Broadband photoluminescence in a ceramic ($\text{Mg}_2\text{SnO}_4\text{--SnO}_2$): Cr^{3+} system

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Abstract

This study reports the synthesis and photoluminescence spectroscopic studies of Cr^{3+} -doped $\text{Mg}_2\text{SnO}_4\text{--SnO}_2$ ceramics. The crystal structure was analyzed by X-ray powder diffraction, and photoluminescence was investigated at room temperature. The diffractogram confirmed the presence of Mg_2SnO_4 and SnO_2 phases. Photoluminescence spectroscopy identified broad and intense emission bands assigned to the Cr^{3+} cation occupation in octahedral Mg_2SnO_4 sites and an orange band assigned to SnO_2 emission. All spectra were analyzed and interpreted according to crystal field theory and Tanabe–Sugano theory for the d^3 electronic configuration. The broad and intense emission band covering the visible/near-infrared region suggests that this system may be a promising material for use as an active medium in a broadband light source at room temperature.

Keywords Optical ceramics · Transition metal complexes · Photoluminescence

1 Introduction

Ceramics with multifunctional applications have been widely explored both commercially and scientifically. The physical properties of ceramics are currently being studied to discover and optimize new applications, with the advantage of being environmentally friendly and relatively inexpensive. A successful example is magnesium stannate (Mg_2SnO_4) ceramics, which exhibit dielectric, semiconductor, photocatalytic and luminescent properties. These properties make these ceramics suitable for applications at high temperatures and frequencies as electronic ceramics in thermally stable capacitors [1, 2]; as monopole antennas for radio and wireless communications [3]; as an alternative anode material in Li-ion batteries [4, 5]; and for photocatalysis [6, 7], optical storage and optical communications [8], among other uses. The synthesis of these ceramics is relatively easy, mostly carried out by solid-state reactions

at high temperatures [1, 5, 9], although other routes have also been explored [4, 6, 10].

Luminescent undoped Mg_2SnO_4 properties are intimately related to its crystal environment. The Mg_2SnO_4 crystal structure is a cubic inverse spinel of the II–IV type (with the molecular formula $\text{A}^{2+}_2\text{B}^{4+}\text{O}^{2-}_4$), where Mg^{2+} and Sn^{4+} are randomly located in octahedral sites, while tetrahedral sites are fully occupied by Mg^{2+} [11–14]. Several authors report the emission of undoped Mg_2SnO_4 through thermoluminescence and photoluminescence mechanisms [8, 11, 15, 16]. Behr [11] and Zhang [15] proposed that the high disorder degree originating from lattice defects is responsible for the luminescent properties of this system. Zhang also observed that the undoped compound exhibits a band centered at 498 nm when irradiated with ultraviolet radiation due to the recombination of oxygen vacancies with crystal structure holes. To the best of our knowledge, no reports on undoped Mg_2SnO_4 emissions in the infrared region are available. The electron

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trapping feature makes magnesium stannate an adequate material for use in optical storage and imaging techniques [15].

The doped Mg_2SnO_4 crystal system has been studied using transition metals and lanthanide cations as activators. Zhang and Li reported the broadband emission of $\text{Mg}_2\text{SnO}_4:\text{Ti}^{4+}$ in the blue–green region under ultraviolet excitation [9, 12]. Li pointed out that Mn^{2+} -doping enlarged the undoped band emission in the green region [9], while other authors have also studied Mn^{2+} -doped samples [17–19]. When doped with divalent cobalt, the compound exhibits an intense broadband in the red–infrared range due to the Co^{2+} activator in tetrahedral sites [20]. Recently, Cai et al. presented results for single-phase $\text{Mg}_{2-x}\text{SnO}_4:\text{Cr}^{3+}$ [21], observing emission bands centered at approximately 750 nm for several Cr^{3+} concentrations. Zhang detailed the photoluminescent properties of $\text{Mg}_2\text{SnO}_4:\text{Eu}^{3+}$, reporting reddish emission at room temperature [22], while Guo analyzed $\text{Mg}_2\text{SnO}_4:\text{Pr}^{3+}$ emissions, detecting bands centered at 530 nm and 570 nm [23].

The crystal structure of tin oxide (SnO_2) is usually reported as rutile type, with tetragonal symmetry where the Sn^{4+} cations are in the center of the octahedra formed by O^{2-} anions [24]. The luminescent properties of this system have been previously investigated by Gu and coauthors, who observed a band in the emission spectrum between 400 and 450 nm [25]. The authors claim that this emission originates from electron transitions mediated by oxygen vacancies. Garcia-Tecedor et al. reported broad emission in undoped SnO_2 [26], with peaks centered at 1.94 eV (639 nm), 2.25 eV (551 nm) and 2.58 eV (480 nm) also originating from oxygen vacancies and surface defects. To the best of our knowledge, no reports of undoped SnO_2 emissions in the infrared region are available.

It is well known that the trivalent chromium cation is used as an activator in ceramic systems, inducing intense red–infrared emission caused by its optical transitions related to the splitting of its energy levels in an octahedral environment. This intense luminescence presents several applications depending on the lattice. For example, $\text{NaAl}(\text{WO}_4)_2:\text{Cr}^{3+}$ has been used as a broadband laser source [27], $\text{LiInSi}_2\text{O}_6:\text{Cr}^{3+}$ in LED-based devices [28], $\text{ZnGa}_2\text{O}_4:\text{Cr}^{3+}$ and $\text{LaAlO}_3:\text{Cr}^{3+}$ in in vivo imaging [29, 30], $\text{LaAlO}_3:\text{Cr}^{3+}$, Ca^{2+} in energy-saving applications [31] and $\text{NaGd}_{0.78}\text{F}_4:\text{Yb}_{0.2}/\text{Er}_{0.02}/\text{Cr}^{3+}_x$ in luminescence-based temperature sensors [32].

In this context, as Mg_2SnO_4 and SnO_2 single phases have been reported as presenting emissions separately at room temperature, the aim of the present study was to investigate whether it is possible to obtain a system exhibiting broadband emissions from the combination of both compounds and the addition of Cr^{3+} as an activator. The

present study reports the structural and photoluminescent properties of a Cr^{3+} -doped $\text{Mg}_2\text{SnO}_4\text{--SnO}_2$ system. Samples were prepared through the solid-state method at high temperatures. The system structure was investigated by X-ray diffraction, and the relevant crystallographic parameters were obtained using the Rietveld method. Elemental analysis was performed using X-ray microfluorescence. Photoluminescence emission and excitation at room temperature were used to identify the optical transitions. The results indicate broadband emission, leading to a system with a photoluminescent signal covering almost the entire visible/near-infrared range.

2 Experimental

Samples were synthesized using the raw chemicals MgO (99%, Riedel-de Hën), SnO_2 (99.9%, Sigma-Aldrich) and Cr_2O_3 (99%, Vetec) as starting materials in powder form to obtain $\text{Mg}_{2(1-x)}\text{Cr}_{2x}\text{SnO}_4$ ($x=0.001$) + SnO_2 . The samples were prepared by the conventional solid-state reaction. Powder oxides were manually weighed and crushed for homogenization. Subsequently, the powder was pressed in an axial direction into 13-mm-diameter and 1-mm-thick pellets under 296 MPa pressure. The pellets were then deposited in alumina crucibles for sintering, undergoing a thermal treatment where they were heated until 1200 °C in an electric furnace under atmospheric pressure at a heating rate of 10 °C/min, remaining at 1200 °C for 6 h. Then, the pellets were removed from the furnace at room temperature, and one pellet was crushed until a homogeneous, thin powder was obtained for the X-ray diffraction experiments.

The diffraction pattern was obtained at room temperature using a Bruker D2 Phaser diffractometer with $\text{Cu-K}\alpha_1$ radiation ($\lambda=1.54056$ Å) operating at 30 kV and 10 mA. Data were collected in a Bragg–Brentano geometry with $15^\circ < 2\theta < 80^\circ$ and a step size of 0.01° . X-ray diffraction data were refined by the Rietveld method using the FullProf package [33] with comparative data from the Inorganic Crystal Structure Database (ICSD). The Rietveld refinement provides information about the space group, lattice parameters and phase quantification.

The sample chemical composition was verified through elemental analysis by X-ray microfluorescence (μXRF) using an M4 Tornado Bruker system with a Rh target X-ray tube operating at 40 kV and 500 μA . The spectra were collected in distinct spots in one pellet for 30 s.

Photoluminescence experiments (emission and excitation spectra) were performed at room temperature using a PTI 300 QuantaMaster spectrofluorometer equipped with a 75 W pulsed xenon lamp operating at 200 Hz and 1 nm spectral resolution. A PTI 914 Photomultiplier Detection

System model R928 (185–900 nm range, peak at 400 nm) was used for signal detection. Filters were used to block excitation and scattered lights in the emission detection apparatus. All photoluminescence spectra were corrected by the apparatus sensitivity response.

3 Results

3.1 Crystal structure and elemental analysis

Figure 1 displays the powder diffractogram recorded at room temperature. The most intense peaks were assigned to the Mg_2SnO_4 phase, while some peaks that did not match this phase were identified to be the SnO_2 phase. Rietveld refinement was performed using cubic Mg_2SnO_4 (ICSD code 28199) and tetragonal SnO_2 (ICSD code 84576) data files as input. According to the refinement, the phase proportion in the sample was 59% Mg_2SnO_4 and 41% SnO_2 . Mg_2SnO_4 crystallized in the $Fd\bar{3}m$ space group with cubic symmetry. The observed SnO_2 phase exhibited a rutile-type structure in the $P4_2/mnm$ space group and tetragonal symmetry. Structural details obtained from the Rietveld refinement are displayed in Table 1. The agreement factors presented in Table 1 indicate good correspondence between the calculated and observed patterns. The goodness-of-fit index (GOF index) extracted from the refinement was 1.6, indicating high refinement quality.

Fig. 1 Powder X-ray diffractogram of the sample. The red circles represent the observed pattern (Y_{obs}), the black line represents the calculated pattern (Y_{calc}), and the blue line represents the difference between the observed and calculated patterns ($Y_{obs} - Y_{calc}$). The green vertical bars represent the Bragg reflection positions of the Mg_2SnO_4 (top) and SnO_2 (bottom) phases

Table 1 Refined crystallographic parameters and agreement factors

Phase	Mg_2SnO_4	SnO_2
ICSD code	28199	84576
Proportion (%)	59	41
Crystal system	Cubic	Tetragonal
Space group	$Fd\bar{3}m$	$P4_2/mnm$
a, b, c (Å)	8.637, 8.637, 8.637	4.737, 4.737, 3.186
α, β, γ (°)	90, 90, 90	90, 90, 90
Cell volume (Å ³)	644.401	71.532

Agreement factors: R_{wp} = 10.1; R_p = 10.5; R_{exp} = 6.3; χ^2 = 2.7; GOF index = 1.6

It was important to estimate the Cr^{3+} occupation position in the identified phases in the sample, keeping in mind that the percentage difference between the atomic radii of the inserted and replaced cations must be lower than 15% [34]. The atomic radius of Mg^{2+} is 0.57 Å when its coordination number (CN) is 4 and 0.72 Å when CN = 6, changing to 0.69 Å and 0.62 Å for Sn^{4+} and Cr^{3+} , respectively, with CN = 6 [35]. Therefore, when assessing ionic radius and cation symmetry, it was noted that Cr^{3+} can replace both Mg^{2+} and Sn^{4+} in octahedral symmetry, since the ionic radius percentage difference is close to 14% between Mg^{2+} and Cr^{3+} , while it is 10% between Sn^{4+} and Cr^{3+} , considering CN = 6 for all cations. When assessing the cation valence involved in the occupation of the octahedral sites (Cr^{3+} , Mg^{2+} and Sn^{4+}), we believe that the most likely replacement to occur will be with Cr^{3+} -occupying octahedral Mg^{2+} sites. This replacement would be more favorable, requiring only one electron to perform charge compensation, and this electron could then be shared by the O^{2-} anions with Cr^{3+} , generating a covalent bond between O^{2-} and Cr^{3+} , allowing for Mg^{2+} replacement.

As mentioned previously, Mg_2SnO_4 contains tetrahedral and octahedral sites, while SnO_2 is composed of Sn^{4+} surrounded by oxygen anions, with octahedral symmetry in a tetragonal system. It is well known that Cr^{3+} tends to preferably occupy octahedral sites. Photoluminescence spectroscopy may indicate the occupation symmetry of Cr^{3+} in the occupied phase(s), according to the position and shape of the observed emission and excitation bands.

The room temperature X-ray microfluorescence spectrum for the sample is depicted in Fig. 2. The measurements were performed in several regions on the sample surface, with similar results showing sample homogeneity. Peaks at 1.2651 keV ($\text{Mg-K}\alpha_1$), 3.4549 keV ($\text{Sn-L}\alpha_1$), 3.6948 keV ($\text{Sn-L}\beta_1$) and 5.4247 keV ($\text{Mg-K}\alpha_1$) were identified. The weakest peaks close to the intense Sn peaks were

Fig. 2 The sample X-ray microfluorescence spectrum. Peaks related to Mg, Sn and Cr are identified in the spectrum. The Rh peak is due to the anode of the X-ray tube

identified as weak Sn lines. The Rh peak was due to the anode of the X-ray tube.

3.2 Emission and excitation spectra

Figure 3 exhibits the photoluminescence spectra of the Cr^{3+} -doped sample with excitations at (a) 300 nm and (b) 450 nm at room temperature. Under 300 nm excitation (Fig. 3a), the sample displayed broad emission in the visible/near-infrared range, exhibiting two intense bands with maxima located at 614 nm and 783 nm, in addition to a

weak signal at 701 nm. The width of the band at 783 nm is related to a characteristic emission from an energy level strongly dependent on the crystal field in an octahedral environment. From this evidence, the band at 783 nm was assigned to the ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ Cr^{3+} transition [36, 37].

Several studies have reported lattice emissions near 500 nm under ultraviolet excitation, originating from the recombination of oxygen vacancies with holes in the Mg_2SnO_4 lattice, probably caused by the number of defects generated by the cation disorder commonly found in the inverse spinel structure [11, 12, 14, 15]. This emission was not observed herein, and the band at 614 nm was far from the previously reported Mg_2SnO_4 emission.

Previous studies have described characteristic undoped SnO_2 emissions of approximately 1.94 eV (639 nm) [26, 38]. Arai and Adachi reported an emission signal at approximately 610 nm ($\lambda_{\text{exc}} = 290$ nm) in undoped SnO_2 nanopowder [39]. Based on these studies, the band located at 614 nm was assigned to the SnO_2 lattice emission. The bluish Mg_2SnO_4 emission mentioned previously at approximately 500 nm was probably hidden by the SnO_2 emission band. Figure 3a displays intense broadband emission over a broad range from the blue to infrared region (450–850 nm), indicating that the $\text{Mg}_2\text{SnO}_4:\text{Cr}^{3+} + \text{SnO}_2$ system was highly effective in achieving a system with intense broadband emission at room temperature.

Figure 3b displays the emission spectrum under 450 nm excitation, exhibiting a broadband located in the near-infrared range with a maximum at 792 nm. Two weak structures were observed in this spectrum at 695 nm and 703 nm. The emission signal increased over twofold

Fig. 3 Photoluminescence spectra of the sample under **a** 300 nm and **b** 450 nm excitation at room temperature. **a** Under 300 nm excitation, the sample exhibited two overlapping bands with maxima at 614 nm and 783 nm. **b** Under 450 nm excitation, the sample

presented a broadband signal with a maximum at approximately 792 nm. One structure is present at 701 nm in the **a** spectrum; two structures are present at 695 nm and 703 nm in the **b** spectrum

(relative to Fig. 3a) under 450 nm excitation. This can be an indication that the main emitting centers in the sample are the Cr^{3+} cations located in the octahedral sites since it is known that wavelengths in the blue region are easily absorbed by Cr^{3+} ions in this coordination. The emission at 792 nm was assigned to the ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ Cr^{3+} transition in octahedral symmetry for the same reasons explained above. The structures overlapping with the broadband at 701 nm in Fig. 3a and 695 nm and 703 nm in Fig. 3b nm were identified as the *R*-lines corresponding to the ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ spin-forbidden Cr^{3+} transition. The splitting of the observed *R*-lines (164 cm^{-1}) in Fig. 3b might indicate that these lines do not belong to the same type of emitting center. The decrease in signal at approximately 854 nm was due to the experimental setup, which did not respond efficiently to wavelengths above this.

Cai and coauthors [21] observed a broadband emission centered at 750 nm for single-phase $\text{Mg}_{2-x}\text{SnO}_4:\text{Cr}^{3+}$ under 470 nm excitation and associated this emission with the presence of Cr^{3+} ions in the Mg_2SnO_4 lattice. The difference between the bands observed herein and the results reported in [21] may be explained mainly by the fact that the sample in [21] was of a single phase, while in the present study, the system contained two phases in which band overlapping was observed.

Considering Fig. 3, it is possible to say that under 300 nm excitation, the luminescent centers from both $\text{Mg}_2\text{SnO}_4:\text{Cr}^{3+}$ and SnO_2 were excited (Fig. 3a), but under 450 nm excitation, only $\text{Mg}_2\text{SnO}_4:\text{Cr}^{3+}$ luminescent centers were excited (Fig. 3b).

Figure 4 depicts the photoluminescence excitation spectrum with monitored emission at 785 nm. The two

Fig. 4 Photoluminescence excitation spectra obtained at room temperature monitored at 785 nm. Black dots indicate the experimental data, green curves represent the Gaussian band fitting, and the red curve represents the Gaussian convolution

bands in the visible region present features related to electronic Cr^{3+} transitions situated in octahedral sites. The band positions were obtained by Gaussian fitting. The band centered at $21,746\text{ cm}^{-1}$ (460 nm) was assigned to the ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_1({}^4\text{F})$ electronic transition, while the band centered at $15,998\text{ cm}^{-1}$ (625 nm) was assigned to the ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_2({}^4\text{F})$ electronic transition. The band shapes and energy intervals are a certain indication that the Cr^{3+} ions were situated in an octahedral environment in the lattice. The emission and excitation results agree with the X-ray fluorescence data since none of the techniques detected possible emitting centers other than chromium atoms.

Transition metal cations in a crystalline environment are subjected to changes in their energy levels due to crystal field action. If this environment presents octahedral or tetrahedral symmetry, these changes can be analyzed using the Tanabe–Sugano theory [40–42], which was developed to estimate the energies involved in the electronic transitions in systems doped by cations with incomplete d shells (d^2 – d^8) and to determine the crystal field strength and the interelectronic parameters from the transition energies. The energy values to be used in the Tanabe–Sugano theory are obtained from the photoluminescence spectra, where the energy of the levels involved in the electronic transitions and the intensity of the crystal field, represented by the *Dq* parameter [42], can then be estimated. The Cr^{3+} cation possesses three electrons in its outer shell (d^3 system). The energy matrices and energy level diagram developed by Tanabe–Sugano were used to understand the photoluminescent properties observed herein [40–43].

Analyzing the d^3 energy level diagram for octahedral symmetry [43], the ground level is labeled ${}^4\text{A}_2({}^4\text{F})$, with the first excited state changing if the cation experiences an intense ($Dq/B > 2.3$) or weak crystal field ($Dq/B < 2.3$), where *B* is the Racah parameter. A weak crystal field environment usually generates a broadband associated with the ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transition, as the ${}^4\text{T}_2({}^4\text{F})$ level is the first excited state, while an intense crystal field environment is correlated with the sharp ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transition since ${}^2\text{E}({}^2\text{G})$ is the first excited state in this situation. Although the broadband signal is related to a weak crystal field, previous studies report broadband emission for $Dq/B > 2.3$ [27, 44].

An interesting case where both transitions can be observed in the same spectrum happens around the crossing level region ($Dq/B \approx 2.3$), where both levels are relatively close to each other. Wojtowicz and coauthors describe two types of coupling between ${}^2\text{E}({}^2\text{G})$ and ${}^4\text{T}_2({}^4\text{F})$ states [45]: the electron–phonon interaction, which can contribute to the mixing of ${}^2\text{E}({}^2\text{G})$ and ${}^4\text{T}_2({}^4\text{F})$ states in a lattice with octahedral site distortion, and the spin–orbit coupling between ${}^2\text{E}({}^2\text{G})$ and ${}^4\text{T}_2({}^4\text{F})$ states,

which breaks the spin multiplicity selection rule, allowing the ${}^2E(^2G) \rightarrow {}^4A_2(^4F)$ transition. These interactions result in broadband emission from the ${}^4T_2(^4F) \rightarrow {}^4A_2(^4F)$ spin-allowed transition accompanied by a structure assigned to the ${}^2E(^2G) \rightarrow {}^4A_2(^4F)$ transition in the emission spectrum.

The Dq and B parameter values are usually determined from the Tanabe–Sugano matrices for d^3 systems [40–43] using the transition energy values obtained from the excitation spectrum as input. The excitation band energies related to the ${}^4A_2(^4F) \rightarrow {}^4T_2(^4F)$ and ${}^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ transitions were used to calculate Dq and B through Eqs. 1 and 2 [43]:

$$E({}^4T_2(^4F)) = 10Dq \quad (1)$$

$$\frac{B}{Dq} = \frac{(\Delta E/Dq)^2 - 10(\Delta E/Dq)}{15[(\Delta E/Dq) - 8]} \quad (2)$$

where $\Delta E = E({}^4T_1(^4F)) - E({}^4T_2(^4F))$.

The calculated values from Eqs. (1) and (2) were $Dq = 1,600 \text{ cm}^{-1}$ and $B = 556 \text{ cm}^{-1}$. The Dq/B ratio was 2.88. This value seemed to be higher than expected for systems containing Cr^{3+} as an activator [46].

Adachi [46, 47] recently proposed a model for the calculation of the Dq and B parameters, starting from the energies of the ${}^2E(^2G)$ and ${}^4T_2(^4F)$ states and the C/B ratio. Assuming $C/B = 4.8$ (a reasonable value for d^3 systems [43]) and using the energies of the ${}^4A_2(^4F) \rightarrow {}^4T_2(^4F)$ transition (band at $15,998 \text{ cm}^{-1}$ in the excitation spectrum) and the ${}^2E(^2G) \rightarrow {}^4A_2(^4F)$ transition (structure at 695 nm ($14,388 \text{ cm}^{-1}$) in the emission spectrum) observed in the present work, the found values of the parameters from the Adachi model were $Dq = 1,600 \text{ cm}^{-1}$ and $B = 691 \text{ cm}^{-1}$, with $Dq/B = 2.32$. The Dq/B value was relatively close to that reported in the literature for oxide systems that use Cr^{3+} as an activator [36, 43].

This Dq/B value obtained from the Adachi model is distinct from the Dq/B ratio obtained using Eqs. (1) and (2), probably due to energy deviations between the observed and expected energies since the energies related to the ${}^4T_1(^4F)$ and ${}^4T_2(^4F)$ states are both used in the B calculation using the energy matrices [46, 47]. The energy of the ${}^4A_2(^4F) \rightarrow {}^4T_1(^4F)$ transition estimated by the Adachi model was $22,771 \text{ cm}^{-1}$, which gives a difference close to 5% of the observed value ($21,746 \text{ cm}^{-1}$), which can be considered a good result.

It is also possible to estimate the energy parameter values using a method where the Dq/B ratio is obtained from the d^3 Tanabe–Sugano diagram alongside the band energy positions observed in the excitation spectrum [48, 49]. Initially, a selected transition will serve as a parameter for indexing the other transitions. In the case of the d^3

system (such as that studied herein), the ${}^2E(^2G) \rightarrow {}^4A_2(^4F)$ transition observed in the emission spectrum was chosen. It is important to note that since the ${}^2E(^2G)$ state can be considered (in the intermediate–strong field region) independent from the crystal field, theoretically, it is expected that its energy position in the emission spectrum will be the same energy position in the excitation spectrum [50]. Therefore, even if it has not been observed in the excitation spectrum, this transition will be compared to the energy positions of the other transitions in the excitation spectrum. For the same reason, this transition was used in the Adachi model described previously. Among the crystal field-dependent transitions, the energy determination of the ${}^4A_2(^4F) \rightarrow {}^4T_2(^4F)$ transition is more accurate than that of ${}^4A_2(^4F) \rightarrow {}^4T_1(^4F)$, where the last transition is found in a higher-lying energy position [46, 47].

The ${}^4T_2(^4F)/{}^2E(^2G)$ energy ratio was obtained using the observed energies of the ${}^4T_2(^4F)$ and ${}^2E(^2G)$ levels, considering ${}^4A_2(^4F)$ as the ground level. With the ${}^2E(^2G)$ energy level used as a reference, it was possible to identify the height of the ${}^4T_2(^4F)$ level in the Tanabe–Sugano diagram, which was ${}^4T_2(^4F)/{}^2E(^2G)$ times the height of the ${}^2E(^2G)$ energy level. For this height (a point on the ${}^4T_2(^4F)$ energy level), the E/B value was obtained on the vertical axis of the Tanabe–Sugano d^3 diagram. Using the energy of the ${}^4A_2(^4F) \rightarrow {}^4T_2(^4F)$ transition observed in the excitation spectrum in E/B , a B value was obtained. A similar procedure was performed for the ${}^4T_1(^4F)/{}^2E(^2G)$ ratio, and a second B value was obtained. In addition, an E/B value can be obtained from the ${}^2E(^2G) \rightarrow {}^4A_2(^4F)$ transition, leading to a third B value. The average B value ($\langle B \rangle$) obtained from this procedure was 690 cm^{-1} , with $Dq = 1,600 \text{ cm}^{-1}$ obtained from the ${}^4A_2(^4F) \rightarrow {}^4T_2(^4F)$ transition. From this method, the Dq/B ratio was 2.32, located close to the crossing level region. The Dq , B and Dq/B values were relatively close to the values determined using the Adachi model [46, 47].

Figure 5 displays an energy level diagram, showing the energy levels involved in the Cr^{3+} excitation and emission processes in the $\text{Mg}_2\text{SnO}_4\text{--SnO}_2$ system. During the excitation process, the Cr^{3+} outer shell electrons are promoted from the ${}^4A_2(^4F)$ ground level to the ${}^4T_1(^4F)$ and ${}^4T_2(^4F)$ excited levels (green arrows in Fig. 5a). After some time, the electrons return to ground level, emitting light with a specific energy. This situation is observed in Fig. 5b and is represented by red arrows. Before arriving at the ground level, the system nonradiatively decays from the higher excited state ${}^4T_1(^4F)$ to the lower ${}^4T_2(^4F)$ and ${}^2E(^2G)$ excited states (black arrows in Fig. 5b), from which they decay again, emitting light.

The energy related to the emission from the ${}^4T_2(^4F)$ state is lower than that observed in the excitation process. This energy difference can be explained by the fact that part of the energy used to excite the system is converted

Fig. 5 Energy level diagram showing the energy levels involved in the Cr^{3+} excitation and emission processes in the $\text{Mg}_2\text{SnO}_4\text{-SnO}_2$ system. The green arrows represent the transitions related to the excitation process, while the red arrows represent the transitions related to the emission process. The black arrows represent the nonradiative transitions

into nonradiative emission (related to lattice vibrations). Therefore, the phonon-assisted emission in the infrared region assigned as the ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ transition occurs at a longer wavelength (and lower energy) than the excitation band assigned to the ${}^4\text{A}_2({}^4\text{F}) \rightarrow {}^4\text{T}_2({}^4\text{F})$ transition. This energy difference (called the Stokes shift) was calculated as $3,372\text{ cm}^{-1}$ using the emission value at 450 nm excitation. A large Stokes shift, as observed in the present study, is advantageous because it is related to a large difference in energy between the emission and excitation bands. This large energy difference between the emission and excitation bands prevents the emitted radiation from being reabsorbed by the activator ions in the vicinity of each emitting ion. Consequently, a large Stokes shift favors luminescence because it avoids intensity losses that could be caused by emitted radiation reabsorption.

Fig. 6 CIE chromaticity diagram for emission under 300 nm excitation at room temperature

The nonradiative processes also populate the ${}^2\text{E}({}^2\text{G})$ level, generating the R-lines to be observed in Fig. 3. The system decays nonradiatively from the ${}^4\text{T}_1({}^4\text{F})$ level, populating the ${}^4\text{T}_2({}^4\text{F})$ and ${}^2\text{E}({}^2\text{G})$ levels, from which radiative transitions to the ground level occur. This behavior was reported by Martín-Rodríguez and coauthors in $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Cr}^{3+}$ nanoparticles [51], where the authors observed sharp lines related to the ${}^2\text{E}({}^2\text{G}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ emission together with a broad emission identified as the ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$ emission at room temperature.

The energy difference between the ${}^2\text{E}({}^2\text{G})$ and ${}^4\text{T}_2({}^4\text{F})$ levels is relatively small (1586 cm^{-1} under 450 nm excitation), considering the ${}^4\text{T}_2({}^4\text{F})$ energy level identified in the excitation spectra and the energy related to the ${}^2\text{E}({}^2\text{G})$ emission observed in the emission spectra. This behavior indicates that the emitting system is near the level crossing point in the d^3 Tanabe–Sugano diagram.

The Dq value (1600 cm^{-1}) is compatible with Cr^{3+} introduced into an octahedral environment, and the Dq/B ratio obtained from the Tanabe–Sugano diagram and the Adachi model [46, 47] indicates that the Cr^{3+} cations are subjected to an intermediate crystal field [36, 52]. The Racah B value is lower than the free-ion value (918 cm^{-1} [43]), which indicates the covalent character of the $\text{Cr}^{3+}\text{-O}^{2-}$ bond. This corroborates the hypothesis that Cr^{3+} occupies the octahedral Mg^{2+} host sites with charge compensation by electron sharing.

Figure 6 exhibits the CIE 1931 chromaticity coordinates determined at room temperature based on emission spectra at 300 nm excitation (Fig. 3a). The calculated x and y color coordinates were 0.4791 and 0.4524 , respectively. The chromaticity coordinate value indicated that sample emission was in the visible region under 300 nm excitation.

This result can be compared to the undoped Mg_2SnO_4 reported by Tsega and coauthors [16], who obtained CIE coordinates in the bluish region of the CIE chromaticity diagram. The sample of the present study had CIE coordinate positions shifted to the orange–yellow region.

The photoluminescence quantum efficiency (QE) was estimated from the emission intensity using the method described in detail in [53]. The obtained value using the results from the emission under 450 nm excitation was 31%. This value can be compared to other Cr^{3+} -doped systems [54–56] and is greater than the value obtained for $\text{LiNbO}_3\text{:ZnO:Cr}^{3+}$ (QE = 10%) [54] and mullite glass (QE = 28%) [55] but very far from that of alexandrite (QE = 95%) [56].

4 Conclusions

The synthesis, crystal structure and photoluminescent properties of an $\text{Mg}_2\text{SnO}_4\text{--SnO}_2$ system with Cr^{3+} cations as activators are presented herein. X-ray diffraction confirmed that Mg_2SnO_4 was accompanied by SnO_2 . X-ray microfluorescence identified the presence of peaks related to Mg, Sn and Cr chemical elements. Peaks related to other elements were not observed, confirming the desired chemical composition. Photoluminescence experiments confirmed that the emission band was an overlapping emission from Cr^{3+} incorporated into the octahedral sites of the Mg_2SnO_4 and SnO_2 emission originating from oxygen vacancies, displaying a broad and intense band in the orange–infrared region. The Dq/B ratio indicated that Cr^{3+} was under an intermediate crystal field, and the Racah B parameter indicated the covalent character of the $\text{Cr}^{3+}\text{--O}^{2-}$ bond. The sample presented an intense emission that covered a large wavelength interval from 450 to 900 nm when excited at 300 nm, indicating that the $(\text{Mg}_2\text{SnO}_4\text{--SnO}_2)\text{:Cr}^{3+}$ material can be used to obtain a light-emitting system at room temperature that covers the visible/near-infrared region.

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Compliance with ethical standards

Conflict of interest The authors declare no conflict of interest.

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