PREPARATION OF DY^{3+}-DOPED CALCIUM MAGNESIUM SILICATE PHOSPHORS BY A NEW SYNTHESIS METHOD AND ITS LUMINESCENCE CHARACTERIZATION

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Abstract

Recently, rare-earth doped alkaline earth silicates have been researched extensively as a new generation of afterglow phosphors. Compared with the conventional sulphide materials used for this purpose, silicates yield luminescence with longer duration time and higher bright, as well as improved chemical stability and lower cost. In the present work, Dy-doped calcium magnesium silicate phosphors were prepared by joining the methods sol-gel and co precipitation. Silica gel was obtained from sodium silicate solution. Ca, Mg and Dy hydroxides, precipitated from chloride solutions with NaOH, were added to the obtained gel. After washing for removal of Cl^- ions, the product was annealed at 1000°C for 2 hours. XRD results confirmed the formation of diopside phase ($CaMgSi_2O_6$). The product was later characterized by SEM and luminescence spectroscopy.

Keywords: Calcium magnesium silicates, dysprosium, luminescence

Introduction

Silicate-based luminescent materials show interesting features, such as: high thermal and chemical stability, water resistance, quantum yield of up to 70% and high radiation intensity. These features come from the weak interaction between the matrix and the activator ion, so the excitation and emission spectra are determined mostly by the nature of the activator ion. Besides, these hosts have a wide band gap and absorb in the far-UV region. [1] These alkaline earth (Ca, Sr, Ba), rare-earth-doped silicates have also been studied as persistent luminescence-phosphors, due to a growing market for their application in traffic signs, decoration and textile printing, among others. Compared with the sulphide materials used earlier, silicate phosphors yield better characteristics, such as longer and brighter luminescence emission, easier preparation and lower cost [2, 3, 4, 5]. Calcium magnesium silicates would be also interesting from the manufacturing point of view, because both calcium and silica are abundant and relatively inexpensive [6, 7]. Some of the compounds existing in the Ca-Mg-Si-O system include diopside ($CaMgSi_2O_6$), akermanite ($Ca_2MgSi_2O_7$), merwinite ($Ca_3MgSi_2O_8$) and monticelite ($CaMgSiO_4$) [8, 9]

Dysprosium (Dy^{3+}) is an important rare earth ion which plays a major role in the production of different types of light-emitting materials. The special interest in Dy^{3+} visible luminescence is due to the existence of two intense bands in the blue (460-480 nm) and yellow (560-580) wavelength regions, that combined at a suitable ratio, will emit white light which, unlike emission from $Eu^{2+/3+}$ ions, is not significantly influenced by the crystal structure and phonon frequency of the host lattice [6, 10]. Consequently, Dy^{3+} activated luminescent materials attracted much attention, because of their significant applications as potential single phase white phosphors [11].

It is well known that the performance of materials highly depends on the synthesis conditions and methods, which play an important role on determination of microstructure, properties and efficiency of these materials. The most commonly used synthesis method for luminescent materials is the solid-state reaction method, which requires high-temperature thermal treatment. Fluxes, such as KCl, LiF, $CaCl_2$, H_3BO_3, can be added to improve crystallization [1, 6, 12].

In order to reduce the sintering temperature, it is necessary to use powders of phosphor compounds in a very small grain size and a narrow size distribution. For this purpose, submicron or even nanosized products have been synthesized by various wet-chemistry methods over the past several years, including hydrothermal synthesis, chemical co-precipitation, sol–gel process, combustion synthesis, etc [12]. The advantages of these wet chemical routes arise from the careful control of composition, which can be achieved by mixing the constituents at molecular level in solution [13]. Several groups have reported particle-size-dependent phenomena in lanthanide-doped nanoparticles that affect emission lifetime, quantum yield and concentration quenching [14].

Although significant progress has been achieved, there are problems; for example, the sol–gel process generally uses metal alkoxides as the starting materials normally, which are very expensive and extremely sensitive to environmental conditions such as moisture, light, and heat. Moisture sensitivity makes it necessary to conduct the experiment in dry boxes or clean rooms. Co-precipitation processes involve repeated washing to eliminate the anions coming from the precursor salts used, making the process complicated and very time-consuming [1].

In the present work, we obtained diopside phase ($CaMgSi_2O_6$) doped with Dy^{3+}, using a combination of sol-gel and coprecipitation methods. Silica gels were obtained using Na_2SiO_3 solution as precursor, instead of silicon alcoxides, and then Ca, Mg and Dy were precipitated using NaOH.

Materials and methods

Starting materials used were: Sodium silicate solution (Na_2SiO_3), choride solutions of calcium ($CaCl_2$), magnesium ($MgCl_2$) and dysprosium (Dy_2Cl_3), HCl 12M and NaOH solution.

Figure 1 shows the flow chart for synthesis of dysprosium-doped calcium magnesium silicates. Table 1 shows the amounts used of each reagent, and correspondent oxides

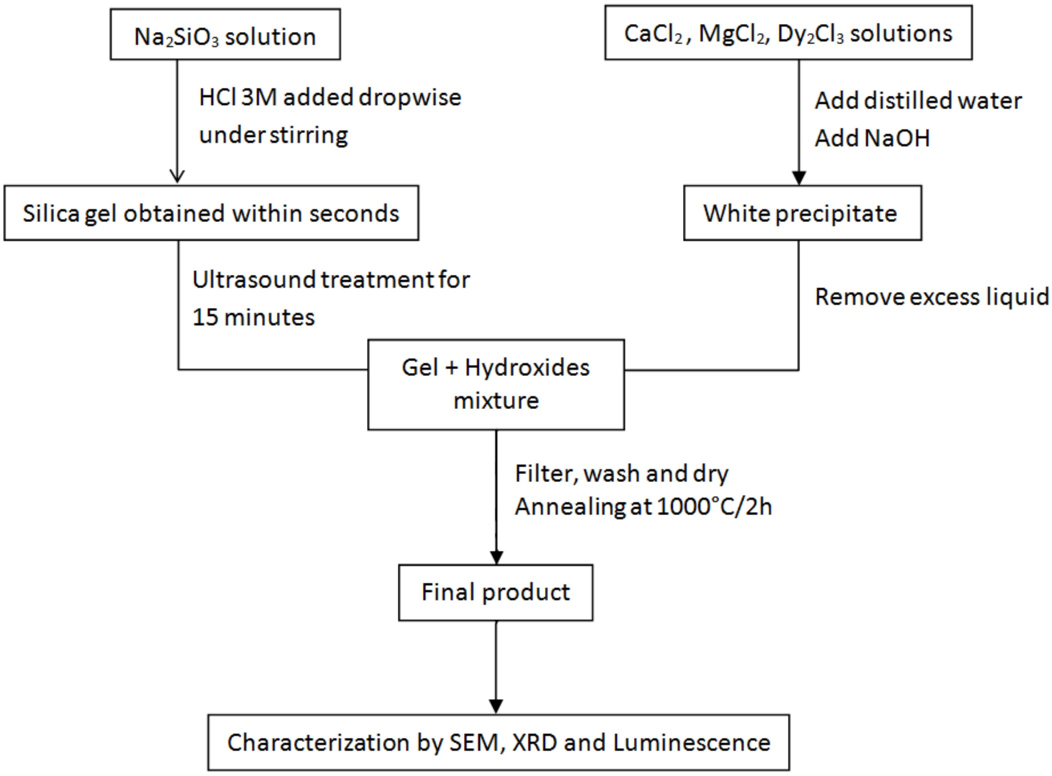


Figure 1: Flow chart for synthesis of dysprosium-doped calcium magnesium silicate

Table 1: Amounts of used materials

Reagent	Correspondent oxide	Oxide amount (mol)
Na_2SiO_3	SiO_2	0,04
$CaCl_2$	CaO	0,02
$MgCl_2$	MgO	0,02
Dy_2Cl_3	Dy_2O_3	0,0001

The product was separated by decantation and the liquid was removed; the process was repeated until no Cl- ions were detected in the liquid by silver nitrate test. The product was dried at 70ºC for 24h; the resulting powder was grounded in mortar and annealed at 1000ºC for 2h. The calcined powder was characterized by XRD, SEM and luminescence.

Results and discussion

Figure 2 shows the XRD pattern of the powder annealed at 1000ºC for 2h (labeled C1-1000).

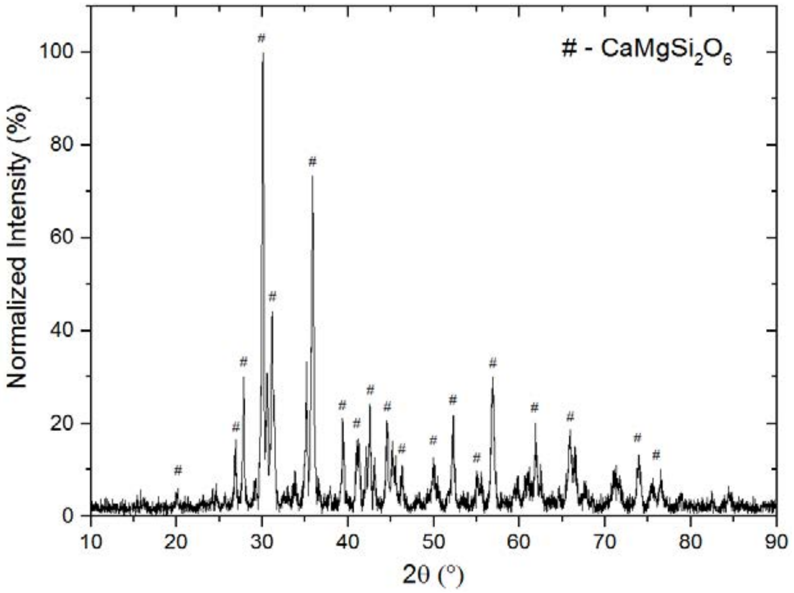
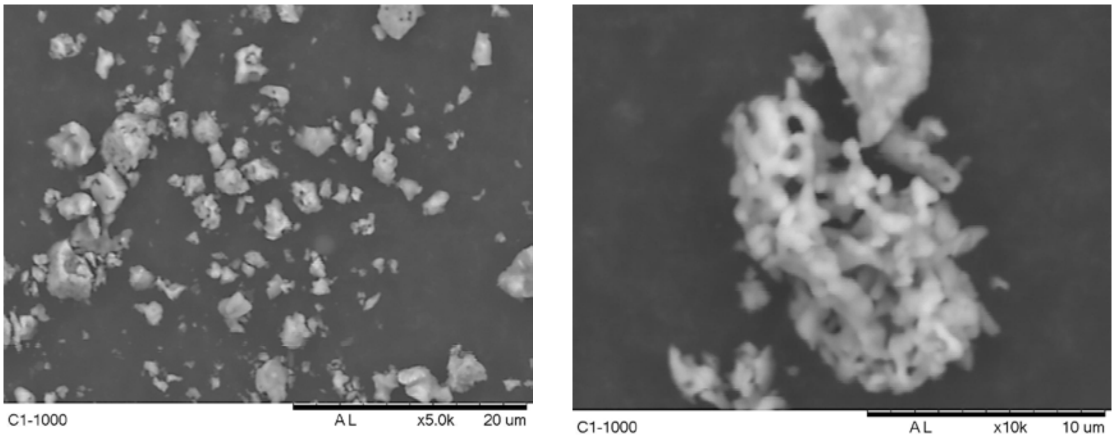


Figure 2: XRD pattern of obtained product, labeled C1-1000

The pattern shown in Fig. 2 presented a strong matched with diopside phase ($CaMgSi_2O_6$, PDF 01-072-1497), with few impurity peaks observed. The diopside mineral belongs to the monoclinic spatial group C2/c, with lattice parameters a = 9,746 Å, b = 8,889 Å, c = 5,251 Å and β = 105,6º [15]

Figures 3a and 3b presents the SEM images for the sample C1-1000.



(a) (b)

Figure 3: SEM images for the sample C1-1000 (a) 5000x magnification (b) 10000x magnification

From Figure 3a, it is verified that the obtained product consists of agglomerates with irregular morphology and narrow size (< 5 μm) distribution. In Figure 3b it is observed that these agglomerates are porous and consisted with connected elongated particles.

Figure 4 presents the excitation and emission spectra of sample C1-1000. The emission spectra were obtained by setting excitation spectra at the wavelength of highest intensity peak (390 nm).

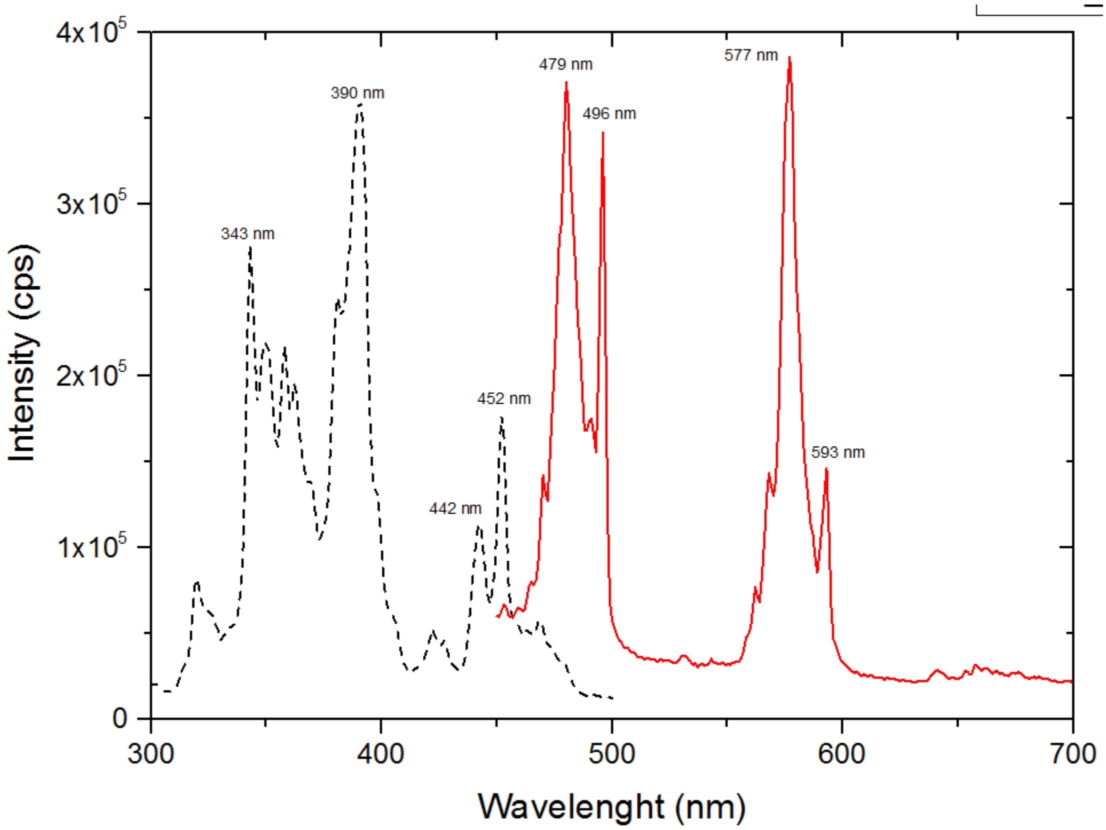


Figure 4: Excitation (black dashed line) and emission spectra (red solid line) of sample C1-1000

The excitation spectra show peaks at 350, 390, 442 and 452 nm. The emission spectra show peaks in the spectral regions of blue and yellow, corresponding to the $^4F_{9/2}$-$^6H_{15/2}$ and $^4F_{9/2}$-$^6H_{13/2}$, transitions of Dy^{3+} respectively, with peaks at 479 and 577 nm showing similar intensities. The emission lines are broadened because there are several Stark levels for the $^4F_{9/2}$-^6H_J transitions. It is well known that the blue-region emission corresponds to the magnetic dipole transition, which hardly varies with the crystal field strength, while the hypersensitive yellow-region emission corresponds to the forced electric dipole transition, which is strongly influenced by the crystal environment [6, 10, 11, 16].

In general, color of any phosphor material is represented by means of color coordinates. Color coordinates are one of the important factors for evaluating phosphors performance. The luminescence color of the sample C1-1000 has been characterized by the CIE (Commission International de l'Eclairage) 1931 chromaticity diagram [6, 10]. The emission spectrum of the sample C1-1000 phosphor was converted to the CIE 1931 chromaticity using the photo-luminescent data and the interactive SpectraLux software [17] as shown in Figure 5.

Every natural color can be identified by (x, y) coordinates that are disposed inside the 'chromatic shoe' representing the saturated colors. Luminescence colors of sample C1-1000 phosphor are placed in the (x = 0.309, y = 0.363), which is represented by the circle symbol [“o”]. The chromatic co-ordinates of the luminescence of this phosphor were measure and reached near to light blue-light green luminescence. The “ideal white light emission” is located on chromaticity coordinates (x = 0.333, y = 0.333) [6, 10, 11, 18].

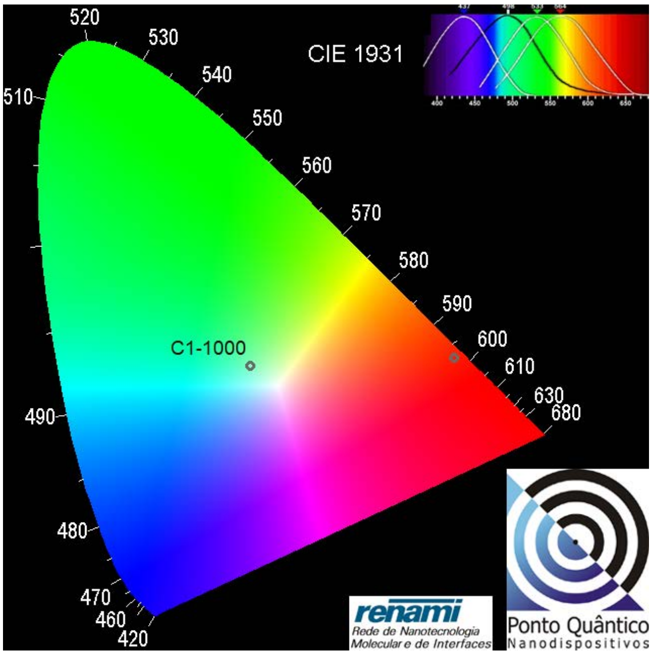


Figure 5: The CIE Coordinate diagram for sample C1-1000

Conclusions

In this work, crystalline, dysprosium-doped calcium magnesium silicate powders were obtained by combining sol-gel and coprecipitation methods. XRD confirmed diopside ($CaMgSi_2O_6$) as the main phase, formed after annealing the precursor powder at 1000ºC for 2 hours. The product also showed the characteristic emission peaks of Dy^{3+}, in the blue and yellow regions, which resulted in an overall light blue-green emission, according to CIE diagram.

Acknowledgments

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