Investigations of $M_3Al_8O_{15}$: Eu^{3+} , Dy^{3+} (M = Ba, Ca, Mg) phosphors

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In this work, aluminate type phosphorescence materials were synthesized via the solid state reaction method and the photoluminescence (PL) properties, including excitation and emission bands, were investigated considering the effect of trace amounts of activator (Eu^{3+}) and co-activator (Dy^{3+}). The estimated thermal behavior of the samples at certain temperatures (> 1000 °C) during heat treatment was characterized by differential thermal analysis (DTA) and thermogravimetry (TG). The possible phase formation was characterized by X-ray diffraction (XRD). The morphological characterization of the samples was performed by scanning electron microscopy (SEM). The PL analysis of three samples showed maximum emission bands at around 610 nm, and additionally near 589 nm, 648 nm and 695 nm. The bands were attributed to typical transitions of the Eu^{3+} ions.

Keywords: aluminate phosphors; solid state reaction method; Eu³⁺; photoluminescence; phase formation

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1. Introduction

Inorganic phosphors are photoluminescent materials which are excited by photons from an external energy source with a wavelength in electromagnetic spectrum range. Their development has been a subject of widespread research over the past decade.

Photoluminescent inorganic phosphors are essentially based on excitation and emission processes. The excited phosphor absorbs energy, then emission takes place by either the host lattice or by impurity ions doped in trace amounts. The emission commonly originates from the impurity ions by exciting with an external energy source. Thus, the emission color can be adjusted by choosing the proper impurity ion, using the same host lattice. Rare-earth (RE) ions are mostly used as impurity ions for phosphors. Extensive research on rare-earth activated phosphors has been carried out because of their important properties, such as luminescent characteristics, thermal stability, environmental friendliness (non-toxic), corrosion-free gas emission, etc. [1, 2]. RE-ions doped materials have attracted considerable attention for a long time due to their significant optical, electronic, chemical characteristics, which are suitable for applications such as solid state lighting (fluorescent or light emitting diodes – LEDs), signs and display devices, radiation dosimetry, X-ray imaging, and sensors; they are also used as other functional compounds [2].

Research has proved that RE activated phosphors can be classified into two types: those with broad and narrow emission bands owing to the df transition and the transition between the f levels, respectively. Eu³⁺/Eu²⁺, Ce³⁺, Tb³⁺, Gd³⁺, Yb³⁺, Dy³⁺, Sm³⁺, Tm³⁺, Er³⁺, Nd³⁺, etc., are the most commonly used activator ions or luminescent centers for inorganic phosphors. Among the inorganic based photoluminescent materials, rareearth-activated alkali aluminates have attracted considerable interest due to their well-known luminescent properties. Until now, a large number of new aluminate phosphors have been developed, i.e. the photoluminescence properties of $Eu^{2+/3+}$, Dy^{3+} , Tb^{3+} , $Pr^{3+/4+}$, Ce^{3+} , etc., single- or codoped strontium, calcium, barium or magnesium

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aluminates have been studied extensively due to their remarkable emission compared to traditional sulfide phosphors [1, 3, 4].

Consequently, as the need for novel phosphors for lighting is one of the most important and urgent challenges, this paper presents our attempts to use the solid state reaction route for the synthesis of some aluminate based phosphors, by substituting europium as activator and dysprosium as co-dopant. In this respect, we aimed to prepare $M_3Al_8O_{15}$ (M = Ba, Ca, Mg) phosphors systems and to investigate them by complementary analysis, i.e. thermal analysis (DTA/TG/DTG before heat treatments), X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence (PL) measurements.

2. Material and methods

Based on previous studies on aluminate type inorganic phosphor systems, the high temperature solid-state reaction method, also known as the ceramic method, was chosen for the production of the samples. As the components of $M_3Al_8O_{15}$: REO M = Ba, Ca, Mg and REO = Eu_2O_3 , Dy₂O₃ were used. Appropriate amounts of high purity raw materials, i.e. $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ (98 %), CaCO₃ (99.9 %), BaCO₃ (99.9 %), Al₂O₃ (99.0 %), Eu₂O₃ (99.99 %) and Dy₂O₃ (99.99 %) were mixed thoroughly and ground in an agate mortar. Subsequently, the well mixed and ground samples were sintered in pure alumina crucibles using an open-atmosphere high-temperature furnace (Protherm PLF 120/5) at 1200 °C for 24 hours, then they were cooled down to room temperature slowly. The synthesized phosphors were ground to powder form for characterization.

After preparing the batches, the thermal analyses, namely 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 performed to study the decomposition and oxidation processes of the precursor. X-ray analysis was carried out after heat treatments, using a BRUKER AXS D8 ADVANCE model X-ray diffractometer, at 40 kV and 30 mA (CuK α radiation) in a step-scan mode (0.02°/2 θ). Scanning electron microscopy (SEM) images were taken on a LEO 440 model scanning electron microscope using an accelerating voltage of 20 kV.

The PL properties, including excitation and emission spectra of the produced phosphors were obtained using a fluorometer (Photon Technology International (PTI), QuantaMasterTM 30).

3. Results and discussion

3.1. Thermal analysis

The thermal behavior of the mixture of all starting materials with a nominal composition, $M_3Al_8O_{15}$:REO (M = Ba, Ca, Mg; REO = Eu₂O₃, Dy₂O₃) system, which included degradable compounds of BaCO₃, CaCO₃, and $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$, was characterized by DTA/TG in the 50 °C to 1300 °C temperature range (Fig. 1 to Fig. 3).

Fig. 1 shows the thermogravimetric analysis curves of all starting materials for $Ba_3Al_8O_{15}:Eu^{3+},Dy^{3+}$ which show a major weight loss between 800 °C to 1200 °C. This weight loss and endothermic peaks are attributed to the decomposing of $BaCO_3$ to CO_2 in the system. The reaction of $BaCO_3$ during heat treatment is given as:

$$BaCO_3 \xrightarrow{\Delta} BaO + CO_2 \tag{1}$$

It can be clearly seen from the DTA/TG curves that BaCO₃ posses three crystallographic structures that are rhombohedral (natural witherite), β -hexagonal and α -cubic forms, depending on the temperature. The phase transformations in BaCO₃ agree with previous studies, including our works. Thus, the first two endothermic peaks are attributed to the orthorhombic to rhombohedral transition at 822 °C and a rhombohedral to cubic phase transition at 983 °C [5].

The total mass loss within 50 °C to 1300 °C is equal to 12.7 %. This result is close to the theoretical mass change which was calculated (\sim 13.0 %).



Fig. 1. DTA/TG curves for Ba₃Al₈O₁₅:Eu³⁺,Dy³⁺ phosphor.

The DTA/TG/DTG analysis results of the starting materials for the second phosphor system, $Ca_3Al_8O_{15}:Eu^{3+},Dy^{3+}$, are given in Fig. 2.



Fig. 2. DTA/TG curves for Ca₃Al₈O₁₅:Eu³⁺,Dy³⁺ phosphor.

The TG curve demonstrates a major weight loss between 600 °C and 900 °C which is due to the decomposition of CaCO₃ and the elimination of CO₂ in the system (Fig. 1). The decomposition reaction during the heating is as follows:

$$CaCO_3 \xrightarrow{\Delta} CaO + CO_2$$
 (2)

Depending on the TG curve, the endothermic peak at 762 $^{\circ}$ C is related to the decomposition

of CaCO₃ [2, 6]. It is clearly proved that the total mass loss ~ 18.0 % of the sample is very similar to the calculated mass loss (~ 18.3 %).

The DTA/TG/DTG analysis results of the starting materials for the last phosphor system, $Mg_3Al_8O_{15}$:Eu³⁺,Dy³⁺, is given in Fig. 3.



Fig. 3. DTA/TG curves for Mg₃Al₈O₁₅:Eu³⁺,Dy³⁺ phosphor.

As shown in Fig. 3, the weight loss in the range of 100 °C to 345 °C and the further decrease between 345 °C and 600 °C can be attributed to the decomposition of $4MgCO_3 \cdot Mg(OH)_2 \cdot 5H_2O$ as the MgO source for the system. The decomposition reactions of this material under heating are as follows:

$$4MgCO_{3} \cdot Mg(OH)_{2} \cdot 5H_{2}O \xrightarrow{\Delta}$$
$$4MgCO_{3} \cdot Mg(OH)_{2} + 5H_{2}O \qquad (3)$$

$$4MgCO_3 \cdot Mg(OH)_2 \xrightarrow{\Delta} 4MgCO_3 + MgO + H_2O$$
(4)

$$4MgCO_3 \xrightarrow{\Delta} 4MgO + 4CO_2$$
 (5)

The first endothermic peak associated with mass loss (TG) occurs at 265 °C which is related to the departure of the hydroxyl group from $Mg(OH)_2$. The second endothermic peak with a greater decrease in mass (TG) at 450 °C proves

the decomposition of MgCO₃ changing into MgO [2, 8]. The TG curve exhibits a total mass loss of about ~25.5 %, which is very similar to the calculated mass loss (~27.0 %) after the decompositions of the sample were completed.

3.2. X-ray diffraction (XRD) analysis and surface morphology

The heat treatments of each studied phosphor system were designed and carried out according to the DTA/TG results. Due to the first crystal formation and completion of decomposition which occurred at about 800 °C, the heat treatments were carried out as a pre-sintering stage at 800 °C for 2 h and the major sintering process at 1200 °C for 24 h for all studied systems. The major sintering process was determined according to the high temperature production process of aluminate systems in previous studies [2]. Therefore the XRD analysis was conducted after the major sinterings.



Fig. 4. XRD pattern for $Ba_3Al_8O_{15}$: Eu^{3+} , Dy^{3+} .

Fig. 4 to Fig. 6 show the XRD patterns for $Ba_3Al_8O_{15}:Eu^{3+},Dy^{3+}, Ca_3Al_8O_{15}:Eu^{3+},Dy^{3+},$ and $Mg_3Al_8O_{15}:Eu^{3+},Dy^{3+},$ respectively.

Although the thermal treatments were carried out for these phosphors according to the DTA/TG results, the XRD results proved that the phosphor samples could not be indexed to any of the desired single phase. It was not possible to synthesize the main crystal structures of the three systems even at high temperatures and long times. Additionally,



Fig. 5. XRD pattern for $Ca_3Al_8O_{15}$:Eu³⁺,Dy³⁺.



Fig. 6. XRD pattern for $Mg_3Al_8O_{15}$: Eu^{3+} , Dy^{3+} .

none of these aluminate structures was reported the literature.

Fig. 7 shows the images obtained from the scanning electron microscopy (SEM) of the phosphors calcined at 1200 °C. The microstructures of the phosphor consist of relatively regular fine grains.

3.3. Photoluminescence properties

Although none of the expected phosphor systems was observed in the obtained XRD patterns, and it was not possible to obtain the desired single phase crystals; all of the PL (excitations and emissions) studies gave remarkable results. The excitation and emission bands occurred owing



to the activated rare-earth ion used for each system, Eu^{3+} , which formed the luminescence center.

Fig. 8 to Fig. 10 show the PL spectra of the three samples which have a similar run because of the same activator, namely the Eu^{3+} -ion.



Fig. 8. PL spectra of $Ba_3Al_8O_{15}$: Eu^{3+} , Dy^{3+} .



Fig. 9. PL spectra of $Ca_3Al_8O_{15}$: Eu^{3+} , Dy^{3+} .

In this research, the PL results of all the samples are both important and striking, despite the XRD results. The PL analyses of the three samples show maximum emission bands at around 610 nm, and additionally near 589 nm, 648 nm and 695 nm, which can be attributed to typical ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions of the Eu³⁺ ion, respectively. The most intense and broad band near 286 nm is the charge-transfer state (CTS) band which proves that the typical Eu³⁺-activated phosphors mostly show strong CTS transition band excitation around 200 nm to 300 nm. Furthermore, the CTS is related



Fig. 10. PL spectra of $Mg_3Al_8O_{15}$:Eu³⁺,Dy³⁺.

to the electron transferred from the oxygen 2p orbital to the empty 4f orbital of europium, which may be ascribed as ligand-to-Eu³⁺ charge-transfer transitions (LMCT). The other bands between 300 nm to 500 nm originate from intra-4f forbidden transitions of Eu³⁺, such as the band at 395 nm, which is associated with the $^{7}F_{0}$ - $^{5}L_{6}$ transition [2, 9, 10]. Typical emission bands of Dy³⁺ ions have not been observed in the PL spectrum of all the phosphor systems.

4. Conclusions

The systems were prepared by a conventional solid-state reaction method under an open atmosphere. The most important conclusion from the results is that although none of the phosphors could be indexed to any crystal system on the basis of XRD patterns, the remarkable PL bands were achieved due to the activator ion, Eu^{3+} . In brief, the PL results proved that all of the Eu^{3+} -activated aluminate type hosts exhibited

similar red emission, i.e. maximum emission bands at around 610 nm, and additional emission bands near 589 nm, 648 nm and 695 nm which were attributed to typical ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{3}$, ${}^{5}D_{0} \rightarrow {}^{7}F_{4}$ transitions of the Eu³⁺ ion, respectively. Consequently, it is concluded that the activator ion based PL results for these phosphors are independent of the phase forming process.

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