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Structural and luminescent properties of a Cr^{3+}/Sm^{3+} doped $GdAlO_3$ orthorhombic perovskite for solid-state lighting applications

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The Cr^{3+} and Sm^{3+} doped $GdAlO_3$ perovskite with formula $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$, was synthesized *via* a solid-state reaction method, and its structure, morphology, and photoluminescence properties were thoroughly investigated. The compound crystallizes in the orthorhombic *Pbnm* space group, with Cr^{3+} transition-metal ions substituting Al^{3+} in the octahedral symmetry site, and Sm^{3+} lanthanide (rare-earth) ions occupying the tetrahedral site. The material's morphology and chemical composition homogeneity were evaluated through Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis. Photoluminescence excitation (PLE) and emission spectra (PL) were used to shed light on the electronic structure of the Cr^{3+} cations, through crystal field analysis in the O_h symmetry site. Theoretical studies enabled the precise assignment of the Cr^{3+} 3d–3d transitions. The intra-configurational 4f–4f transitions of Sm^{3+} resulted in a variety of excitation bands appearing in the high-wavelength range of the PLE spectrum. The photoluminescence studies supported the occurrence of energy transfer in the doped $GdAlO_3$ perovskite between Gd^{3+}, Sm^{3+} and Cr^{3+} ions. The obtained results suggest the high potential of the synthesized material for solid state lighting applications.

1. Introduction

The investigation of rare-earth-doped luminescent materials has unlocked new avenues of innovation, driving advancements across various high-tech industries.[1] Among these, white light-emitting devices (LEDs) stand out due to their exceptional luminescent properties. In the context of global energy challenges and the growing threat of climate change, the need for innovative and efficient phosphors tailored for solid-state lighting (SSL) is critical.[2,3] The demand for novel phosphors used in SSL displays and lamps continues to rise, driven by their prolonged lifespan, high luminescence efficiency, and contribution to sustainable environmental practices.[4–8]

Aluminate-based host matrices have garnered significant attention as ideal candidates for phosphor development due to their superior crystallinity, excellent luminous characteristics, straightforward synthesis, favorable color parameters, and exceptional chemical and thermal stability. Their high heat resistance further enhances their suitability for doping with various ions, enabling the creation of materials optimized for diverse applications.[9,10] Consequently, aluminate-based materials have been extensively investigated and have found applications in energy harvesting for flat-panel displays,[11] SSL,[12] scintillators,[13] optical lasers,[14] light-emitting diodes,[15] photonic storage devices, and remote sensing technologies.[16]

Among these materials, gadolinium aluminate ($GdAlO_3$), featuring an orthorhombic perovskite crystal structure (*Pnma* space group), is a particularly notable example. $GdAlO_3$ is uniquely suited for multifunctional applications due to its robust thermal and chemical stability, compatibility with rare-earth dopants, and excellent energy transfer characteristics. These properties make it an attractive host matrix for developing phosphors with tailored optical and magnetic functionalities. While gadolinium can be expensive, the strategic use of $GdAlO_3$ in doped compositions mitigates costs,[17] and its performance advantages justify its use in niche applications such as magneto-optoelectronics and hybrid devices requiring simultaneous photoluminescent and magnetic properties.[18–20] Furthermore, $GdAlO_3$ based materials show promise for energy storage and conversion technologies, adding to their appeal as next-generation phosphor materials.

Cr^{3+} ions were selected as primary activators due to their well-established photoluminescent properties, including intense and tunable red emissions. To further enhance the

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material's spectral characteristics, Sm^{3+} was introduced as a codopant. Sm^{3+} was chosen for its ability to enhance red luminescence and its potential to act as an energy transfer mediator, facilitating a synergistic effect with Cr^{3+}. This combination is particularly relevant for applications requiring optimized spectral output, such as full-spectrum lighting or display technologies. Moreover, the dopant combination leverages the perovskite structure of $GdAlO_3$ to enable efficient energy transfer and tailored luminescent properties.

In this investigation, we synthesized and characterized the structural and luminescence properties of a Cr^{3+} doped orthorhombic $GdAlO_3$ perovskite phosphor, codoped with Sm^{3+} to achieve the composition $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$. This study aims to elucidate the fundamental mechanisms governing the optical properties of $GdAlO_3$ doped with Cr^{3+} and Sm^{3+}, thereby fostering further exploration into the potential of complex oxides doped with transition and rare-earth elements for advanced technological applications. The findings presented here demonstrate the promise of this novel material for applications in solid-state lighting.

2. Materials and methods

In this study, $GdAlO_3$ perovskite was synthesized *via* solid-state method. High-purity gadolinium oxide (Gd_2O_3) and aluminum oxide (Al_2O_3) powders were weighted in stoichiometric ratio to form the base material. To introduce chromium and samarium doping, appropriate amounts of samarium oxide (Sm_2O_3) and chromium oxide (Cr_2O_3) were added, ensuring the desired doping level of $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$. The solid-state method was chosen for its robustness and ability to exert precise control over reaction conditions. Following preannealing at 700 °C for 24 hours to remove volatile inorganic materials, the mixture was ground using an agate mortar and pestle to ensure intimate mixing of the reactants. The resulting mixture was then sintered at 1200 °C for 24 hours, promoting atomic and ionic diffusion essential for the formation of the desired doped $GdAlO_3$ compound. The high temperature during sintering facilitated the incorporation of Cr^{3+} and Sm^{3+} ions into the crystal lattice, ensuring the development of the desired orthorhombic crystal structure. Finally, the sintered material was compacted into pellets with a diameter of 8 mm, which were used in the subsequent characterization and analyses experiments.

Characterization of the newly synthesized compound was undertaken using different techniques. The material was first analyzed by powder X-ray diffraction (X-ray Siemens D5000, with $\lambda = 1.5406$ Å CuK_α radiation). Data was collected within the 20–100° 2θ range, with a step size of 0.02°. Subsequently, photoluminescence emission (PL) and excitation (PLE) measurements were collected in a Horiba-Jobin-Yvon Fluorolog 322, operating in time-resolved mode (using a pulsed lamp) with a 0.05 ms delay after-flash. The morphology of the material and its chemical homogeneity were investigated by scanning electron microscopy (SEM), using a TESCAN VEGA3 SBH instrument equipped with an X-ray energy dispersive microscopy (EDS) detector. Image analysis was carried out using the ImageJ software,[21] and structure analysis was undertaken using the Visualization Electronic and Structural Analysis (VESTA) software.[22–24]

Table 1 CIE parameters for the red luminescence color of the synthesized Cr^{3+}/Sm^{3+} doped $GdAlO_3$ phosphor

x	y	CCT (K)	CP (%)
0.62157	0.37383	1892.46	87.08

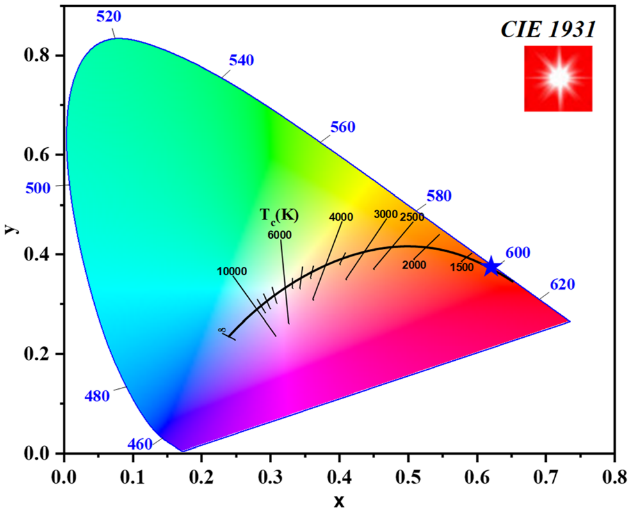

Fig. 1 The CIE graph for the studied Cr^{3+}/Sm^{3+} doped $GdAlO_3$ phosphor.

Raman spectra were collected (with 4 cm^{-1} spectral resolution) in a LabRAM HR Evolution Raman microscope (Horiba Scientific) with a 600 g mm^{-1} grating. The excitation was provided by a He–Ne laser ($\lambda = 633$ nm), which was focused on the sample to a ~1 mm spot using a 100× objective. The applied laser power of ~0.2 mW at the sample resulted in no detectable heating or degradation. The collection time was 10 s with 100 accumulations being averaged to generate the final spectra.

The chromaticity coordinates (x, y) of the synthesized $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$ phosphor were determined using the CIE 1931 color space from its emission spectrum under 377 nm excitation. The correlated color temperature (CCT) and color purity (CP) values were calculated based on established methods.[25,26] The resulting parameters are presented in Table 1, demonstrating the material's potential for applications in warm white light-emitting diodes (LEDs).

Fig. 1 shows the CIE 1931 chromaticity diagram for the $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$ phosphor, generated from the emission spectrum under 377 nm excitation, where the coordinates are positioned in the reddish-orange region.

3. Results and discussion

3.1 Powder X-ray diffraction analyses

Powder X-ray diffraction (PXRD) is a powerful technique for elucidating crystal phases, lattice parameters, and overall

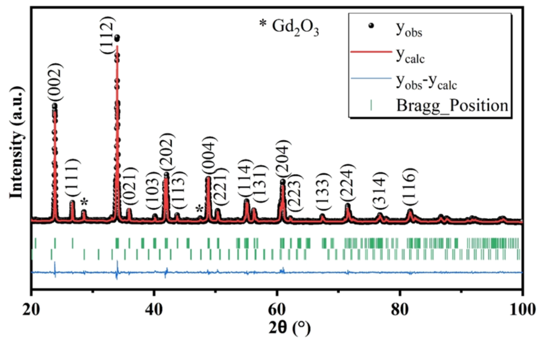

Fig. 2 Results of the performed Rietveld refinement for $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$.

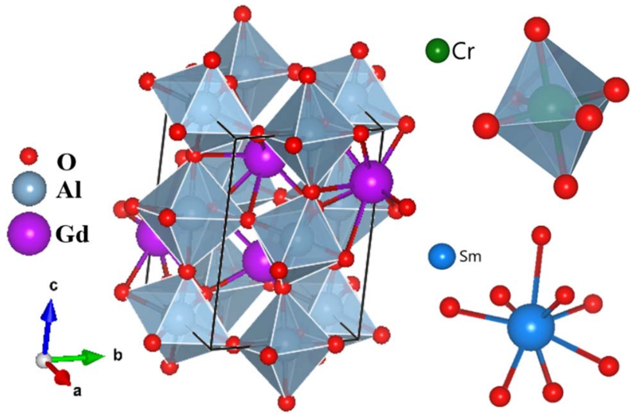

Fig. 3 Illustration (Vesta software images) of the structure of the $GdAlO_3$ perovskite, and of the 8-coordinated SmO_8 and 6-coordinated (octahedral) CrO_6 units.

structural characteristics of solid materials. To determine the phases present in the synthesized material, its PXRD diffraction pattern (Fig. 2) was obtained and compared with ICDD (International Center for Diffraction Data) database. The observed peaks could be successfully indexed to a primitive orthorhombic crystal lattice, within the *Pbnm* space group. The identification process used standard JCPDS data files [$GdAlO_3$ 46-0395; Gd_2O_3 88-2165]. Rietveld refinement revealed the presence of two phases, the predominant one corresponding to the perovskite compound and the minor to Gd_2O_3. The presence of the Gd_2O_3 as impurity in the sample is consistent with previous studies,[27] where this impurity was also observed. Table 2 presents the refined crystallographic parameters, with the agreement between calculated and observed profiles being satisfactory, as indicated by a χ^2 value of 1.7. The fit quality between the observed and calculated diffraction patterns is reflected by $R_p = 17.6$, $R_{wp} = 14.2$, and $R_e = 10.9$. While, R_p (profile *R*-factor) is a measure of the agreement between the observed and calculated diffraction profiles, R_{wp} (weighted profile *R*-factor) is similar to R_p but takes into account the statistical weights of the observed intensities and R_e (expected *R*-factor) represents the ideal *R*-factor that would be obtained if the model perfectly fits the data, considering only statistical uncertainties. Fig. 3 depicts the structures of the $GdAlO_3$ perovskite, where Al^{3+} and Gd^{3+} cations are bonded to six and eight oxygen atoms, respectively. Al^{3+} ions occupy an octahedral (O_h) coordination site corresponding to corner-sharing AlO_6 octahedra with tilt angles of 24°, while Gd^{3+} stay in a coordination site whose symmetry is C_s. The compound presents four shorter and two longer Al–O bond lengths, along with two inequivalent O^{2-} sites. In the first site, O^{2-} is bonded in a 5-coordination geometry to three equivalent Gd^{3+} and two equivalent Al^{3+} cations; in the second, O^{2-} is bonded in a 4-coordination geometry to two equivalent Gd^{3+} and two equivalent Al^{3+} cations. Upon doping, Cr^{3+} and Sm^{3+} cations are hypothesized to replace Al^{3+} and Gd^{3+}, respectively, due to the close match in their ionic radii. Cr^{3+} (0.615 Å in octahedral coordination) is similar in size to Al^{3+} (0.535 Å), making it a suitable substitute at the Al^{3+} site. Similarly, the ionic radius of Sm^{3+} (1.079 Å in nine-fold coordination) closely matches that of Gd^{3+} (1.053 Å), facilitating substitution at the Gd^{3+} site.

Table 2 Cell parameters and volume resulting from the Rietveld refinement for the synthesized compound, and statistical indicators

Formula	$Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$	R_p	17.6
Space group	*Pbnm*	R_{wp}	14.2
a (Å)	5.251_7	R_e	10.9
b (Å)	5.299_8	χ^2	1.7
c (Å)	7.445_8	Gd_2O_3 (%)	3.050_1
V (Å^3)	207.240_1	SEM (nm)	177

3.2 EDS and particles morphology studies

Scanning electron microscopy (SEM) was employed to investigate the morphology of particles of the synthesized compound. Fig. 4 shows the presence of agglomerated and irregularly

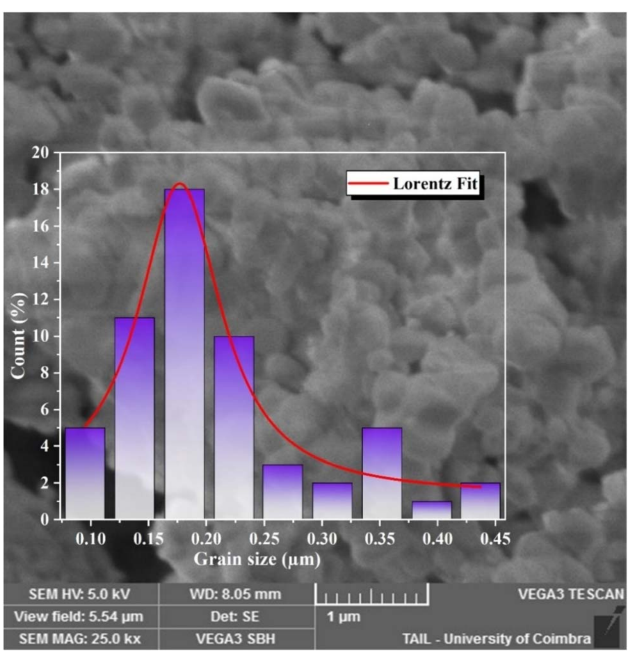

Fig. 4 SEM image and particle size distribution histogram of the synthesized compound, and results of the Lorentz fit to the distribution data.

shaped grains, resulting from the substantial surface area of the particles and their interaction *via* weak van der Waals forces. The average particle size distribution, determined by Lorentz fitting using the ImageJ software, shows a peak centered at 177 nm.

To confirm the chemical composition of the sample, its EDS spectrum was collected (Fig. 5). The spectrum exhibits characteristic peaks of all expected elements (Gd, Cr, Al, Sm, O) confirming the presence of these elements in the sample. The low-energy peaks correspond to lighter elements like Al and O, while the intermediate-energy peaks are attributed to Cr, Sm, and Gd, with distinct signals from their L and K edges. High-energy peaks, primarily from the K edges of Gd, also show some overlap from Sm, consistent with their atomic characteristics. All peaks are clearly labeled in the spectrum for clarity.

The elemental distribution maps, presented in the smaller images on the right of Fig. 5, provide a visual representation of the spatial distribution of the elements in the sample. While the main inset (colorful grain map) shows some inhomogeneity in the intensity of elemental signals, this variation is likely due to factors such as sample morphology, local concentration differences, or surface roughness, which can affect signal intensities. Despite these minor variations, the maps demonstrate significant co-localization of the elements, indicating a uniform distribution across the sample. This is further supported by the composite overlay of the elemental maps, where no regions are completely absent of any detected elements, confirming the overall homogeneity of the elemental distribution.

Table 3 provides the results of the quantitative analysis of the elements present in the sample, which show good agreement with the theoretical values for the expected composition. The observed differences between the nominal composition and EDS results, particularly for Cr and Sm, are attributed to the limitations of EDS in quantifying trace elements and matrix effects. Despite these minor discrepancies, the elemental maps confirm a homogeneous distribution of elements across the sample.

Table 3 Elemental composition obtained from the EDS data of the studied sample and theoretical values for $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$

Element	Series	Experimental (weight%)	Error (%)	Theoretical (weight%)	Experimental (atomic%)
Al	K	16.19	1.61	14.57	17.56
Cr	K	0.30	0.09	0.14	0.23
Sm	L	2.92	0.18	0.41	1.13
Gd	L	80.59	3.92	84.88	81.08
Total		100.00		100.00	100.00

3.3 Raman spectroscopy analyses

The symmetry analyses of *Pbnm* space group symmetry perovskites of general formula ABO_3 has been detailed by Chopelas, who has performed a systematic study of the Raman spectra of 30 different aluminate orthorhombic perovskites with emphasis on $YAlO_3$ and $GdAlO_3$.[28] In the Brillouin zone center, the 24 Raman active optical modes span the symmetry species $7A_g + 7B_{1g} + 5B_{2g} + 5B_{3g}$. Chopelas has observed and assigned twenty of these modes for $GdAlO_3$ using single crystal polarized Raman spectroscopy with excitation at 488.0 or 457.9 nm (Ar^+ laser).[28]

The Raman spectra of $GdAlO_3$ and of the synthesized $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$ compound obtained in the present study using 633 nm excitation are shown in Fig. 6, together with the difference spectrum obtained by subtracting

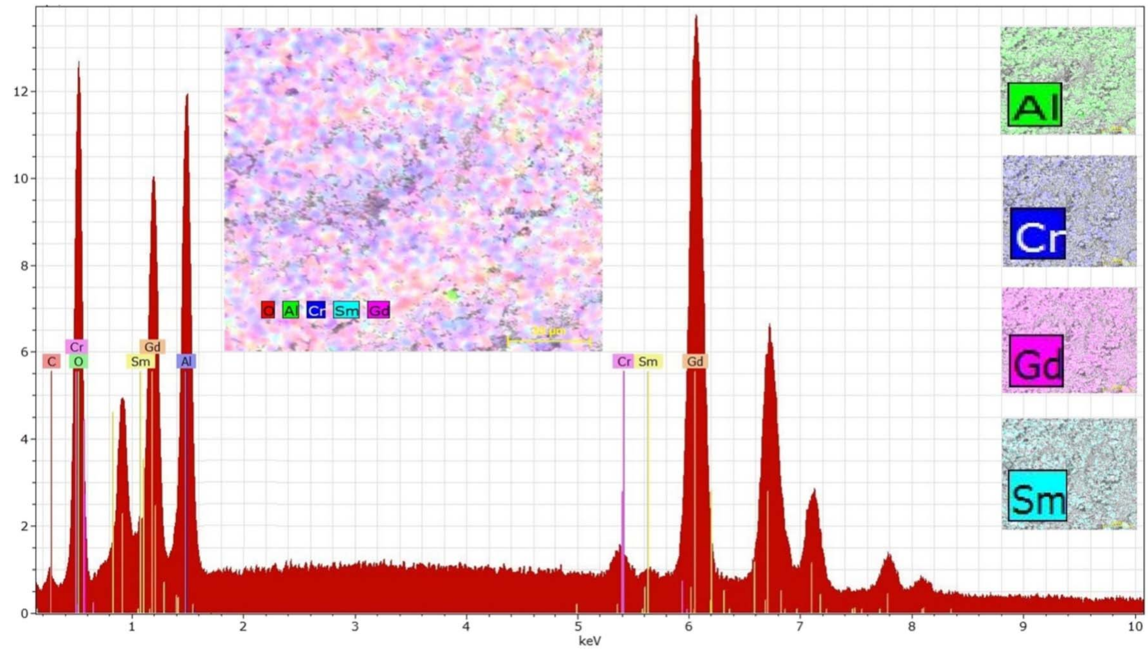

Fig. 5 EDS spectrum of $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$ and elements distribution maps.

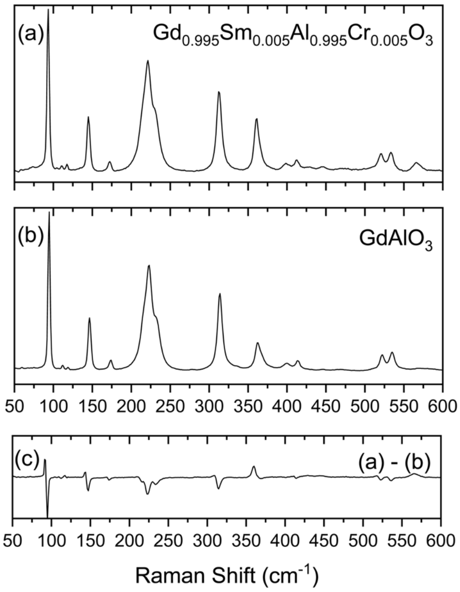

Fig. 6 Raman spectra of the prepared compound (a) compared to that of undoped $GdAlO_3$ (b). Plot (c) is the difference spectrum obtained by subtracting the spectrum of the undoped $GdAlO_3$ perovskite from that of the prepared compound.

the spectrum of the undoped $GdAlO_3$ perovskite from that of the newly prepared compound. The difference spectrum allows to better notice the spectral changes due to the presence of the dopant atoms, which for most of the bands correspond to small shifts to lower frequency. These changes could be anticipated considering the much larger mass of chromium compared to aluminum (51.996 *vs.* 26.9815). On the other hand, the mass difference between gadolinium and samarium is small (157.2 *vs.* 150.4) so that the effects of the substitution of Gd^{3+} ions by Sm^{3+} at the level of substitution in the studied compound could be expected to lead to experimentally non-detectable perturbations in the frequencies of the modes where the movements of these atoms play a major role.

The collected spectrum of the undoped $GdAlO_3$ compound follows closely those reported before.[28,29] Assignments are given in Table 4, which includes also the data for the studied Sm^{3+}/Cr^{3+} doped compound. Compared to the previous investigations,[28,29] the present results have allowed to propose assignments for the 4 modes not yet firmly assigned before: the assignment of the A_g mode 6 proposed by Gouadec *et al.*[29] was confirmed to the band now located at 445.0 cm^{-1} (440 cm^{-1} as reported before[29]), and the B_{1g} modes 4 and 6 are assigned to bands observed at 280.0 and 570.0 cm^{-1}, respectively, at frequencies in the ranges observed for other orthorhombic *Pbnm* aluminium oxide perovskites;[29] the B_{2g} mode 1 that had been previously ascribed to the band at 146 cm^{-1}, is now reassigned to the band observed at 119.0 cm^{-1}, while the band at 146 cm^{-1} is reassigned to the B_{2g} mode 2 (this band is also assigned to the A_g mode 2, following the assignments proposed

Table 4 Assignment of the Raman spectra of $GdAlO_3$ and of $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$

		$GdAlO_3$			$Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$
Symmetry	Mode	This study	28	29	This study
A_g	1	94.5	95	93.5	93.0
	2	146.5	146	146	145.0
	3	233.0	232	233	233.0
	4	314.0	313	315	313.0
	5	362.0	368	366	361.0[b]
	6	445.0	—	440	427.0/445.0[c]
	7	535.0	536	534	533.5
B_{1g}	1	112.0	111	—	111.0
	2	162.0	160	—	159.0
	3	222.5	222	223	221.0
	4	280.0	—	—	278.0
	5	414.0	414	405	412.0
	6	512.0	512	—	508.0
	7	570.0	—	—	566.0
B_{2g}	1	119.0	—	—	117.5
	2	146.5	146[a]	146	145.0
	3	400.0	398	399	399.0
	4	468.0	475	470	468.0
	5	522.0	523	522	521.0
B_{3g}	1	174.0	174	172	172.0
	2	217.0	217	215	217.0
	3	334.0	323	—	334.0
	4	400.0	400	399	399.0
	5	551.0	551	—	547.0

[a] Assigned in [28] to the B_{2g} 1 mode. [b] This band is among all bands the one undergoing the largest frequency shift and broadening, indicating that the movement of the Al^{3+}/Cr^{3+} ions have a large contribution to the corresponding vibration. [c] The appearance of the additional low-frequency band is, with all probability, a consequence of the Al^{3+} by Cr^{3+} substitution.

before;[28,29] see Table 4). The assignment of all other modes follows those previously suggested.[28,29]

The analysis of the Raman spectra provided new data for the undoped material that allowed for fine tuning of the assignments for that material, and are completely new for the synthesized doped material.

3.4 Photoluminescence measurements

3.4.1 Photoluminescence emission spectrum (PL). The room temperature PL spectra of $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$ and $GdAlO_3$ compounds are shown in Fig. 7. The spectra were collected in time-resolved mode (using a pulsed lamp) with excitation at 377 nm and with a 0.05 ms delay after flash. The intense and well-resolved line observed at 726 nm is ascribed to a Cr^{3+} 3d–3d transition from the excited $^2E_g(^2G)$ to the ground $^4A_{2g}(^4F)$ state.[30] This emission, with its remarkable tissue-penetrating capability and minimal tissue damage, makes the synthesized compound a promising candidate for *in vivo* imaging applications and optoelectronic devices.

Additionally, an emission line at 735 nm, commonly observed in systems containing high concentrations of Cr^{3+} ions (*e.g.*, $GaAlO_3:Cr^{3+}$, $LaAlO_3:Cr^{3+}$ (ref. 31)), is likely due to energy transfer between exchange-coupled Cr^{3+} pairs and individual Cr^{3+} ions. Emission bands observed at 720, 704, 697, and 680 nm are attributed to the Gd^{3+} 4f–4f transitions ($^6P_j \rightarrow {}^8S_{7/2}, j = 3/2, 5/2$ and $7/2$). Bands at 660 nm ($^4G_{5/2} \rightarrow {}^6H_{11/2}$), 647 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$), 600 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$), and 564 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$) are assigned to Sm^{3+} 4f–4f transitions.[32]

3.4.2 Photoluminescence excitation spectra (PLE). Fig. 8 presents the PLE spectra of the studied doped material at room temperature, collected with emission at 600 and 697 nm. The spectrum monitored at $\lambda_{em} = 697$ nm spectra present a narrow UV excitation band corresponding to Gd^{3+} 4f–4f transition, located at 275 nm and assigned to the absorption $^8S_{7/2} \rightarrow {}^6I_{11/2}$, and a broad band located at 326 nm, due to the $^8S_{7/2} \rightarrow {}^6P_j$ transition.[33] Two additional broad bands in the visible region correspond to Cr^{3+} 3d–3d transitions: 564 nm ($^4A_{2g}(^4F) \rightarrow {}^4T_{2g}(^4F)$) and 418 nm ($^4A_{2g}(^4F) \rightarrow {}^4T_{1g}(^4F)$).

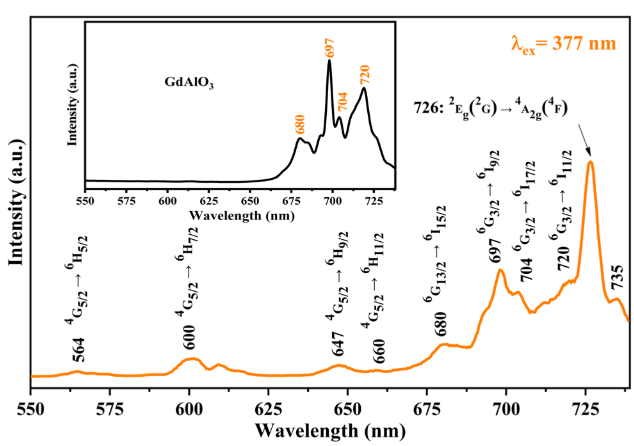

Fig. 7 Comparison between the $GdAlO_3$ and $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$ PL spectra (collected with excitation at 377 nm).

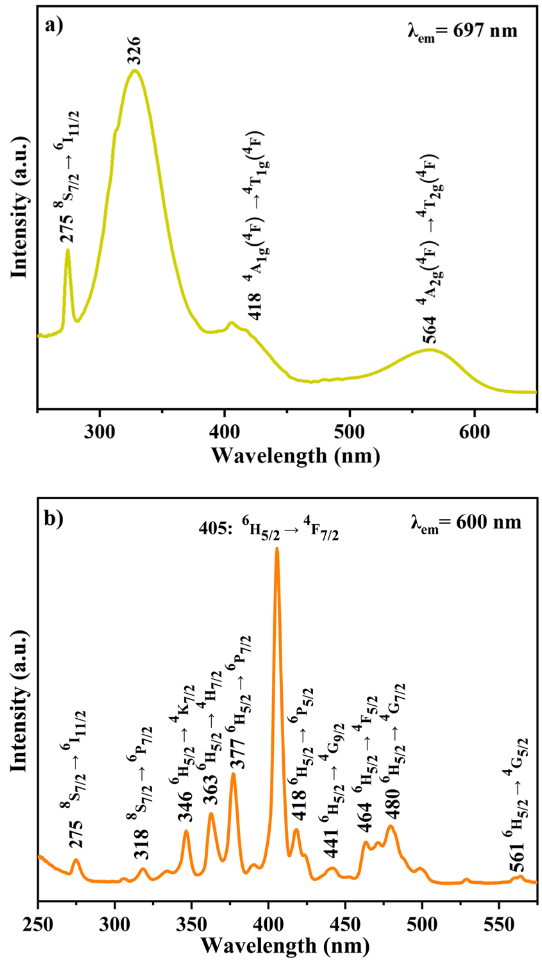

Fig. 8 PLE spectra of the studied doped perovskite monitored at (a) 697 and (b) 600 nm.

In contrast, the PLE spectrum monitored at $\lambda_{em} = 600$ nm reveals multiple excitation bands above 340 nm, arising from intra-configurational 4f–4f transitions of Sm^{3+}.[34] These bands, detailed in Table 5, correspond to transitions from the ground state $^6H_{5/2}$ to various excited states (*e.g.*, $^4K_{7/2}$, $^4H_{7/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^6P_{5/2}$, $^4G_{9/2}$, $^4F_{5/2}$, $^4G_{7/2}$, $^4G_{5/2}$).[35,36] Weak excitation peaks at 275 nm ($^8S_{7/2} \rightarrow {}^6I_{11/2}$) and 318 nm ($^8S_{7/2} \rightarrow {}^6P_{7/2}$) further confirm the occurrence of energy transfer from Gd^{3+} to Cr^{3+} ions.

Table 5 Excitation transitions of $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$

Transition for Sm^{3+} (ion)	Wavelength (nm)
$^6H_{5/2} \rightarrow {}^4K_{7/2}$	346
$^6H_{5/2} \rightarrow {}^4H_{7/2}$	363
$^6H_{5/2} \rightarrow {}^6P_{7/2}$	377
$^6H_{5/2} \rightarrow {}^4F_{7/2}$	405
$^6H_{5/2} \rightarrow {}^6P_{5/2}$	418
$^6H_{5/2} \rightarrow {}^4G_{9/2}$	441
$^6H_{5/2} \rightarrow {}^4F_{5/2}$	464
$^6H_{5/2} \rightarrow {}^4G_{7/2}$	480
$^6H_{5/2} \rightarrow {}^4G_{5/2}$	561

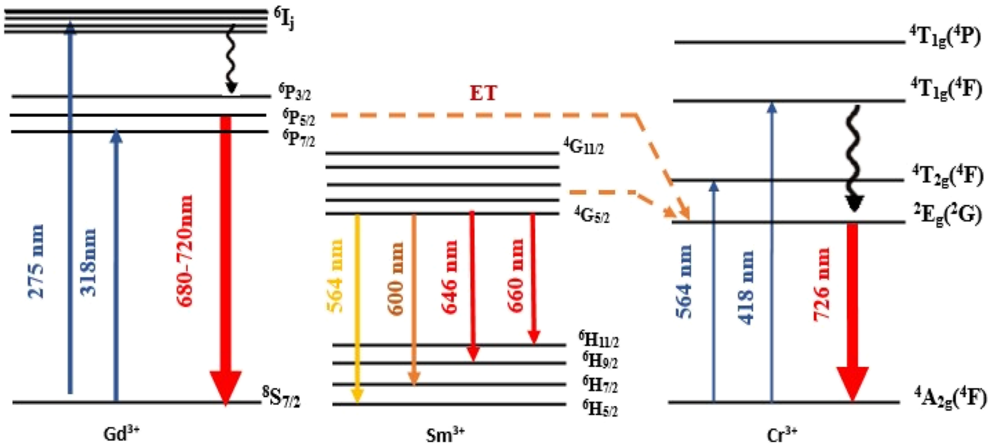

Fig. 9 Energy transfer between Gd^{3+}, Sm^{3+} and Cr^{3+} ions.

3.4.3 Energy transfer mechanism. The luminescence of Cr^{3+} can be further enhanced by the presence of lanthanides due to the energy transfer (ET) from Gd^{3+} and Sm^{3+} to Cr^{3+}. The photoluminescence (PL) spectrum of $GdAlO_3{:}Cr^{3+}$ and Sm^{3+} shows a decrease in the emission intensity of the Gd^{3+} ion at 697 nm and 720 nm ($^6P_J \rightarrow {}^8S_{7/2}$) compared to the emission intensity in the undoped $GdAlO_3$ spectrum (Fig. 7). We also notice that the red line at 726 nm, corresponding to the main luminescence $^2E_g(^2G) \rightarrow {}^4A_{2g}(^4F)$ from $GdAlO_3{:}Cr^{3+}$ and Sm^{3+}, is intense. This observation confirms the significant energy transfer from Gd^{3+} and Sm^{3+} ions to the Cr^{3+} dopant ions, which further enhances the luminescence of the Cr^{3+} ions. Energy transfer occurs from the Gd^{3+} emissions at 697 nm and 720 nm ($^6P_J \rightarrow {}^8S_{7/2}$) to the emission of Cr^{3+} ions. Additionally, energy transfer from Sm^{3+} emissions at 564 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$; green), 600 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$; yellow), 647 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$; orange), and 660 nm ($^4G_{5/2} \rightarrow {}^6H_{11/2}$; red) further enhances the $^2E_g(^2G) \rightarrow {}^4A_{2g}(^4F)$ emission as shown in Fig. 9. The higher excited states $^4T_{1g}(^4P)$, $^4T_{1g}(^4F)$, $^4T_{2g}(^4F)$ relax non-radiatively to the lowest excited state $^2E_g(^2G)$ of Cr^{3+}, which then undergoes radiative relaxation from the $^2E_g(^2G)$ state to the ground state $^4A_{2g}(^4F)$.

3.4.4 Potential energy surface. In transition ion complexes, electronic transitions are essentially electric dipolar in nature. The d–d transitions for transition metal complexes are in principle prohibited by Laporte's rule.[37] Nevertheless, observation of these transitions can be explained by vibronic coupling (coupling between vibrational and electronic wave functions). For example, for an octahedral complex, it can be assumed that some of the vibrations distort the octahedron in such a way that the center of symmetry is destroyed. The states of the configuration d^n then no longer strictly preserve their character g and the transitions, normally prohibited by Laporte's rule, become "slightly permitted".[37] Vibronic origins are mainly associated with odd-parity vibrational modes. Table 6 gives the selection rules for the Cr^{3+} ion occupying an O_h site in the studied doped perovskite. As shown in the table, the Cr^{3+} 3d–3d transitions observed in the PLE (Fig. 10) are governed by the vibronic mechanism that allow non-graded parity modes (a_{1u}, a_{2u}, t_{1u}, t_{2u} and e_u).

Table 6 Selection rules for electronic transitions of Cr^{3+} occupying an O_h site symmetry in the studied doped perovskite

d–d transitions	Electric dipole transition (odd vibrational mode that makes the transition permitted) $\langle \Gamma_i \vert T_{1u} \vert \Gamma_f \rangle \Gamma_u = A_{1g}$
$^4A_{2g}(^4F) \rightarrow {}^4T_{2g}(^4F)$	a_{1u}, t_{1u}, t_{2u}, e_u
$^4A_{2g}(^4F) \rightarrow {}^4T_{1g}(^4F)$	a_{2u}, t_{1u}, t_{2u}, e_u

To better understand the absorptions and emissions observed in the PLE and PL spectra of the studied compound, the coupled potential energy surface model was used. To simplify the model, a single normal coordination coordinate Q was considered. Due to the characteristics of the electronic transition, which is an intra-configuration d–d excitation, the potential energy minima of the doublet $^2E_g(^2G)$ and fundamental $^4A_{2g}(^4F)$ states are considered to be at the same configuration ($Q = 0$ Å) and have the same vibrational frequency. As the metal–ligand antibonding molecular orbitals are populated by d–d excitation, the minimum potential energy of the states $^4T_{2g}(^4F)$, $^4T_{1g}(^4F)$ and $^4T_{1g}(^4P)$ is shifted by the quantity ΔQ relative to the minimum of the $^2E_g(^2G)$ state.

The potentials for the excited states $^2E_g(^2G)$, $^4T_{2g}(^4F)$, $^4T_{1g}(^4F)$ and $^4T_{1g}(^4P)$ are as follows:

$$V(^2E_g(^2G)) = 1/2(kQ^2) + E_{ZPL}(^2E_g(^2G)) \quad (1a)$$

$$V(^4T_{2g}(^4F)) = 1/2(k(Q - \Delta Q_1)^2) + E_{ZPL}(^4T_{2g}(^4F)) \quad (1b)$$

$$V(^4T_{1g}(^4F)) = 1/2(k(Q - \Delta Q_1)^2) + E_{ZPL}(^4T_{1g}(^4F)) \quad (1c)$$

$$V(^4T_{1g}(^4P)) = 1/2(k(Q - \Delta Q_1)^2) + E_{ZPL}(^4T_{1g}(^4P)) \quad (1d)$$

where $E_{ZPL}(^2E_g(^2G))$, $E_{ZPL}(^4T_{2g}(^4F))$, $E_{ZPL}(^4T_{1g}(^4F))$, and $E_{ZPL}(^4T_{1g}(^4P))$ are the energies of the minima for the $^2E_g(^2G)$, $^4T_{2g}(^4F)$, $^4T_{1g}(^4F)$ and $^4T_{1g}(^4P)$ states, respectively, and k is the Raman frequency of $GdAlO_3$ assigned to the ground and excited states. The adiabatic potential state surfaces, obtained from eqn (1) are depicted in Fig. 10.

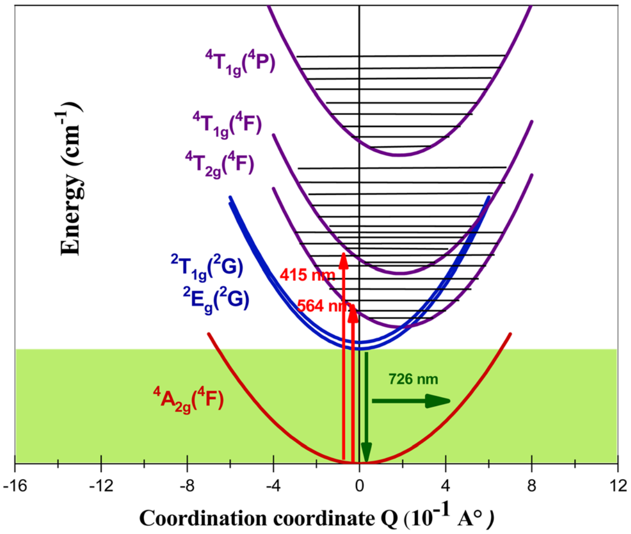

Fig. 10 Adiabatic potential energy curves for $^2E_g(^2G)$, $^4T_{2g}(^4F)$, $^4T_{1g}(^4F)$ and $^4T_{1g}(^4P)$ states.

3.4.5 Crystal field analysis of Cr^{3+} in $GdAlO_3$ and relevance to PLE and PL spectra. The electronic structure of Cr^{3+} in $GdAlO_3$ can be ascertained by employing the Crystal Field Theory (CFT). In this work, we expand on previous studies by providing a more detailed analysis of the crystal field effects and their influence on the photoluminescence (PL) behavior of Cr^{3+} in this host material. The Cr^{3+} ion energy levels are assessed using a complete Hamiltonian, and the crystal field strength (D_q), as well as the Racah parameters (B and C), are found by analyzing the optical PLE and PL spectra.

The Cr^{3+} ion energy levels are assessed using the complete Hamiltonian:[38–50]

$$H = H_0 + H_{ee}(B, C) + H_{Trees}(\alpha_{Trees}) + H_{CF}(D_q) + H_{SO}(\zeta) \quad (2)$$

where H_0 is the configuration Hamiltonian, H_{ee} is the electron–electron repulsion Hamiltonian,[51–53] H_{SO} is the spin–orbit coupling Hamiltonian, the H_{Trees} Hamiltonian included the Trees correction,[54,55] and H_{CF} is the crystal field Hamiltonian for octahedral symmetry (O_h):[56–58]

$$H_{CF} = 21D_q\left[C_0^{(4)} + \sqrt{\frac{5}{14}}\left(C_0^{(4)} + C_{-4}^{(4)}\right)\right] \quad (3)$$

In eqn (2) and (3) the parameter D_q represents the ligand field splitting, while numerical techniques are used to specifically calculate the matrix elements for the $C_q(k)$ operators, as described in ref. 59. The α_{Trees} and ζ parameters are calculated using the following equations:[54–56]

$$\alpha_{Trees} = N^4\alpha_0$$

and

$$\zeta = N^2\zeta_0 \quad (4)$$

with:

$$N^2 = \frac{1}{2}\left(\sqrt{\frac{B}{B_0}} + \sqrt{\frac{C}{C_0}}\right) \quad (5)$$

where, N is the reduction factor.[60]

Table 7 Optical parameter values for the theoretical study of $GdAlO_3:Cr^{3+}$

Parameter	Value [this study]	Parameter	Value[43,51]
D_q (cm^{-1})	1773	B_0 (cm^{-1})	918
B (cm^{-1})	617	C_0 (cm^{-1})	4133
C (cm^{-1})	3045	α_0	30
α (cm^{-1})	21.12	ζ_0	275
ζ (cm^{-1})	230.75		
D_q/B	2.87		
C/B	4.94		

Table 8 Experimental and calculated energies (cm^{-1}) of $GdAlO_3:Cr^{3+}$

O_h	E_{obs}	E^*_{cal} [this work]	E^{a*}_{cal} [this work]
$^4A_{2g}(^4F)$	0	0	0
$^2E_g(^2G)$	—	13 767	13 896 (4)
$^2T_{1g}(^2G)$		14 282	14 404 (4)
			14 461 (2)
$^4T_{2g}(^4F)$	17 730	17 730	17 637 (2)
			17 692 (4)
			17 802 (2)
			17 806 (4)
$^2T_{2g}(^2G)$	—	20 897	20 966 (4)
			21 072 (2)
$^4T_{1g}(^4F)$	23 923	24 097	23 988 (4)
			23 997 (2)
			24 002 (2)
			24 006 (4)
$^2A_{1g}(^2G)$	—	29 333	29 514 (2)
$^2T_{1g}(^2P)$	—	31 342	31 541 (2)
			31 587 (4)
$^2T_{1g}(^2H)$	—	31 653	31 744 (2)
			31 918 (4)
$^2E_g(^2H)$	—	33 266	33 397 (4)
$^2T_{1g}(^2H)$	—	36 101	36 161 (2)
			36 196 (4)
$^4T_{1g}(^4P)$	—	38 348	38 208 (2)
			38 223 (4)
			38 326 (4)
			38 361 (2)
$^2T_{2g}(^2H)$	—	40 349	40 252 (2)
			40 355 (4)
$^2A_{2g}(^2F)$	—	41 673	41 683 (2)
$^2T_{2g}(^2_aD)$	—	49 008	49 258 (2)
			49 369 (4)
$^2T_{2g}(^2F)$	—	50 418	50 335 (4)
			50 455 (2)
$^2E_g(^2_aD)$	—	50 334	50 564 (4)
$^2T_{1g}(^2F)$	—	54 944	54 841 (2)
			54 966 (4)
$^2T_{2g}(^2_bD)$	—	68 763	68 605 (4)
			68 804 (2)
$^2E_g(^2_bD)$	—	72 704	72 761 (4)

We derived a stable crystal-field and Racah parameters for Cr^{3+} ions, which allow to calculate the electronic energy levels of $Cr^{3+}(3d^3)$ ions in the O_h symmetry site of a Cr^{3+} doped $GdAlO_3$ perovskite ($GdAlO_3$:Cr^{3+}). The free ion Cr^{3+} parameters B_0, C_0, α_0 and ζ_0 are listed in Table 7.[41–43] The crystal-field strength parameter D_q was computed using the energy of the quartet excited state $^4T_{2g}(^4F)$, and the Racah parameters B and C were calculated based on the observed excited states of the $^4T_{1g}(^4F)$ quartet and the $^2E_g(^2G)$ doublet, decreasing in relation to their values for the free ion due to the covalency effect. The values of α and ζ were obtained using eqn (3)–(5). The calculations were done using a custom code that was developed in our laboratory, by S. Kammoun, using the Maple 2024 software. The calculated energies (Table 8) are in excellent agreement with the experimental findings of Yeung *et al.*,[61] thus validating our computational method.

Electrons are usually transferred from one atom to another during ionic bonding, producing positively and negatively charged ions. Eqn (6) allows to evaluate the type of bonding for Cr^{3+} in $GdAlO_3$:Cr^{3+}.[62] In this equation, h is a measure of the degree of electron delocalization between the cation to the ligands. For the considered system, the constant k is equal to 0.21.[63,64]

$$h = \left[\frac{B_0 - B}{B_0 k}\right] \tag{6}$$

The calculated large value for h (1.44) indicates a high degree of d-electron delocalization, revealing the high ionic character of the bonds established between Cr^{3+} ions and their ligands.

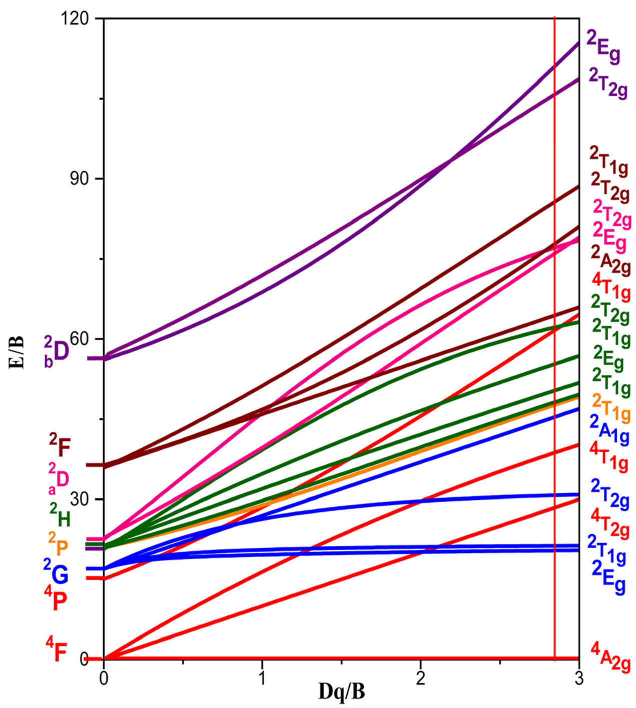

Fig. 11 Tanabe–Sugano energy-levels diagram highlighting the case of $Cr^{3+}(3d^3)$ ion doped into the octahedral symmetry site of $GdAlO_3$, as expressed by the vertical line for $D_q/B = 2.87$.

The basic optical characteristics of $3d^n$ transition-metal ions doped into crystalline hosts can be explained by the crystal-field model. The Tanabe–Sugano energy-level diagram presented in Fig. 11 shows how the ratio D_q/B affects the electronic energy levels of $3d^n$ trivalent ionic species in the octahedral site of the $GdAlO_3$ host. The vertical line in Fig. 11 for $D_q/B = 2.87$ corresponds to Cr^{3+} doped into the $GdAlO_3$ perovskite in an octahedral site symmetry.

The theoretical study for determining the electronic structure of Cr^{3+} ion in $GdAlO_3$:Cr,Sm using crystal field theory confirms that this ion replaces Al^{3+} at an octahedral site. Indeed, there is a satisfactory agreement between the experimental and theoretical levels, considering that Cr^{3+} replaces Al^{3+} at an octahedral site. The importance of the theoretical study using crystal field theory lies in the fact that it confirms the oxidation state and the site occupied by the Cr^{3+} ion. Also, it is only through this theoretical study that the d–d transitions can be accurately assigned, as these transitions vary for the same ion depending on the matrix (intermediate crystal field).

4. Conclusion

In conclusion, the orthorhombic $Gd_{0.995}Sm_{0.005}Al_{0.995}Cr_{0.005}O_3$ sample, synthesized through the solid-state reaction method, underwent comprehensive investigation of its structure, morphology, and photoluminescence properties. The material crystallized in the orthorhombic *Pbnm* space group, with Cr^{3+} ions substituting for Al^{3+} ions in octahedral site symmetry within the $GdAlO_3$:Sm^{3+}, Cr^{3+} matrix. Examination *via* Scanning Electron Microscopy (SEM) and Energy Dispersive X-ray analysis confirmed the morphology and homogeneity of the sample's chemical composition. Photoluminescence excitation (PLE) and photoluminescence (PL) spectra revealed the electronic structure of Cr^{3+} ions in the O_h symmetry site, with theoretical studies allowing for precise attribution of their 3d–3d transitions. Additionally, intra-configurational 4f–4f transitions of Sm^{3+} resulted in various excitation bands observed in the PLE spectrum at higher wavelengths. Moreover, the photoluminescence studies give additional support to the occurrence of energy transfer among Gd^{3+}, Sm^{3+}, and Cr^{3+} ions. Based on these findings, the synthesized nanophosphor samples demonstrate strong potential for applications in solid-state lighting.

Data availability

Data are available upon request to the authors.

Conflicts of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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