

The effect of ligand-to-Eu³⁺ charge-transfer transitions (LMCT) on the photoluminescence intensity of M₂SiO₄: Eu³⁺ (M = Ca, Zn) type phosphors

ESRA ÖZTÜRK*, ERKUL KARACAĞLU

Department of Metallurgical and Materials Engineering, Faculty of Engineering,
Karamanoğlu Mehmetbey University, Karaman, 70200, Turkey

In this study, silicate systems, M₂SiO₄ (M = Ca, Zn) were produced by solid state reaction and doped with 1 mol% Eu³⁺ rare-earth ion. Their heat treatments, which were conducted at 1200 °C and above for minimum 3 hours under an open atmosphere, were applied according to the DTA/TG results. Powder X-ray diffraction XRD analyses were performed to determine the phase properties of the phosphor systems after the sintering process. It was proved that the structures of two of the phosphor systems were well formed in except that the Zn₂SiO₄ had some ZnO secondary phases. The expected photoluminescence (PL) results were presented and the transitions of the Eu³⁺ ions were observed for both phosphors.

Keywords: *silicate phosphor; solid state reaction method; luminescence; Eu³⁺*

1. Introduction

For a long time, considerable effort has been given to the development of inorganic phosphors due to their wide applications for coatings in lamps (fluorescent), light emitting diodes (LEDs), cathode ray tubes, flat panel displays, electroluminescent and optoelectronic devices, radiation detectors in medical imaging systems, etc. [1, 2].

Silicate-based inorganic phosphors offer superior properties due to their stable crystal structure, thermal stability, wide energy band gap, low cost, non-toxicity, multi-color phosphorescence, high resistance to acid, alkali and oxygen, transparency in the ultraviolet (UV) to visible range, wide energy band gap (5.5 eV), etc. [1, 3].

Among the rare-earth (RE) ions, the divalent (Eu²⁺) and trivalent (Eu³⁺) europium play an important role in blue to red emission, depending on the structure. The optical spectra of the Eu²⁺ and Eu³⁺ centers in solids or host structures can be easily differentiated. The photoluminescence (PL) properties of the Eu³⁺ ions originate from

the intra-configurational 4f⁶ → 4f⁶ parity forbidden transitions [2, 4]. The corresponding emission spectrum comprises narrow and intense lines in the red region, the energies of which are practically independent of the host lattice. Moreover, the PL properties of Eu²⁺ ions result from the 4f⁶5d¹ → 4f⁷ parity allowed transition and the emission spectrum shows a broad band whose energy greatly depends on the crystal environment. Therefore, the Eu²⁺ ion provides good PL properties in that the color depends on the host lattice and can vary from UV to red region. It can also be mentioned that materials containing both Eu²⁺ and Eu³⁺ ions are potentially very interesting phosphors with a high color rendering index (CRI) [4].

The structural properties of orthosilicate (Ca₂SiO₄), which is a well-known silicate type structure, have been investigated in detail. It was found that Ca₂SiO₄ has five polymorphs which can be divided into hexagonal α, orthorhombic α'_H, α'_L, γ and monoclinic β forms. The two phases which are observed at ambient conditions are phase γ, which is thermodynamically more stable and can therefore be obtained at higher temperatures, and phase β. The β → γ transition temperature is about 550 °C at ambient pressure [4].

*E-mail: esracircir@gmail.com

The willemite (Zn_2SiO_4) host, which is also a well-known silicate type structure activated with rare-earth or transition metal ions, has been investigated and used extensively for PL applications, such as for luminescent materials in lamps, LEDs, cathode ray tubes (CRTs), plasma display panels (PDPs), laser crystals, upconversion luminescent materials, etc, due to its unique luminescent properties, a wide energy band gap (5.5 eV), and excellent chemical stability. This structure shows polymorphic phases α and β ; the α -phase exhibits a stable structure, while the β -phase has a metastable crystal structure [1, 3, 5–7].

When all this information is taken into account, these two silicate type hosts can be said to exhibit good thermal and chemical stability, and the Eu^{3+} ion is an ideal red phosphor activator due to its $4f^6$ electronic configuration. Therefore, in this study, Eu^{3+} doped silicate-type red color emitting phosphors, namely $\text{Ca}_2\text{SiO}_4:\text{Eu}^{3+}$ and $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$, which can be effectively excited by UV-source, were successfully synthesized by means of solid state reaction method.

2. Experimental

2.1. Materials and methods

In this research, the solid state reaction method was chosen to synthesize the phosphor systems, and high purity CaCO_3 (99.9 %), ZnO (99.9 %), SiO_2 (99.9 %) and Eu_2O_3 (99.99 %) raw materials were used to form $\text{M}_2\text{SiO}_4:1 \text{ \% mol Eu}^{3+}$ ($\text{M} = \text{Ca, Zn}$). The constituents were thoroughly mixed and ground in an agate mortar to obtain a homogeneous mixture. The dry-mixed compositions were then pre-heated at 800 °C for 2 hours taking into consideration the DTA/TG results. Then the phosphor systems, namely $\text{Ca}_2\text{SiO}_4:\text{Eu}^{3+}$ and $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$, were sintered in pure alumina crucibles at different sintering conditions. The sintering processes were performed at 1200 °C for 2 h and at 1220 °C for 8 h under an open atmosphere to get the $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ system phosphor. To obtain the $\text{Ca}_2\text{SiO}_4:\text{Eu}^{3+}$ system phosphor, a sintering process at 1250 °C for 3 h was carried out. Then the sintered phosphors were cooled

down slowly to room temperature. The synthesized phosphors were dry-milled to a powder form for characterization.

Differential thermal analysis (DTA) and thermogravimetric (TG) analysis (Seiko Instruments Inc./Exstar TG/DTA 6200) at a heating rate of 10 °C/min from room temperature to 1300 °C were conducted to analyze the decomposition and oxidation process of the phosphor systems. After the heat treatments, which were applied taking into account the DTA/TG results, a BRUKER AXS D8 ADVANCE model X-ray diffractometer (XRD), run at 40 kV and 30 mA ($\text{CuK}\alpha = 1.5406 \text{ \AA}$ radiation) in a step-scan mode ($0.02^\circ/2\theta$), was employed to determine the phases after the sintering processes. Finally, the photoluminescence (PL) properties, and the excitation and emission spectra of the phosphors were analyzed by a fluorometer (Photon Technology International, PTI, QuantaMaster™ 30).

3. Results and discussion

3.1. Thermal analysis

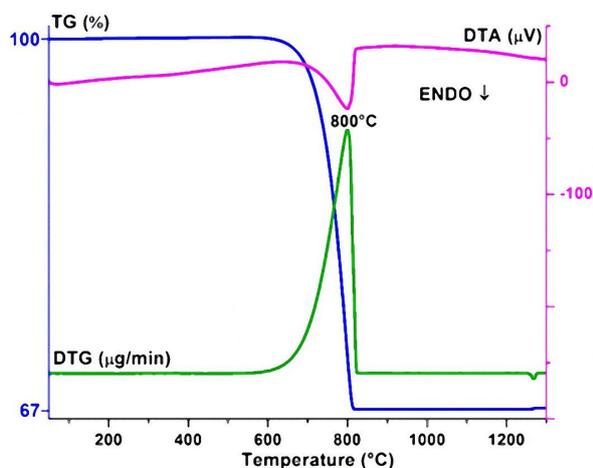
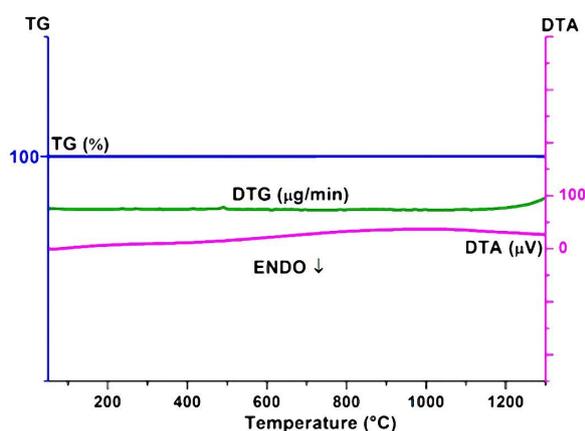
Among the phosphors used in this study, only the $\text{Ca}_2\text{SiO}_4:\text{Eu}^{3+}$ system contained a degradable reactant, namely CaCO_3 . Despite this, the DTA/TG analyses were carried out between 50 °C and 1300 °C in both phosphor systems (Fig. 1 and Fig. 2).

The major weight loss between 600 °C and 900 °C is related to the decomposition of CaCO_3 or the elimination of CO_2 in the system (Fig. 1). The decomposition reaction under heating is given as follows:



The endothermic peak at 800 °C is associated with the decomposition of CaCO_3 which transforms into CaO [8]. The TG curve shows a total mass loss equal to 33.5 %, which is almost similar to the calculated mass loss ($\sim 33.7 \%$).

As shown in Fig. 2, it is clearly seen that the TG curve does not show any significant weight loss in the applied temperatures range [9]. This is not surprising as the sample had no carbonate or hydrate

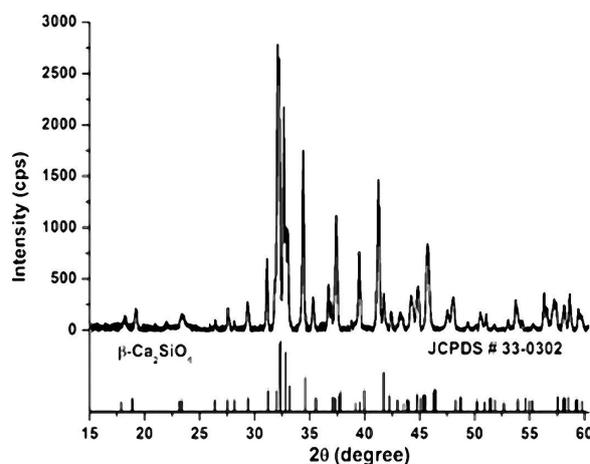
Fig. 1. DTA/TG curves of Ca₂SiO₄:Eu³⁺.Fig. 2. DTA/TG curves of Zn₂SiO₄:Eu³⁺.

phases. Therefore, there was also no physically adsorbed water. Furthermore, the raw material such as ZnO, led to the complete formation of the phosphor system. The DTA curve does not exhibit any defined endothermic/exothermic peaks, as expected.

3.2. X-ray diffraction (XRD) analysis

Heat treatments of the samples were carried out in accordance with to the thermal analysis results. Therefore, to eliminate the volatile components, a pre-sintering at 800 °C for 2 h was applied to the samples. The major sintering processes determined the phases which developed.

The XRD pattern of Ca₂SiO₄:Eu³⁺ is shown in Fig. 3. All the lines have been indexed by

Fig. 3. XRD pattern of Ca₂SiO₄:Eu³⁺ sintered at 1250 °C for 3 h.

considering the patterns of standard β-Ca₂SiO₄ (PDF 00-033-0302). Since the ionic radius of Eu³⁺ (0.095 nm) is close to that of Ca²⁺ (0.099 nm) and the ionic radius of Si⁴⁺ (0.054 nm) is very small compared with Eu³⁺, the Eu³⁺ rare-earth as a dopant ion has not significantly influenced the host or the XRD patterns. Therefore, it is obvious that the Eu³⁺ ions substitute for Ca²⁺ sites in β-Ca₂SiO₄. In this system, the β-Ca₂SiO₄ has a monoclinic structure with the lattice parameters $a = 9.31 \text{ \AA}$, $b = 6.76 \text{ \AA}$, $c = 5.51 \text{ \AA}$, $\alpha = \gamma = 90^\circ$ and $\beta = 94.46^\circ$, based on the space group of P₂₁/n (14) and two different Ca sites, Ca (1) and Ca (2) [10, 11].

The XRD patterns of Zn₂SiO₄:Eu³⁺ sintered at different temperatures are given in Fig. 4.

The diffraction pattern of Zn₂SiO₄:Eu³⁺ that was sintered at 1220 °C for 8 h is well matched with the PDF 00-037-1485 card except for some secondary ZnO lines. The phosphor system has a trigonal-hexagonal structure with the lattice parameters $a = 13.94 \text{ \AA}$, $b = 13.94 \text{ \AA}$, $c = 9.31 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$ and $\gamma = 120^\circ$. The point to be noted here is that the last applied sintering temperature (1220 °C) is still not sufficient to form the single Zn₂SiO₄ phase. Therefore, increasing the sintering temperature and/or time may cause complete elimination of the ZnO secondary phase as the Zn and Si elements on the surface

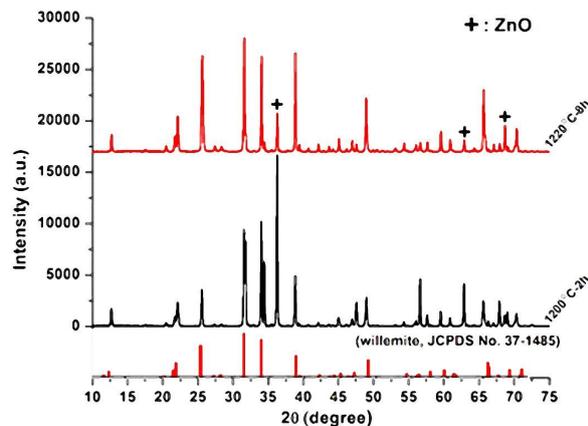


Fig. 4. XRD patterns of $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ sintered at $1200\text{ }^\circ\text{C}$ for 2 h and $1220\text{ }^\circ\text{C}$ for 8 h.

appear to be mobile enough to move and diffuse inside the porous body and cause the formation of the Zn_2SiO_4 phase [1, 12].

3.3. Photoluminescence properties

The samples show PL properties with the excitation and emission bands. Fig. 5 shows the PL spectra of the $\text{Ca}_2\text{SiO}_4:\text{Eu}^{3+}$ phosphor excited at 282 nm.

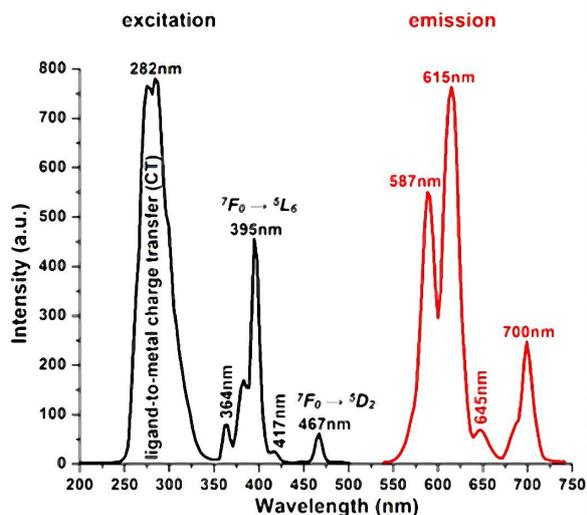


Fig. 5. PL spectra of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{3+}$ phosphor.

The broad and the most intense excitation band near 282 nm is the charge-transfer state (CTS) band, because of an electron transferred from the oxygen 2p orbital to the empty 4f orbital

of europium, which may be ascribed to a ligand-to- Eu^{3+} charge-transfer transition (LMCT). The sharp excitation peaks in the range from 290 nm to 500 nm are associated with typical intra-4f transitions of the Eu^{3+} ion [13].

All the emission bands are attributed to transitions of the Eu^{3+} ion: at 580 nm to 610 nm from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ which is the most intense and is caused by magnetic dipole transitions between the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ states, at 610 nm to 635 nm from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ which result from electronic dipole transitions between the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ states, and at 707 nm from ${}^5\text{D}_0 \rightarrow {}^7\text{F}_4$. The ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ (613 nm) transition is forbidden (f-f intra-configurational transition) for the Eu^{3+} ions located on the sites that deviate from the inversion center of symmetry. Therefore, it shows a significant and intense red emission band at 615 nm [1, 2].

The PL spectra of the $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ phosphor under excitation at 465 nm and maximum emission at 618 nm occur in the red region (Fig. 6).

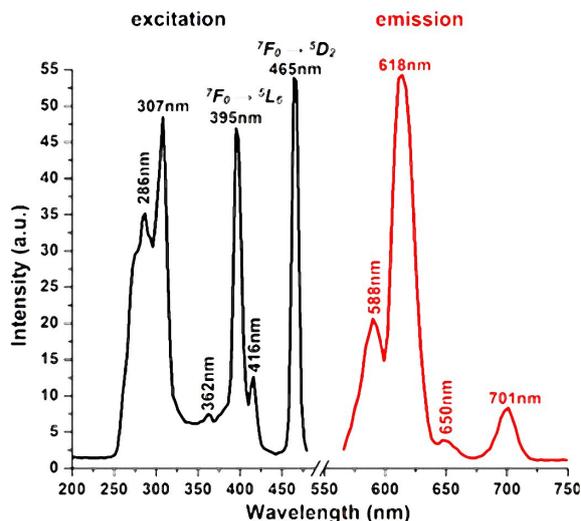


Fig. 6. PL spectra of $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ phosphor.

It has been proved that all the excitation and emission bands are attributed to transitions of Eu^{3+} , so this study revealed similar results to the $\text{Ca}_2\text{SiO}_4:\text{Eu}^{3+}$ system phosphor. It should be noted that the maximum excitation of the $\text{Zn}_2\text{SiO}_4:\text{Eu}^{3+}$ system phosphor is different from that of $\text{Ca}_2\text{SiO}_4:\text{Eu}^{3+}$. While the maximum

excitation of Zn₂SiO₄:Eu³⁺ at 282 nm, attributed to ligand-to-Eu³⁺ (O²⁻-Eu³⁺) charge-transfer transition (LMCT), was induced because of the electron transfer from 2p orbitals of O²⁻ ions to 4f shells of Eu³⁺ ions, the Ca₂SiO₄:Eu³⁺ revealed the excitation maximum at 465 nm which was associated with ⁷F₀ → ⁵D₂ transitions of Eu³⁺ in the host lattice [1, 13].

4. Conclusions

The hosts, Ca₂SiO₄ and Zn₂SiO₄, which were activated with Eu³⁺, were prepared successfully by the solid state reaction method according to the DTA/TG results. While the Ca₂SiO₄:Eu³⁺ system phosphor was well crystallized and indexed, the Zn₂SiO₄:Eu³⁺ phosphors had some secondary phases which were indexed as ZnO, although the sintering temperature and time of sintering were increased. The PL analysis revealed that the two phosphors with different hosts exhibit similar emissions in the red region that are attributed to transitions of the Eu³⁺ ion. The point to be considered is that the PL intensities of the two phosphor systems are quite different from each other, i.e. the Ca₂SiO₄ system is more intense than the Zn₂SiO₄ one. Furthermore, the ligand-to-Eu³⁺ charge-transfer transition (LMCT) with an excitation band at 282 nm gives the most dominant peak for Zn₂SiO₄:Eu³⁺ in comparison to the other excitation bands in the same system. Therefore, there is very high energy transfer to Eu³⁺ transitions causing steadily growing emission intensity.

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