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Thermal and Optical Analysis of the Doped Cerium Calcium Aluminate Obtained by the Gel Process Using Ethylenediamine Tetraacetic Acid

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Abstract: In this work, we synthesized calcium aluminates doped with trivalent cerium ions (Ce^{3+}) by gel process with ethylenediamine tetraacetic acid (EDTA) as a chelating agent. The synthesized material was characterized by means of thermogravimetry and differential thermal analysis and spectrofluorimetry. The results were similar to literature.

Keywords: Calcium aluminate, cerium ions, luminescence.

1. Introduction

The calcium aluminate ($CaAl_2O_4$) is an oxide with spinel structure of normal type with close-packed face-centered-cubic with *Fd3m* space group symmetry [1]. $CaAl_2O_4$ powders can be synthesized by gel process. This process synthesizes fine and homogeneous powders in low temperature, high homogeneity of the matrix and activating agents, among others [2]. In this study, it was synthesized calcium aluminate through the gel process using ethylenediamine tetraacetic acid (EDTA) doped with trivalent cerium ions.

2. Materials and Methods

Two syntheses were performed, the first one with 1.0 % mol Ce^{3+} in the matrix of $CaAl_2O_4$ and other with 0.5% mol cerium ions. Synthesis of doped cerium calcium aluminate ($CaAl_2O_4$:Ce^{3+} (1.0%)) was made separately. Synthesis of $CaAl_2O_4$:Ce^{3+} (1.0%) was made by mixing NH_4OH solution in EDTA solution. Then, it was added solutions of $Al(NO_3)_3$ and $Ca(NO_3)_2$. This mixture was placed on a heating plate at about 80°C

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with continuous slow stirring for 2 hours to evaporate water. After this time, it was added a solution of $Ce(NO_3)_3$ (1%mol), increasing at 140 ºC the temperature of the heating plate, keeping the mixture with continuous stirring to form a viscous solution and gelled until to dry. Solution of $Ce(NO_3)_3$ was made dissolving cerium oxide (Aldrich, 99.9%) in concentrated nitric acid solution (pH=1.0), then diluting until the pH=4.0 by evaporation cycles.

The solid formed in this phase is called precursor. The precursor was pre-calcined at 200°C in a muffle furnace, pulverized and calcined with temperature ramp of 20°C/min until 800°C for 2 hours. This calcination at 800ºC synthesized fine product. Synthesis of the $CaAl_2O_4:Ce^{3+}$ (0.5%) was made the same way, just replacing the cerium nitrate (1.0%) solution for 0.5%. Powders of $CaAl_2O_4:Ce^{3+}$ were characterized using thermogravimetry (TGA) and differential thermal analysis (DTA) using Shimadzu Thermal Analyzer model DTG-60H and spectrofluorimetry with a Shimadzu model RFPC-450 spectrofluorimeter.

3. Results and Discussion

The thermal characterization techniques were thermogravimetry (TGA) and differential thermal analysis (DTA), which were done simultaneously. These techniques were employed in the analysis of precursor powders of the $CaAl_2O_4:Ce^{3+}$ (0.5%) and the $CaAl_2O_4:Ce^{3+}$ (1.0%). The results for these precursors are shown in Fig. 1.

The TGA curves shown in Fig. 1 show that there was a marked weight loss below 700°C. This indicated that the precursors of doped aluminates did not absorb humidity and had high content of EDTA derivatives, this may be due to pre-calcination at a temperature 200°C, lower than the final calcination. Another observation in Fig. 1 is the similarity of the endothermic and exothermic peaks in the DTA curve, indicating that the phases were similar [3].

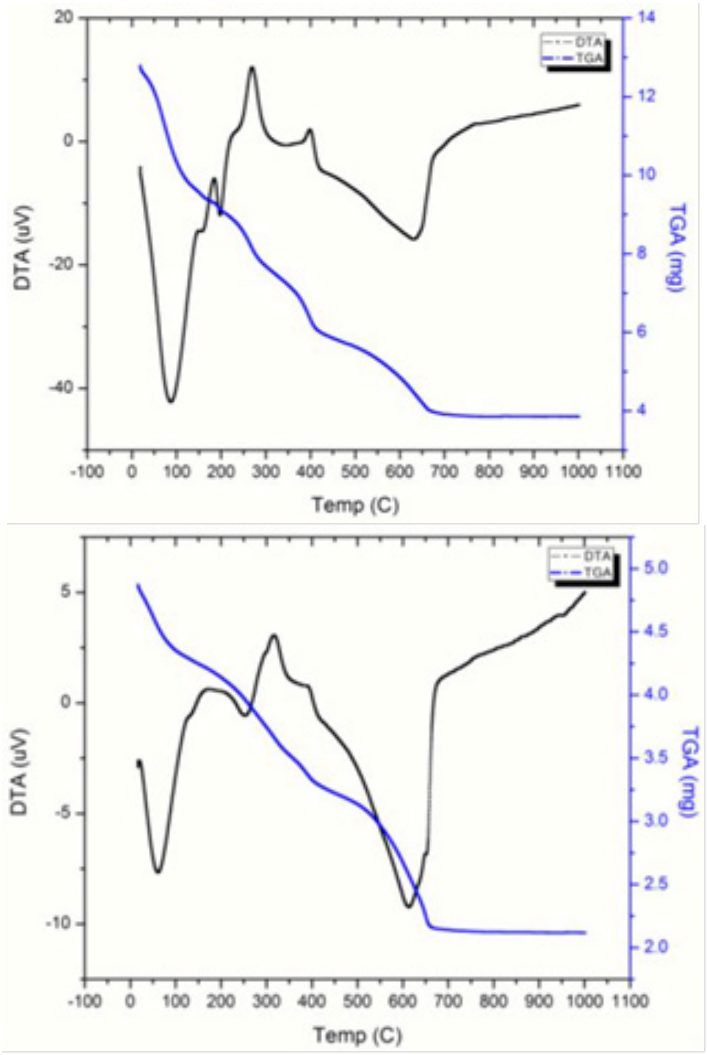

Fig. 1 TGA and DTA curves for the doped calcium aluminate precursor with Ce^{3+} (1.0%) (Top) and Ce^{3+} (0.5%) (Bottom)

The optical characterization technique used was spectrofluorimetry, it was used to analyze luminescence of Ce^{3+} doped aluminate calcined at 800 °C. The emission and excitation spectra obtained on spectrofluorimetry were normalized to facilitate comparison between them. After normalization of the spectra, it was performed comparison of the wavelengths of the spectra obtained with the energy level diagrams shown in the literature [4, 5]. The results are shown in Fig. 2 and 3. Fig. 2 shows the emission spectra of $CaAl_2O_4:Ce^{3+}$ (1.0%) and $CaAl_2O_4:Ce^{3+}$ (0.5%) in the top and bottom plots, respectively. The wide emission band of both materials indicated that the optical transition is type d-f [6]. Fig. 3 shows the excitation spectra for the emission of $CaAl_2O_4:Ce^{3+}$ (1.0%) and $CaAl_2O_4:Ce^{3+}$ (0.5%) in the top and bottom plots, respectively. The both spectra have peaks of the maximum wavelength and similar energy, Fig. 3 (right), with wavelength of 222 nm, corresponding to the energy of 45045 cm^{-1} and Fig. 3 (left) had peak at 224 nm, with energy at 44642 cm^{-1}.

This energy is attributed to optical 4f-5d transition, characteristic of the Ce^{3+}. This transition 4f-5d is due to electric dipole transition of the Ce^{3+} ion 4f electrons allowed from the ground state $^1F_4$ (^2F term) deployed by spin-orbit (sub-levels$^2F_{5/2}$ and $^2F_{7/2}$) to the 5d excited state [4].

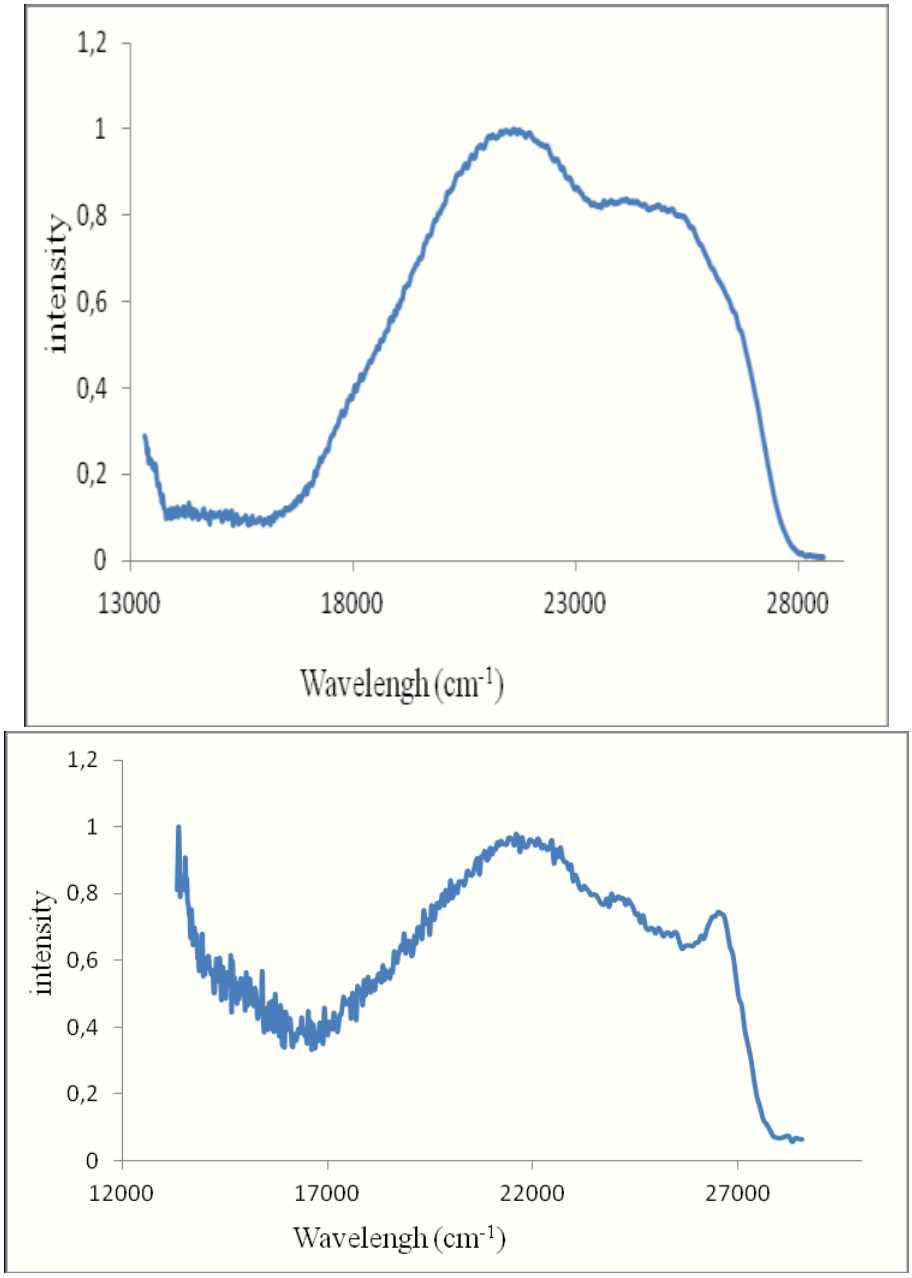

Fig. 2 Emission spectra with λ_{exc} = 275nm of the calcium aluminate doped with Ce^{3+}. (Bottom) $CaAl_2O_4:Ce^{3+}$ (1.0%) (Top) $CaAl_2O_4:Ce^{3+}$ (0.5%).

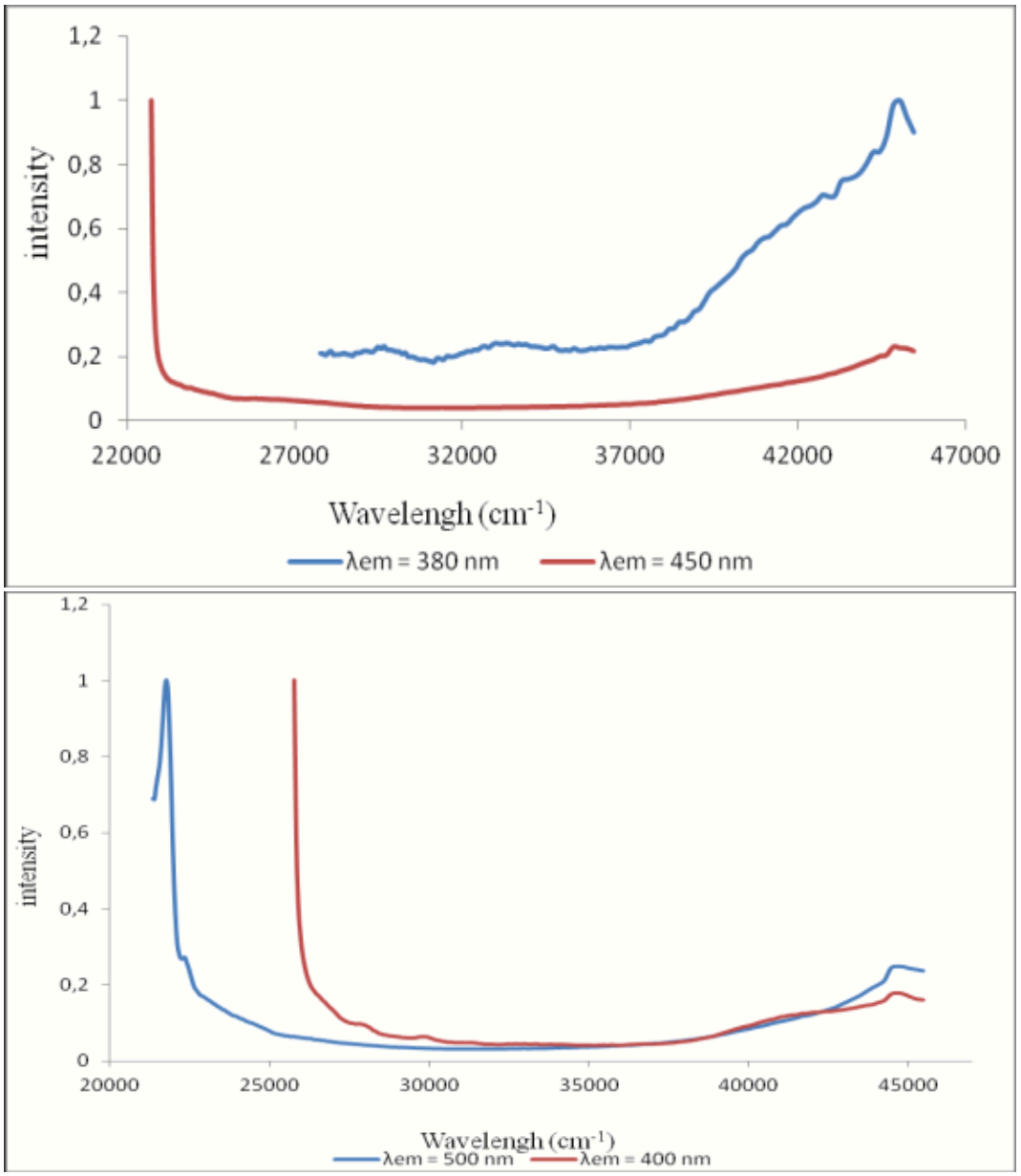

Fig. 3 Excitation spectra for the calcium aluminate doped with Ce^{3+}. (bottom) $CaAl_2O_4:Ce^{3+}$ (1.0%) (Top) $CaAl_2O_4:Ce^{3+}$ (0.5%).

4. Conclusion

It is observed that the gel is very efficient route for the synthesis of calcium aluminates doped with lanthanide ions and by doping the matrix of calcium aluminates with cerium ionis very effective for the study of luminescence in blue region of visible spectrum.

Acknowledgments

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