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Synthesizing and photoluminescence properties of Eu^{3+}-doped germanate and Dy^{3+}-doped silicate hosts

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ABSTRACT

The Eu^{3+}-doped germanate (Mg_4GeO_6 and Ba_2GeO_4) and Dy^{3+}-doped silicate (Li_3SiO_4) hosts were prepared by solid state reaction in this study. Dy^{3+}-ion for Mg_4GeO_6 and Ho^{3+}-ion for both Ba_2GeO_4 and Li_3SiO_4 were used as co-dopants for these systems. The heat treatments were performed with reference to the DTA/TG results. The repeated and increased heat treatments used for the systems, the single phase crystals determined by the powder x-ray diffraction (XRD) analysis. Thus, the Mg_4GeO_6 and Ba_2GeO_4 systems formed additionally, the Li_3SiO_4 system could not be formed or indexed for any phase. Considerable photoluminescence (PL) thermoluminescence (TL) results were achieved due to the transitions of the Eu^{3+}-, Dy^{3+}- and Ho^{3+}-ions.

1. Introduction

For many years, scientists have desired to develop novel hosts as well as activators for inorganic phosphor systems which have high efficiency and chemical stability under room temperature for next generation applications. At first, traditional phosphors were developed which used rare-earth or transition-metal-activated sulfides such as ZnS, SrS, and CaS. Then, aluminates, silicates or other systems with more effective properties were evolved. The color of phosphor systems depends on the host structures as well as commonly used activator ions, which are generally rare-earth ions and the emission color can be changed from violet to red in the visible region. Inorganic phosphors are popular because of their wide applications for coatings in conventional fluorescent lamps, cathode ray tubes, flat panel displays, light emitting diodes (LEDs), optoelectronic devices, radiation detectors in medical imaging systems, etc. [1].

Silicate and silicate-germanate based phosphors have been researched along time for use as the emitting materials of cathode ray tube (CRT) screens and displays. The production of red-green-blue (RGB) emitters can be achieved by changing the chemical compositions by incorporating different transition metals or rare-earth activators to the structure. Moreover germanates can be used for important applications due to their dielectric, optical and acoustic–optical properties [2,3]. Furthermore, it is well known that inorganic silicate phosphor systems have excellent properties due to their thermal stability, low cost of production, non-toxicity, strong crystal structure and stability, multi-color photoluminescence, wide energy band gap, high resistance to acid, alkali and oxygen, emissions in the ultraviolet (UV) to visible range, etc. [4,5].

In this research, an Eu^{3+} doped as well as Dy^{3+} co-doped germanate type, namely Mg_4GeO_6 and Ba_2GeO_4 phosphors, and also a Dy^{3+}-doped as well as Ho^{3+} co-doped Li_3SiO_4, silicate phosphor were investigated as to their PL properties including excitations and emissions.

2. Material and methods

The materials for this research were produced via the solid state reaction method. In this context, high purity raw materials were selected to produce the phosphors, i.e. $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$ (A.R.), GeO_2 (99.9%), Eu_2O_3 (99.99%), Dy_2O_3 (99.99%), $BaCO_3$ (99.9%), Ho_2O_3 (99.99%), Li_2CO_3 (99.9%), SiO_2 (99.9%). First of all, for all systems, the raw materials were ground well and at the same time mixed according to the stoichiometric rates of phosphors in an agate mortar to obtain a homogeneous powder. The dry-milled compositions were then examined with thermal analysis (DTA/TG). Based on the thermal analysis results, the pre-heating stage was applied at 1073 K (800 °C) for 2 h.

Then, all the expected phosphor systems were sintered with the same heat treatment process, namely at 1473 K (1200 °C) for 24 h. Additionally, the Mg_4GeO_6:Eu^{3+},Dy^{3+} and Ba_2GeO_4:Eu^{3+},Ho^{3+} products were subjected to sintering conditions of 1523 K (1250 °C) for 24 h under open atmosphere. Supplemental heat treatments were

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applied to determine the XRD results of the two systems.

Then the sintered materials were cooled down to room temperature slowly. The end products were dry-milled to powder form to carry out characterizations.

The 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 1573 K (1300 °C) were run to analyze the decomposition and the oxidation process of the phosphor systems. After the DTA/TG and thereafter the heat treatments, a BRUKER AXS D8 ADVANCE model X-ray diffractometer (XRD), which was run at 40 kV and 30 mA (Cu-Kα radiation) in a step-scan mode (0.02°/2θ), was employed to determine the phases after the sintering processes. The morphology and particle size distributions of the powder form phosphors were determined by a LEO 440 scanning electron microscope (SEM). Finally, the photoluminescence (PL) properties, including the excitation and emission spectra of the products, were analyzed by a spectrophotometer (Photon Technology International, PTI), QuantaMaster™ 30). In order to investigate the thermoluminescence trap parameters the samples were annealed at 600 °C for 15 min to erase any residual information before the subsequent irradiation for the thermoluminescence (TL) experiments. All annealing treatments were carried out microprocessor controlled electrical oven, which is able to control the temperature to within ± 1 °C. Each powder samples was spread on very thin aluminum disks, about 10.0 ± 0.1 mg and was irradiated at room temperature using the beta rays from a calibrated ^{90}Sr–^{90}Y source. The typical strength of the source is about ≅7.44 Gy/min. After irradiation, the glow curve of the sample was recorded for a constant (β = 2 °C/s) heating rate. The time duration between irradiation and TL reading was always kept constant at about 10 s. The glow curves of the irradiated sample were measured between 40 °C and 400 °C using an RA-04 manual type TLD Reader-Analyzer, which has a photomultiplier tube and is interfaced to a PC on which the signals were studied and analyzed.

The standard thermal quenching procedure [6] was applied to Mg_4GeO_6: Eu^{3+}, Dy^{3+} to eliminate the number of overlapping peaks. T_s was chosen as 200 °C.

Reusability of the all the phosphors was investigated and tested by using a standard irradiation-readout-annealing cycles and statistical analysis [6,7]. The sample was annealed at 873 K (600 °C) for 15 min and was exposed to β-ray irradiation for 10 min and then the glow curve was recorded between 40 and 400 °C. All steps were repeated 10 times, the glow curve intensities were compared and the sample variability index was calculated. The index gives a measure of the reproducibility of the TL materials, and is given as [7];

$$\text{Index} = [(\%\text{mCV})^2 - (\%\text{CV})^2]^{1/2} \tag{1}$$

Here, CV and *m*CV are the covariance and average covariance for each phosphor, respectively.

The kinetic orders of the phosphor samples were examined by using the additive dose procedure [6] for different β radiation doses (37.5–150 Gy) and variation in the temperatures (T_M) of maximum TL intensity was compared. According to fundamental TL models [6], it is noted that for TL glow peaks following first-order kinetics, T_M does not depend on the administered dose.

All the recorded glow curves were analyzed using a glow curve analyzing program, which was developed at the Reactor Institute at Delft, The Netherlands [8] and FOM values of the fits were also calculated.

3. Results and discussion

3.1. Thermal analysis

For the first phosphor system, Mg_4GeO_6:Eu^{3+}, Dy^{3+}, there is only one raw material that can be decomposed, namely $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$. Therefore, the DTA/TG/DTG curves were related only to this reactant which is shown clearly in Fig. 1.

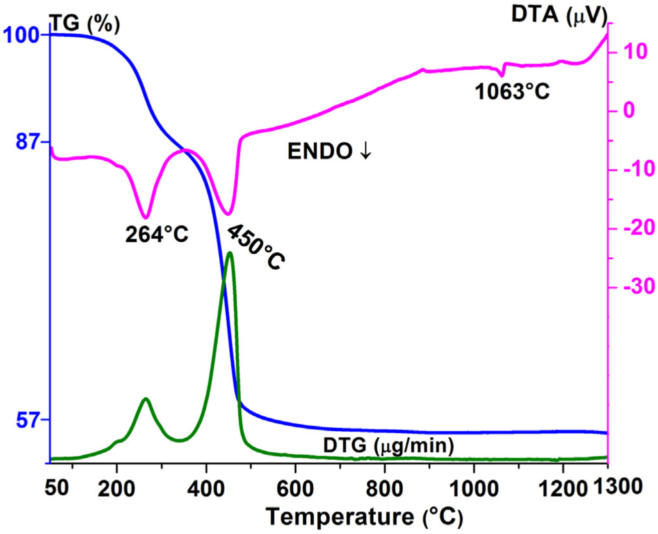

Fig. 1. DTA/TG/DTG curves of the starting materials of Mg_4GeO_6: Eu^{3+}, Dy^{3+}.

As shown by Fig. 1, the weight losses starting from 473 to 623 K (200–350 °C) and a further decrease from 623 to 873 K (350–600 °C) are due to decomposition of $4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O$. The thermal behavior of this material's reactions under heating can be summarized as follows:

$$4MgCO_3{\cdot}Mg(OH)_2{\cdot}5H_2O \overset{\Delta}{\rightarrow} 4MgCO_3{\cdot}Mg(OH)_2 + 5H_2O \tag{2}$$

$$4MgCO_3{\cdot}Mg(OH)_2 \overset{\Delta}{\rightarrow} 4MgCO_3 + MgO + H_2O \tag{3}$$

$$4MgCO_3 \overset{\Delta}{\rightarrow} 4MgO + 4CO_2 \tag{4}$$

The first endothermic peak (at 264 °C) is associated with the departure of the hydroxyl group from $Mg(OH)_2$. The second endothermic peak (at 450 °C) shows the decomposition of $MgCO_3$ which changes into MgO [9,10]. The TG curve exhibits a total mass loss equal to ~43.0%, which is almost the same as the calculated mass loss (~44.5%) for completed decompositions. The endothermal peak at 1336 K (1063 °C) is believed to be the first crystallization temperature at which the formation of phases can be achieved using the solid state-assisted process.

Fig. 2 shows the thermal behavior of Ba_2GeO_4: Eu^{3+}, Ho^{3+} as DTA/TG/DTG curves. It can be seen that the major weight loss within the

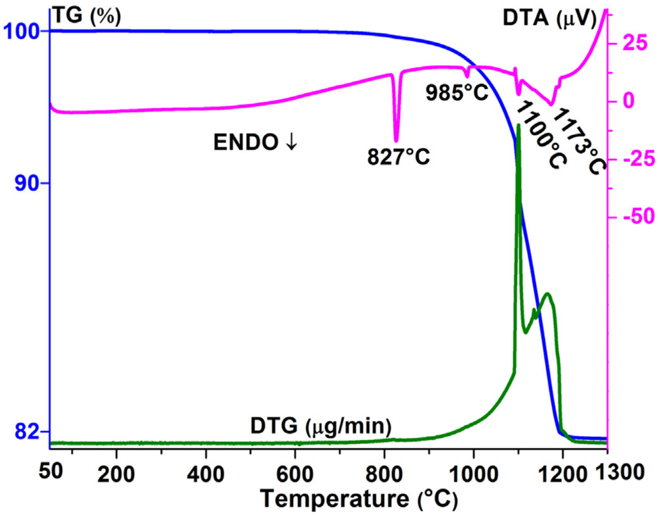

Fig. 2. DTA/TG/DTG curves of the starting materials of Ba_2GeO_4: Eu^{3+}, Ho^{3+}.