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Investigation on the structural and photoluminescent properties of chromium-doped ceramics cordierite

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ABSTRACT

This work presents the investigation about the structural and optical properties of a doped-chromium system containing cordierite ($Mg_2Al_4Si_5O_{18}$) as main phase. The sample composition and the structural data were obtained from X-ray diffraction (XRD) measurements and the results were analyzed by Rietveld method. Photoluminescence (PL) spectra under several excitation wavelengths and photoluminescence excitation (PLE) measurements were performed. The obtained results from PL and PLE experiments are evidences that Cr^{3+} occupies octahedral sites in this ceramic system. By correlating the optical results, the crystal field parameter (Dq) and Racah interelectronic repulsion parameters (B and C) were calculated and discussed according to the Tanabe-Sugano (TS) theory for d^3 transition metals in octahedral sites.

1. Introduction

The search for new materials with low cost and simple fabrication for optical applications has been the aim of many researches for several years. A new approach is related to the investigation of systems whose optical properties have not been entirely explored, despite other physical features of these systems which were exhaustively studied. In this way, we focus in studying ceramic systems which may present broad emission spectra when transition metals are inserted in their crystal environment. The insertion of transition metal cations of iron group originated from Ti, V, Cr, Fe, Mn, Ni and Co atoms may generate luminescence in a broad range covering from the visible to near infrared region of the electromagnetic spectrum. The luminescence of these systems leads these materials to present potential applications in the development of new tunable lasers [1], *in vivo* imaging [2,3], white emission sources [4–6], illumination [7], photoelectric devices [8], night-vision surveillance [9] and other optical devices [10–15], only to mention a few examples.

In this work we investigated a very known system due to its thermal and electrical properties and also for being a promissing material for optical devices due to its potential optical features. The cordierite ceramic compound, with chemical formula $Mg_2Al_4Si_5O_{18}$ can be present in three distinct polymorphs [16–18]: the α-cordierite (also known as indialite) in hexagonal structure (space group $P6/mcc$), with stable form around 1450–1460 °C; the β-cordierite, presenting stability at temperatures lower than 1450 °C with orthorhombic symmetry (space group $Cccm$) and the μ-cordierite, metastable, consisting of a solid solution with β-quartz structure.

Its physical properties include chemical, mechanical and thermal stability, porosity, low expansion thermal coefficient, resistance to thermal shocks, low dielectric constant, resistance to corrosion and even magnetic features [17,19–21]. These features besides its low cost and easy fabrication are advantageous for several applications in electronics, catalysis, membranes manufacturing, refractory materials, engineering industry and gas control systems, for example [17,22–24]. Several works report the preparation of solid solutions containing distinct dopants, which may modify their physical properties [17,18,21,25,26].

The system under investigation can be considered a versatile material, according to its physical properties described above and due to its optical properties, specially the photoluminescent features. Spinolo et al. [27] investigated the absorption and photoluminescent of the Fe–Mn co-doped cordierite, showing that iron and manganese cations can ocuppy tetrahedral and octahedral sites, giving rise to several transitions detected in the optical spectra of the sample due to crystal field. Miletich et al. [28] presented a study of optical absorption spectroscopy with trivalent iron ions inserted in the cordierite sites showing a strong absorption in the blue region of visible spectrum. Zhou et al. [21] reported

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the luminescence of cordierite when doped with Eu^{2+} ions evidencing a red-shift in the emission bands of this sample when K^+ and Rb^+ are inserted in the system replacing Mg^{2+}. Some papers also investigated the optical properties of trivalent chromium in cordierite glass sites at low temperatures, as reported by Champagnon et al. [29,30]. Capobianco et al. [31] performed a study of the optical properties of cordierite at low temperatures containing other oxide phases with likely Cr^{3+} occupation. Rossi et al. [32] investigated the luminescent features of nanostructured chromium-doped cordierite oxide at room and low temperatures.

In this way, the aim of the present work is to investigate the photoluminescent properties of the cordierite system when trivalent chromium is used as impurity, using a simple, low cost preparation route to obtain the cordierite phase. The sample was investigated by X-ray diffraction and the diffractogram was used in the Rietveld refinement for investigation of the crystal structure. SEM and EDX were used for determination of sample composition and morphology. The optical properties were investigated using photoluminescence (PL) and excitation photoluminescence (PLE) experiments at room temperature. The obtained photoluminescence spectra show a broad band with several structures in the visible-near infrared region. The structures found in the spectra were related to the sites occupied by Cr^{3+} ions in octahedral environment. By correlating the optical results, the crystal field parameter (*Dq*) and Racah interelectronic repulsion parameters (*B* and C) have been evaluated and discussed according to the Tanabe-Sugano theory for d^3 transition metals in octahedral sites.

2. Experimental details

Silicon oxide (SiO_2), aluminum oxide (Al_2O_3), magnesium oxide (MgO) and chromium oxide (Cr_2O_3) in powder form with high purity level ($\geq$ 99.9%) were weighed at stoichiometric proportions to obtain 1 g of cordierite containing 0.1 at% of Cr^{3+}. The powder oxides were mixed into a solution containing 50% of distilled water and 50% of glacial acetic acid [33]. The mixture was slowly heated to fully evaporate the liquid and, after the evaporation, the volume was reduced. The remaining mixture was dried at 100 °C in furnace during 12 h to remove humidity. After that, the solid solution was put into an alumina crucible for thermal treatment in air furnace at 800 °C during 12 h. At the end of the first thermal treatment, the furnace was switched off and left to cool until room temperature by inertia. The powder was removed from the furnace at room temperature and compacted in pellets with 1.0 cm diameter under pressure of 2 tons. The pellets were heated at 1350 °C during 12 h. After synthesis, a small part of the powder was reground until a homogeneous and thin powder was obtained for X-ray diffraction experiments.

X-ray powder diffraction data were obtained at room temperature, using a X Pert Pro Panalytical diffractometer with Cu-Kα radiation ($\lambda = 1.54056$ Å), 40 kV and 40 mA. Data were collected in the $10° < 2\theta < 100°$ range in a Bragg-Brentano geometry, with a step size of 0.01° and a counting time of 1 s per step. The structure pattern was refined by Rietveld method for identification of the space group, lattice parameters and phase quantification. SEM images and EDX analysis were obtained with a FEI Quanta 400 Microscope connected to a EDS Bruker Quantax 800 system.

Photoluminescence measurements at room temperature were performed using a solid state laser with 532 nm/50 mW as excitation source, modulated by a chopper *Newport* 75160 with variable speed operating at 200 Hz. A spectrometer *Acton* AM510 was used to scan the emission, in the 600–850 nm range, with 1 nm/step. A photomultiplier *Newport Oriel* 77348 with the signal amplified by a *Princeton* lock-in 5209 were used to signal detection. Emission, excitation spectra and emission decay data were acquired in a spectrofluorimeter *PTI 300 QuantaMaster* equipped with a pulsed Xenon lamp using a spectral resolution of 2 nm in the visible region with 1 nm/step. All data were corrected by the apparatus sensitivity response.

3. Crystal structure and morphology

Fig. 1 shows the diffractogram of the sample. The Rietveld method was used to refine the data using *Fullprof* package [34]. The quantitative analysis obtained from refinement identified the presence of four phases in the sample: the main phase α-cordierite $Mg_2Al_4Si_5O_{18}$ (also known as indialite) with 56.64% of relative phase composition, followed by a small quantity (9.20%) of the $MgAl_2O_4$ spinel phase. The refinement also identified the presence of some reactants in the final sample: α-Al_2O_3 (19.51%) and SiO_2 (14.65% in relative phase composition).

Details of the Rietveld refinement and the ICSD codes of the phases used for the 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. The pseudo-Voigt profile function was used during the refinement. Agreement factors and the difference between the calculated and observed profiles were evaluated at each refinement cycle to determine the refinement quality, and their values are also presented in Table 1. The weighted profile R_{wp} factor is related to the quantity to be minimized and it is the most direct measure for monitoring the refinement convergence; its value should approach to the statistically expected R_{exp} value. The ratio between the two quantities is known as the goodness-of-fit *S*. The mathematical expressions for these quantities can be found in literature [35,36]. The phase quantitative analysis was calculated from refinement of the scale factors. The goodness-of-fit factor *S* extracted from refinement was 1.5, indicating the very good quality of refinement.

The appearing of the spinel additional phase accompanied by reactants traces is very common during cordierite synthesis, as reported by some authors [17,24,37]. However, it is important to

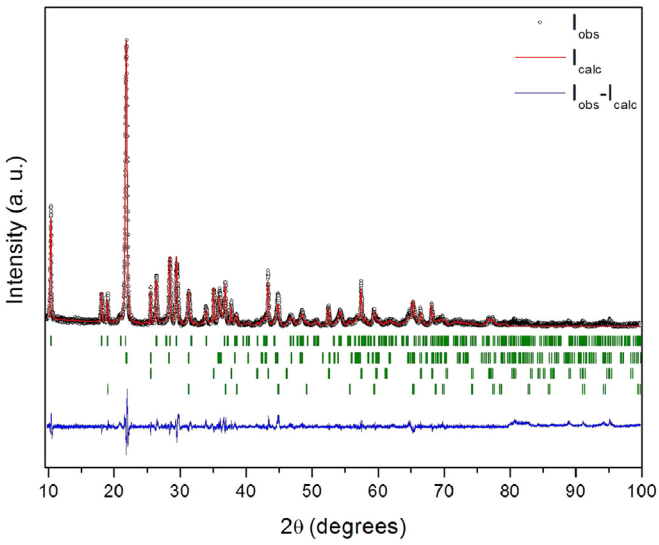

Fig. 1. Powder X-ray diffractogram of the sample. The open circles represent the observed pattern, the red line represent the calculated pattern and the blue line is the difference between the calculated and observed patterns. The green vertical bars represent the reflections of the observed phases in the following order (from top to bottom): $Mg_2Al_4Si_5O_{18}$, SiO_2, α-Al_2O_3 and $MgAl_2O_4$. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)