Synthesis and Characterization of CaMgSi$_2$O$_6$ Activated by Eu^{2+}

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Abstract. Rare earth silicate based M$_n$MgSi$_2$O$_{5+n}$ (M = Ca, Sr or Ba and n=1-2) phosphors, have attracted interest of researchers due to their high efficiency as a host, excellent thermal and chemical stability and high brightness adding to their low cost. These phosphors showed great potential in various applications such as fluorescent lamps, white light emitting diodes, and display components. High temperature solid-state reactions are usually employed to synthesize those compounds. This paper proposes an alternative method of obtaining nanophosphor host based on Eu-doped CaMgSi$_2$O$_6$ (CMS:Eu), persistent luminescence phosphor. Sol gel technique combined to a modified molten salt method was used. The resulted powder was calcined for 3h under an atmosphere of 5% H$_2$ and 95% Ar$_2$. Phase identification by XRD and the measurements of photoluminescence (PL) and photoluminescence excitation (PLE) were performed. Single phased CMS:Eu with persistent luminescence characteristics was prepared.

Introduction

Photoluminescent materials, also called phosphors, have been widely studied since earliest times [1]. They have found a wide variety of applications [2], including information displays, lighting, medical X-ray monitors, X-ray-improving and scintillation, *etc*. Among these materials, the persistent luminescent ones can emit visible light for 24+ h after the irradiation (UV-lamp, sun light, fluorescent tubes, *etc.*). Until early 1990, sulfide phosphors continued to be the commercial persistent luminescence phosphors. However, over the last 20 years, a new class of aluminate persistent luminescence phosphors has attracted attention, since the sulfide phosphors are not stable and not bright enough for many applications. Rare earth (RE)-doped alkaline earth aluminate phosphors have attracted attention of researchers due to their high brightness, long duration and excellent photo resistance [3, 4]. However, these hosts showed to be water sensitive. More recently, silicate-based phosphors [5] have attracted the attention of researchers due to their high chemical and thermal stabilities, water resistance, tunable color emission and low cost [6, 7, 8]. The interest for those materials, in recent years, is triggered by the growing application market such as traffic signs, emergency exit indicator, textile printing, and decorations, *in-vivo* bio imaging, *etc.* [9].

Alkaline earth silicates are suitable luminescent hosts with a stable crystal structure, like CaMgSi$_2$O$_6$ (CMS) [10, 11]. Many different CMS luminescence materials can be prepared by doping with different ions, where the emission arises from *e.g.* exclusively from Eu^{2+} (CMS:Eu^{2+} or CMS:Eu^{2+},Dy/Nd) [12] or combined with different ions like Eu^{3+} (CMS:Eu$^{2+/3+}$) [11,13,14] or Mn^{2+} (CMS:Eu^{2+}, Mn^{2+}) [15]. The emission of Eu^{2+} doped materials arises from the parity allowed 4f^7→4f^{6}5d^1 transition [16, 17]. Although, the 4f electrons of Eu^{2+} are not very sensitive to changes on the crystal field strength due to the shielding function of the outer shells, the 5d electrons are very sensitive [18]. The peak positions in the emission spectra depend on the nature of the Eu^{2+} surroundings, and consequently, Eu^{2+} ions can emit in different regions of the UV-vis spectrum by changing the crystal field [19].

Many methods have been developed to prepare persistent luminescence materials, such as solid state reaction method [20, 21], co-precipitation method [11], sol-gel process [22], spray pyrolysis method [23] and combustion method [24]. In this study a modified sol-gel followed by molten salt

method to synthesized CMS:Eu phosphor particles was proposed. Solution of $NaSiO_3$, Eu_2O_3, CaO, and MgO were used as starting materials. Gel of silica was obtained by acid catalyzed reaction using high acid chloride solution of Eu, Ca, and Mg. The thermal treatment of the gel allowed the molten salt process. Luminescence properties (PL) under UV light excitation and photoluminescence X-ray diffraction (XRD) of the obtained CMS:Eu were investigated.

Experimental

The $CaMgSi_2O_6$:Eu (CMS:Eu) material with 0.03 mol-% of Eu_2O_3 (calculated on the basis of the Ca^{2+} amount) was prepared by a modified sol-gel followed by molten salt method. The starting materials were CaO, MgO, Eu_2O_3 and Na_2SiO_3 solution. Stoichiometric amounts of CaO, MgO and Eu_2O_3 were initially solved by a previous calculated volume of 12M HCl. This volume of acid is enough keep an acid medium when this solution is added to the Na_2SiO_3 one, allowing the acid catalyzed reaction of the gel formation. Then CaO, MgO and Eu_2O_3 in HCl acid solution were added under stirring to the Na_2SiO_3 solution. After 2 h, a gel formation was observed which was dried on a hot plate at 250 °C. The dried powder was heated at 900°C for 1 h to perform the molten salt process. The resulted product was washed until no chloride ions were detected by $AgNO_3$ solution. After washing, the material was again dried and calcined at 900°C for 4 h. Finally, the sample was heated in a tube oven in a reducing atmosphere of Ar_2/H_2 (95:5) at 900°C for 4 h to perform the $Eu^{3+} \rightarrow Eu^{2+}$ reduction. The prepared CMS:Eu powders were characterized by XRD (CuKα radiation, λ: 1.5418 Å) to verify the crystalline phases. The UV excited spectra were measured with a SPEX Fluorolog-2 spectrofluorometer equipped with two 0.22 m SPEX 1680 double grating monochromators. A 450 W Xenon lamp was used as the irradiation source.

Results and Discussion

The XRD patterns (Fig. 1) of synthesized CMS:Eu powder exhibit mainly the monoclinic diopside phase of $CaMgSi_2O_6$ (JCPDS 78-1390), indicating that no significant Eu-related impurity was formed by Eu dopping. Since Eu^{2+} and Ca^{2+} have the same charge, and similar ionic radii (Eu^{2+}: 1.17 and Ca^{2+} 1.00 Å, both with coordination number CN 6 [25]), no big distortions are expected. In the case of Eu^{3+} doping, the ionic radii are even closer (Eu^{3+}: 0.947 Å, CN: 6), but the different charges implies in charge compensation processes in order to keep the charge balance. A peak at 21.89° can be observed, which can be assigned to the formation of the quartz phase of silica (JCPDS 86-1564), which is probably due to the excess amount of silica source in the synthesis.
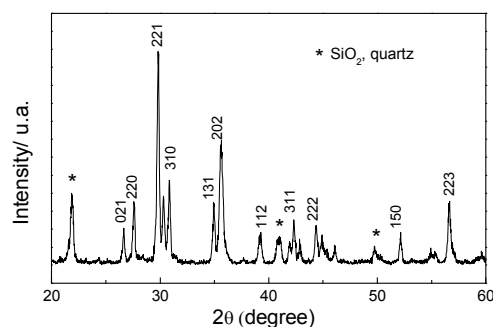

Fig.1- XRD patterns of synthesized CMS:Eu calcined in air at 900°C for 1h and submitted to reduction in Ar_2/H_2 (95:5) atmosphere at 900°C for 4 h.

The PL excitation spectra of CMS:Eu phosphor with emission monitored in the Eu^{2+} emission at 448 nm is shown in Fig. 2. It is observed a broad absorption band at 300–400nm in the UV range which is attributed to the parity-allowed transition from the $4f^7$ ground state of Eu^{2+} to the $4f^65d$ excited state [7] . It is also observed a low intensity excitation peak at 392 nm, indicating that even with the hydrogen-reducing atmosphere there is still some trivalent europium ions in the host. The presence of this band might indicate energy transfer process from Eu^{3+} to Eu^{2+}.
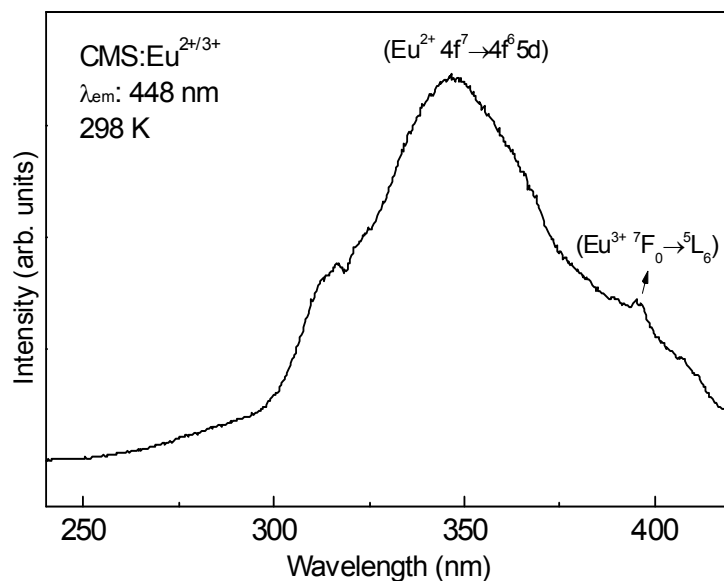
Fig.2- PL excitation (λ_{em}: 448 nm) spectra of the synthesized and reduction submitted CMS:Eu.

The excitation spectrum measured monitoring Eu^{3+} $^5D_0 \rightarrow ^7F_1$ emission at 583 nm (Fig. 3) shows the Eu^{3+} 4f-4f intraconfigurational transitions, with maximum at 391 nm ($^7F_0 \rightarrow ^5L_6$). It can also be observed a broad band centered at 265 nm (~4.7 eV) attributed to the ligand to metal charge transfer (LMCT) transition $O^{2-}(2p) \rightarrow Eu^{3+}$. The energy of the LMCT band in this material is similar to the one found in $Sr_2MgSi_2O_7$ (5.0 eV) [26] and indicates the position of the Eu^{2+} ground state level in relation to the valence band of the host [27].
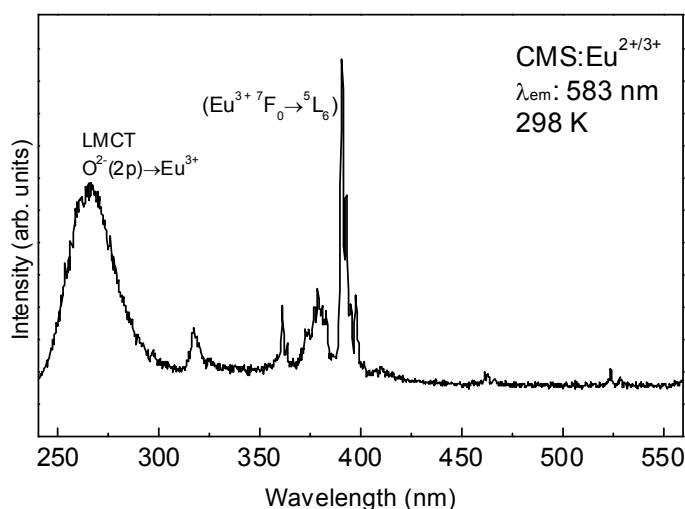

Fig.3- PL excitation (λ_{em}: 583 nm) spectra of the synthesized and reduction submitted CMS:Eu.

The emission spectrum of the CMS:Eu under excitation at the Eu^{2+} $4f^7 \rightarrow 4f^6 5d^1$ absorption in 345 nm (Fig. 4) shows a broad emission with its maximum at about 448 nm arising from the $4f^6 5d^1 \rightarrow 4f^7$ transition of Eu^{2+}. It is worth noting that no Eu^{3+} emission can be observed under Eu2+ excitation indicating that there is no $Eu^{2+} \rightarrow Eu^{3+}$ energy transfer. This fact can be justified by the much faster lifetime of the parity allowed transitions of Eu^{2+} (µs) compared to the parity forbidden of Eu^{3+} (ms).
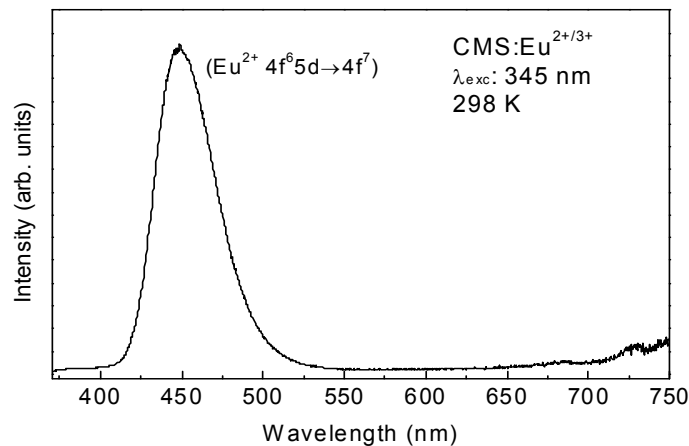
Fig.4- PL emission (λ_{exc}: 345 nm) spectra of the synthesized and reduction submitted CMS:Eu.

The emission spectrum excited at Eu^{3+} $^7F_0 \to {}^5L_6$ absorption in 395 nm (Fig. 5) exhibits both the Eu^{2+} and Eu^{3+} emission transitions. The presence of only the Eu^{2+} band in the 448 nm region indicates that there is indeed energy transfer from $Eu^{3+} \to Eu^{2+}$, since the excitation spectrum (Fig. 2) showed Eu^{3+} transitions when monitoring a Eu^{2+} emission.

The Eu^{3+} transitions range from 578 to 720 nm arising from the transitions $^5D_0 \to {}^7F_J$, J: 0 (578 nm), 1 (583), 2 (621), 3 (660) and 4 (706). The very low intensity of the electric dipole $^5D_0 \to {}^7F_2$ transition compared to the magnetic dipole $^5D_0 \to {}^7F_1$ one indicates that Eu^{3+} occupies a site with center of inversion, where the hypersensitive $^5D_0 \to {}^7F_2$ is strictly forbidden.

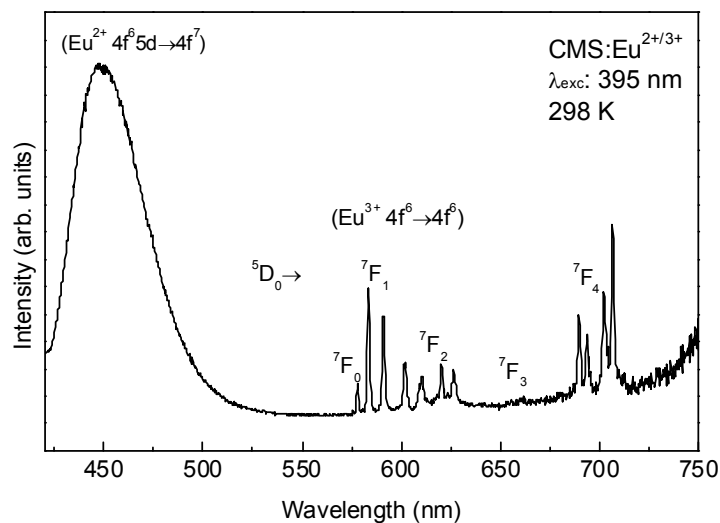Fig. 5- PL emission (λex = 395 nm) spectra of the synthesized and reduction submitted CMS:Eu.

Conclusions

Eu^{2+} doped $CaMgSi_2O_6$ phosphor was successfully prepared using a modified sol gel method followed by the molten salt technique. From XRD patterns of the synthesized powder sample of CMS:Eu, diopside crystalline phase was identified as main crystalline phase. The compound presents both oxidation states of Eu (2+ and 3+) as indicated by the excitation and emission spectra. Besides, energy transfer was observed from Eu^{3+} to Eu^{2+}, but not in the opposite way due to the energy levels position and the faster decay time of the divalent form compared to Eu^{3+}. The emission spectrum under Eu3+ absorption shows that Eu occupies a center of inversion site since the hypersensitive transitions possess very low intensity. The suggested method is promising to synthetize phosphor compounds.

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