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# Preparation and optical properties of trivalent europium doped into cordierite using the sol–gel process

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## Abstract

The photoluminescence properties of the  $\text{Eu}^{3+}$  ion doped into  $\alpha$ -cordierite were studied based on the excitation and emission spectra and lifetime measurements. These samples were prepared by the sol–gel method and calcined by heating the xerogel at different temperatures: 873, 1133, 1223 and 1473 K. X-ray diffraction patterns were used to characterize the luminescent material. The  ${}^5D_0 \rightarrow {}^7F_0$  transition of the samples exhibits only one broad peak arising from the inhomogeneous linewidth of the amorphous phase, except for the ceramic material obtained at 1473 K that presents two peaks. Also, in the latter case the luminescence decay lifetime exhibits a bi-exponential fit when excited at 280 nm, corroborating that the  $\text{Eu}^{3+}$  ion exists in two sites of symmetry. The experimental intensity parameter  $\Omega_2$  ( $10.0 \times 10^{-20} \text{ cm}^2$ ) indicates a moderately polarizable chemical environment around the  $\text{Eu}^{3+}$  ion. The emission spectra of the  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}:\text{Eu}^{3+}$  samples calcined at 873, 1133 and 1223 K also presented inhomogeneous profiles for the  ${}^5D_0 \rightarrow {}^7F_J$  transitions suggesting disorder of the material. On the other hand, the sample calcined at 1473 K shows narrow bands indicating the crystalline form. The emission quantum efficiency ( $\eta$ ) of the  $\alpha$ -cordierite system is also discussed.

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**Keywords:** Cordierite; Europium; Sol–gel process; Luminescence properties

## 1. Introduction

The sol–gel process has been used to prepare amorphous or crystalline materials from liquid-phase to apply in ceramic coatings to metal surfaces [1,2]. Recently, this method has been utilized to synthesize either thin films or bulky samples of nanoporous amorphous silica materials in the nanotechnology and nanoscience area with new development of optical materials [1,3,4].

Magnesium  $\alpha$ -cordierite,  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ , is a promising ceramic material for technological applications due to easy preparation, chemical and thermal durability and mechanical properties resistant to corrosion at higher temperature [1].

Piriou et al. [5,6] have studied luminescent properties of magnesium cordierite ( $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ ) doped with

$\text{Eu}^{3+}$  ion prepared by sol–gel routes using tetraethyl orthosilicate (TEOS) and acetylacetonate compounds. It was also evidenced the  $\text{Eu}^{3+}-\text{O}^{2-}$  association by luminescence study of  $\alpha$ -cordierite, mulite and hydroxyapatite [5]. Based on time-resolved spectroscopy it was possible to distinguish two sites (A and B) for the  $\alpha$ -cordierite structure [7]. The luminescence study of  $\text{Cr}^{3+}$  doped in cordierite glass  $\text{MgAl}_2\text{O}_4$  nanocrystal was reported [8].

$\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  occurs in two polymorphic forms. This system at high temperature presents a hexagonal structure space group  $P6/mcc$ , stable above 1450°C, where  $\text{Al}^{3+}$  and  $\text{Si}^{4+}$  ions are distributed over two sets of tetrahedral sites and the  $\text{Mg}^{2+}$  ion is in octahedral coordination [9].

Capobianco et al. [10] reported the laser-excited fluorescence and crystal field analysis of  $\text{Eu}^{3+}$  in cordierite glass obtained by a solid-state reaction.

The photoluminescent properties of the trivalent rare-earth ions ( $\text{RE}^{3+}$ ) doped in sol–gel derived from solid

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matrix have increased considerably in the last decades due to advances in the area of micro-lasers, luminescent labels, optical amplification, electroluminescence and optical components [4,11–13]. The  $4f$  orbitals are shielded from the chemical environment by the  $5s5p$  orbitals, which produce very narrow bands in their electronic spectra from the compounds in the gas and solid-state phases or in solution.  $\text{Eu}^{3+}$  ion is the most commonly used in photoluminescent studies due to the presence of the very narrow band with high intensity red emission. In the  ${}^5D_0 \rightarrow {}^7F_0$  transition, both the excited and ground states are non-degenerated and may suggest that the  $\text{Eu}^{3+}$  ion occupies identical site symmetries of the type  $C_s$ ,  $C_n$  or  $C_{nv}$  which facilitates the interpretation of the spectral data and provides information on the eventual existence of more than one site symmetry being occupied by the  $\text{Eu}^{3+}$  ion. Another advantage of using this ion is that the  ${}^5D_0 \rightarrow {}^7F_1$  transition is usually taken as a reference transition [14] because it is allowed by magnetic dipole, and consequently the crystal field does not considerably alter the intensity of this transition.

This work reports the photoluminescence investigations of  $\text{Eu}^{3+}$  ion into cordierite matrix prepared by the sol–gel process using silicic and citric acids and sodium metasilicate calcined at different temperatures. Our analysis is mainly devoted to the study of the influence of the cordierite host on the photoluminescent properties arising from the energy transfer to the rare-earth ion. In addition, the  $\text{Eu}^{3+}$ -matrix interaction is studied via luminescence spectroscopy based on the experimental intensity parameters, emission quantum efficiency and the lifetime of the emitter  ${}^5D_0$  level.

## 2. Experimental section

### 2.1. Preparation of the samples

The ceramic materials in powder form were prepared from a sodium metasilicate ( $\text{Na}_2\text{SiO}_3 \cdot 5\text{H}_2\text{O}$ ) aqueous solution, 20 w/o, which was passed through a previously treated bed of solid ion exchange resin ( $\text{H}^+$  form). A vacuum pump was used to help the liquid elution from the resin. The silicon concentration in the eluted liquid was determined by titration [15]. Depending on the silicon concentration, solid aluminum ( $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ), magnesium ( $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ) and trivalent europium nitrate ( $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ), and citric acid were added to the silicic acid aqueous solution in amounts to keep the molar ratio of Si:Al:Mg:Eu, citric acid equal to 5:2.15:2.25:0.0076:2.15. The obtained sol was covered and kept in repose until the gel formation. All chemicals were analytical grade from Merck. The ionic exchanger was IR120 from Rohm and Haas. The xerogel was prepared by heating the formed gel in an oven at 323 K for 20 days, at 723 K for 30 h and at 873 K

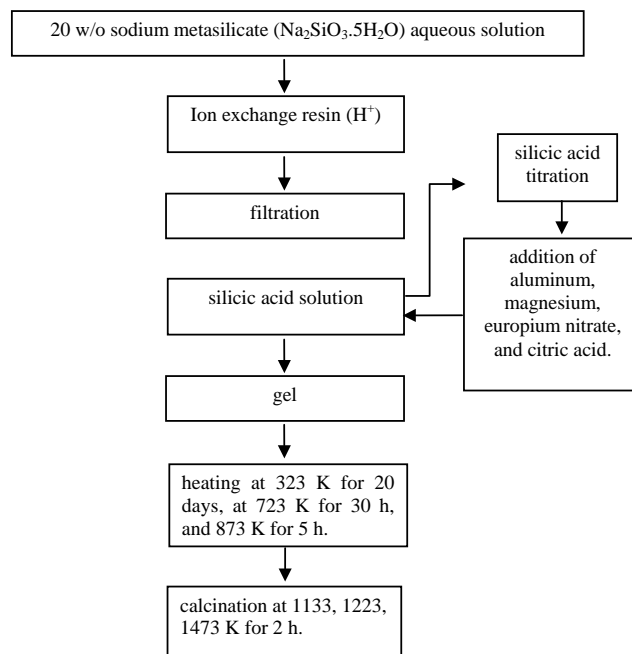


Fig. 1. Flow chart of preparation of  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}:\text{Eu}^{3+}$  cordierite powder.

for 5 h. Several crucibles containing the xerogels were taken to an oven for 2 h, which had its temperatures previously stabilized at 1133, 1223 and 1473 K (Fig. 1).

### 2.2. Measurements

The X-ray diffraction patterns were registered on a diffractometer, Shimadzu model XRD 6000 using  $\text{CuK}\alpha$  radiation, in the range of  $10\text{--}80^\circ$  ( $2\theta$ ) at  $2^\circ/\text{min}$  using the powder X-ray diffraction method.

The excitation and emission spectra at room and liquid nitrogen temperature were collected at an angle of  $22.5^\circ$  (front face) in a spectrofluorimeter (SPEX-Fluorolog 2) with double grating 0.22 m monochromators (SPEX 1680) and a 450 W Xenon lamp as the excitation source. A spectroscopy computer DM3000F controlled this apparatus. The solid samples were maintained in a quartz dewar flask at 77 K. The lifetime measurements were recorded at 298 K using the phosphorimeter (SPEX 1934D) accessory coupled with the spectrofluorimeter.

## 3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of the samples of cordierite doped with  $\text{Eu}^{3+}$  ion calcined at 873, 1133, 1223 and 1473 K. The XRD patterns present no Bragg reflections for the samples calcined at 873, 1113 and 1223 K confirming the amorphous phase. On the other hand, for the sample calcined at 1473 K, the XRD patterns present well-defined reflections indicating

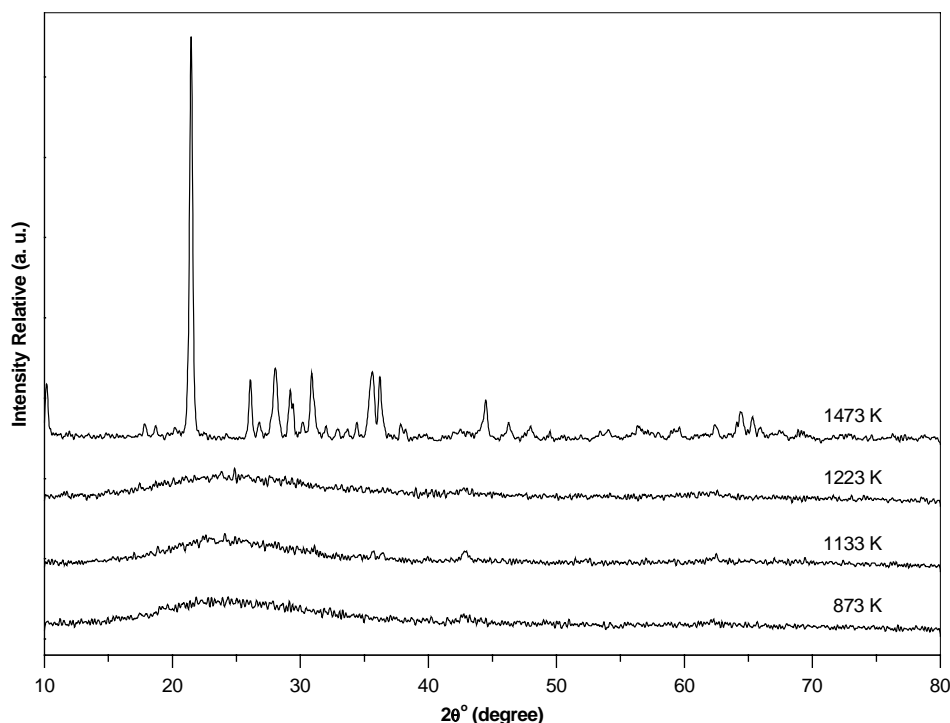


Fig. 2. X-ray diffraction patterns of cordierite doped with europium ion treated in the following temperatures (K): (a) 873; (b) 1133; (c) 1223 and (d) 1473.

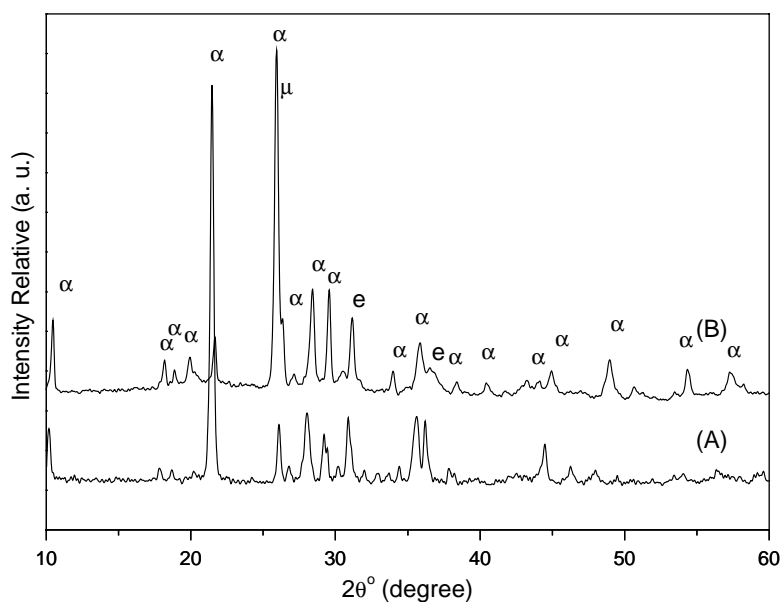


Fig. 3. X-ray diffraction patterns of (A) cordierite doped with  $\text{Eu}^{3+}$  ion and (B) cordierite (where  $\alpha = \alpha$ -cordierite,  $\mu = \mu$ -cordierite and  $e = \text{spinel}$ ).

a crystalline phase of  $\alpha$ -cordierite, which suggests an effective action of the citric acid on the cordierite crystallization.

The X-ray diffraction patterns of the cordierite doped with europium ion (A) and cordierite (B) prepared by the sol-gel method calcined at 1473 K for 2 h is shown in Figs. 3(A) and (B), respectively. It is observed in

Fig. 3(B) diffraction peaks at  $d = 0.451, 0.343, 0.225$  and  $0.186$  nm, which correspond to  $\mu$ -cordierite (ASTM 14-249), peaks at  $d = 0.286, 0.244, 0.202$ , and  $0.142$  nm relative to spinel  $\text{MgO} \cdot \text{Al}_2\text{O}_3$  (ASTM 21-1152), and peaks at  $d = 0.848, 0.489, 0.467, 0.409, 0.338, 0.313, 0.302$ , and  $0.264$  nm, which correspond to the crystalline phase of  $\alpha$ -cordierite (ASTM 13-293). These data show

the crystallization of  $\alpha$ -cordierite, without the crystallization of  $\mu$ -cordierite, which is very common in this type of system [15]. Nevertheless, the samples doped with  $\text{Eu}^{3+}$  ion show peaks at the same positions ( $2\theta$ ) as  $\alpha$ -cordierite, however the relative intensities are different. This alteration should be provoked by changes in the cordierite cell parameters due to the introduction of rare-earth ion into the crystalline cell. The  $\alpha$ -cordierite exists in a stable high-temperature phase while the  $\mu$ -cordierite is found in a metastable low-temperature phase [16].

### 3.1. Photoluminescent study

The excitation spectra of the  $\text{Eu}^{3+}$  ion doped into  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$  matrix were obtained at room temperature ( $\sim 298$  K) in the range of 250–590 nm with emission monitored in the hypersensitive  ${}^7F_0 \rightarrow {}^5F_2$  transition at about 612 nm (Fig. 4). It is noted a broad low intensity band in the range of 250–320 nm corresponding to the ligand-to-metal charge-transfer states from the  $\text{O} \rightarrow \text{Eu}^{3+}$  transitions at around 280 nm. The LMCT bands are enveloped with sharp lines at around 380, 298, 302

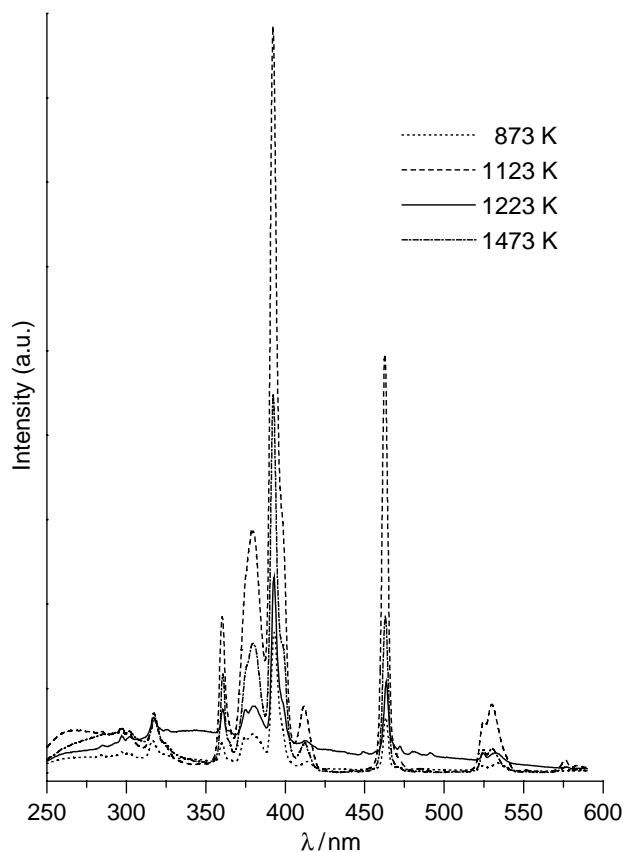


Fig. 4. Excitation spectra of  $\text{Eu}^{3+}$  doped into cordierite matrix obtained upon heating at the following temperatures (K): (a) 873 (solid line); (b) 1133 (dash line); (c) 1223 (dot line) and 1473 (dash dot line) with emission monitored in the hypersensitive  ${}^5D_0 \rightarrow {}^7F_2$  transition around 615 nm, at 298 K.

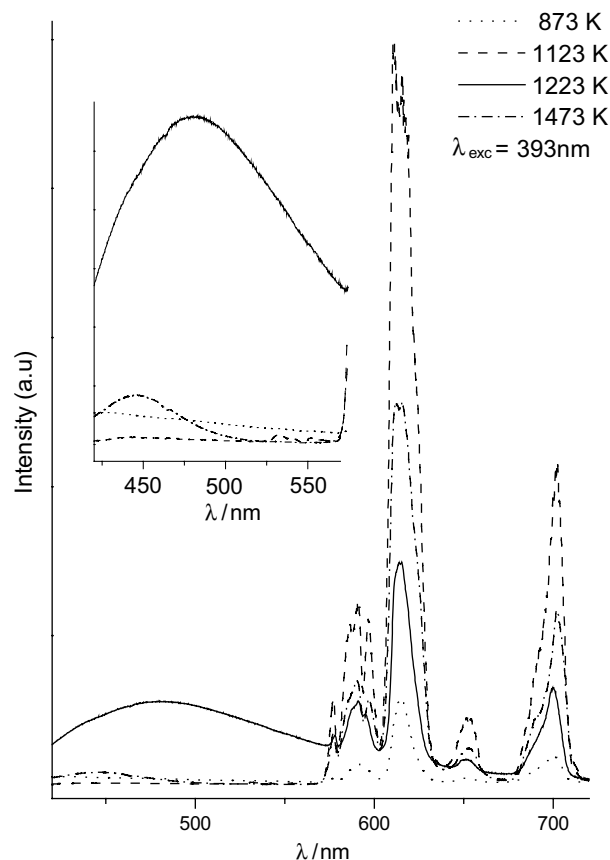


Fig. 5. Emission spectra of the  $\text{Eu}^{3+}$  doped into cordierite matrix calcined at the following temperatures: (a) 873 (solid line); (b) 1123 (dash line); (c) 1223 (dot line) and 1473 K (dash dot line) under excitation at the  ${}^5L_6$  transition around of 393 nm of the  $\text{Eu}^{3+}$  ion, at 298 K.

and 318 nm, corresponding to the  ${}^7F_0 \rightarrow {}^5F_{2,4}$  and  ${}^5H_3$  transitions arising from the  $\text{Eu}^{3+}$  ion. The excitation spectra also present sharp lines referent to the  ${}^7F_0 \rightarrow {}^5D_J$  ( $J = 0 - 4$ ) and  ${}^7F_0 \rightarrow {}^5L_J$  ( $J = 6, 7$ ) transitions characteristic of the  $\text{Eu}^{3+}$  ion, confirming the presence of the rare-earth ion into the cordierite matrices.

Fig. 5 shows the emission spectra of the cordierite samples in the range from 420 to 720 nm, under excitation into the  ${}^7F_0 \rightarrow {}^5L_6$  transition of the  $\text{Eu}^{3+}$  ion ( $\sim 393$  nm); at room temperature broadened bands in the range of 420–570 nm are noted (Fig. 5, inset) corresponding to the ligand-to-metal charge-transfer states from the  $\text{O} \rightarrow \text{Eu}^{3+}$  transitions. Also noted for the cordierite calcined at 1473 K (Fig. 5, inset) is that the LMCT bands are enveloped with low intensity lines at around 540 and 555 nm, corresponding to the  ${}^5D_1 \rightarrow {}^7F_{1,2}$  transitions from the  $\text{Eu}^{3+}$  ion. These emission spectra in the range of 570–720 nm present broadened bands arising from the  ${}^5D_0 \rightarrow {}^7F_J$  ( $J = 0 - 4$ ) transitions due to inhomogeneous broadening of the transitions, suggesting that the cordierite samples present an amorphous phase. In contrast, the homogeneous linewidth of the  ${}^5D_0 \rightarrow {}^7F_J$  transitions from the

$\text{Eu}^{3+}$  ion in crystalline compounds have very sharp lines.

When the emission spectra of the cordierite samples are monitored with excitation at 280 nm corresponding to the  $\text{O} \rightarrow \text{Eu}^{3+}$  LMCT show the same broad spectral profiles as those excited at 393 nm, except for the cordierite sample calcined at 1473 K. Fig. 6 shows the emission spectrum of the sample calcined at 1473 K which presents the sharp lines indicative of the crystalline phase. Additionally, this spectrum shows two peaks around 573 and 577 nm corresponding to the  ${}^5D_0 \rightarrow {}^7F_0$  transition suggesting two different chemical environments around the  $\text{Eu}^{3+}$  ion, which is corroborated by the  $\alpha$ -cordierite structure containing two sites (A and B), as reported in Ref. [6].

The hypersensitive  ${}^5D_0 \rightarrow {}^7F_2$  transition around 612 nm and  ${}^5D_0 \rightarrow {}^7F_1$  around 590 nm contain more than  $(2J+1)$  components indicating also that the  $\text{Eu}^{3+}$  ion is founded at more than one site and reinforcing the presence of two sites for the  $\alpha$ -cordierite structure calcined at 1473 K. The same spectral profiles were observed for the emission spectra recorded at 77 K indicating that there are no structural changes in the compounds when the temperature is lowered.

The  $\Omega_\lambda$  experimental intensity parameters for  $J-J'$  transitions contain the contributions from the forced electric dipole and dynamic coupling mechanism. These parameters can be estimated theoretically from structural data or determined experimentally from absorption or

emission spectra. It is important to study the influence of europium ion doped in the  $\alpha$ -cordierite matrix,  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}:\text{Eu}^{3+}$ , on the luminescence behavior by determining the radiative contribution for the depopulation of the emitter level,  ${}^5D_0$ , and consequently the emission quantum efficiency. In this case we have to consider the spectral data at room temperature using the  ${}^5D_0 \rightarrow {}^7F_2$  and  ${}^5D_0 \rightarrow {}^7F_4$  transitions from the  $\text{Eu}^{3+}$  ion to determine the  $\Omega_\lambda$  ( $\lambda = 2$  and 4) experimental intensity parameters. Since the intensity of a magnetic dipole transition ( ${}^5D_0 \rightarrow {}^7F_1$ ) is relatively insensitive to the ligand field around the  $\text{Eu}^{3+}$  ion, it may be used as reference. The emission intensity,  $I = \hbar \omega A N$ , is expressed in terms of the surface under the emission curve where  $\hbar \omega$  is the transition energy,  $N$  is the population of the emitter level ( ${}^5D_0$ ) and the Einstein's coefficient of spontaneous emission [17–19],  $A$ , in this case may be given by

$$A = \frac{4e^2\omega^3}{3\hbar c^3} \left( \frac{1}{2J+1} \right) \left[ \frac{n_0(n_0^2+2)^2}{9} \right] \times \sum_{\lambda=2,4} \Omega_\lambda \langle {}^5D_0 | U^{(\lambda)} | {}^7F_J \rangle^2, \quad (1)$$

where  $n_0(n_0^2+2)^2/9$  is a Lorentz local field correction. The reduced matrix elements in Eq. (1) were taken from Ref. [20]. In this case the  $A$  values are obtained by using the relation:  $A_{0-\lambda} = A_{0-1}(S_{0-\lambda}/S_{0-1})(\sigma_\lambda/\sigma_1)$ , where  $S_{0-\lambda}$  is the area under the curve related to the  ${}^5D_0 \rightarrow {}^7F_\lambda$  transition obtained from the spectral data,  $\sigma_\lambda$  is the barycenter of the  $0-\lambda$  transition and  $A_{0-1}$  is the Einstein's coefficient for the  $0-1$  magnetic dipole transition.

The lifetime ( $\tau$ ), non-radiative ( $A_{\text{nrad}}$ ) and radiative ( $A_{\text{rad}}$ ) rates are related through the following equation  $A_{\text{tot}} = 1/\tau = A_{\text{rad}} + A_{\text{nrad}}$ , where the  $A_{\text{rad}}$  rate was obtained by summing over the radiative rates  $A_{0J}$  for each  ${}^5D_0 \rightarrow {}^7F_J$  transitions is given by  $A_{\text{rad}} = \sum_J A_{0J}$ . The emission quantum efficiency of the emitter  ${}^5D_0$  level is given by

$$\eta = \frac{A_{\text{rad}}}{A_{\text{rad}} + A_{\text{nrad}}}. \quad (2)$$

Table 1 presents the experimental intensity parameters ( $\Omega_2$  and  $\Omega_4$ ) for the xerogel samples calcined at 873, 1133, 1223 and 1473 K. The highest value of the  $\Omega_2$  parameters ( $\sim 10.7 \times 10^{-20} \text{ cm}^2$ ) for the crystalline  $\alpha$ -cordierite doped with europium ion,  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}:\text{Eu}^{3+}$ , calcined at 1473 suggests the highest hypersensitive behavior of the  ${}^5D_0 \rightarrow {}^7F_2$  transition. This fact suggests that the  $\text{Eu}^{3+}$  ion in this  $\alpha$ -cordierite sample is in a more polarizable environment than in the amorphous systems. It can also be observed that the  $\text{Eu}^{3+}$  ions in  $\alpha$ -cordierite are not in a highly polarizable environment as can be observed for the  $[\text{Eu}(\text{TTA})_3(\text{H}_2\text{O})_2]$  complex ( $\Omega_2 = 30 \times 10^{-20} \text{ cm}^2$ ), where

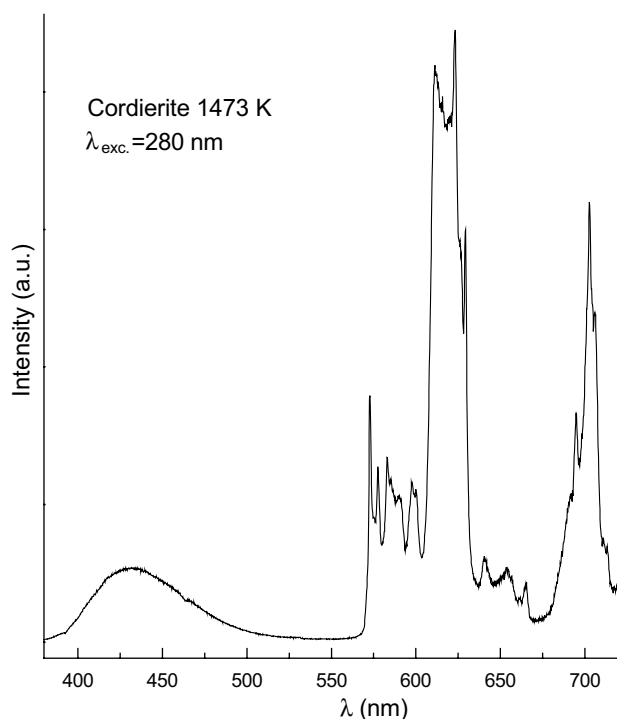


Fig. 6. Emission spectrum of  $\text{Eu}^{3+}$  doped in cordierite matrix calcined at 1473 K temperature with excitations monitored at:  $\text{O} \rightarrow \text{Eu}$  LMCT band around 280 nm, at 298 K.

Table 1

Experimental intensity parameters ( $\Omega_i$  and  $R_{02}$ ), emission quantum efficiency ( $\eta$ ), lifetime ( $\tau$ ), non-radiative ( $A_{\text{nrad}}$ ) radiative ( $A_{\text{rad}}$ ) and total ( $A_{\text{total}}$ ) rates for the  $\text{Eu}^{3+}$  ion doped into cordierite matrix calcined at different temperatures

Annealing temperatures (K)	$A_{\text{rad}}$ ( $\text{s}^{-1}$ )	$A_{\text{nrad}}$ ( $\text{s}^{-1}$ )	$A_{\text{tot}}$ ( $\text{s}^{-1}$ )	$\Omega_2$ ( $10^{-20} \text{ cm}^2$ )	$\Omega_4$ ( $10^{-20} \text{ cm}^2$ )	$R_{02}$	$\tau$ (ms)	$\eta$ (%)
1473	519	309	828	10.7	10.2	0.017	1.207	62
1223	424	977	1401	8.2	8.7	0.010	0.714	30
1133	489	56	545	10.2	9.0	0.019	1.833	90
873	482	607	1089	9.9	9.2	0.011	0.918	44

TTA = thenoyltrifluoroacetate [14] indicating a smaller electric dipole character to the  ${}^5D_0 \rightarrow {}^7F_2$  transition for the cordierite systems.

As can be seen, the highest value of the  $\Omega_4$  parameter was determined for the crystalline  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}:\text{Eu}^{3+}$  sample, calcined at 1473 K. Besides, it is observed that the samples present similar values of  $\Omega_4$  and  $\Omega_2$  parameters, except for the sample calcined at 1133 K suggesting moderately sensitive behaviors of the  ${}^5D_0 \rightarrow {}^7F_4$  transition. It is considered that the  $\Omega_2$  parameter depends rather on the lower rank components of the crystal field and dynamic coupling interactions, while the  $\Omega_4$  parameter depends rather on the corresponding higher components [21–24].

Based on the luminescence decay curves for all of the samples (figure not shown) recorded at room temperature (excitation at 280 nm) were determined the lifetime values (Table 1) of the emitter  ${}^5D_0$  level of the  $\text{Eu}^{3+}$  ion. The decay curves of the  $\alpha$ -cordierite samples present a bi-exponential behavior, indicating that there is more than one type of environment around the  $\text{Eu}^{3+}$  ion. This suggests other depopulation channels for the  ${}^5D_0$  level of  $\text{Eu}^{3+}$  ion. In contrast, the luminescence decay curves of the samples calcined at 873, 1133 and 1223 K temperatures are better fitted as mono-exponential behavior.

The emission quantum efficiencies ( $\eta$ ) result from a balance between the radiative ( $A_{\text{rad}}$ ) and non-radiative ( $A_{\text{nrad}}$ ) decay rates arise from the  ${}^5D_0$  level. As can be seen in Table 1 the highest value of  $\eta$  was determined in a sample calcined at 1133 K due to the lowest contribution of the non-radiative decay rate ( $A_{\text{nrad}} = 56 \text{ s}^{-1}$ ) and considering that the radiative decay rates of all samples present the same order of magnitude.

Table 1 also shows the  $R_{02}$  intensity parameter, which is the ratio between the intensities of the  ${}^5D_0 \rightarrow {}^7F_0$  and  ${}^5D_0 \rightarrow {}^7F_2$  transitions. The  $R_{02}$  parameter gives information on the J-mixing effect associated with the  ${}^5D_0 \rightarrow {}^7F_0$  transition [25]. This effect is mainly due to the mixing between the  ${}^7F_2$  manifold and the  ${}^7F_0$  level though the rank-two components of the ligand field. By comparison among the cordierite systems calcined at different temperatures, the following order for the magnitude of the J-mixing effect is proposed:  $1133 \approx 1473 > 873 \approx 1223 \text{ K}$ .

## 4. Conclusions

The cordierite samples were prepared by the sol-gel method and calcined at different temperatures 873, 1133, 1223 and 1473 K. X-ray diffraction patterns suggest the predominance of the  $\alpha$ -cordierite phase calcined at 1473 K. In the case of  $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}:\text{Eu}^{3+}$  obtained at the highest temperature the  ${}^5D_0 \rightarrow {}^7F_0$  transition splitting in two peaks when excited at 280 nm suggesting the existence of two local site symmetries for the  $\text{Eu}^{3+}$  ion chemical environment, which is corroborated by the  $\alpha$ -cordierite structure containing two sites. This result was consistent with the bi-exponential behavior of the luminescence decay curves that suggest a crystalline phase of the  $\alpha$ -cordierite sample. The value of the  $\Omega_2$  intensity parameter ( $10.0 \times 10^{-20} \text{ cm}^2$ ) for all samples reflects a moderately polarizable chemical environment around the  $\text{Eu}^{3+}$  ion. In amorphous phase, the effects of a distribution of different symmetry sites occupied by the rare-earth ion produce the inhomogeneous line broadening of  ${}^5D_0 \rightarrow {}^7F_J$  transitions.

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