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# Photoluminescence of the $Mg_2Al_4Si_5O_{18}$-$Al_2O_3$-$MgAl_2O_4$-$SiO_2$ ceramic system containing $Fe^{3+}$ and $Cr^{3+}$ as impurity ions

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ABSTRACT

This work presents the results of photoluminescence, excitation and radiative decay time for a ceramic system containing $Mg_2Al_4Si_5O_{18}$-$Al_2O_3$-$MgAl_2O_4$-$SiO_2$ with $Fe^{3+}$ and $Cr^{3+}$ as impurity ions. Emission data were obtained using several excitation wavelengths and the excitation data were acquired for the most intense emission bands. The optical results were analyzed according to the Tanabe-Sugano (TS) theory from which the crystalline field parameter *Dq* and Racah parameters *B* and *C* were obtained for the $Fe^{3+}$ and $Cr^{3+}$ sites. The results indicate that the $Fe^{3+}$ and $Cr^{3+}$ ions occupy tetrahedral and octahedral sites, respectively. The emission from $Fe^{3+}$ and $Cr^{3+}$ ions causes an intense and broad band ranging between 350 nm and 850 nm, showing that this material is a potential tunable radiation source at room temperature.

## 1. Introduction

Transition-metal doped materials have been studied exhaustively because they present interesting optical properties, such as high reflectance and broad emission and absorption bands in visible and infrared regions [1–4]. Due to these broad bands, many of these emitting materials can be used as tunable radiation sources in optical devices at room temperature or in pigments [5–7]. Some recently produced examples are the $MAl_{12}O_{19}$:$Fe^{3+}$ (M = Ca, Sr, Ba) phosphors that present intense emission in the near infrared region, between 700 nm and 850 nm, in which the emission was associated with $Fe^{3+}$ ions in octahedral sites [8]. According to the authors these materials are appropriate for use in high-resolution bioimaging. Another example is the $Zn_3Ga_2Ge_2O_{10}$ doped with $Cr^{3+}$, which is a sunlight-activated long-persistent luminescence material with a broad emission band in the red-infrared region, ranging between 650 nm and 1000 nm [9].

$Fe^{3+}$-$Cr^{3+}$ co-doped materials are interesting because it is possible to achieve an emission band from the visible to infrared regions of the electromagnetic spectrum, with an overlap of emissions from $Fe^{3+}$ and $Cr^{3+}$ ions. The emission band is possible because generally the stronger absorption band of the $Cr^{3+}$ is outside the luminescence region of the $Fe^{3+}$ ions, and vice-versa [10,11]. Some literature papers have presented simultaneous doping with $Fe^{3+}$ and $Cr^{3+}$ ions [12,13]. For example, in Ref. [12] the authors show results for the $\gamma$-$Al_2O_3$, in which broad bands ranging between 600 nm and 850 nm are observed, with the barycenter and the broadening dependent on the $Fe^{3+}$/$Cr^{3+}$ ratio.

In an earlier paper [1] photoluminescence results of the $Mg_2Al_4Si_5O_{18}$-$Al_2O_3$-$MgAl_2O_4$-$SiO_2$ system doped with $Cr^{3+}$ were presented. The spectra showed a broad band from the visible to infrared region, generated by an overlapping of emissions from several optical centers present in the sample. The aim of the present work is to produce and investigate the same system, now containing two different impurities, $Fe^{3+}$ and $Cr^{3+}$.

The choice of the $Mg_2Al_4Si_5O_{18}$-$Al_2O_3$-$MgAl_2O_4$-$SiO_2$ system was motivated by its property of having appropriate sites for trivalent doping ions occupation. Due to a low doping level, the probable distance among the impurities should be enough for the interaction between doping ions or pair formation to not occur.

In this work photoluminescence, excitation and radiative decay time for a ceramic system containing $Mg_2Al_4Si_5O_{18}$-$Al_2O_3$-$MgAl_2O_4$-$SiO_2$ with low quantities of $Fe^{3+}$ and $Cr^{3+}$ ions are presented. Photoluminescence spectra present broad bands assigned to $Fe^{3+}$ and $Cr^{3+}$ transitions in tetrahedral and octahedral sites, respectively. From the excitation data, and according to the Tanabe-Sugano (TS) theory, the crystalline field parameter *Dq* and Racah

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parameters *B* and *C* were obtained for the $Fe^{3+}$ and $Cr^{3+}$ sites.

## 2. Material and methods

The sample was prepared with the ultrapure (99.9%) oxides MgO, $SiO_2$, α-$Al_2O_3$, and $Fe_2O_3$. The masses of the raw oxides were weighed for the production of 2 g of the $Mg_2Al_{4\text{-}x}Fe_xSi_5O_{18}$ (cordierite phase) with x = 0.02, which is equivalent to the substitute 0.5% of the total number of $Al^{3+}$ ions in the molecular formula by the same number of $Fe^{3+}$ ions. The powder was mixed manually for 2 h and compressed into small dishes at 2 ton, which were put into an alumina crucible. During the next step the dishes were calcined in an air furnace at 1350 °C for 12 h, after which the furnace was switched off and cooled down to room temperature by thermal inertia.

X-ray data were acquired at room temperature by a *XPert Pro PANalytical* diffractometer (40 kV, 40 mA, with Cu-Kα radiation, with $\lambda = 1.54056$ Å). The data were refined using the Rietveld method with the *FullProf* package [14], for quantification and identification of the space group and lattice parameters for each crystallographic phase. A pseudo-Voigt (pV) profile function was used to fit the diffracted peaks.

Photoluminescence and excitation data at room temperature were obtained using a spectrofluorimeter *PTI 300 QuantaMaster* equipped with a 75 W pulsed Xenon lamp with a spectral resolution of 2 nm in the visible region. The data were corrected as a result of the experimental response.

## 3. Results and discussion

Fig. 1 shows the sample diffractogram and its respective Rietveld refinement. The circles ($I_{obs}$) are the experimental data. The Rietveld refinement result is the blue solid line ($I_{calc}$), calculated with the pseudo-Voigt (pV) profile function. The vertical bars are the Bragg reflections and the bottom line is the difference between the experimental data and the calculated data. The results indicate that the sample contains the following phases: $Mg_2Al_4Si_5O_{18}$, $MgAl_2O_4$, and non-reacted α-$Al_2O_3$ and $SiO_2$, identified by the Bragg lines (from top to bottom, respectively) in the Inorganic Crystal Structure Database (ICSD) [15] and American Mineralogist Crystal Structure Database (AMCSD) [16] data files.

Table 1 summarizes the refined values for cell parameter, space group, crystal system and fraction (%) of the phases. The obtained value for the "Goodness of Fit" [14] was S = 2.4, which is an acceptable value for samples with two or more phases [17].

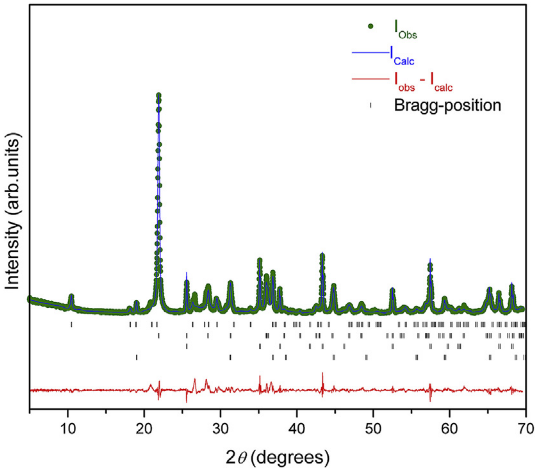

**Fig. 1.** X-ray diffraction data and Rietveld refinements for the sample. The Bragg lines (vertical bars) are associated with the phases $Mg_2Al_4Si_5O_{18}$, $MgAl_2O_4$, α-$Al_2O_3$, and $SiO_2$ (from top to bottom, respectively).

The structure of the $Mg_2Al_4Si_5O_{18}$ is formed by six units of Si/$AlO_4$ in which Al and Si ions are in tetrahedral sites coordinated by $O^{-2}$ ions [18]. The $MgAl_2O_4$ is a partially inverse spinel, in which the cations $Mg^{2+}$ and $Al^{3+}$ occupy tetrahedral and octahedral sites with the inversion parameter, thus being a fraction of the tetrahedral sites occupied by $Al^{3+}$ ions which vary from 0.1 to 0.6. So, in this phase $Al^{3+}$ in octahedral and tetrahedral sites [19] is expected. Concerning the $Al_2O_3$, this phase has a crystal structure in which the oxygen ions are arranged into hexagonal packing with $Al^{3+}$ ions occupying octahedral positions [20]. Therefore, the crystallographic phases have several $Al^{3+}$ sites convenient for $Fe^{3+}$ and $Cr^{3+}$ substitution.

Fig. 2 shows the time resolved photoluminescence data obtained at room temperature with (a) several excitation wavelengths for the emission range 600 nm–800 nm and, (b) excitation with a wavelength of 280 nm for emission range 350 nm–800 nm.

Fig. 2(a) demonstrates that the time resolved emission spectra depend upon the excitation wavelength. The spectra show a narrow peak at 690 nm when the sample is excited with 400 nm, 450 nm, 500 nm, 530 nm, and 550 nm. The most intense emission at 690 nm was achieved with 530 nm excitation. Besides the narrow line at 690 nm, a broad and intense band with barycenter at 770 nm can be observed. This band appears clearly with 400 nm wavelength excitation, but the intensity was enhanced with the excitation at 350 nm and 300 nm (higher intensity of the band).

Fig. 2(b) shows the photoluminescence spectrum obtained with excitation of 280 nm, in which it is possible to observe a new band with barycenter at 475 nm. However, the band at 690 nm was not detected.

To clarify the emission channels we have performed excitation measurements at room temperature (Fig. 3) with the emission monitored at 690 nm (dashed line) and 770 nm (solid line).

The excitation spectrum of the emission at 690 nm (14,493 $cm^{-1}$) (Fig. 3, dashed line) shows two broad bands at 417 nm (23,980 $cm^{-1}$) and at 568 nm (17,606 $cm^{-1}$). The shape and wavelength intervals of the bands are similar, respectively, to the ${}^4A_2({}^4F)\rightarrow{}^4T_1({}^4F)$ and ${}^4A_2({}^4F)\rightarrow{}^4T_2({}^4F)$ transitions of $Cr^{3+}$ in octahedral sites [13,21–23]. This result clearly shows that the sample contains $Cr^{3+}$ impurities, and we believe that it is very likely that our sample was contaminated with a small amount of $Cr^{3+}$ ions during the manufacturing process.

From the energy positions of the barycenter of the bands and using the solutions of Tanabe-Sugano matrices for $d^3$ electronic configuration (Eqs. (1)–(3)) [21–23], the crystal field parameter *Dq* and Racah parameters *B* and *C* were calculated:

$$E\,({}^4T_2) = 10\,Dq \tag{1}$$

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

$$\frac{E({}^2E)}{B} \cong \frac{3.05C}{B} + 7.90 - 1.80\frac{B}{Dq} \tag{3}$$

In equations (1)–(3), $E({}^4T_2)$ is the energy of the ${}^4A_2\rightarrow{}^4T_2({}^4F)$ transition and $\Delta E$ is the energy difference between the barycenter of the ${}^4A_2\rightarrow{}^4T_2({}^4F)$ and the ${}^4A_2\rightarrow{}^4T_1({}^4F)$ bands from the excitation spectrum. The $E({}^2E)$ is the energy of transition ${}^2E({}^2G)\rightarrow{}^4A_2({}^4F)$ obtained from the emission spectrum. As the ${}^2E({}^2G)$ energy level is independent from the crystalline field, the energy value of absorption and emission transition between ${}^2E({}^2G)$ and ${}^4A_2({}^4F)$ energy levels is the same [21].