

# Structural and photoluminescent properties of the $\text{MgGa}_2\text{O}_4:\text{Co}^{2+}$ ceramic compound revisited after two decades

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**Abstract:** In this work, we revisit and show how the structural and photoluminescent properties of the  $\text{MgGa}_2\text{O}_4$  ceramic compound have been kept unchanged for more than two decades. The obtained results confirm the high quality, radiative efficiency, and chemical stability of this ceramic, proving that the material is a strong candidate to be used in optical device applications with relatively long useful life.

**Keywords:** ceramic compound; cobalt; solid-state reaction; photoluminescence

## 1 Introduction

The study of materials with luminescent properties has been active for several decades, and in the last few years, the research in this area has been focused on the development of new systems with optimized optical properties. The research is intensified for materials that, beyond presenting remarkable luminescent properties, also present features satisfying certain market requirements, such as long life usefulness and radiative efficiency. This causes a direct impact on the production cost, with raw material economy resulting in optimized financial costs, also being environmentally friendly. Transition metals and rare earth doped materials exhibit such features, being widely used in several applications as solid-state lasers [1,2], scientific research [3,4], medicine and dosimetry [5–7], and sensing and optical communications [8], just to name a few examples.

In the scientific literature, it is possible to find several works concerning the photoluminescent properties of

optical systems doped with transition metals [3,4,9]. Cobalt is one of the transition metals exhibiting luminescent properties when inserted in ceramic hosts. Particularly, the cobalt ion is found in several oxidation states (+2, +3, and +4) and in distinct crystal environments, but the divalent state is well known by its capacity to generate luminescence in the visible and infrared regions [10–12]. From the point of view of the energy level structure, the divalent ion  $d^7$  in tetrahedral coordination presents a level splitting similar to the  $d^3$  ion's level splitting in octahedral coordination, where the ground level is the  ${}^4A_2({}^4F)$  and the first excited energy levels are  ${}^4T_2({}^4F)$ ,  ${}^4T_1({}^4F)$ , and  ${}^4T_1({}^4P)$  for small values of  $Dq/B$  [9]. In the absence of spin-orbit coupling, only the  ${}^4T_2({}^4F) \rightarrow {}^4A_2({}^4F)$  transition is detected in the visible region, with the appearing of a broad and intense emission band, due to the fact that the  ${}^4T_2({}^4F)$  energy level is strongly dependent on the crystal field parameter  $Dq$ , generating a spin-allowed transition.

Sosman *et al.* [13,14] investigated the  $\text{MgGa}_2\text{O}_4$  system doped with  $\text{Co}^{2+}$  two decades ago. This compound presents a partially inverted spinel structure, where the tetrahedral sites are occupied by  $\text{Ga}^{3+}$  ions and the octahedral sites contain  $\text{Ga}^{3+}$  and  $\text{Mg}^{2+}$  ions

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randomly distributed. It was reported by Sosman and collaborators an intense luminescence at 77 K for this system, with an emission band at the visible region with barycenter around 675 nm, attributed to the  $\text{Co}^{2+}$  transition in tetrahedral coordination site [13], but the luminescence at room temperature was not explored in the mentioned paper.

In the present work, we report measurements performed on the same  $\text{MgGa}_2\text{O}_4:\text{Co}^{2+}$  (0.1%) sample produced 24 years ago, whose results can be seen in Refs. [13] and [14]. The aim of this work is to investigate whether the photoluminescence early observed in this sample at low temperature also occurs at room temperature and whether some luminescence features as emission band profile and energy position remain with the change of temperature and time. It is of great importance the study of the optical properties at room temperature, since this is the temperature of interest in most optical devices. Fourier transform infrared spectroscopy and X-ray diffraction at room temperature were also performed to determine if the structure suffered degradation and if the crystal structure profile remained unchanged after this long time. The results of this brief study can open a way for the development and improvement of this material, which keeps the luminescent properties and its composition stable for several decades besides exhibiting intense emission in the visible at low and room temperature, even with the compound stored in adverse conditions of temperature and humidity.

## 2 Experimental details

$\text{Mg}_{1-x}\text{Co}_x\text{Ga}_2\text{O}_4$  compound with  $x=0.001$  was synthesized by conventional solid-state reaction, using magnesium oxide (MgO), gallium oxide ( $\text{Ga}_2\text{O}_3$ ), and cobalt II carbonate ( $\text{CoCO}_3$ ) with high purity in stoichiometric quantities. The reactants were mixed and sintered at 1673 K in vacuum furnace during 48 h, in order to assure that the cobalt ions acquire the divalent state. Further information concerning the preparation method can be found in other references [13,14]. The sample was prepared in 1991 and stored under environmental conditions of Rio de Janeiro city, Brazil, where the temperature changes in the range of 21–42 °C and the average air relative humidity is around 80% during the year. After stored under these conditions for more than two decades, the sample still presents the deep blue color reported in the 1992 work [13],

indicating that there is not an apparent degradation even under the adverse storage conditions.

To investigate possible degradation suffered by the sample, it was performed Fourier transform infrared spectroscopy measurements, using a ThermoScientific spectrometer model NICOLET iS50 FT-IR, with resolution of  $4\text{ cm}^{-1}$ .

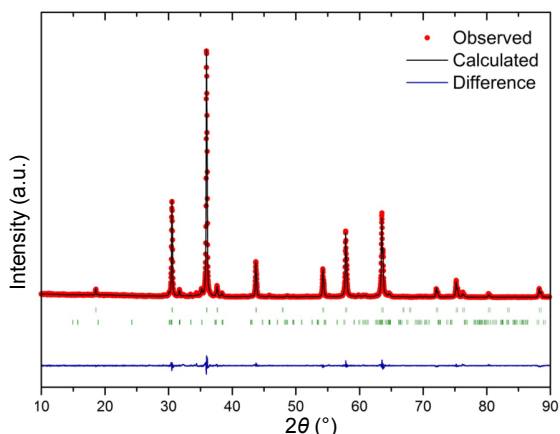
To investigate if any crystal structural change occurred over the years, X-ray diffraction experiments were performed at room temperature. It was used an X-Pert Pro Panalytical diffractometer working at 40 kV and 40 mA (Cu  $K\alpha$  radiation,  $\lambda = 1.54056\text{ \AA}$ ). Data were collected in the range of  $10^\circ < 2\theta < 90^\circ$  in Bragg–Brentano geometry with  $0.02^\circ$  step and 100 s/step. The structure pattern was refined by Rietveld method for identification of the space group, lattice parameter, and phase quantification.

Photoluminescence measurements at room temperature were performed in 2014 using a solid-state laser with 532 nm/50 mW as excitation source, modulated by a chopper with variable speed Newport model 75160 operating at 200 Hz. One spectrometer Acton model AM510 was used to scan the emission in the range of 600–800 nm with 1 nm/step. To detect the signal, we used a photomultiplier Newport Oriel model 77348 with the signal amplified by a Princeton lock-in model 5209. All data were corrected by the apparatus sensitivity response.

## 3 Results and discussion

The X-ray powder diffractogram of the sample is shown in Fig. 1. Two phases are identified in the 1991 synthesized compound: the main phase  $\text{MgGa}_2\text{O}_4$  followed by a small quantity of  $\text{Ga}_2\text{O}_3$ . For the present work, the structural data were refined using the FullProf Suite [15] using the data corresponding to the  $\text{MgGa}_2\text{O}_4$  (ICSD code 61449) and  $\text{Ga}_2\text{O}_3$  (ICSD code 83645) as basis.

Details of the Rietveld refinement can be seen in Table 1. Input data related to the experimental conditions and the structural data of each identified phase were introduced in the software in order to compare data with the experimental diffractogram, with 13 refined parameters. The profile shape used was the Pseudo-Voigt and the background was fit in linear interpolation mode between a set of background points with refinable heights. The weighted profile factor  $R_{\text{wp}}$ , the reduced chi-square  $\chi^2$ , and the difference between



**Fig. 1** Sample diffractogram showing the observed profile (red circles), calculated profile from Rietveld refinement (black line), and the difference between the calculated and observed profile (blue line).

the calculated and observed profiles were evaluated at each refinement cycle to determine the refinement quality. The phase qualitative analysis can be calculated from refinement of the scale factors, where the most intense peaks are always related to the predominant phase.

The main phase  $MgGa_2O_4$  crystallizes in the cubic symmetry  $Fd3m$  space group with lattice parameter  $a = 8.2780 \text{ \AA}$  and volume  $V = 567 \text{ \AA}^3$ ; the secondary phase  $Ga_2O_3$  belongs to the monoclinic space group  $C12/m1$ , with lattice parameters  $a = 12.2325 \text{ \AA}$ ,  $b = 3.0409 \text{ \AA}$ ,  $c = 5.8091 \text{ \AA}$ ,  $\beta = 103.8285^\circ$ , and volume  $V = 210 \text{ \AA}^3$ . The quantitative analysis obtained from the refinement indicates the proportions of 88.8% for the main phase  $MgGa_2O_4$  and 11.2% for the secondary phase  $Ga_2O_3$ . The value of the  $S$  parameter is 1.3, which indicates the high quality of the refinement. Further details about the quality factors and crystal structure of the main and secondary phases can be seen in Tables 1–3. Comparing the results of X-ray diffraction acquired in 2014 with the data obtained in 1991 [13], we do not notice any

**Table 1** Rietveld quality parameters and FWHM factors

$R_p$ (profile factor)	10.5
$R_{wp}$ (weighted profile factor)	12.5
$R_{exp}$ (expected weighted profile factor)	9.43
$\chi^2$	1.75
$S (= R_{wp}/R_{exp}, \text{goodness of fit})$	1.3
FWHM ( $MgGa_2O_4$ ) (profile function: Pseudo-Voigt)	$U = 0.021780$ $V = -0.002049$ $W = 0.010391$
FWHM ( $Ga_2O_3$ ) (profile function: Pseudo-Voigt)	$U = 0.034640$ $V = -0.006243$ $W = 0.001769$

**Table 2** Crystallographic parameters of the main phase

Molecular formula		$MgGa_2O_4$ (ICSD 61449)				
Proportion		88.8%				
Formula weight		4259.96				
Crystal system		Cubic				
Space group		$Fd3m$				
Unit cell dimensions		$a = b = c = 8.2780 \text{ \AA}; \alpha = \beta = \gamma = 90^\circ$				
Cell volume		$567 \text{ \AA}^3$				
Formula units per cell		8				
Density calculated		5.32				
Temperature		300 K				
Atomic coordinate						
Atom	Oxidation	Wyck	Occ	X	Y	Z
Mg1	+2.00	8a	0.05177	0.12500	0.12500	0.12500
Ga1	+2.00	16d	0.05938	0.12500	0.12500	0.12500
Mg2	+3.00	8a	0.02860	0.50000	0.50000	0.50000
Ga2	+3.00	16d	0.11943	0.50000	0.50000	0.50000
O1	-2.00	32e	0.35029	0.25376	0.25376	0.25376

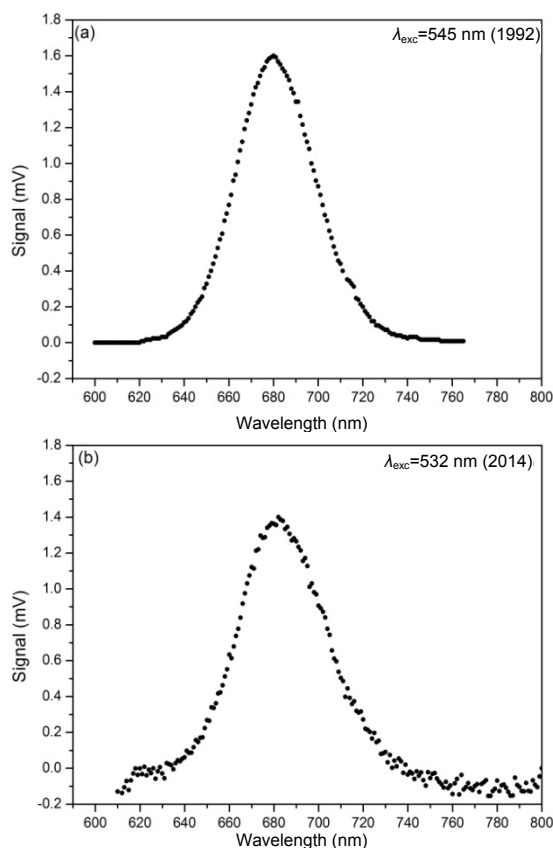
**Table 3** Crystallographic parameters of the secondary phase

Molecular formula		$Ga_2O_3$ (ICSD 83645)				
Proportion		11.2%				
Formula weight		817.97				
Crystal system		Monoclinic				
Space group		$C12/m1$				
Unit cell dimensions		$a = 12.2325 \text{ \AA}; b = 3.0407 \text{ \AA}; c = 5.8091 \text{ \AA}; \alpha = \gamma = 90^\circ; \beta = 103.8285^\circ$				
Cell volume		$210 \text{ \AA}^3$				
Formula units per cell		4				
Density calculated		5.96				
Temperature		300 K				
Atomic coordinate						
Atom	Oxidation	Wyck	Occ	X	Y	Z
Ga1	+3.00	4i	0.50000	0.09050	0.00000	0.79460
Ga2	+3.00	4i	0.50000	0.15866	0.50000	0.31402
O1	-2.00	4i	0.68134	0.16450	0.00000	0.10980
O2	-2.00	4i	0.48473	0.17330	0.00000	0.56320
O3	-2.00	4i	0.69843	-0.00410	0.50000	0.25660

chemical degradation or significant changes in the structure, which points to the high quality and long durability of the material.

The obtained Fourier transform infrared spectroscopy measurements show only a noise profile, which confirms that the sample does not suffer any kind of degradation by the moisture and/or  $CO_2$  presence in the air, or any another organic component.

The unpublished luminescence spectrum obtained at room temperature in 1992 can be seen in Fig. 2(a). The excitation source was a 1 kW xenon lamp positioned at  $\lambda_{exc} = 545 \text{ nm}$  and it is possible to observe a symmetrical emission broadband, with maximum intensity at 680 nm. In Fig. 2(b), it is shown the emission spectrum of the same sample at room temperature, but now acquired in 2014 with a laser as excitation source operating at  $\lambda_{exc} = 532 \text{ nm}$ .



**Fig. 2** Luminescence spectra at room temperature of  $\text{MgGa}_2\text{O}_4:\text{Co}^{2+}$  (0.1%). (a) Spectrum obtained in 1992 with excitation source (Xe lamp) positioned in 545 nm; (b) spectrum obtained in 2014 with excitation source in 532 nm (solid-state laser).

In the 2014 spectrum, the luminescence consists of a broad band in the visible–near infrared region with maximum intensity at 682 nm. This emission band corresponds to the spin-allowed electronic transition  ${}^4\text{T}_2({}^4\text{F}) \rightarrow {}^4\text{A}_2({}^4\text{F})$  of the  $\text{Co}^{2+}$  ion in tetrahedral coordination site. In Table 4, it is shown a comparison between the luminescence data obtained at room temperature in 1992 and 2014: the wavelength of the respective excitation sources ( $\lambda_{\text{exc}}$ ), the wavelength where the maximum intensity of the broad band occurs ( $\lambda_{\text{em}}$ ), and the FWHM in nm and  $\text{cm}^{-1}$  units.

In the 1992 paper [13], the authors presented the emission spectra of this compound, and reported the emission band obtained at 77 K with maximum

**Table 4** Data comparison extracted from the 1992 and 2014 spectra at room temperature

Year	$\lambda_{\text{exc}}$ (nm)	$\lambda_{\text{em}}$ (nm)	FWHM	
			(nm)	( $\text{cm}^{-1}$ )
1992	545	680	41	885
2014	532	682	43	940

intensity at 675 nm. The photoluminescence measurements reported in the present work correspond to the same sample (not the same sample synthesized again, but the same sample used in the 1991 measurements), whose spectrum at room temperature was not published until now (Fig. 2(a)). Comparing both spectra obtained at room temperature in 1992 and 2014, it is noticed a small shift to higher wavelength (lower energy) in the band maximum intensity, which is explained by the use of distinct equipment to acquire both spectra in distinct times.

A very important difference between experiments is related to the excitation wavelength of the sample. In the excitation spectrum [13], we see that the intensity of the luminescence at 680 nm is about 20% higher when the sample is excited with 545 nm than with 532 nm wavelength. This fact can contribute to the signal difference (of 0.2 mV) observed in the spectra showed in this paper. In this way, we are able to say that exciting the sample using 545 nm is more favorable than using 532 nm, because the former generates a more intense signal than the latter.

The luminescence lifetime, calculated by the shift phase method [16] is around 8  $\mu\text{s}$ , a characteristic value for systems containing  $\text{Co}^{2+}$ , and this value has the same order of magnitude of the value previously reported [14]. The same magnitude of the lifetime in both measurements indicates that the radiative transitions are originated from the same emission state and that this state was kept unchanged over the years. This observation indicates that the environment of the dopant ion remains unchanged, without crystallographic variation, as observed also in the X-ray results.

## 4 Conclusions

After 24 years stored, we performed photoluminescence measurements at room temperature in the  $\text{MgGa}_2\text{O}_4$  with 0.1% of cobalt sample to verify if the optical properties early observed in the material changed during this long time. Concerning the structural features, we did not observed any chemical degradation and structural changes in the sample. The optical properties remain unchanged even after this long time, with the appearing of the same broad band and an intense luminescence already reported in previous works at low temperature. We observed a significant shift in the emission band and the radiative lifetime with the change of temperature and time, indicating that the site

remains unchanged even after the time, temperature, and humidity actions. Such observations show that the studied material presents high quality and efficiency, non-reactivity, longevity, and stability, which makes it a very good system as a material for technological applications with relatively long useful life.

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