a dedicated aluminum cylinder and covered completely with acetone. The cylinder was inserted into the extraction chamber, which was sealed and connected to the high-pressure tubing. The lower connections were checked for leakage while submerged in water, and the upper connections were checked with soapy water.

The chamber was placed in an ice-water bath and maintained at approximately 0 °C. Liquid CO₂ was introduced at an initial flow rate of 1 mL min⁻¹. The back-pressure controller was set to 55 bar, and the inlet valve was opened slowly until the chamber reached the target pressure. Rapid pressure changes were avoided during the initial filling stage. If the pressure increased above 55 bar, the back-pressure set point was raised gradually, up to approximately 60 bar, until solvent discharge occurred; the set point was then returned to 55 bar.

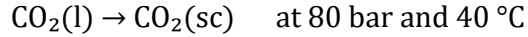
After the pressure had remained stable at 55 bar for 30 min, the CO₂ flow rate was increased to 2 mL min⁻¹. Extraction was continued for 4 h at 0 °C and 55 bar. The pressure was then increased from 55 to 80 bar in steps of 1 bar every 20–30 s. The ice bath was removed, the chamber was dried externally, and the oven temperature was increased to 40 °C in steps of 1 °C every 20–30 s.

At 80 bar and 40 °C, the CO₂ was above its critical point. The inlet valve was closed, the pump was stopped, and the samples were held under static supercritical conditions for 1.5 h. The chamber was then depressurized at a rate of 1 bar every 1.5 min until atmospheric pressure was reached. After complete depressurization, the chamber was opened and the aerogels were recovered.

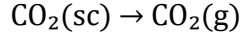
During the first stage, acetone was extracted from the gel pores by flowing liquid CO₂:



Raising the system to 80 bar and 40 °C converted the pore fluid to the supercritical state:



The absence of a liquid-gas interface under supercritical conditions limits capillary stress during drying. Slow depressurization then removes CO₂ from the pores:



2.4 Heat treatment and crystallization

The dried aerogels were calcined in air at selected temperatures between 800 and 1000 °C. The samples were heated at 10 °C min⁻¹ and held at the target temperature for 2 h. Thermal treatment removed residual water, hydroxyl groups, anions, and organic species and promoted crystallization of the mixed Y-Al-Cr oxide network.

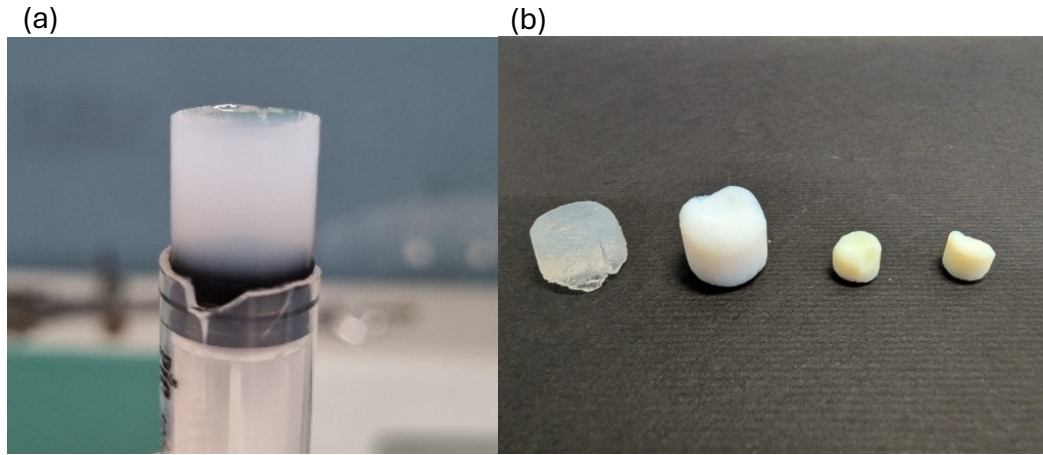
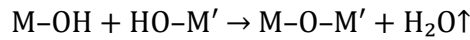
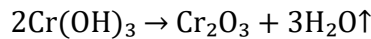
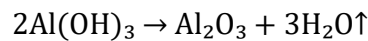
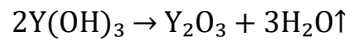


Figure 2.2: Representative YAG:Cr³⁺ aerogel monoliths (a) GEL and (b) from left to right comparison of gel, aerogel and aerogels after heat treatment.

Condensation and dehydroxylation during heating can be represented by:

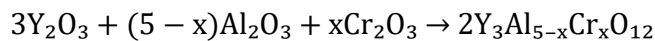


For the idealized individual hydroxides, the corresponding oxide-forming reactions are:

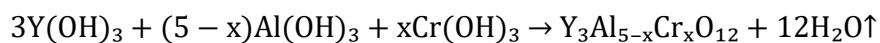


These equations are stoichiometric representations. In the prepared aerogel, the three cations were already mixed within one amorphous hydroxo/oxo network.

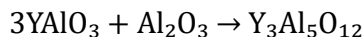
The overall garnet-forming reaction can be written from the component oxides as:



An equivalent idealized equation written from the metal hydroxides is:



The phase transformation proceeds through an amorphous precursor and may include intermediate yttrium aluminate phases before formation of cubic YAG. The undoped limiting reaction between YAlO_3 and alumina is:



2.5 Characterizations

The structural, microstructural, compositional, textural, and optical properties of the samples were examined by X-ray diffraction, transmission electron microscopy, selected-area electron diffraction, energy-dispersive X-ray spectroscopy, nitrogen adsorption-desorption analysis, photoluminescence excitation and emission spectroscopy, and temperature-dependent luminescence measurements.

2.5.1 X-ray diffraction

X-ray powder diffraction (XRPD) patterns of the aerogels were recorded at room temperature using a PANalytical Empyrean diffractometer in Bragg-Brentano parafocusing geometry. The instrument was equipped with a PIXcel3D-Medipix3 1×1 area detector and used $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The X-ray tube operated at 40 kV and 40 mA, and data were collected at a rate of 1° per 80 s. For the perovskite samples, XRPD patterns intended for Rietveld refinement were acquired with the same instrument using an acquisition time of 500 s. Phase identification was used to follow the formation of intermediate yttrium aluminate phases and cubic YAG as a function of calcination temperature. Apparent crystallite sizes were estimated from selected reflections using the Scherrer equation:

$$D = K\lambda / (\beta \cos \theta) \quad (14)$$

where D is the apparent crystallite size, K is the shape factor, λ is the X-ray wavelength, β is the full width at half maximum in radians, and θ is the Bragg angle.

2.5.2 Scanning electron microscopy and EDX

Scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) were carried out on a Hitachi S-3400N microscope operating at $[10]$ kV. The powders were dispersed on carbon tape and coated with a thin gold–palladium layer to avoid charging. SEM images were taken to look at particle shape, surface texture, how strongly the particles were agglomerated, and how these features changed after calcination. EDX was used to measure the elemental composition and to check whether Al and Y were evenly distributed in the samples. Point analyses were collected at three randomly chosen areas, The Al/Y ratios found this way were compared with the nominal values from the synthesis.

2.5.3 Transmission electron microscopy, SAED

Transmission electron microscopy (TEM), selected-area electron diffraction (SAED), were performed using an FEI Tecnai G2 F20 S/TEM operated at 200 kV. The microscope was

equipped with a Schottky field-emission source, S-TWIN pole pieces, a Gatan MultiScan CCD camera (Model 794),. TEM images were used to examine particle morphology, particle size, network connectivity, and the changes produced by calcination. SAED was used to assess local crystallinity,. Particle diameters were measured from calibrated TEM images using ImageJ and are reported as mean values with standard deviations.

2.5.4 Nitrogen adsorption-desorption analysis

Nitrogen adsorption-desorption isotherms were measured at -196 °C using a Micromeritics TriStar II Plus instrument. Before analysis, the samples were degassed at 60 °C for 12 h under a pressure of 2×10^{-2} mmHg. The specific surface area was calculated from the adsorption isotherm using the Brunauer-Emmett-Teller (BET) method. The specific pore volume was determined from the quantity of nitrogen adsorbed after capillary condensation. The pore-size distribution was obtained by the Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherm.

2.5.5 Photoluminescence (PL) and Photoluminescence Excitation (PLE):

Room-temperature photoluminescence (PL) and photoluminescence excitation (PLE) spectra were recorded using a Varian Cary Eclipse fluorescence spectrophotometer (Agilent Technologies). The instrument is equipped with a pulsed xenon flash lamp operating at 80 Hz with a pulse width of approximately 2 μ s and a peak power equivalent to 75 kW, and uses two Czerny-Turner monochromators with a spectral range of 200–900 nm and a wavelength accuracy of ± 1.0 nm. Detection is performed by a red-sensitive photomultiplier tube extending sensitivity up to 900 nm. For PL measurements, the excitation wavelength was fixed at 442 nm, corresponding to the $^4A_2 \rightarrow ^4T_1$ absorption band of Cr^{3+} , while the emission was scanned across the Cr^{3+} emission region. For PLE measurements, the excitation monochromator was scanned from 450 to 700 nm while the emission was monitored sequentially at three wavelengths: 687 nm (R_1 zero-phonon line of the ^2E state), 704 nm (phonon sideband region), and 750 nm (broad $^4T_2 \rightarrow ^4A_2$ emission band). This allowed the relative contribution of each excitation pathway to the different emission channels to be assessed. All spectra were recorded at room temperature on powder samples without further preparation.

2.5.6 Temperature dependence luminescence

Temperature-dependent photoluminescence spectra were recorded using a Acton SpectraPro 2150i spectrograph coupled to a Princeton Instruments PIXIS 100 CCD detector attached to a spectrometer equipped with a 300 grooves/mm grating blazed at 500 nm. The detector was operated in high-capacity mode with a gain of 3 and an integration time of 1 s. The emission slit was set to the minimum aperture to maximise spectral resolution. Excitation was provided by a 405 nm laser, coinciding with the broad $^4A_2 \rightarrow ^4T_1$ absorption band of Cr^{3+} in YAG, at a power adjusted according to the sample to avoid photodamage and local heating effects. Scattered laser light was rejected using a 500 nm long-pass filter placed in the collection path before the spectrometer entrance slit, ensuring that only the Cr^{3+} emission band between 670 and 750 nm reached the detector. All instrumental parameters were kept strictly constant across the full temperature range to ensure that any change in the photoluminescence signal could be attributed solely to temperature and not to variations in measurement conditions.

Temperature control was provided by a Linkam THMS600 heating and cooling stage (Linkam Scientific Instruments, UK), covering the range from -150°C to 500°C with a temperature stability better than 0.1°C . Sub-ambient temperatures were achieved using a liquid nitrogen cooling pump. A dry nitrogen purge was maintained throughout the experiment to prevent condensation at low temperatures and sample oxidation at high temperatures. At each temperature setpoint, a heating rate of $20^{\circ}\text{C}/\text{min}$ was applied, followed by a hold time of 6 minutes 15 seconds before acquisition to ensure thermal equilibration of the sample.

2.5.7 PL decay curve measurements: Lifetime evaluation

Photoluminescence decay measurements were performed using a custom LabVIEW-based acquisition system interfaced with a LeCroy WaveJet 354A digital oscilloscope (500 MHz bandwidth, 2 GS/s sampling rate). The sample was excited with a pulsed 442 nm laser and the emitted light was collected and directed through a spectrometer equipped with a 300 grooves/mm grating blazed at 500 nm, with grating positioning controlled by a Vexta PK244M-01A stepper motor. Decay curves were recorded sequentially at five emission wavelengths — 678, 687, 707, 724, and 750 nm — spanning the full Cr^{3+} emission band, by stepping the grating to each position in turn. A 500 nm long-pass filter was placed in the collection path to reject scattered laser light. The luminescence signal was detected by a photomultiplier tube (PMT), whose output was recorded by the oscilloscope and averaged over multiple acquisitions to improve the signal-to-noise ratio. Temperature control was provided by the Linkam THMS600 heating and cooling stage (Linkam Scientific Instruments, UK), covering the range from -150°C to 500°C with a temperature stability better than 0.1°C . Sub-ambient temperatures were achieved using a liquid nitrogen cooling pump. All five emission wavelengths were measured at each temperature before moving to the next setpoint.

3. RESULTS AND DISCUSSION

3.1 Structural and morphological characterization

First, the effect of temperature on the morphology and crystalline structure stabilization was investigated by combining electron microscopy (SEM/TEM), N_2 physisorption and diffraction (XRPD and electron diffraction) analyses.

3.1.1 Temperature effect on density

A clear effect of annealing temperature can already be seen from the appearance of the samples (Figure 3.1). As the calcination temperature increases, the aerogel monoliths shrink in both diameter and height, while their bulk density increases. This section examines these changes using the dimensional, mass, and density measurements obtained for the 1 mol% Cr YAG aerogel in the as-dried state and after annealing at 800, 900, and 1000 °C (Figure 3.2). The observed shrinkage and densification are then compared with the phase changes identified by XRPD in Section 3.1.2.

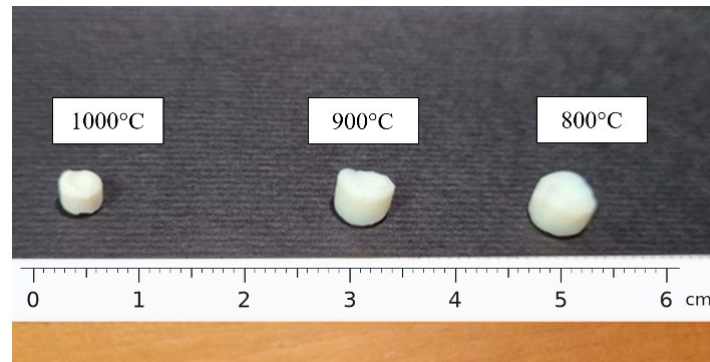


Figure 3.1: Photographs of 1 mol% Cr^{3+} YAG aerogel monoliths after annealing at 800, 900, and 1000 °C.

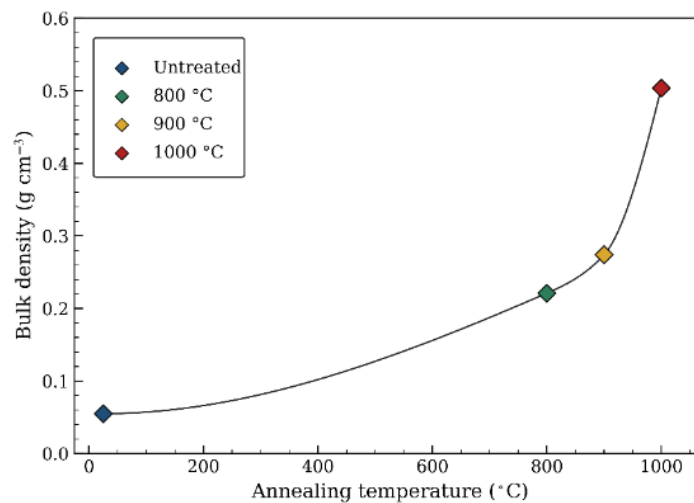


Figure 3.2: Bulk density of the 1 mol% Cr^{3+} YAG aerogel as a function of annealing temperature

The as-dried monolith has a bulk density of 0.055 g cm^{-3} , which corresponds to approximately 1.2% of the theoretical density of dense YAG, 4.55 g cm^{-3} . The estimated void fraction is therefore about 98.8%, confirming the highly porous nature of the as-dried material. The bulk density increases progressively with annealing temperature, as shown in Figure 3.2, although the extent of densification differs between the investigated temperature ranges.

After annealing at $800 \text{ }^{\circ}\text{C}$, the density increases from 0.055 to 0.221 g cm^{-3} , corresponding to an increase by a factor of approximately 4. Since no crystalline phase is detected by XRPD within this temperature range, this initial densification is mainly associated with the removal of adsorbed water, residual solvent, and remaining organic species from the amorphous precursor. Dihydroxylation and partial shrinkage of the gel network may also contribute to the reduction in volume.

Between 800 and $900 \text{ }^{\circ}\text{C}$, the density increases only slightly, from 0.221 to 0.274 g cm^{-3} , corresponding to a factor of approximately 1.24. This change occurs at the same temperature at which the metastable hexagonal YAlO_3 phase, YAH, appears in the XRPD pattern. The relatively small increase in density suggests that the formation of YAH mainly involves structural rearrangement within the amorphous oxide network rather than extensive collapse of the monolith.

A more pronounced increase is observed between 900 and $1000 \text{ }^{\circ}\text{C}$, where the density rises from 0.274 to 0.504 g cm^{-3} , corresponding to a factor of approximately 1.84. This temperature range coincides with the conversion of YAH into cubic YAG. The phase transformation is therefore accompanied by further shrinkage and a reduction in the internal free volume of the material.

Despite this densification, the bulk density of the sample annealed at $1000 \text{ }^{\circ}\text{C}$ remains only about 11% of the theoretical density of dense YAG. The corresponding estimated void fraction is approximately 89%, showing that the monolith does not transform into a dense ceramic under the applied heat-treatment conditions. Instead, a substantial fraction of the porous volume is retained after crystallization of the cubic YAG phase.

Bulk density measurements provide information on the overall degree of densification but do not distinguish between open and closed pores or determine the dimensions of the remaining pores. The specific surface area, pore volume, and pore-size distribution are therefore evaluated separately by nitrogen physisorption, as discussed in Section 3.1.6.

Table 3.1. Dimensions, mass, volume, and bulk density of the 1 mol% Cr³⁺ YAG aerogel before and after annealing.

SAMPLE	DIAMETER	HEIGHT	VOLUME	WEIGHT	DENSITY
YAG:Cr 1% untreated	1 cm	1 cm	0.785 cm ³	0.0431 g	0.055 g/cm ³
YAG:Cr 1% 800 °C	6 mm	5 mm	0.141 cm ³	0.0313 g	0.221 g/cm ³
YAG:Cr 1% 900 °C	5 mm	4 mm	0.079 cm ³	0.0215 g	0.274 g/cm ³
YAG:Cr 1% 1000 °C	4 mm	3 mm	0.038 cm ³	0.0190 g	0.504 g/cm ³

3.1.2 Crystalline phase evolution and identification: XRPD Analysis

The crystallographic evolution of the 1 mol% Cr YAG aerogel-derived material was investigated by X-ray powder diffraction (XRPD) after annealing at 850, 900, 950 and 1000 °C for 2 h in oven. The four patterns are shown in Figure 5.3, together with the reference patterns for cubic Y₃Al₅O₁₂ (YAG, ICSD, space group *Ia-3d*) and hexagonal YAlO₃ (YAH, space group *P6₃/mmc*).

The sample annealed at 850 °C shows only two broad features centered at approximately $2\theta = 30^\circ$ and 50° , with no distinct Bragg reflections. The material is therefore considered amorphous within the detection limit of the measurement. After annealing at 900 °C, the broad amorphous background is replaced by sharp reflections assigned to the metastable hexagonal YAH phase, while no YAG reflections are detected. The formation of YAH as the first crystalline phase agrees with the behavior commonly reported for sol–gel-derived Y–Al–O precursors, where the amorphous oxide first crystallizes into a metastable hexagonal aluminate before converting to the thermodynamically stable garnet phase [32].

At 950 °C, reflections from both YAH and YAG are present with comparable intensities. This confirms that the sample is in an intermediate stage of transformation and that the conversion of YAH into YAG occurs progressively between 900 and 1000 °C. After annealing at 1000 °C, all observed reflections can be indexed to cubic YAG. No residual YAH peaks or additional reflections attributable to Al₂O₃, Y₂O₃, orthorhombic YAlO₃, or Y₄Al₂O₉ are visible. The sample annealed at 1000 °C can therefore be regarded as phase-pure cubic YAG. This sample was selected for the subsequent structural and optical measurements.

The broad YAG reflections are a clear indication of the nanocrystalline nature of the crystallites. The corresponding crystallite size is evaluated from the diffraction-peak broadening through the Scherrer equation. The mean crystallite size of the phase-pure YAG obtained at 1000 °C was estimated from the broadening of the diffraction peaks through the Debye–Scherrer equation equal to 29 nm.

The phase evolution observed by XRPD is also consistent with the bulk-density results discussed in Section 3.1.1. The smaller increase in density between 800 and 900 °C occurs during the transformation from the amorphous precursor to YAH, whereas the larger increase between 900 and 1000 °C accompanies the conversion of YAH into cubic YAG. The

diffraction and density measurements therefore describe the same sequence of structural changes.

This general picture is consistent with the reported YAG:Cr aerogel system. The untreated material is predominantly amorphous and highly porous, the sample treated at 950 °C corresponds to an intermediate mixed-phase region, and the sample treated at 1000 °C approaches a more homogeneous YAG phase. At the same time, the monolith shrinks and densifies during heating while preserving its overall shape. These observations indicate that crystallization of the host and loss of porosity proceed together, and that the optical behavior of the final material must be understood in relation to this structural evolution.

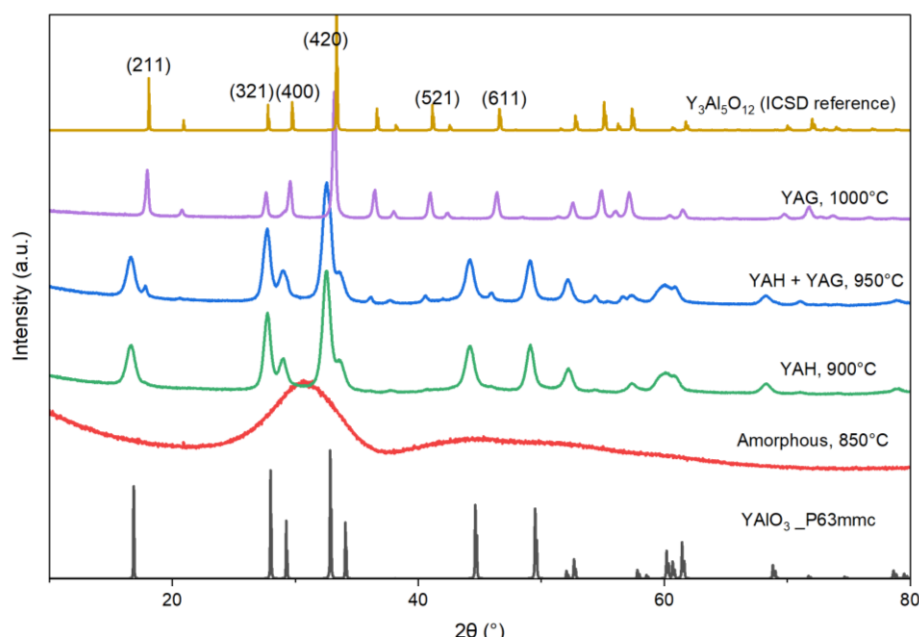


Figure 3.3: XRPD patterns of the 1 mol% Cr aerogel-derived material after annealing at 850, 900, 950 and 1000 °C, with the ICSD references for cubic $\text{Y}_3\text{Al}_5\text{O}_{12}$ (top) and hexagonal YAlO_3 (bottom).

3.1.3 Morphological evolution from SEM

The morphology of the YAG:Cr³⁺ 1% aerogels was studied by SEM before and after annealing at 950 and 1000 °C. The images were recorded at 5.0 kV using secondary electrons at $\times 30,000$ and $\times 100,000$ magnification.

The untreated aerogel (Figure 3.4, a-b) shows an open and highly porous network made of small, poorly defined particles. Individual particles are difficult to distinguish, which is consistent with the amorphous structure observed by XRPD. The very low bulk density of 0.055 g cm⁻³ also confirms the large amount of free volume in the untreated sample.

After annealing at 950 °C (Figure 3.4, c-d), the particles become more clearly defined. The network is more compact, but the porous structure is still visible. Small necks between neighboring particles can also be observed. In addition, two families of particles with different sizes are visible, suggesting the presence of two different entities. This morphology agrees with the mixed YAH + YAG phase identified by XRPD.

At 1000 °C (Figure 3.4, e-f), the material consists of uniform well-defined, mainly rounded nanoparticles. The particles are connected by more pronounced necks, indicating the beginning of sintering. Despite the densification, large voids remain between the particles, showing that the material is still porous and not fully dense.

Overall, the SEM images show a gradual change from an amorphous porous network to a more crystalline and interconnected nanoparticle structure with increasing annealing temperature. The detailed surface area and pore-size distribution are discussed later using nitrogen adsorption–desorption measurements.

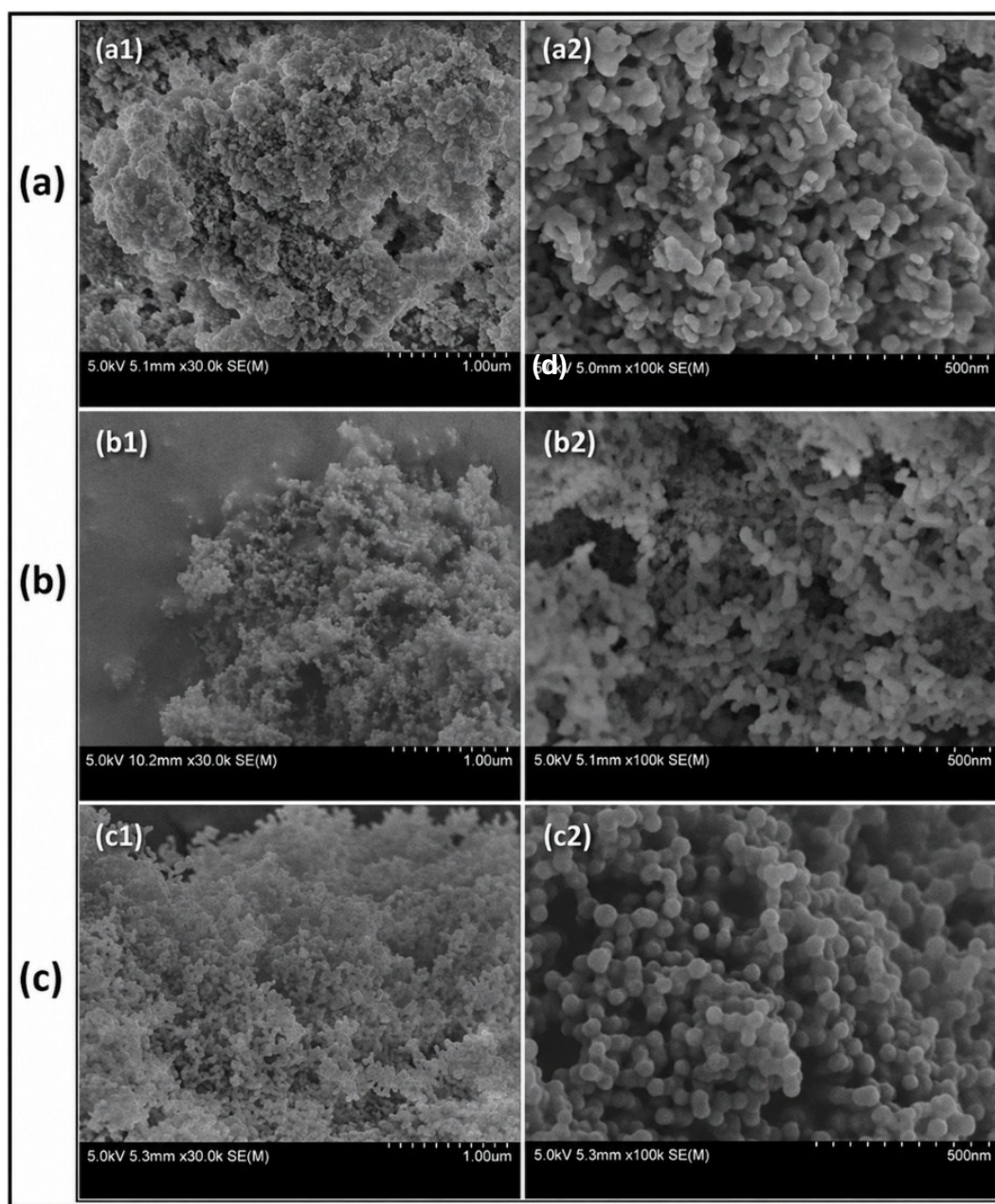


Figure 3.4: SEM micrographs of the 1 mol% Cr³⁺ YAG aerogel: untreated (a), annealed at 950 °C (b), and annealed at 1000 °C (c), recorded at ×30,000 (left) and ×100,000 (right).

3.1.4 Chemical composition from EDS

As example, the elemental composition of the untreated and 1000 °C samples was examined by EDS using the average of three spectra. Oxygen and Si are excluded from the calculation, and the results were compared with the nominal YAG composition. As shown in Figure 3.5, the analyzed areas were chosen at random across the sample. The maps indicate that Y and Al are evenly distributed, with no regions of local enrichment or depletion. The quantitative values, however, should be treated with care: each analysis covers only a limited area of the sample, so the measured Al/Y ratios give an indication of the composition rather than an accurate value for the material as a whole. The corresponding results are given in Figure 3.6. For ideal YAG, the expected Al/Y ratio is 1.67. For the nominal 1 mol% Cr composition, $\text{Y}_3\text{Al}_{4.95}\text{Cr}_{0.05}\text{O}_{12}$, the calculated ratio is 1.65. The sample annealed at 1000 °C gives an Al/Y ratio of 1.36, while the untreated sample gives a lower value of 1.23 shown in Table 3.2. Both values are below the nominal composition, indicating a higher relative Y content or lower relative Al content in the regions examined by EDS on that certain chosen area.

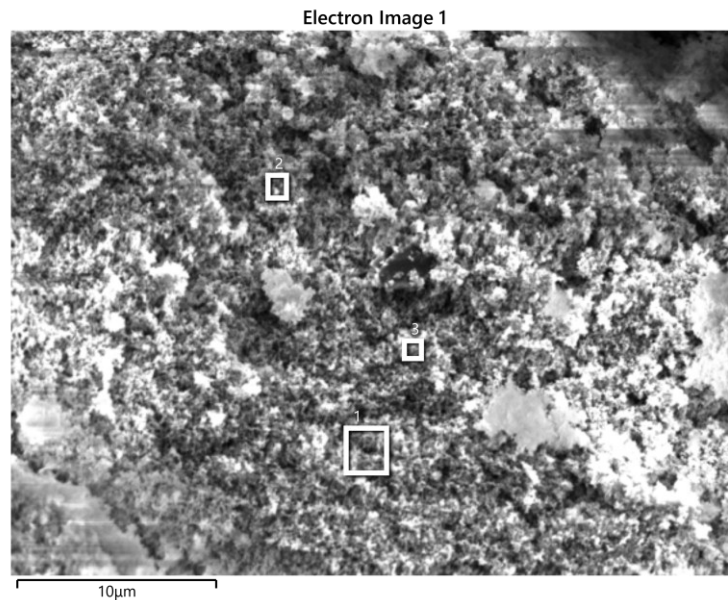


Figure 3.5: Random selected area on sample

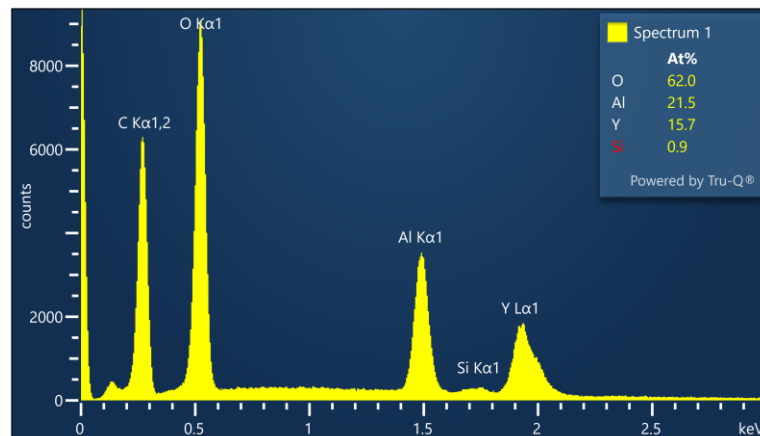


Figure 3.6: EDX result of YAG:Cr^{3+} , 1000°C

The Al/Y ratio becomes closer to the expected YAG value after annealing at 1000 °C, which may be related to the structural reorganization and crystallization occurring during heat treatment. However, the measured value still differs from the nominal ratio, so the EDS results should be considered semi-quantitative.

Chromium was not detected in either sample by EDS. The nominal Cr concentration is only 0.63 at.% when oxygen is excluded, which is close to the practical detection limit of conventional EDS. Therefore, the absence of a measurable Cr signal does not necessarily indicate the absence of Cr in the material. The incorporation of Cr³⁺ is instead supported by the characteristic Cr³⁺ photoluminescence discussed in the optical characterization section.

Overall, the EDS measurements confirm the presence of Y and Al as the main cations of the material, while the quantitative Al/Y ratios show some deviation from the nominal YAG composition.

Table 3.2. EDS-derived cation composition and Al/Y ratio of the untreated and 1000 °C samples (average of three spectra; O and Si excluded).

Sample / composition	Basis	Al %	Y %	Cr %	Al/Y ratio
Ideal YAG	(Y ₃ Al ₅ O ₁₂)	62.50%	37.50%	0	1.67
Lab report YAG:Cr 1%	(Y ₃ Al _{4.95} Cr _{0.05} O ₁₂)	61.88%	37.50%	0.63%	1.65
YAG:Cr 1%, 1000 °C EDS	average of 3 spectra, O excluded	57.69%	42.31%	not detected	1.36
YAG:Cr 1%, untreated EDS	average of 3 spectra, O excluded	55.18%	44.82%	not detected	1.23

3.1.5 Transmission Electron Microscopy (TEM) analysis

Transmission electron microscopy (TEM) and high-resolution TEM (HRTEM) were performed on the untreated 1 mol% Cr YAG aerogel and on the samples annealed at 950 and 1000 °C, to visualize the morphology at the nanoscale and to confirm the phase evolution identified by XRPD (Section 3.1.2) at the lattice level.

The TEM images of the untreated monolith (Figure 3.7, a–b) reveal a three-dimensional interconnected network of nanoparticles with sizes of a few tens of nanometers, forming the mesoporous architecture inherited from the wet gel and preserved through the supercritical CO₂ drying step. No evident lattice fringes are observed at higher magnification, and the selected-area electron diffraction (SAED) pattern (Figure 3.7 c) consists exclusively of broad diffuse rings without any sharp Bragg reflections as expected for an amorphous aerogel.

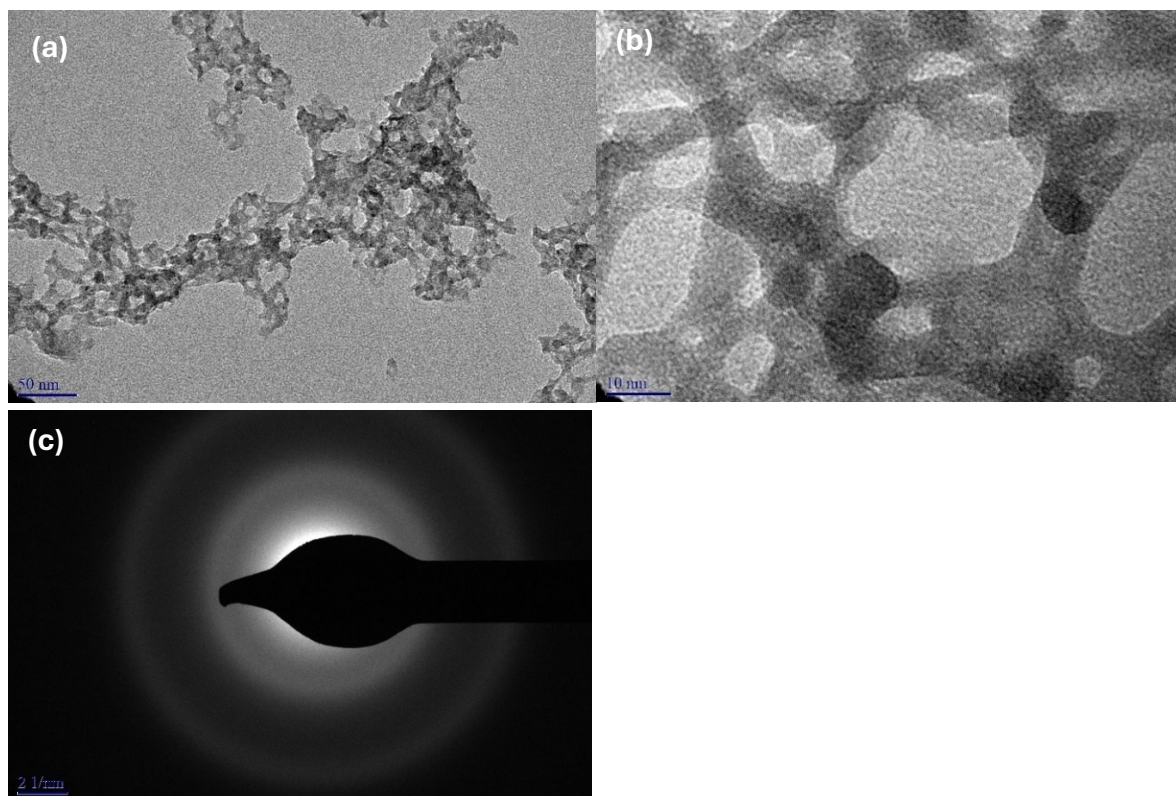


Figure 3.7: TEM images and SAED pattern of the untreated 1 mol% Cr³⁺ YAG aerogel, showing an interconnected amorphous nanoparticle network.

The mixed-phase composition of the 950 °C sample identified by XRPD in Section 3.1.2 was investigated at the nanoscale by TEM and HRTEM (Figure 3.8).

At lower magnifications (Figure 3.8 a-b), the TEM images reveal a bimodal population of nanoparticles coexisting within the aerogel-inherited porous network. A first population consists of larger, rounded, well-defined particles with diameters in the range of $\approx 20\text{--}40$ nm, indicating a well-crystallized state. A second population consists of considerably smaller particles ($\approx 5\text{--}15$ nm) with less-defined outlines, interconnected with the larger particles into the same framework. The simultaneous presence of the two populations in the same field of view (as in the case of SEM analysis) is the direct nanoscale signature of a two-phase system, consistent with the mixed YAH + YAG composition identified by XRPD.

HRTEM analysis of a representative nanoparticle (Figure 3.8, c-d) resolves lattice fringes with an interplanar spacing of $d = 5.23$ Å. The corresponding Fast Fourier Transform (Figure 3.8, c), which acts as a local selected-area electron diffraction pattern, confirms this measurement: several diffraction spots are found at a common radius from the FFT centre, all corresponding to $d = 5.23$ Å and forming the ring highlighted in FFT. The presence of a whole family of spots along the same ring — rather than a single Bragg pair — indicates that the analysed region contains multiple crystalline domains sharing the same d -spacing but with different orientations, that is, a polycrystalline assembly of grains all belonging to the same lattice family. The measured value of 5.23 Å is in excellent agreement with the theoretical (002) reflection of hexagonal YAlO₃ (YAH, space group $P6_3/mmc$, $c = 10.52$ Å; theoretical $d(002) = 5.23$ Å). The FFT is therefore unambiguously assigned to the (002) family of YAH,

providing direct nanoscale evidence for the presence of the metastable hexagonal aluminate phase.

Direct HRTEM identification of the YAG lattice was not attempted in this analysis, since the presence of YAG at 950 °C is independently and unambiguously established by the XRPD pattern of Figure 3.3, which shows both YAH and YAG reflections in comparable intensities. The morphological identification of the two nanoparticle populations follows naturally from the crystallization pathway of aerogel-derived Y–Al–O systems: YAH nucleates first from the amorphous precursor and grows as an assembly of small nanocrystallites, while YAG forms subsequently through solid-state reaction between YAH and residual amorphous alumina, and the YAG grains grow at the expense of the surrounding YAH. The smaller nanoparticles in the TEM images are therefore attributed to residual YAH, and the larger nanoparticles to YAG that has already formed and coarsened. The 950 °C sample thus represents the transition regime of the crystallization pathway, in which YAG has nucleated and grown but the YAH → YAG transformation is not yet complete — precisely the interpretation given by the XRPD analysis in Section 3.1.2, now confirmed at the nanoscale by direct TEM imaging.

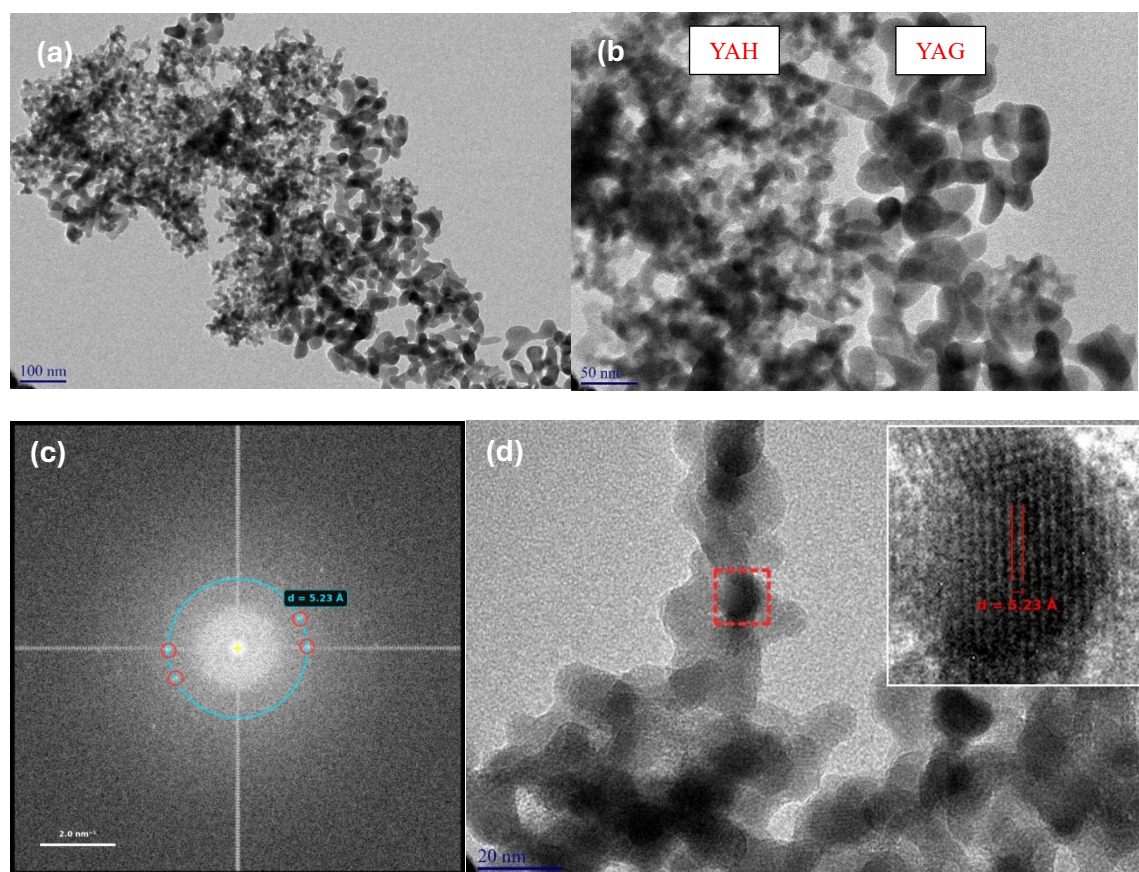


Figure 3.8: TEM, HRTEM, and FFT analysis of the 1 mol% Cr³⁺ sample annealed at 950 °C, showing the mixed YAH + YAG microstructure and a YAH lattice spacing of approximately 5.23 Å.

At 1000 °C, TEM shows well-crystallized quasi-spherical nanoparticles distributed in the aerogel-inherited network (Figure 3.9). The particle-size distribution obtained from ImageJ analysis of 97 nanoparticles gives a mean diameter of 34.9 ± 8.7 nm, in agreement with the mean crystallite size of 29 nm obtained from Scherrer analysis. The small difference between the two values TEM measures the physical envelope of each nanoparticle, whereas Scherrer probes the coherent-diffraction domain indicates that each nanoparticle is essentially a single crystallite, at most decorated by a thin disordered surface layer, in agreement with the behaviour reported for YAG:Cr³⁺ nanopowders of comparable size [44].

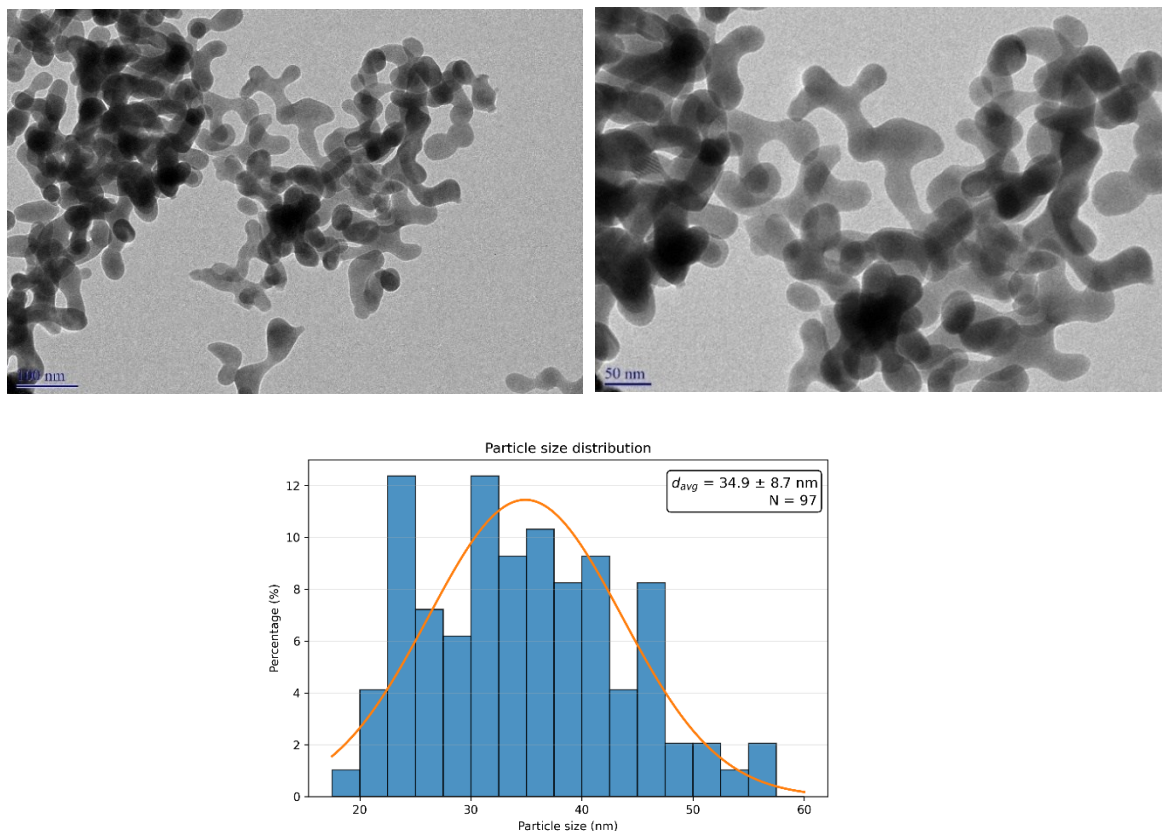


Figure 3.9: TEM images and particle-size distribution of the 1 mol% Cr³⁺ sample annealed at 1000 °C. The mean particle diameter is 34.9 ± 8.7 nm ($N = 97$).

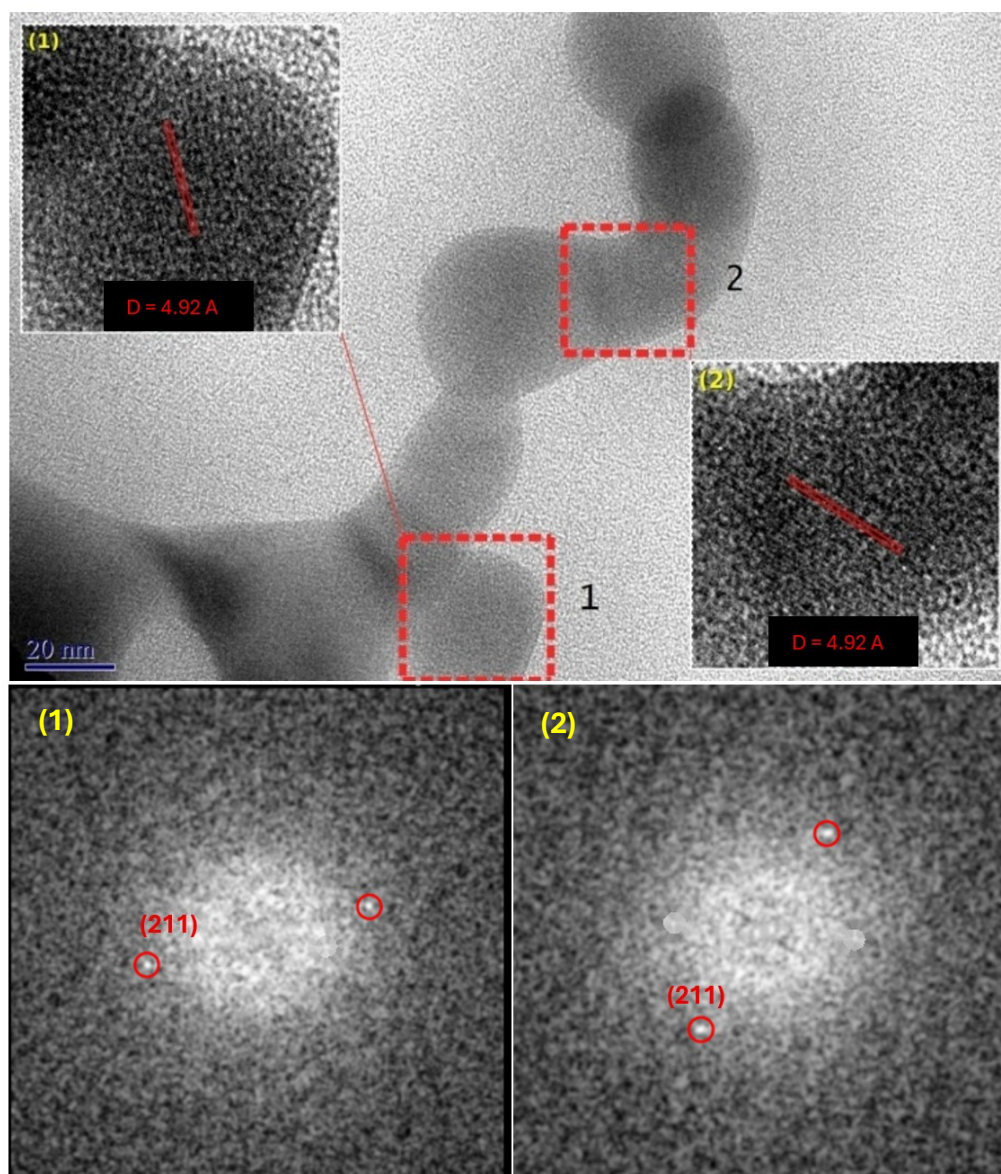


Figure 3.10: HRTEM and FFT analysis of the 1 mol% Cr^{3+} sample annealed at 1000 °C, showing lattice fringes with $d \approx 4.92 \text{ \AA}$ assigned to the YAG (211) planes.

The nanoscale lattice structure of the 1000 °C sample was investigated by high-resolution TEM (HRTEM) supported by Fast Fourier Transform (FFT) analysis of two independent regions of the same TEM micrograph. The two regions, labelled 1 and 2 in Figure 3.10, correspond to different nanoparticles of the aerogel-derived network and are analysed here to test the reproducibility of the lattice-plane identification across the sample.

The high-resolution insets (1) and (2) in Figure 3.10 show clearly resolved lattice fringes in both nanoparticles, with a common interplanar spacing of $d = 4.92 \text{ \AA}$ measured directly from the fringe periodicity along the red reference line. This value is in exact agreement with the theoretical d-spacing of the (211) reflection of cubic YAG calculated from the refined lattice parameter $a = 12.065 \text{ \AA}$ reported in references. The two nanoparticles are therefore both identified as cubic YAG.

The HRTEM + FFT analysis therefore provides a direct nanoscale confirmation of the phase identification made by XRPD in Section 3.1.2, and shows that the phase-pure cubic YAG identity of the 1000 °C sample is preserved at the single-nanoparticle level.

3.1.6 N₂ physisorption analysis: Isotherms and pore size distribution curves

Nitrogen physisorption was used to examine how the textural properties of the aerogel changed during calcination. The measurements had two main purposes. First, they were used to determine whether the main characteristics of the aerogel, particularly its high specific surface area *S* and open mesoporous structure, were retained after the heat treatment required for YAG crystallization. Second, they provide information relevant to the spectroscopic results discussed later in this chapter. The surface-to-volume ratio influences the fraction of Cr³⁺ ions located close to the particle surface, where their local environment and crystal field may differ from those in the bulk lattice.

Measurements were carried out on the untreated aerogel and on samples calcined at 900, 950 and 1000 °C. Specific surface areas were calculated using the BET method from the linear region of the adsorption isotherm. Cumulative pore volumes and average pore diameters were obtained from the desorption branch using the BJH method. The results, together with the corresponding phase assignments, are presented in Table 3.3 and Figure 3.11.

Table 3.3. Textural parameters of the aerogel-derived YAG:Cr³⁺ powders as a function of calcination temperature, obtained from nitrogen adsorption–desorption isotherms at 77 K.

Sample / calcination T	S (BET) [m ² g ⁻¹]	V (BJH des.) [cm ³ g ⁻¹]	d (BJH des.) [Å]	V (micropore) [cm ³ g ⁻¹]
Untreated	301.18	2.2923	376.7	0.0757
900 °C	86.45	0.5093	352.1	0.0256
950 °C	77.62	0.4882	376.6	0.0229
1000 °C	65.36	0.3814	391.5	0.0197

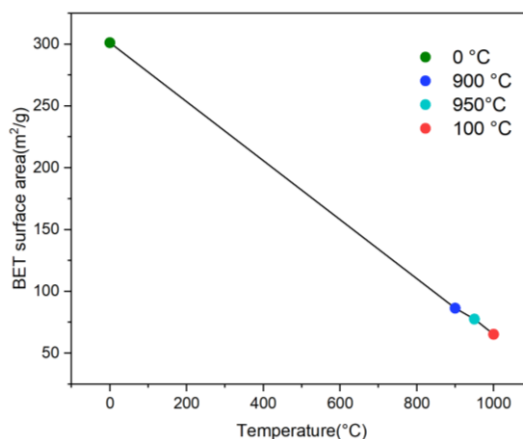


Figure 3.11: Comparison of BET surface area in 4 different temperature

The untreated aerogel has a high specific surface area of 301.18 m² g⁻¹ and a pore volume of 2.2923 cm³ g⁻¹, consistent with its low bulk density of 0.055 g cm⁻³ in section 3.1.1. After calcination at 900 °C, these values decrease sharply to 86.45 m² g⁻¹ and 0.5093 cm³ g⁻¹, corresponding to losses of 71 % and 78 %. XRPD shows that this major change coincides with crystallization of the amorphous material into metastable hexagonal YAH. The increase in bulk density to 0.274 g cm⁻³ in section 3.1.1 further indicates densification of the aerogel network, accompanied by coarsening and loss of smaller pores. Thus, the main textural collapse occurs during YAH formation rather than during the later transformation to YAG, which is completed at 1000 °C.

Above 900 °C the behavior changes markedly. Between 900 and 1000 °C the surface area falls only from 86.45 to 65.36 m² g⁻¹, a further reduction of 24 %, and the pore volume from 0.5093 to 0.3814 cm³ g⁻¹. Over this same interval the material completes the YAH → YAG transformation and reaches phase purity, and the crystallite size grows to 29.3 ± 5.0 nm (Section 3.1.2); yet the textural parameters change by a comparatively modest amount. The reason is that the two intervals are governed by different densification mechanisms. Once a continuous crystalline framework has been established, viscous flow is no longer available and further coarsening must proceed by solid-state diffusion, which is orders of magnitude slower at these temperatures. Crystallization therefore stabilizes the surviving mesoporous architecture rather than destroying it, and this is the practical reason why a phase-pure, high-surface-area YAG:Cr³⁺ powder can be obtained from this route at all.

The micropore volume decreases monotonically from 0.0757 cm³ g⁻¹ in the green body to 0.0197 cm³ g⁻¹ at 1000 °C, a reduction of 74 %, indicating that the narrowest pores are progressively sealed by heat-induced atomic rearrangement. It is worth noting, however, that micropores never account for more than about 5 % of the total pore volume in any of the samples, and that their relative contribution remains essentially constant across the series (3.3 % in the green body, 5.2 % at 1000 °C). The textural evolution of this material is therefore governed almost entirely by the mesopore network; the loss of surface area cannot be attributed to the closure of microporosity alone.

The average pore diameter d_{avg} behaves non-monotonically: it decreases from 37.7 nm in the green body to 35.2 nm at 900 °C, then rises again to 37.7 nm at 950 °C and 39.2 nm at 1000 °C. This apparent widening of the pores with increasing temperature is counter-intuitive. The quantity reported is not a mode of the pore-size distribution but a ratio of two cumulative quantities, computed on the assumption of an array of uniform, non-intersecting cylindrical pores:

$$d_{avg} = \frac{4V_p}{S_{BJH}} \quad (15)$$

where V is the cumulative BJH desorption pore volume and S the corresponding cumulative desorption surface area. Being an area-weighted mean, it responds to changes in the shape of the distribution as much as to uniform shrinkage of the pores. The initial decrease between the green body and 900 °C reflects the collapse of the widest and most fragile pores of the aerogel

skeleton, which carry a large share of the total volume. Above 900 °C the trend reverses: the narrower mesopores are eliminated preferentially by diffusion-driven neck growth, so that the surviving population becomes increasingly dominated by the larger and thermally more stable pores and the mean shifts upward to 39.2 nm at 1000 °C. The increase therefore reports the selective removal of small pores, not the growth of individual pores, and is a signature commonly observed in sintered aerogels.

A useful cross-check against the structural characterization is obtained by converting the BET surface area into the diameter of a non-porous sphere having the same specific surface area,

$$d_{\text{BET}} = \frac{6}{\rho S_{\text{BET}}} \quad (16)$$

where $\rho = 4.55 \text{ g cm}^{-3}$ is the theoretical density of YAG. For the 1000 °C sample this yields an equivalent particle diameter of approximately 20 nm, to be compared with the volume-weighted crystallite size of $29.3 \pm 5.0 \text{ nm}$ obtained from the Scherrer analysis in Section 3.1.2. The agreement in order of magnitude confirms that the powder consists of loosely connected nanocrystals rather than dense sintered agglomerates, in line with the morphology observed by SEM (Section 3.1.3) and HRTEM (Section 3.1.5). The fact that the equivalent BET diameter lies somewhat below the crystallite size shows that part of the measured area is internal — porosity retained within and between the crystallites — which is exactly what the residual pore volume of $0.3814 \text{ cm}^3 \text{ g}^{-1}$ quantifies.

Taken together, these measurements establish that the severe thermal treatment required to crystallize phase-pure YAG does not collapse the material into a dense solid. After calcination at 1000 °C the powder retains a specific surface area of $65.36 \text{ m}^2 \text{ g}^{-1}$ and a pore volume of $0.3814 \text{ cm}^3 \text{ g}^{-1}$ — 22 % and 17 % of the green-body values respectively — within a mesoporous framework whose characteristic dimension remains a few tens of nanometers. This outcome is significant in two distinct respects.

3.2 Optical investigation

3.2.1 Room-temperature PL and PLE analysis

The optical properties of the YAG:Cr³⁺ aerogels were first examined at room temperature by steady-state photoluminescence (PL) and photoluminescence excitation (PLE) measurements using the 1 mol% Cr sample annealed at 1000 °C. The PL spectrum was recorded under excitation at 450 nm, corresponding to the $^4\text{A}_2 \rightarrow ^4\text{T}_1$ absorption band of Cr³⁺. PLE spectra were recorded monitoring the emission at 687, 704, and 750 nm, covering the main Cr³⁺ emission region from the sharp $^2\text{E} \rightarrow ^4\text{A}_2$ *R*-line to the longer-wavelength phonon sidebands. The PL and PLE spectra are shown in Figure 3.12.

The PLE spectrum shows two broad excitation bands, the first with a barycenter at 440 nm and the second centered at 606 nm. They are assigned to the spin-allowed $^4\text{A}_2 \rightarrow ^4\text{T}_1$ and $^4\text{A}_2 \rightarrow ^4\text{T}_2$ transitions of octahedrally coordinated Cr³⁺. Converted to wavenumbers, the bands lie at $22\,727$ and $16\,502 \text{ cm}^{-1}$, giving a separation of $\Delta E = 6226 \text{ cm}^{-1}$ between the two ^4T states.

The energy levels of a d^3 ion in an octahedral environment are described by three parameters. The crystal-field strength Dq measures how strongly the ligand field splits the 3d orbitals, and $10Dq$ (Equation 17) is the energy gap between the t_{2g} and e_g sets. The Racah parameters B and C describe the electron–electron repulsion within the 3d shell: B governs the separation between terms of the same spin multiplicity and is the parameter most sensitive to covalency, while C is needed in addition to B to place the spin-forbidden doublet states such as ^2E . All three can be extracted directly from the spectroscopic analysis.

The $^4T_2$ band position is a direct measure of the crystal-field splitting,

$$10Dq = E(^4T_2) \quad (17)$$

which gives $Dq = 1650 \text{ cm}^{-1}$. B follows from the separation of the two spin-allowed bands through the standard relation

$$\frac{B}{Dq} = \frac{\left(\frac{\Delta E}{Dq}\right)^2 - 10\left(\frac{\Delta E}{Dq}\right)}{15\left(\frac{\Delta E}{Dq} - 8\right)} \quad (18)$$

where $\Delta E = E(^4T_1) - E(^4T_2)$ is the separation between the two spin-allowed bands.

With $\Delta E/Dq = 3.77$, this yields $B/Dq = 0.371$, so $B = 611 \text{ cm}^{-1}$ and $Dq/B = 2.70$. C is then obtained from the position of the spin-forbidden ^2E level, which appears at 687 nm (14 556 cm^{-1}), using:

$$\frac{E(^2E)}{B} = 3.05 \frac{C}{B} + 7.9 - 1.8 \frac{B}{Dq} \quad (19)$$

rearranged as:

$$C = \frac{E(^2E) - 7.9B + 1.8 \frac{B^2}{Dq}}{3.05} \quad (20)$$

which gives $C = 3323 \text{ cm}^{-1}$ and $C/B = 5.43$.

These values agree with those reported for Cr^{3+} at the Al^{3+} octahedral site in YAG [51]. The reduction of B relative to the free-ion value of about 918 cm^{-1} reflects the covalency of the Cr–O bond in the garnet lattice, while $Dq/B = 2.69$ places the ion firmly in the strong-field region of the Tanabe–Sugano diagram, where ^2E lies below $^4T_2$.

This crystal-field strength is what makes the material usable as a Boltzmann thermometer: ^2E is the lowest excited state, but $^4T_2$ sits close enough above it that thermal population of the broad band becomes appreciable on heating, producing the two-channel emission analyzed in the following section.

The PL spectrum recorded under 450 nm excitation contains strong, narrow emission features centered at approximately 687.6, 706 nm and other minor peaks assigned to the $^2E \rightarrow ^4A_2$ R -line emission of Cr^{3+} in YAG and its sidebands, respectively. In addition to the sharp R -line emission, weaker vibronic features extend toward longer wavelengths, from about 700 to 800

nm. These bands arise from coupling between the Cr^{3+} electronic transition and lattice vibrations of the YAG host.

At room temperature, the broad ${}^4\text{T}_2 \rightarrow {}^4\text{A}_2$ emission is much weaker than the sharp ${}^2\text{E} \rightarrow {}^4\text{A}_2$ emission and cannot be clearly separated in the spectrum under the present measurement conditions. Its contribution becomes more evident as the temperature increases and is discussed in the temperature-dependent PL analysis in Section 3.2.2.

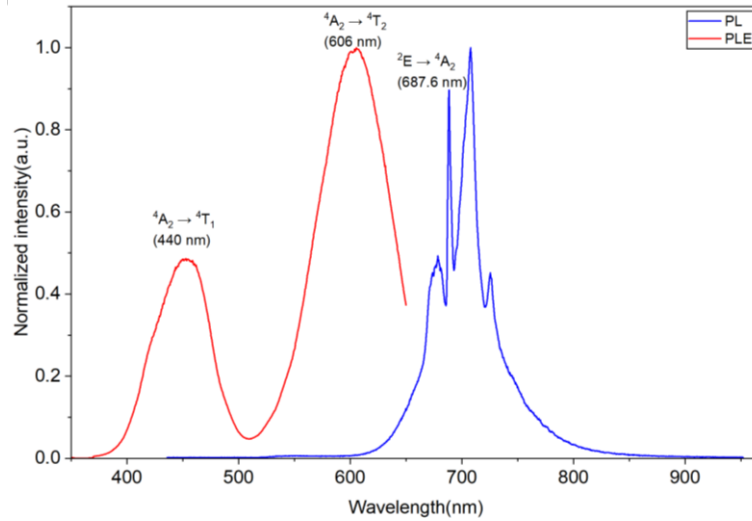


Figure 3.12: Room-temperature PL and PLE spectra of the 1 mol% Cr^{3+} YAG sample annealed at 1000 °C.

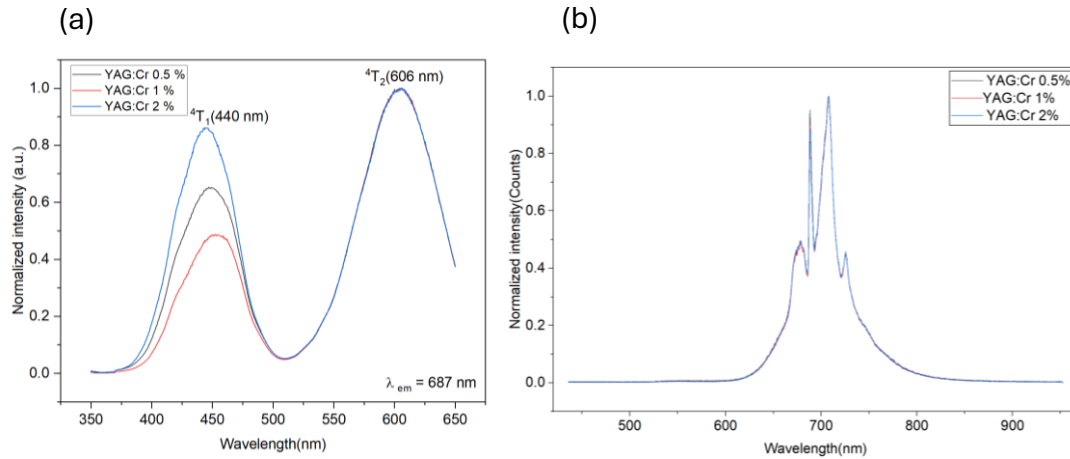


Figure 3.13: Normalized (a) PLE and (b) PL spectra of the 0.5, 1, and 2 mol% Cr^{3+} YAG samples monitored at 687 nm.

The effect of Cr^{3+} concentration on the PLE spectrum was also examined for samples containing 0.5, 1, and 2 mol% Cr by monitoring the emission at 687 nm, as shown in Figure 3.13 (a). The overall shape and position of the two main excitation bands remain similar for all three compositions. The ${}^4\text{A}_2 \rightarrow {}^4\text{T}_1$ band occurs between approximately 440 and 454 nm, while the ${}^4\text{A}_2 \rightarrow {}^4\text{T}_2$ band remains near 605–606 nm. Within the experimental uncertainty, no clear shift of either excitation band is observed with increasing Cr^{3+} concentration. Figure 3.13(b) shows normalized PL spectra of three different concentrations without change in the

position of the peaks related to ^2E and its side bands. This suggests that the average local crystal-field environment around Cr^{3+} remains similar over the investigated concentration range. The absence of a measurable shift in the PLE band positions also allows the temperature-dependent optical response of the different Cr^{3+} concentrations to be compared using the same electronic-state assignments.

3.2.2 PL temperature dependence

Temperature-dependent emission spectra were recorded for the 1 mol% Cr^{3+} powder annealed at 1000 °C, using the Linkam THMS600 stage. The sample was held in the stage over the interval -150 to 600 °C, the temperature being changed between setpoints at a controlled rate of 20 °C min^{-1} and held for 2 min at each setpoint before acquisition, so that the powder and the stage block were thermally equilibrated before the spectrum was taken. Liquid nitrogen was used for the sub-ambient part of the series.

Spectra were collected with a 300 gr mm^{-1} grating blazed at 500 nm, chosen so that the full emission envelope — from the anti-Stokes side of the R-line to the long-wavelength tail of the $^4T_2$ band. The integration time was 1 s, with the detector operated in high-capacity mode at gain 3, and the emission slit set to the smallest available width to preserve as much spectral resolution as the grating allows. Excitation was provided by the 405 nm source, with the excitation power adjusted for each sample so that the strongest feature in the low-temperature spectrum remained within the linear response range of the detector; the power was then held constant throughout a given temperature series. Because the thermometric analysis in the following sections is based on an intensity ratio between two features of the same spectrum, the absolute excitation power does not affect the result, but keeping it fixed within a series avoids any drift in the relative band shapes.

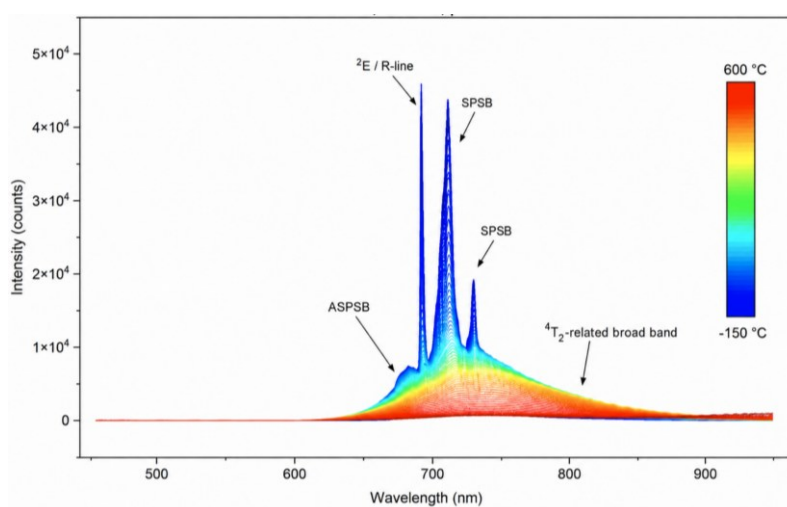


Figure 3.14: Temperature-dependent emission spectra of aerogel-derived $\text{YAG}:\text{Cr}^{3+}$ (1 mol%, annealed at 1000 °C), recorded from -150 °C to 600 °C under 442 nm excitation. The colour scale runs from blue (-150 °C) to red (600 °C). Labelled features: the $^2E \rightarrow ^4T_2$

As it can be seen in Figure 3.14, the low-temperature spectrum is dominated by the sharp ${}^2E \rightarrow {}^4A_2$ *R*-line. On the long-wavelength side, Stokes phonon sidebands are observed near 707 and 724 nm, while a weaker anti-Stokes sideband appears near 678 nm. Similar features have been reported for YAG:Cr³⁺, with Stokes sidebands at 708 and 725 nm and an anti-Stokes sideband at 675 nm [29]. Stokes sidebands involve the emission of lattice phonons, whereas anti-Stokes sidebands involve phonon absorption and therefore become more pronounced as the temperature increases [51]. The strength of these vibronic features is related to electron–phonon coupling. For Cr³⁺, this coupling has been reported to be weaker in YAG than in YGG, which has been attributed to the lower covalency of the aluminate host [39]. A much weaker anti-Stokes sideband (ASPSB) appears on the short-wavelength side of the *R*-line near 678 nm; this feature requires the absorption of a phonon from an already thermally populated mode, so it is barely visible at –150 °C and grows steadily as the temperature rises.

As the temperature increases, the sharp ${}^2E$ -related features broaden and decrease in relative intensity [44]. At the same time, a broad ${}^4T_2 \rightarrow {}^4A_2$ emission band develops because of thermal population of the ${}^4T_2$ state [51]. In the present sample, this broad band is centered approximately in the 730–750 nm region and becomes the main contribution above about 300 °C. At the highest temperatures, the total emission intensity also decreases, indicating thermal quenching. Thermally activated non-radiative relaxation may contribute to this decrease.

The redistribution of intensity between the sharp and broad features is a physically important observation. The ${}^4T_2$ state lies a few hundred wavenumbers above ${}^2E$ in this host, so at low temperature it is essentially unpopulated and all emission proceeds through the long-lived ${}^2E$ level. As $k_B T$ becomes comparable to the ${}^4T_2$ – ${}^2E$ separation, thermal population of ${}^4T_2$ becomes significant, and because the ${}^4T_2 \rightarrow {}^4A_2$ transition is spin-allowed its radiative rate is orders of magnitude larger than that of ${}^2E \rightarrow {}^4A_2$. A modest fractional population of ${}^4T_2$ therefore produces a disproportionately large contribution to the emitted intensity, which is why the broad band overtakes the *R*-line group well before the two states are equally populated. Provided the two states remain in fast thermal equilibrium, the ratio of their emitted intensities follows the Boltzmann distribution, and this is what makes the material a self-referencing ratiometric thermometer. The quantitative treatment of this ratio, including the spectral deconvolution required to separate the two contributions, is presented in Section 3.2.5.

Two points are important for the analysis that follows. Below about 0 °C, the ${}^4T_2$ contribution is very weak compared with the sharp ${}^2E$ -related emission. In this region, the integrated area of the broadband becomes difficult to determine accurately from the spectral fit. For this reason, the lowest-temperature data were not included in the Boltzmann calibration. At higher temperatures, the sharp emission features remain visible over a broad temperature range, allowing both the ${}^2E$ and ${}^4T_2$ contributions to be followed during heating. These two limits define the temperature range used for the *LIR* analysis.

The spectra also give information about the quality of the YAG:Cr³⁺ obtained by the aerogel route. The position of the *R*-line, the presence of the phonon sidebands, and the increase of the broad ${}^4T_2$ emission with temperature is all consistent with Cr³⁺ incorporated in a crystalline YAG host. This agrees with the structural results in Section 3.1, where the sample annealed at

1000 °C was identified as cubic YAG. The optical results therefore support the conclusion that the supercritical drying and subsequent heat treatment produce a well-crystallized YAG:Cr³⁺ material.

3.2.3 Temperature-dependent photoluminescence: powder and monolith

Temperature-dependent emission measurements were carried out on the 1 mol% Cr³⁺ sample annealed at 1000 °C, using both ground powder and an intact monolith. The powder measurements covered the temperature range from –150 to 600 °C, while the monolith was measured from –100 to 600 °C. In both cases, the same excitation system was settled. The corresponding spectra are shown in Figures 3.15 (a and b).

Different temperature-control procedures were used for the powder and the monolith because of their different thermal behavior. In the Linkam THMS600 stage, the sample is heated by conduction from the block underneath it, while the control thermocouple measures the temperature of the heating block rather than the temperature directly inside the sample. For a thin powder layer, thermal equilibration is relatively fast, and measurements were therefore performed using a heating rate of 20 °C min⁻¹ with a dwell time of 2 min at each temperature.

The monolithic sample was approximately 2 mm thick and required a slower heating procedure. Because of the low thermal conductivity of the porous aerogel-derived material, the temperature at the upper surface may differ from that of the heating block. This is particularly important because luminescence was collected from the upper surface, which is furthest from the heat source. A temperature gradient through the monolith can therefore influence the measured luminescence intensity ratio. For this reason, the heating rate was reduced to 3.3 °C min⁻¹ and the sample was held at each temperature for 20 min before acquisition. This longer equilibration time was used to reduce transient temperature differences within the sample and to obtain a more stable optical signal. The PL of monolithic and powder are shown in Figure 3.15 a,b.

The longer dwell time reduces temperature changes associated with heating or cooling, although a small steady-state temperature gradient may remain across the monolith. Heat is continuously lost from the exposed surface through convection and thermal radiation and must be transferred through the sample from the heating stage. Because of the low thermal conductivity and finite thickness of the monolith, the actual temperature of the measured surface may therefore differ slightly from the temperature indicated by the stage, particularly toward the limits of the investigated temperature range. This possible difference should be considered when interpreting the absolute temperature calibration of the monolithic sample.

Figure 3.16 (a) compares the PL spectra at 100 °C of the powder and the monolith annealed at 1000 °C, both normalized to their maximum near 708 nm. The two samples show the same Cr³⁺ emission features, but the balance between the sharp and broad components is different.

The origin of this difference was examined by deconvoluting both series with the same model and the same integration limits, so that the results could be compared directly. The ²E–⁴T₂ separation obtained from the same deconvolution is 860 ± 15 cm⁻¹ for the powder and 851 ±

42 cm^{-1} from 0°C to 400°C (Figure 3.16 b) for the monolith, in agreement within the uncertainties, and the corresponding relative sensitivities at 300 K are 1.38 and 1.36 % K^{-1} .

The difference lies instead in the position of the $^4\text{T}_2$ band. At 0 °C it is centred at 711 nm in the powder and at 698 nm in the monolith, a separation of about 260 cm^{-1} , and on heating it red-shifts more than three times faster in the powder, 0.044 nm K^{-1} against 0.013 nm K^{-1} . The width of the band behaves almost identically in the two samples, the fitted effective phonon energies being 929 and 903 cm^{-1} . The $^4\text{T}_2$ minimum in the powder is thus displaced further along the configurational coordinate and couples more strongly to the lattice, which broadens the emission and extends it to longer wavelengths without altering the $^2\text{E}-^4\text{T}_2$ separation. This accounts for both the weaker apparent *R*-line and the longer red tail seen in Figure 3.15.

The two forms therefore share the same thermometric parameters but not the same emission profile, and each requires its own *LIR* calibration. This is probably due to the different average temperature in the powder and monolithic samples; the fact that the curves are parallel suggests that the monolithic sample experiences an apparent lower temperature with respect to the powder due to the different thermalization in the stage. Waiting for a longer time could have been led to the same results.

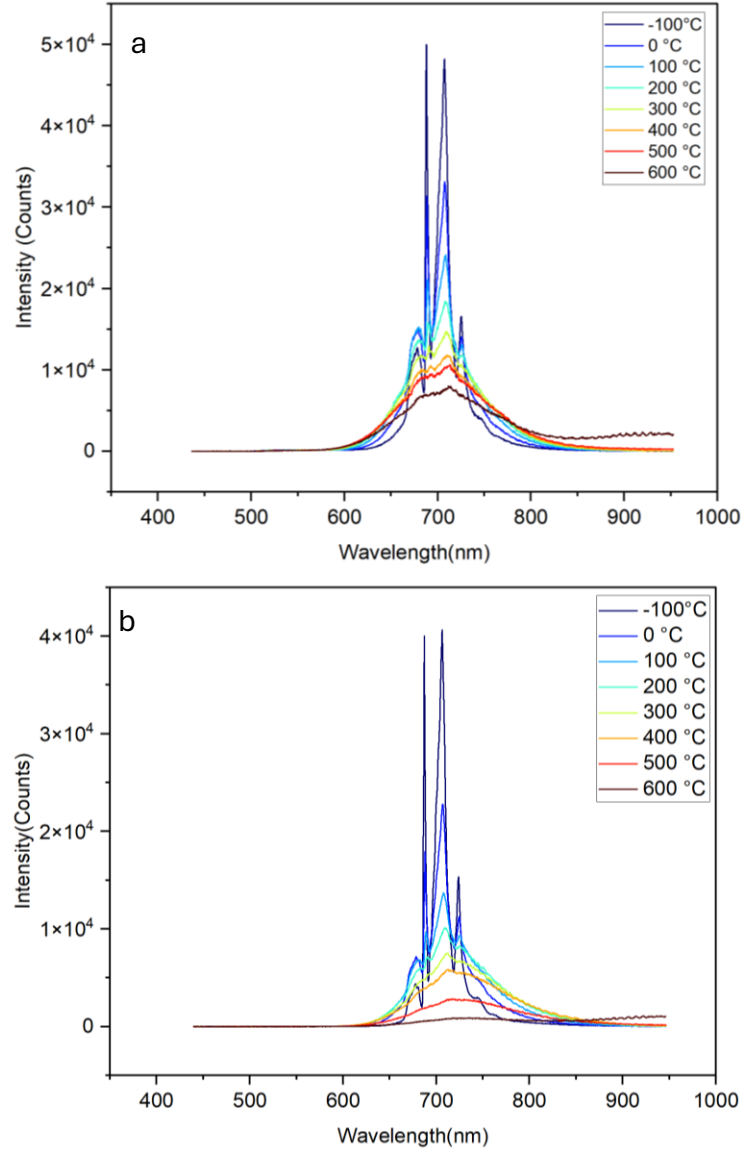


Figure 3.15: Temperature-dependent emission spectra of the 1 mol% Cr^{3+} YAG sample measured as (a) intact monolith and (b) powder under same excitation.

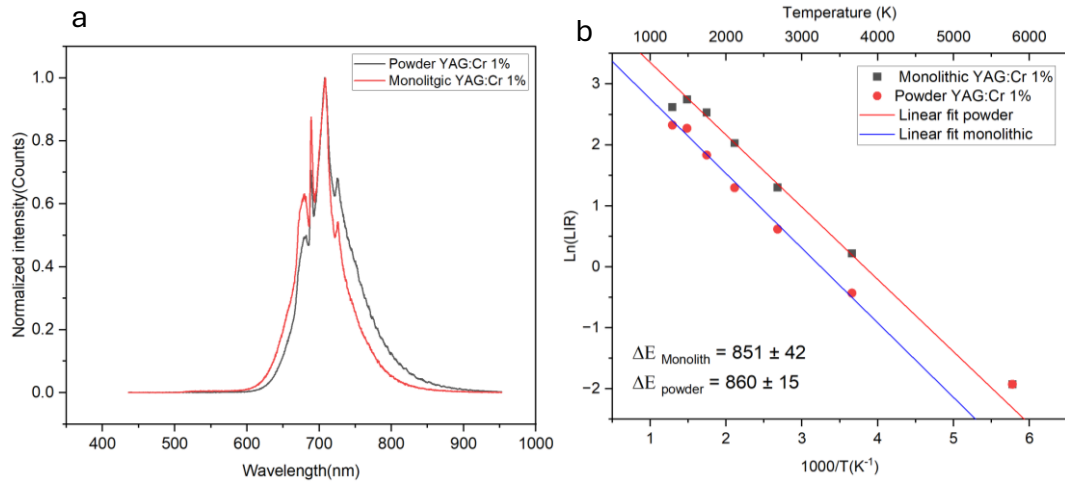


Figure 3.16: (a) Normalized plot between two forms of YAG:Cr^{3+} , 1000°C at 100°C (b) Arrhenius representation of $\ln(\text{LIR})$

3.2.4 Spectral deconvolution

The reduced model used in section 3.2.3 treats the whole ${}^2E$ manifold as one fixed profile, taken from the coldest measured spectrum and simply scaled, broadened and shifted with temperature. This is what made the powder and the monolith directly comparable, since neither sample imposes its vibronic structure on the other. But it also means the R_1 line and its sidebands are never separated: the model gives the integrated ${}^2E$ and ${}^4T_2$ areas and nothing more.

That is not enough for what follows. The sidebands are needed individually their temperature dependence carries the electron–phonon coupling, and the anti-Stokes-to- R_1 ratio provides the second thermometric mechanism of Section 3.2.5. The powder was measured at 69 temperatures in 10 °C steps, which easily supports a more detailed fit. The full series was therefore decomposed into nine Gaussians, resolving each vibronic component separately. Where the two models overlap they agree, giving ΔE values within about 4% of each other.

The ${}^2E$ R -line, its phonon sidebands, and the broad ${}^4T_2$ emission overlap strongly, especially at intermediate and high temperatures. Direct integration of fixed wavelength regions would therefore lead to contributions from more than one emission component. To separate these contributions, each spectrum was fitted using nine Gaussian functions.

Six Gaussians were used for the phonon sidebands of the ${}^2E \rightarrow {}^4A_2$ transition. These included two anti-Stokes sidebands, centered near 671 and 678 nm, and four Stokes sidebands centered near 699, 707, 713, and 725 nm. The six sidebands were fitted using a fixed FWHM.

The R_1 line was fitted separately using a narrow Gaussian with an independent FWHM. This allowed the R -line to remain considerably narrower than the phonon sidebands.

The broad ${}^4T_2 \rightarrow {}^4A_2$ emission was described using two Gaussian components. The first broad component was centered between approximately 700 and 730 nm, while the second described the longer-wavelength part of the band between approximately 730 and 760 nm. Two broad components were required because the ${}^4T_2$ emission is asymmetric and cannot be described satisfactorily by a single Gaussian over the full spectral range.

In total, the fitting model contained 22 adjustable parameters. The spectra were fitted over the 660–790 nm range using the same parameter limits at every temperature. The spectrum recorded at 60 °C was used as the starting point because both the sharp ${}^2E$ -related emission and the broad ${}^4T_2$ contribution is clearly present at this temperature. The fitted parameters obtained at 60 °C were then used as initial values for the neighboring temperatures, proceeding separately toward higher and lower temperatures.

This procedure reduced abrupt variations between consecutive fits and provided a consistent description of the spectra over the complete temperature range.

The nine-Gaussian model reproduces the measured spectra well over most of the investigated temperature range. The coefficient of determination is generally higher than 0.99 and exceeds 0.995 between approximately –30 and 400 °C, where the signal-to-noise ratio is highest. Representative fits at –80, 0, 100, 300, and 600 °C are shown in Figure 3.17.

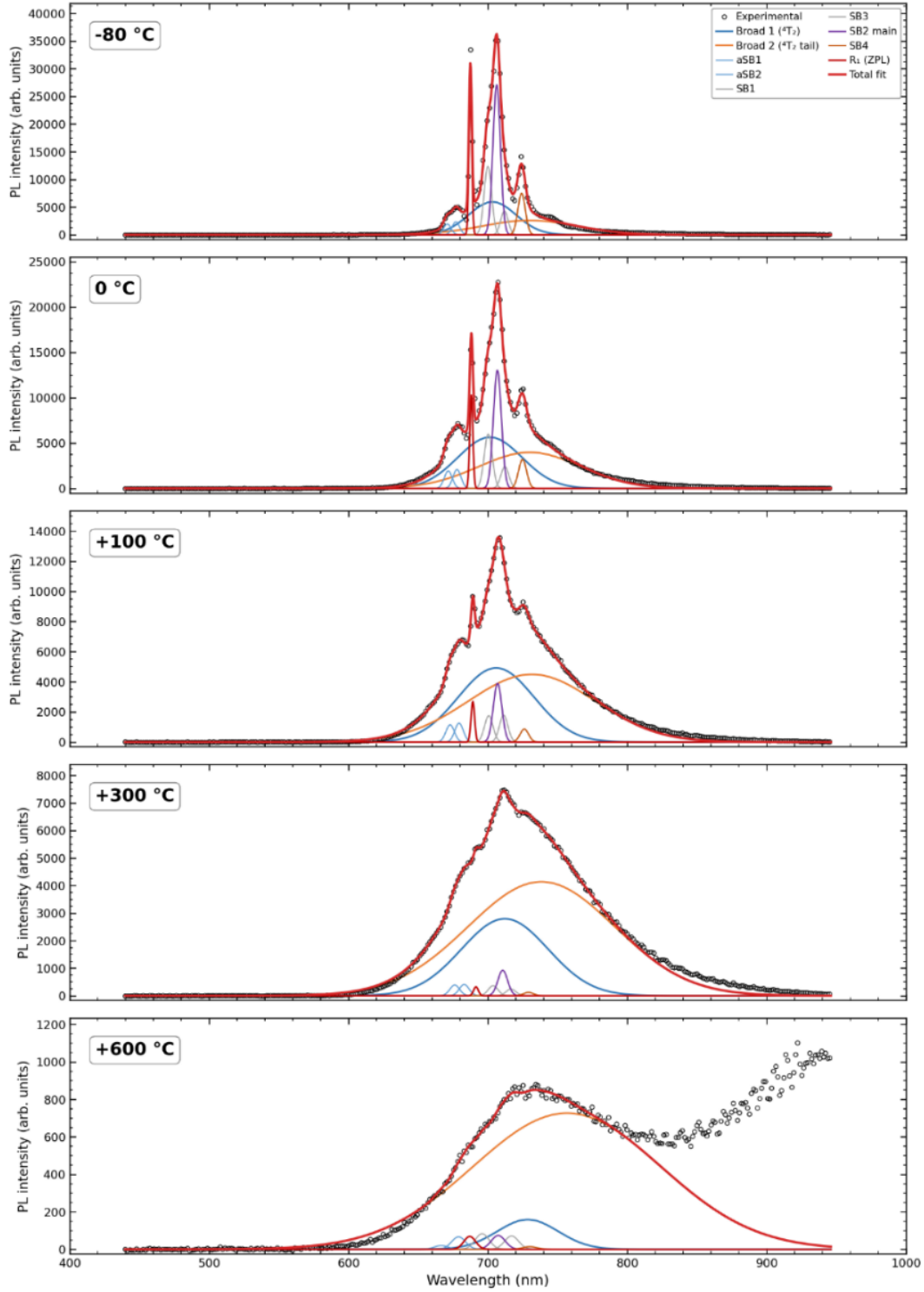


Figure 3.17: Representative nine-Gaussian fits of the YAG:Cr³⁺ emission spectra at selected temperatures.

At the lowest temperatures, between -80 and -30 °C, the R^2 values decrease slightly to approximately 0.990 – 0.995 . In this region, the R_l line becomes very narrow and approaches

the spectral resolution of the measurement. Its shape is also not perfectly described by a Gaussian function. The deviations are mainly confined to the R -line region and have a smaller effect on the broad ${}^4T_2$ contribution, which extends over a wider wavelength range.

At temperatures above approximately 400 °C, the R_1 contribution becomes very small compared with the broad ${}^4T_2$ emission. The uncertainty associated with the fitted R_1 parameters therefore increases at high temperature. In contrast, the broad-band areas remain well defined because they account for most of the measured emission.

The fitted areas of the broad components can therefore be followed over the complete temperature range, while the ${}^2E$ contribution is determined most accurately in the low- and intermediate-temperature region. The integrated areas returned by the 9-Gaussian deconvolution were grouped into four quantities: ZPL (R_1 area), ASPSB ($aSB1 + aSB2$), SPSB ($SB1 + SB2 + SB3 + SB4$), and Total (sum of the seven ${}^2E$ components). Their change during temperature range (-150 to 600) can be seen in Figure 3.18.

ZPL and SPSB both decrease monotonically from 2.7 to 0.5 units and from 14 to 3 units respectively reflecting the thermal depopulation of ${}^2E$ towards ${}^4T_2$. Their ratio SPSB/ZPL stays roughly constant, confirming that the Stokes sidebands share the same electronic origin as R_1 (Figure 3.18). The different temperature behavior of the anti-Stokes phonon sideband can be explained by considering the thermal population of phonons. The average number of phonons with energy $\hbar\omega$ is given by the Bose–Einstein distribution, (21) for the ${}^2E$ depletion. The Bose–Einstein occupation factor describes the average population of a phonon mode with energy $\hbar\omega$ at a given temperature T . Here, $\hbar$ is the reduced Planck constant, ω is the phonon angular frequency, k_B is the Boltzmann constant, and T is the absolute temperature.

This relation is particularly relevant for the anti-Stokes phonon sideband, since an anti-Stokes transition requires the absorption of a phonon that is already thermally populated in the crystal. At low temperatures, the phonon population is small and, consequently, anti-Stokes transitions are less probable. As the temperature increases, the phonon population also increases, enhancing the probability of phonon-assisted anti-Stokes transitions.

$$n(\hbar\omega) = \frac{1}{\exp\left(\frac{\hbar\omega}{k_B T}\right) - 1} \quad (21)$$

In the high-temperature limit, where $k_B T \gg \hbar\omega$, the Bose–Einstein occupation factor can be approximated as:

$$n(\hbar\omega) \approx \frac{k_B T}{\hbar\omega} \quad (22)$$

Under these conditions, the phonon population increases approximately linearly with temperature. This temperature-dependent increase in phonon occupation helps explain the

different behavior of the anti-Stokes phonon sideband compared with the zero-phonon line and the Stokes phonon sideband.

The Total intensity of ${}^2E$ falls smoothly from 18 to 5 units in the same interval. This decrease of the ${}^2E$ manifold, together with the concurrent growth of the ${}^4T_2$ broadband, produces the strong temperature dependence of the *LIR* analyzed in Section 3.2.5.

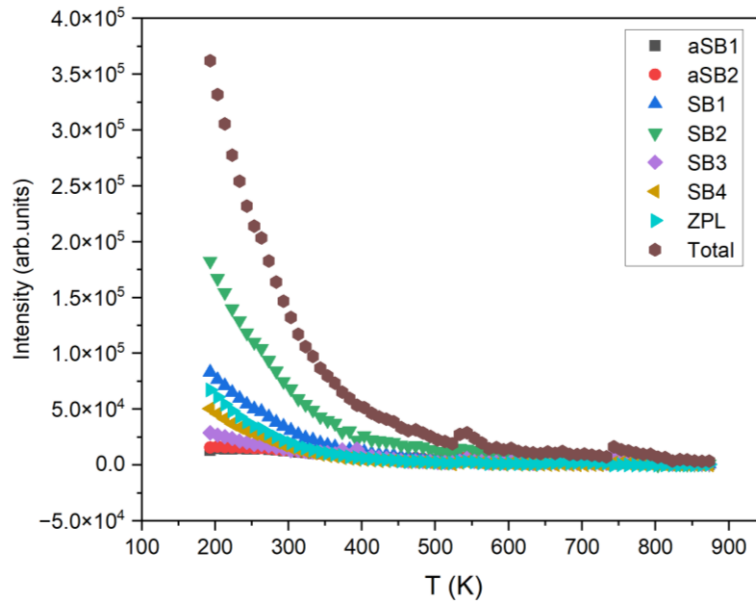


Figure 3.18: Temperature dependence of the fitted ${}^2E$ emission components obtained from the nine-Gaussian spectral deconvolution

3.2.5 Luminescence intensity ratio and Boltzmann analysis in high temperatures

The luminescence intensity ratio was calculated from the areas obtained from the Gaussian fitting. The total ${}^4T_2$ contribution was taken as the sum of Broad 1 and Broad 2, while the ${}^2E$ contribution was calculated from the R_1 line together with the six phonon sidebands. The LIR_{TE} was therefore defined as mentioned in formula (6). Using the complete ${}^2E$ emission contribution, rather than only the R_1 -line, avoids dependence on an arbitrary choice of individual sidebands. Similar approaches have been used for Cr^{3+} -based thermometers reported in the literature [40, 43, 44]. The Boltzmann constant was expressed in spectroscopic units as, allowing the fitted energy separation to be obtained directly in cm^{-1} .

Figure 3.19a shows the Arrhenius representation of $\ln(LIR_{TE})$ as a function of $1000/T$. The data are approximately linear between 293.15 K and 453.15 K, while deviations become more pronounced outside this interval.

At temperatures above approximately 473.15 K (200 °C), the simple Boltzmann model no longer describes the experimental data as closely. At these temperatures, thermal quenching and other non-radiative processes may contribute to the population and depopulation of the excited states. At low temperatures, below approximately 293.15K (20 °C), the $^4T_2$ contribution becomes relatively weak. At -80 °C, for example, its fitted area is only about 10% of the R_1 contribution, which increases the relative uncertainty associated with the broad-band area.

For these reasons, the Boltzmann fit was performed over the 293.15 K and 453.15K (20–180 °C) interval, where the Arrhenius plot shows the best linearity. The linear least-squares fit gives:

$$\Delta E = 890 \pm 10 \text{ cm}^{-1} (R^2 = 0.9986)$$

The value $\Delta E = 890 \pm 10 \text{ cm}^{-1}$ obtained here is between the reported ranges (from 800 to 1000 cm^{-1}) for YAG:Cr³⁺. The relative sensitivity at 100 °C (0.92 % K⁻¹) remains comparable to that of single-crystal YAG:Cr³⁺ and the good linearity obtained between 293.15 K and 453.15 K (20 and 180 °C) indicates that the temperature dependence of the ^2E and $^4T_2$ populations can be described well by the Boltzmann law within this interval. Outside this range, the increasing deviation from linearity suggests that additional processes should be considered [54-56].

The Boltzmann fit (Figure 3.19(a)) was carried out over the range 293.15 to 453.15 K where the Arrhenius plot is most linear. Extending the upper bound to 463.15 K (190 °C) leaves the extracted ΔE essentially unchanged (878 ± 12 vs $890 \pm 10 \text{ cm}^{-1}$), while extending the lower bound below 293.15 K (20 °C) produces a gradual decrease of the fitted slope. The decrease with lower bound reflects the increasing relative uncertainty of the $^4T_2$ area at temperatures where the broadband contributes less than 15 % of the total emission and is not associated with a real change in the electronic gap. For this reason, the 293.16 - 453.15 K interval is adopted as the primary fitting range, and the value $\Delta E = 890 \pm 10 \text{ cm}^{-1}$ is reported as the intrinsic ^2E – $^4T_2$ energy gap

The relative thermal sensitivity S_r of the 1 mol% Cr³⁺ sample reaches approximately 1.39 %·K⁻¹ at 30 °C and decreases to approximately 0.72 %·K⁻¹ at 150 °C, as shown in Figure 3.19b and reported in Table 3.4. At 100 °C, the calculated relative sensitivity is approximately 0.92 %·K⁻¹.

These values are comparable to those reported for other Cr³⁺-based Boltzmann thermometers, measured based on lifetime temperature dependent both in single-crystal YAG:Cr³⁺ (~1 % K⁻¹ at room temperature)[47] and in Cr³⁺-doped nanocrystalline garnets (0.8–1 % K⁻¹ around room temperature)[31]. The methodological framework and the sensitivity range are also consistent with the values reported for the analogous Bi₂Ga₄O₉:Cr³⁺ system by the same Gaussian

deconvolution approach [40]. Because k_B and T^2 are the same for all these hosts, the small differences in S_r reflect only the differences in ΔE , which follow the crystal-field trends.

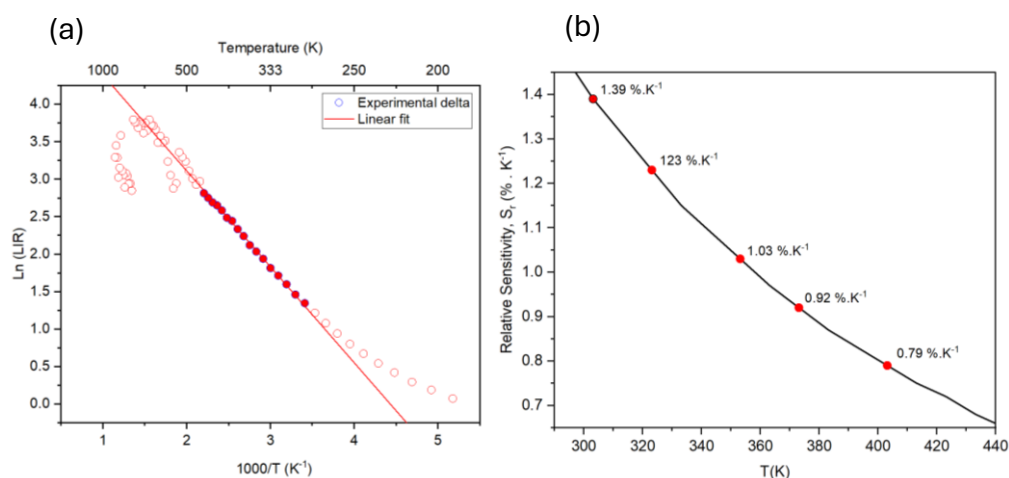


Figure 3.19: (a) Arrhenius representation of $\ln(LIR)$ and (b) relative thermal sensitivity of the 1 mol% Cr^{3+} YAG sample over the selected Boltzmann-fit interval.

Table 3.4. relative and absolute sensitivities of the 1 mol % Cr sample in the 30–150 °C linear range

T (°C)	T (K)	S_r (% K^{-1})	S_a ($\times 10^{-3} K^{-1}$)
20	293.15	1.49	59.9)
30	303.15	1.39	59.3
40	313.15	1.31	63.6
50	323.15	1.23	67.8
60	333.15	1.15	71.9
70	343.15	1.09	75.8
80	353.15	1.03	79.5
90	363.15	0.97	83.1
100	373.15	0.92	86.5
110	383.15	0.87	89.7
120	393.15	0.83	92.8
130	403.15	0.79	95.7
140	413.15	0.75	98.4
150	423.15	0.72	100.9
160	433.15	0.68	100.5
170	443.5	0.65	102.1
180	453.15	0.62	103.9

3.2.6 Low temperature ratiometric thermometry: Stokes/anti-Stokes phonon sidebands

The ${}^4T_2/{}^2E$ Boltzmann analysis described in the previous subsections is reliable only when both spectral contributions can be determined with sufficient precision. In the 1 mol% Cr^{3+} sample, the broad ${}^4T_2$ emission becomes very weak below 0 °C. The global nine-Gaussian fit can still reproduce the spectrum well in this region, but the uncertainty of the small ${}^4T_2$ area becomes large compared with its fitted value. For this reason, the ${}^4T_2/{}^2E$ ratio is not used as the main low-temperature thermometric parameter. The same spectra, however, contain a second temperature-dependent signal to be used: the anti-Stokes and Stokes phonon sidebands of the ${}^2E \rightarrow {}^4A_2$ transition.

The use of these sidebands for thermometry is supported by recent work on d^3 transition-metal ions. Wang et al. used Stokes and anti-Stokes sidebands of Cr^{3+} in $BaAl_4Sb_2O_{12}$ to construct a ratiometric thermometer and reported a maximum relative sensitivity of 3.12% K^{-1} at 150 K [55]. However, the SPSB and ASPSB were not well-resolved and the equation used was improper. A related approach was reported for Mn^{4+} , which has the same d^3 electronic configuration, where the anti-Stokes/Stokes intensity ratio was used from cryogenic temperature toward room temperature [56], [57], [58]. These studies show that the phonon sidebands can provide a useful temperature readout when the higher electronic state used in a conventional Boltzmann ratio becomes too weak to measure accurately.

For a vibronic transition, the Stokes sideband is produced when a phonon is created during emission, whereas the anti-Stokes sideband requires the absorption of a phonon that is already present in the lattice. The temperature dependence therefore comes from the thermal occupation of the phonon mode. In the one-phonon approximation, the mean occupation number of a mode with energy ϵ_{ph} is given by the Bose–Einstein distribution:

$$\bar{n} = \frac{1}{\exp(\frac{\epsilon_{ph}}{k_B T}) - 1} \quad (23)$$

For the same phonon mode, the anti-Stokes contribution is proportional to $\bar{n}$, while the Stokes contribution is proportional to $\bar{n} + 1$ [58]. For a single matched phonon pair, their ratio therefore has an Arrhenius form. In the present analysis several sidebands are integrated together, so a prefactor C is retained to account for different sideband strengths, spectral response, and the fact that the numerator and denominator do not represent one single phonon mode:

$$LIR_{AS/S} = \frac{I_{AS}}{I_S} = C \frac{\bar{n}}{1 + \bar{n}} = C \exp(-\frac{\epsilon_{ph}}{k_B T}) \quad (24)$$

Here LIR denotes the phonon-sideband intensity ratio. The prefactor would approach unity only for an ideal pair of corresponding sidebands with the same coupling and detection factors. This point is important for the present YAG: Cr^{3+} spectra because two anti-Stokes components and four Stokes components are combined. The fitted energy should therefore be interpreted as an effective energy describing the sideband manifold rather than as the energy of one uniquely identified YAG normal mode.

No additional spectral fit is required for the low-temperature analysis. The six phonon-sideband Gaussians already obtained in Section 5.2.4 are used directly. The anti-Stokes intensity is defined as the sum of the fitted areas at approximately 671 and 678 nm, while the Stokes intensity is the sum of the fitted areas at approximately 699, 707, 713, and 725 nm:

$$I_{AS} = A_{671} + A_{678}$$

$$I_S = A_{699} + A_{707} + A_{713} + A_{725}$$

The R_1 zero-phonon line is excluded because it does not require phonon creation or annihilation, and the ${}^4T_2$ broadband is excluded because it belongs to a different electronic transition. Summing the sidebands on each side of R_1 also reduces the influence of small point-to-point changes in the area of an individual Gaussian. At the same time, this summation means that the result represents an effective phonon-sideband response. From the fitted wavelengths, the individual sideband offsets from R_1 cover several hundred cm^{-1} , so a single fitted energy cannot be assigned to only one of these components.

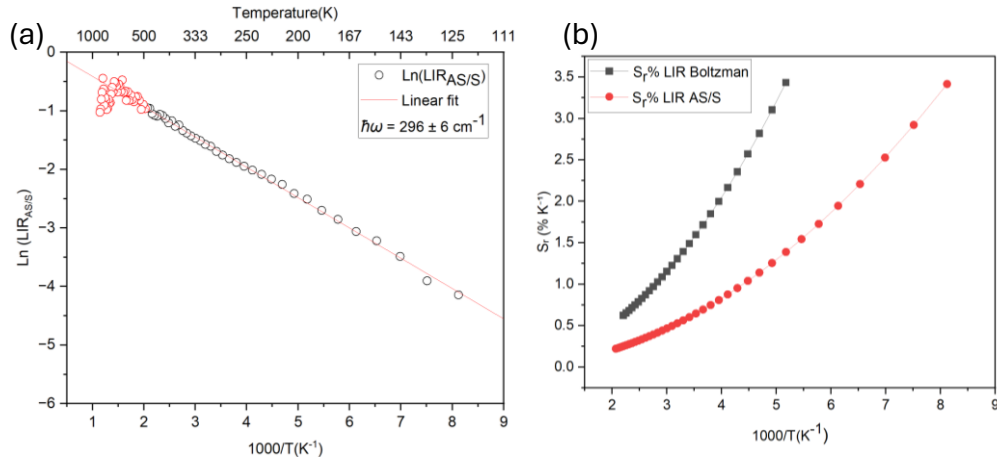


Figure 3.20: Low-temperature Boltzmann thermometry of YAG:Cr³⁺ 1 mol % aerogel powder based on the Stokes/anti-Stokes phonon-sideband LIR. (a) Bose–Einstein linear fit of $\ln(LIR)$ vs $1000/T$ over -150 to $+210$ °C gives $\hbar\omega = 296 \pm 6 \text{ cm}^{-1}$ ($R^2 = 0.996$). (b) Complementary S_r of the low- T sideband LIR and the high- T ${}^4T_2/{}^2E$ LIR, covering -150 to $+210$ °C.

Figure 3.20(a) shows $\ln(LIR_{AS/S})$ as a function of $1000/T$. The data remain close to a linear Arrhenius dependence from -150 to $+210$ °C. Above this range, the increasing contribution of the broad ${}^4T_2$ emission produces stronger overlap with the phonon-sideband envelope and the simple low-temperature relation becomes less reliable. A linear least-squares fit over -150 to $+210$ °C gives $LIR_{AS/S}(T) = 0.777 \cdot \exp(-296 \text{ cm}^{-1}/k_B T)$, with $R^2 = 0.9962$. In this notation k_B is expressed in spectroscopic units ($k_B/hc = 0.6950 \text{ cm}^{-1} \text{ K}^{-1}$). Equivalently, using $c_2 = hc/k_B = 1.4388 \text{ cm K}$, the fitted calibration can be written in a dimensionally explicit form as:

$$LIR_{AS/S}(T) = 0.777 \exp\left[-\frac{c_2 \times 296 \text{ cm}^{-1}}{T}\right] = 0.777 \exp(-425.9 \text{ K}/T) \quad (25)$$

The fitted value of $296 \pm 6 \text{ cm}^{-1}$ should be regarded as an effective phonon energy for the integrated sideband ratio rather than the frequency of one specific YAG normal mode. This distinction is important because the present $LIR_{AS/S}$ combines two anti-Stokes and four Stokes

components, so several lattice vibrations can contribute to the fitted value. A unique mode assignment would require an independent vibrational measurement, such as Raman or infrared spectroscopy, together with a mode-by-mode analysis of the sidebands.

Comparison with previous YAG:Cr³⁺ studies support this interpretation. Zhang and Grattan reported a strong *R*-line phonon sideband approximately 400 cm⁻¹ from the R₁ line [47]. When their temperature-dependent YAG:Cr³⁺ lifetime data were represented with a single effective phonon, they obtained $h\nu = 336 \text{ cm}^{-1}$ for the 288–550 K range. Extending the fit to 77–550 K gave a lower effective value of 191 cm⁻¹, which they attributed to the greater contribution of lower-energy phonons at low temperature. Shen and Bray [51] later derived an effective phonon density of states directly from the low-temperature Cr³⁺:YAG vibronic sideband and used an odd-parity phonon energy of about 400 cm⁻¹, corresponding to the most intense sideband feature, in their lifetime analysis. High-resolution spectroscopy by Nie et al.[43] also resolved several lower-energy phonon contributions in YAG:Cr³⁺, including features at 124, 142, 162, 184, and 196 cm⁻¹, and emphasized that several vibrational and multiphonon contributions can enter the sideband structure. The present value of $296 \pm 6 \text{ cm}^{-1}$ therefore lies within the range expected for Cr³⁺–lattice coupling in YAG and is close to the 336 cm⁻¹ effective value obtained from the lifetime analysis of Zhang and Grattan.

For the calibration in Equation (20), the relative and absolute sensitivities follow directly from the derivative of *LIR*. With $\varepsilon_{\text{ph}} = hc\tilde{\nu}_{\text{eff}}$, they are:

$$S_r(T) = \frac{1}{LIR} \left| \frac{d LIR}{dT} \right| = \frac{c_2 \tilde{\nu}_{\text{eff}}}{T^2} \quad (26)$$

$$S_a(T) = \left| \frac{d LIR}{dT} \right| = LIR(T) \frac{c_2 \tilde{\nu}_{\text{eff}}}{T^2} \quad (27)$$

The relative sensitivity reaches 2.81 %·K⁻¹ at –150 °C (123 K) and decreases with increasing temperature to 0.23 %·K⁻¹ at +200 °C. The absolute sensitivity shows a broad maximum near 213 K (about –60 °C), where the fitted model gives approximately $1 \times 10^{-3} \text{ K}^{-1}$. Selected values calculated from Equation (21) are listed in Table 3.5.

Table 3.5. Calculated phonon-sideband intensity ratio and thermometric sensitivities for the 1 mol% YAG:Cr³⁺ aerogel.

Temperature (°C)	Temperature (K)	S _r (% K ⁻¹)	S _a (K ⁻¹)
–150	123.15	2.81	6.87×10^{-4}
–100	173.15	1.42	9.43×10^{-4}
–70	203.15	1.03	9.85×10^{-4}
–50	223.15	0.86	9.86×10^{-4}
0	273.15	0.57	9.33×10^{-4}
+20	293.15	0.50	9.01×10^{-4}
+100	373.15	0.37	8.54×10^{-4}
+200	473.15	0.23	8.89×10^{-4}

The maximum value of $S_r = 2.81 \text{ \%}\cdot\text{K}^{-1}$ at 123 K is of the same order as the $3.12 \text{ \%}\cdot\text{K}^{-1}$ reported at 150 K for the Cr³⁺ sideband thermometer of Wang et al. [55]. These comparisons

support the use of the sideband ratio as a low-temperature thermometric signal, but they should not be treated as a direct ranking of the materials because the hosts, spectral integration procedures, excitation conditions, and detectors are different.

In conclusion, the phonon-sideband ratio and the ${}^4T_2/{}^2E$ ratio probe two different energy scales of the same Cr^{3+} center. The low-temperature calibration is controlled by the thermal occupation of lattice vibrations and gives $\tilde{\nu}_{eff} = 296 \pm 6 \text{ cm}^{-1}$. The higher-temperature calibration is controlled by redistribution between the ${}^2E$ and ${}^4T_2$ electronic states and gives $\Delta E_{TE} = 890 \pm 10 \text{ cm}^{-1}$. Their useful ranges are therefore different. In the present measurements, $LIR_{AS/S}$ is calibrated from 123.15 to 483.15 K (-150 to $+210 \text{ }^\circ\text{C}$), whereas the ${}^4T_2/{}^2E$ ratio is calibrated from 253.15 to 453.15 K (20 to $180 \text{ }^\circ\text{C}$).

The new $LIR_{AS/S}$ calibration overcomes the limitations of the Boltzmann-based LIR approach and covers a wider temperature range (Figure 3.20 (b)), including the region that was previously not accessible with the primary calibrations. As a result, the dual-mode thermometric response can now be described continuously over a broader temperature interval.

The use of different thermometric channels in different temperature ranges has also been demonstrated in other garnet systems. Back et al. [59], for example, used two different Boltzmann ratios in the same Nd^{3+} -doped garnet to obtain a low-temperature calibration from 100 to 220 K and a separate high-temperature calibration beginning near 300 K.

It is also important to distinguish theoretical sensitivity from practical precision. For an ideal Boltzmann ratio, the relative sensitivity contains a $1/T^2$ term and does not simply decrease on cooling. The practical limitation of the ${}^4T_2/{}^2E$ thermometer below $0 \text{ }^\circ\text{C}$ is instead that the ${}^4T_2$ emission becomes too weak to be reliable. The phonon-sideband ratio extends the useful measurement toward lower temperature because the anti-Stokes components remain measurable in the present spectra, but it will also fail at sufficiently low temperature when the anti-Stokes signal approaches the noise level. The lower limit of 123 K is therefore an experimental limit of the present data set, not a fundamental lower temperature limit of the method.

The low-temperature analysis adds a second thermometric use to the same temperature-dependent emission series. It also shows that the aerogel-derived $YAG:Cr^{3+}$ preserves not only the ${}^2E$ – ${}^4T_2$ electronic coupling used for the higher-temperature thermometer, but also the resolved vibronic structure of the ${}^2E \rightarrow {}^4A_2$ emission needed for phonon-sideband thermometry. Within the validated intervals, the same Cr^{3+} -doped aerogel can therefore be read using an electronic-state ratio at higher temperature and a phonon-sideband ratio at lower temperature.

3.2.7 Effect of Cr^{3+} concentration on thermometry behavior

Figure 3.21 shows PL spectra of 3 different concentration of $\text{YAG}:\text{Cr}^{3+}$ and Figure 3.22(a) compares the normalized room-temperature emission spectra of the 0.5, 1, and 2 mol% Cr^{3+} samples. The positions of the *R*-line and phonon sidebands, as well as the overall shape of the broad emission contribution, remain almost identical over the concentration range investigated. This indicates that the average local crystal-field environment of Cr^{3+} does not change strongly between 0.5 and 2 mol%. However, similar room-temperature spectral shapes do not necessarily imply identical temperature-dependent population dynamics. The energy separation obtained from the Boltzmann analysis depends on the evolution of the ${}^2\text{E}/{}^4\text{T}_2$ intensity ratio with temperature and may therefore be affected by signal-to-noise ratio, fitting range, and concentration-dependent relaxation processes.

The same analysis was used to samples containing 0.5, 1, and 2 mol% Cr^{3+} . All three samples were prepared using the same synthesis procedure and annealed at 1000 °C. The same nine-Gaussian fitting model was used for the temperature-dependent spectra of each composition.

The emission intensity of the 0.5 and 2 mol% samples was lower than that of the 1 mol% sample (Figure 3.22 (b)), resulting in a larger uncertainty in the fitted spectral areas. The temperature interval used for the Boltzmann fit (Figure 3.22(c)) was therefore adjusted for each composition. The 0.5 mol% sample was fitted over approximately 293.15-393.15, while the 2 mol% sample was fitted over approximately 301.15-373.15 K. The results are summarized in Table 3.6.

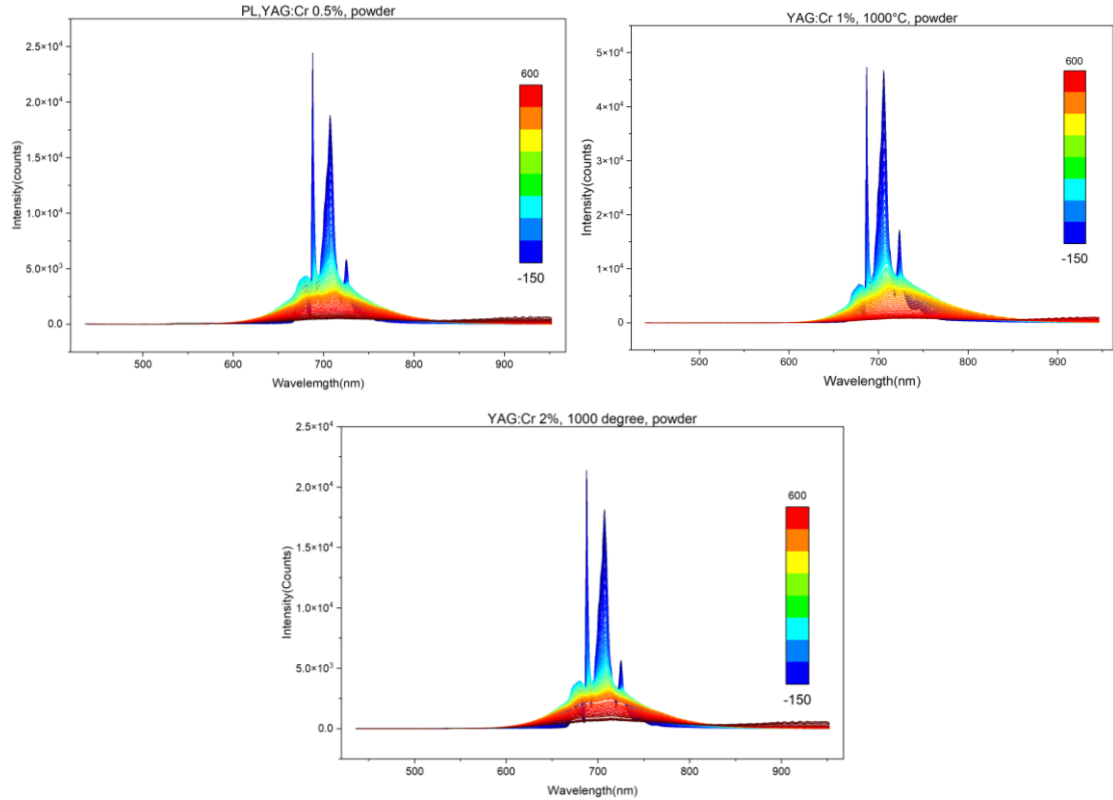


Figure 3.21: (a,b) Room-temperature emission spectra of $\text{YAG}:\text{Cr}^{3+}$ samples containing 0.5, 1, and 2 mol% Cr^{3+} ,

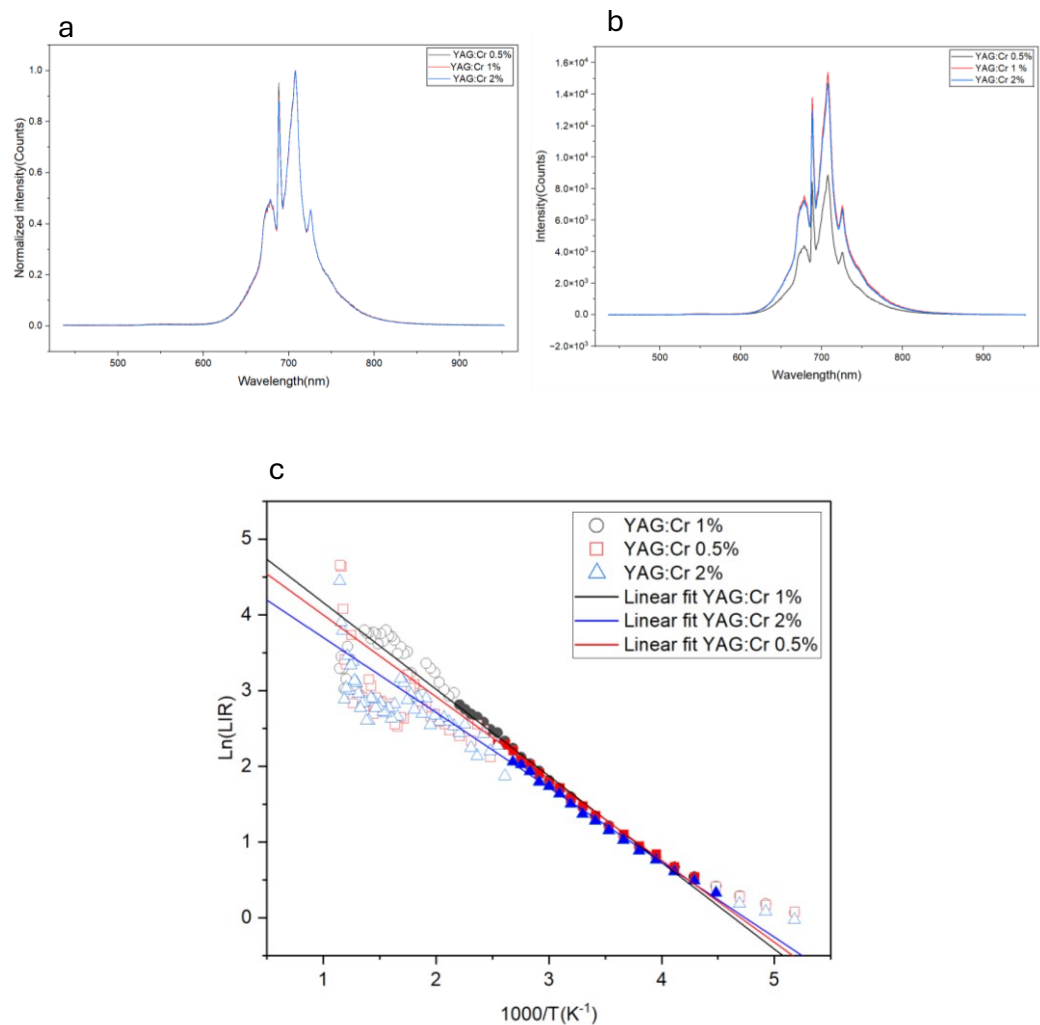


Figure 3.22: (a) Room-temperature emission spectra of YAG:Cr³⁺ samples containing 0.5, 1, and 2 mol% Cr³⁺, normalized to their respective maxima. (b) not normalized room temperature PL of 3 different concentrations. (c) comparison of LIR in 3 different concentrations.

Table 3.6. Energy separation and relative thermal sensitivity obtained from the LIR analysis for the three Cr³⁺ concentrations.

Cr ³⁺ content	Boltzmann-fit range (°C)	Boltzmann-fit range (K)	ΔE (cm ⁻¹)	S _r at 100 °C (% K ⁻¹)
0.5 mol%	20–120 °C	293–393 K	750 ± 55	0.79
1.0 mol%	20–180 °C	293–453 K	890 ± 10	0.92
2.0 mol%	30–100 °C	303–373 K	753 ± 74	0.78

Among the three compositions investigated, the 1 mol% sample therefore gives the most favorable thermometric response.

The lower fitted value obtained for the 0.5 mol% sample may partly arise from the weaker luminescence signal and the resulting uncertainty in the LIR values. Since the PLE measurements do not show a clear change in the crystal-field band positions with concentration, the difference should not automatically be interpreted as a large change in the intrinsic Cr^{3+} electronic structure.

For the 2 mol% sample, the lower apparent energy separation may also be influenced by concentration-dependent interactions between Cr^{3+} ions. As the Cr^{3+} concentration increases, the average distance between neighboring activator ions decreases, which can increase energy-transfer and non-radiative relaxation processes. Concentration quenching of Cr^{3+} luminescence has previously been reported in Cr:YAG, particularly at higher Cr^{3+} contents [60]. However, the present measurements alone do not allow the lower value to be assigned exclusively to cross-relaxation.

The differences in the fitted ΔE values should therefore be interpreted with caution. In particular, the three compositions were fitted over different temperature intervals, and the Arrhenius plots show some deviation from ideal linear behavior outside the central temperature range. The lower values obtained for the 0.5 and 2 mol% samples may partly arise from the weaker emission intensity and the corresponding uncertainty in the spectral deconvolution. For the 2 mol% sample, additional Cr–Cr interactions and concentration-dependent non-radiative processes may also contribute. Consequently, the fitted ΔE values should be regarded as effective activation energies obtained from the selected Boltzmann ranges rather than as direct evidence that the fundamental crystal-field splitting changes strongly with Cr^{3+} concentration.

The concentration study therefore shows that all three compositions display temperature-dependent changes in the ^2E and $^4T_2$ emission components, but the 1 mol% sample provides the most consistent Boltzmann fit, the smallest uncertainty in ΔE , and the highest relative sensitivity within the investigated series.

3.2.8 Temperature dependence of the ^2E lifetime

The luminescence intensity ratio discussed in the previous subsection provides an estimate of ΔE from the relative areas of two emission components. The temperature dependence of the Cr^{3+} luminescence lifetime offers a second and independent way to examine the same ^2E – $^4T_2$ coupling.

As reported by Back et al. for $Bi_2Ga_4O_9:Cr^{3+}$ [61], lifetime measurements are generally less affected by changes in excitation intensity, absorption efficiency, or sample position than measurements based only on emission intensity. The lifetime is also sensitive to the interaction between the Cr^{3+} excited states and lattice vibrations, which is important for the thermal behavior of transition-metal ions.

For this reason, the lifetime was measured over the temperature range from -150 to 500 °C, covering nearly the same range used for the steady-state emission measurements. The resulting temperature dependence was then used to compare with, and independently check, the ΔE value obtained from the LIR analysis and to investigate the potential of the use of lifetime as thermal sensor.

Following the procedure commonly used for Cr^{3+} systems with a strong crystal field, the effective lifetime τ was obtained by fitting the linear part of the semi-logarithmic decay curve with a mono-exponential function:

$$I(t) = I_0 \exp\left(-\frac{t}{\tau}\right) \quad (28)$$

where $I(t)$ is the emission intensity at time t after the excitation pulse, I_0 is the intensity extrapolated to $t = 0$, and τ is the effective decay time. In logarithmic form, the fitted linear region is described by:

$$\ln[I(t)] = \ln I_0 - \frac{t}{\tau} \quad (29)$$

Figure 3.23 (a) shows lifetime in different temperature at 687 nm belongs to ^2E transition. In this figure, the slope of $\ln[I(t)]$ against t is equal to $-1/\tau$. The fast component observed during the first few microseconds and the noisy part at long decay times were excluded from the fit range. The fast component is much weaker than the main decay and represents only a small fraction of the excited-state population. The fits show good agreement with the experimental data, with R^2 values above 0.994 over the full temperature range and typically above 0.999 between -150 and 500 °C, as listed in Table 5.4. The lifetime decreases continuously from 8.14 ms at -150 °C to 0.078 ms at 500 °C. This decrease covers more than two orders of magnitude.

A similar temperature dependence has been reported for $\text{YAG}:\text{Cr}^{3+}$ single crystals by Zhang and Grattan [47]. The result therefore shows that the aerogel-derived $\text{YAG}:\text{Cr}^{3+}$ sample has a similar temperature-dependent decay behavior to the bulk material ensuring its reliability.

In Cr^{3+} systems with an intermediate and strong crystal field, the ^2E and $^4\text{T}_2$ excited states are coupled through spin-orbit interaction. Because of this coupling, the $^2\text{E} \rightarrow ^4\text{A}_2$ emission gains some allowed $^4\text{T}_2$ character. If the two states behave as a coupled system, the decay time should be similar at different emission wavelengths belonging to the same $^2\text{E}-^4\text{T}_2$ manifold [61].

Figure 3.23(b) shows the decay curves measured at 300 °C at 678, 687, 707, 724, and 750 nm. Each curve was fitted with a mono-exponential function. The corresponding lifetimes are represented in Table 3.7. The values differ by less than 5%, which is within the experimental variation of the measurements.

Table 3.7. Mono-exponential lifetime values obtained at different wavelength at 300°C.

Wavelength (nm)	τ_{eff} (μs)	τ_{eff} (ms)
678	226.416	0.2264
687	228.766	0.2288
707	231.938	0.2319
724	229.641	0.2296
750	222.422	0.2224

A similar agreement was observed at the other temperatures. This shows that the decay time is essentially independent of the selected emission wavelength. The result supports the coupling between the ^2E and $^4\text{T}_2$ states and indicates that the lifetime measured at 687 nm can be used as a representative value for the temperature-dependent decay of the Cr^{3+} emission.

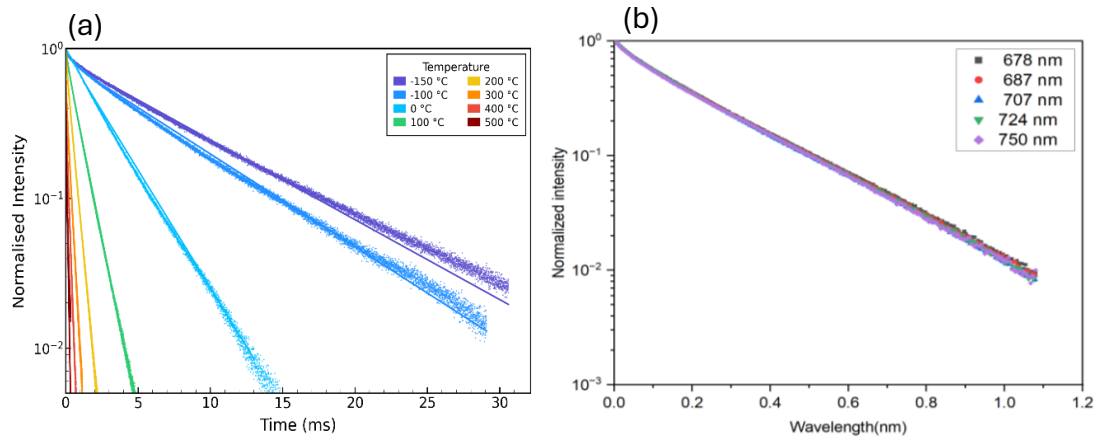


Figure 3.23: (a) Luminescence-decay analysis of the 1 mol% Cr^{3+} YAG sample: temperature-dependent decay at 687 nm, (b) comparison of decay curves at different emission wavelengths at 300 °C, and representative mono-exponential fit results.

Table 3.8. Mono-exponential lifetime values obtained at 687 nm as a function of temperature.

Temp °C	τ lifetime ms	R ²
-150	8.1424	0.999326
-100	7.0129	0.998622
0	2.7590	0.999239
100	0.9062	0.999312
200	0.4136	0.999622
300	0.2406	0.999189
400	0.1572	0.998489
500	0.0781	0.994260

Figure 3.24(a) shows the temperature dependence of the lifetime on a logarithmic scale between -150 and 500 °C. The lifetime decreases continuously from 8.21 ms to 0.068 ms, but not at a uniform rate. The strongest decrease occurs between -100 and 100 °C, where the lifetime falls by more than a factor of seven. Between 100 and 400 °C the change becomes much slower, and a second faster decrease appears above 400 °C. Figure 3.24 (b) shows the corresponding sensitivity and Table 3.9 lists the absolute sensitivity, obtained by numerical differentiation of the measured lifetimes, together with the relative sensitivity S_r calculated from the fitted model. The model gives a maximum of $1.21\% \text{ K}^{-1}$ at 252 K and remains above $0.5\% \text{ K}^{-1}$ between 171 and 755 K . This behavior suggests that more than one thermally activated process contributes to the decay of the Cr^{3+} emission. At low and intermediate temperatures, the decrease in lifetime can be related to thermal population of the $^4\text{T}_2$ state and to the coupling between the ^2E and $^4\text{T}_2$ states. At higher temperatures, an additional non-radiative relaxation process may become important, further shortening the lifetime.

To describe how the lifetime changes with temperature, the perturbation model developed by Grinberg and co-workers for the coupled ^2E – $^4\text{T}_2$ states of 3d^3 ions [62] is used. The model was applied in the form later adopted by Back et al. for Cr^{3+} ions in intermediate and strong crystal fields [61]. Within the adiabatic approximation, the wavefunction of the mixed ^2E – $^4\text{T}_2$ emitting state can be expressed as the product of its electronic and vibrational components:

$$\varphi_e(r) \cong \alpha_{11} \varphi_E(r) \left(\frac{1}{2}\right) + \alpha_{12} \varphi_T(r) \left(\frac{3}{2}\right) \quad (30)$$

The electronic wavefunction contains contributions from both the ^2E and $^4\text{T}_2$ states because of spin–orbit coupling. The coefficients α_{11} and α_{12} describe the mixing between these two states, while the labels $1/2$ and $3/2$ refer to the spin quantum numbers of the doublet ^2E and quartet $^4\text{T}_2$ states, respectively.

Because the ^2E and $^4T_2$ excited states lie close in energy, spin–orbit coupling mixes them, and the wavefunction of the emitting level is written as a linear combination of the two zeroth-order states. The vibrational wavefunction can be written in a similar form represent in Eq (31) where $\chi_E^0(Q)$ and $\chi_T^0(Q)$ are the unperturbed ^2E and $^4T_2$ wavefunctions at the configurational coordinate Q , and β_{11} and β_{12} are the mixing coefficients. The admixture of $^4T_2$ character described by β_{12} is what gives the nominally spin-forbidden $^2E \rightarrow ^4A_2$ emission a finite radiative rate.

$$\chi_v(Q) \approx \beta_{11}\chi_E^0(Q) + \beta_{12}\chi_T^0(Q) \quad (31)$$

In the harmonic approximation, the ground state $^4A_2$ and the excited states ^2E and $^4T_2$ are represented by parabolic potential-energy curves in the single-configurational-coordinate diagram. The $^4A_2$ and ^2E states have approximately the same equilibrium coordinate, while the $^4T_2$ curve is displaced. The energy associated with this displacement is described by $S\hbar\omega$, where S is the Huang–Rhys parameter and $\hbar\omega$ is the effective phonon energy.

Two energy separations are considered in this model. The first, ΔE , is the energy difference between the minima of the ^2E and $^4T_2$ states and is also the quantity used in the Boltzmann thermometric analysis. The second, $\Delta E'$, includes the contribution associated with the displacement of the $^4T_2$ potential-energy curve:

$$\Delta E' = E_T^0 - E_E^0 = \Delta E + S\hbar\omega \quad (32)$$

$\Delta E'$ is therefore the energy quantity used in the treatment of the spin–orbit mixing between the two excited states.

By combining the spin–orbit mixing with the thermal population of the $^4T_2$ state, Back et al. [61] used an expression for the temperature-dependent lifetime:

$$\tau_E(T) = \left| \tau_T \frac{1 + 3 \exp\left(-\frac{\Delta E}{k_B T}\right)}{\left(\frac{V_{SO}}{\Delta E'}\right)^2 \left[1 + \left(\frac{\Delta E'}{\Delta E}\right)^2 e^{-S}\right] + 3 \exp\left(-\frac{\Delta E}{k_B T}\right)} \right| \quad (33)$$

In this expression, τ_T is the intrinsic radiative lifetime of the quartet component, V_{SO} is the spin–orbit coupling strength between ^2E and $^4T_2$, and ΔE is the energy separation between the two states. The factor of 3 in the Boltzmann term accounts for the relative degeneracy of the states in the model.

At low temperature, thermal population of the $^4T_2$ state is small and the lifetime approaches a nearly constant value. As the temperature increases, the $^4T_2$ state becomes progressively

populated and the lifetime decreases. In the present case, Equation 33 describes the experimental $\tau(T)$ dependence reasonably well up to approximately 200 °C.

At temperatures above about 400 °C, a second decrease in lifetime becomes visible. To account for this high-temperature behavior, the model can be extended by including an additional non-radiative decay channel from the $^4T_2$ state. This process is described by an activation energy E_{nr} and a parameter q related to the relative non-radiative decay rate. The extended expression reported by Back et al.[61] is:

$$\tau_E(T) = \tau_T \frac{1 + 3\exp\left(-\frac{\Delta E}{k_B T}\right) + \exp\left(-\frac{E_{nr}}{k_B T}\right)}{\left(\frac{V_{SO}}{\Delta E'}\right)^2 \left[1 + \left(\frac{\Delta E'}{\Delta E}\right)^2 e^{-S}\right] + 3\exp\left(-\frac{\Delta E}{k_B T}\right) + q\exp\left(-\frac{E_{nr}}{k_B T}\right)} \quad (34)$$

Equation (34) contains seven fitting parameters. Among them, ΔE is the main parameter of interest in this work because it can be compared directly with the value obtained from the *LIR* analysis. The other parameters describe the spin–orbit interaction, electron–phonon coupling, and high-temperature non-radiative decay.

However, the present lifetime dataset contains only eight independent temperature points. Fitting seven correlated parameters to eight data points does not provide enough information to determine all parameters independently. A very high R^2 can therefore be obtained even when the uncertainties of the individual fitting parameters are large. In the work of Back et al. [46], additional quantities such as the effective phonon energy were determined independently, which reduced the number of free parameters.

For this reason, Equation (33) was used for the main determination of ΔE in the present work, while Equation (34) was used only to check whether the second high-temperature decrease in lifetime could be described by an additional thermally activated process.

Equation (33) was fitted independently to the lifetime data measured at 678, 687, 707, The average value was:

$$\langle \Delta E \rangle_{\text{lifetime}} = 917 \pm 10 \text{ cm}^{-1}$$

$$\langle \Delta E \rangle_{\text{LIR}} = 890 \pm 10 \text{ cm}^{-1}$$

The fitted parameters were of the same order of magnitude as those reported for other Cr^{3+} systems. For the aerogel-derived $\text{YAG}:\text{Cr}^{3+}$ sample, the fit gives approximately $\tau_T = 88 \text{ } \mu\text{s}$, $\Delta E' = 2465 \text{ cm}^{-1}$, $S = 3.05 \pm 0.08$, and $V_{SO} = 222 \text{ cm}^{-1}$. The value of 222 cm^{-1} used for the spin–orbit coupling constant sits comfortably within what has been reported for Cr^{3+} in garnets. Shen and Bray derived a value of $207 \pm 9 \text{ cm}^{-1}$ for YAG by averaging two perturbation schemes, Grinberg gives 219 cm^{-1} for the same host, and the value rises to 279 cm^{-1} in GGG and 319 cm^{-1} in GSGG as the field weakens. The $^4T_2$ – ^2E separation of 917 cm^{-1} is also in line with the figure of roughly 1000 cm^{-1} that follows from the zero-phonon energies of the two states. A Huang–Rhys factor of 3.05 falls between the value near 2.5 reported for YAG and

the larger ones found in weaker-field hosts such as CaHfO_3 (3.2) and ZnGa_2O_4 (5.3), which is what one would expect for a strong-field garnet. Finally, the activation energy of 3038 cm^{-1} for the non-radiative channel is close to the 2823 cm^{-1} that Back and co-workers obtained for $\text{Bi}_2\text{Ga}_4\text{O}_9\text{:Cr}^{3+}$ with the same model, though it rests on only the three highest-temperature points and should be read as an order of magnitude rather than a precise figure [51], [61], [63].

The two ΔE values are the same. This agreement is useful because the two methods are based on different measurements. The LIR method uses the relative integrated areas of the ^2E and $^4\text{T}_2$ emission components, whereas the lifetime method follows the time-dependent decay of the excited-state population.

The similar ΔE values obtained from the two analyses therefore support the interpretation of the measured temperature dependence in terms of thermal coupling between the ^2E and $^4\text{T}_2$ states. It also shows that the value obtained from the spectral deconvolution is consistent with the independent lifetime measurements.

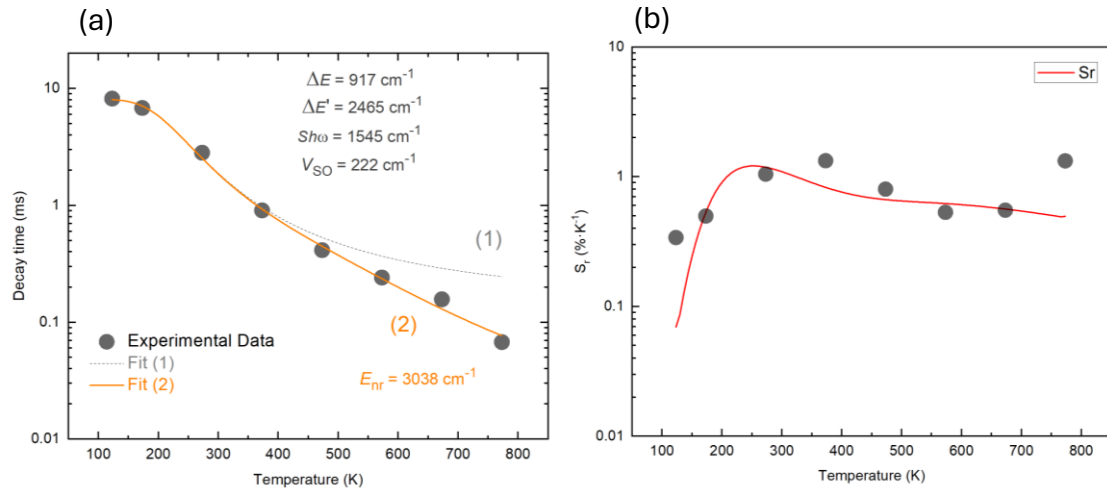


Figure 3.24: (a) Temperature dependence of the Cr^{3+} luminescence lifetime measured at 678, 687, 707, and 724 nm, shown on linear and logarithmic scales and (b) and the corresponding relative sensitivity

Table 3.9 Relative sensitivity and absolute sensitivity based on perturbation model

T (°C)	T (K)	τ (ms)	S_a (ms K^{-1})	S_r (% K^{-1})
-150	123	8.2075	0.0279	0.055
-100	173	6.8140	0.0339	0.536
0	273	2.8207	0.0295	1.183
100	373	0.9059	0.0120	0.827
200	473	0.4140	0.0033	0.666
300	573	0.2414	0.0013	0.621
400	673	0.1574	8.69×10^{-4}	0.564
500	773	0.0677	8.97×10^{-4}	0.486

4. CONCLUSIONS

In this work, Cr³⁺-doped YAG was prepared by an epoxide-assisted sol–gel route followed by solvent exchange, supercritical CO₂ drying, and thermal treatment. The aim was to obtain crystalline YAG:Cr³⁺ while preserving part of the porous structure of the aerogel and to determine whether the Cr³⁺ optical response could be used for luminescence thermometry over a wide temperature range.

The structural analysis showed that the phase formation strongly depends on the annealing temperature. The material remained amorphous at 850 °C, while the metastable hexagonal YAlO₃ phase appeared at 900 °C. At 950 °C, YAH and YAG were both present, whereas annealing at 1000 °C produced cubic YAG with no secondary phases detected by XRPD. The crystallite size was approximately 29 nm, in good agreement with the mean particle size of 34.9 ± 8.7 nm obtained from TEM. These results confirm that the aerogel route can produce nanocrystalline YAG after thermal treatment at 1000 °C.

The development of the crystalline phase was accompanied by shrinkage and loss of porosity. Nevertheless, the material remained far from a dense ceramic. The bulk density increased from 0.055 g cm⁻³ in the untreated aerogel to 0.504 g cm⁻³ after annealing at 1000 °C, corresponding to only about 11% of the theoretical density of YAG. The BET surface area decreased from 301.18 to 65.36 m² g⁻¹ and the pore volume from 2.2923 to 0.3814 cm³ g⁻¹. SEM and TEM images also showed that the final material consists of interconnected nanoparticles separated by residual voids. The 1000 °C treatment therefore allows crystallization of YAG while retaining a significant part of the porous structure produced by the aerogel route.

The optical measurements showed the characteristic behavior of Cr³⁺ in the YAG crystal field. At low temperature, the emission is dominated by the sharp ²E → ⁴A₂ R-line and its phonon sidebands. With increasing temperature, the ²E emission decreases and broadens, while the broad ⁴T₂ → ⁴A₂ contribution becomes progressively stronger. This change reflects the thermal population of the ⁴T₂ state from the lower ²E state and provides the basis for ratiometric temperature sensing.

For temperatures between 293.15 – 453.15 K (20 and 180 °C), the ratio between the integrated ⁴T₂ and ²E emission areas follows the expected Boltzmann dependence. For the 1 mol% Cr³⁺ sample, the fit gives an energy separation of $\Delta E = 890 \pm 10$ cm⁻¹ with R² = 0.9986. The relative thermal sensitivity reaches approximately 1.39% K⁻¹ at 30 °C and decreases to about 0.72% K⁻¹ at 150 °C. At 100 °C, the relative sensitivity is approximately 0.92% K⁻¹. These values show that the aerogel-derived material retains the thermally coupled ²E–⁴T₂ behavior known for conventional YAG:Cr³⁺.

The temperature-dependent lifetime measurements provide an independent check of this result. The lifetime decreases from approximately 8.14 ms at –150 °C to 0.078 ms at 500 °C. Measurements performed at different emission wavelengths give similar decay times at the same temperature, supporting the coupling between the ²E and ⁴T₂ excited states. The perturbation-model analysis gives an energy separation of approximately 917 ± 10 cm⁻¹, in good agreement with the value obtained from the intensity-ratio analysis. The agreement

between the two methods indicates that the fitted energy separation is associated with the same $^2E-^4T_2$ thermal coupling rather than with the details of a particular fitting procedure.

At temperatures below room temperature, the $^4T_2$ contribution becomes too weak for reliable use of the $^4T_2/^2E$ ratio. In this region, however, the Stokes and anti-Stokes phonon sidebands of the $^2E \rightarrow ^4A_2$ transition provide a second thermometric parameter. The ratio between the integrated anti-Stokes and Stokes sidebands follows a thermally activated behavior between -150 and $+210$ °C. The fit gives an effective phonon energy of $\hbar\omega_{\text{eff}} = 296 \pm 6 \text{ cm}^{-1}$ with $R^2 = 0.9962$. The maximum relative sensitivity is approximately **2.81% K⁻¹ at -150 °C**. This value decreases with increasing temperature, as expected from the thermal population of the phonon modes involved in the anti-Stokes process.

The fitted phonon energy should be regarded as an effective value because the thermometric parameter contains several Stokes and anti-Stokes components rather than a single vibrational mode. Nevertheless, the value is consistent with phonon energies previously associated with Cr^{3+} vibronic coupling in YAG. The preservation of clearly resolved Stokes and anti-Stokes sidebands after the aerogel synthesis and crystallization treatment also shows that the local Cr^{3+} environment retains the vibronic structure characteristic of crystalline YAG.

The two ratiometric methods therefore operate in complementary temperature ranges. The phonon-sideband ratio provides the most useful response from approximately **123 to 293 K**, while the $^4T_2/^2E$ ratio provides a reliable calibration between approximately **273 and 453 K**. The same Cr^{3+} center can therefore be used through two different temperature-dependent processes: phonon population at low temperature and thermal redistribution between the ^2E and $^4T_2$ excited states at higher temperature. This extends the useful temperature range of the aerogel-derived material without introducing a second luminescent dopant.

Also the influence of Cr^{3+} concentration was studied using 0.5, 1, and 2 mol% samples. Their normalized room-temperature spectra were very similar, indicating that the average Cr^{3+} environment remains comparable over this concentration range. However, the 1 mol% sample gave the most reliable temperature calibration, with the smallest uncertainty in ΔE and the highest relative sensitivity among the three compositions. The lower signal intensity of the 0.5 and 2 mol% samples increases the uncertainty of the spectral decomposition, while concentration-dependent interactions may also contribute at the higher Cr^{3+} content. For the conditions investigated in this work, the 1 mol% composition therefore provides the best thermometric performance.

The comparison between powder and monolith samples showed similar spectral features and temperature-dependent behavior, indicating that grinding does not significantly alter the Cr^{3+} emitting environment. The main limitation of the monolith is thermal rather than optical. Because of the low thermal conductivity of the porous material, the temperature of the emitting surface may differ from the temperature measured by the heating stage. Longer equilibration times are therefore required, and direct measurement of the monolith surface temperature would improve future calibration. The two forms therefore share the same thermometric parameters but not the same emission profile, and each requires its own *LIR* calibration

Overall, this work shows that nanocrystalline YAG:Cr³⁺ can be prepared in aerogel-derived form while retaining significant porosity and the characteristic optical behavior of Cr³⁺ in the YAG lattice. The porous structure does not prevent the establishment of the ²E–⁴T₂ thermal equilibrium required for Boltzmann thermometry, and the resolved phonon sidebands provide an additional temperature-sensitive parameter at lower temperatures. The combination of these two mechanisms gives the material a wider useful temperature range than would be obtained from the ⁴T₂/²E ratio alone.

The main result of this work is therefore the demonstration that the known thermometric behavior of YAG:Cr³⁺ can be preserved in a low-density, nanocrystalline and highly porous material. The aerogel form adds structural properties that are not available in dense YAG, including high surface area and accessible porosity, while maintaining the Cr³⁺ optical response required for temperature sensing.

Future work should include repeated heating and cooling cycles to determine reproducibility and hysteresis, direct measurement of temperature resolution and uncertainty, and independent measurement of the true surface temperature of the monolith. Further compositional analysis would also help clarify the distribution of Cr³⁺ and the origin of the differences observed among the three dopant concentrations. Finally, testing the material as a porous coating or in contact with flowing gases, liquids, or catalytic systems would allow the practical advantages of the aerogel structure to be assessed.

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