



Study on preparation and luminescent properties of Eu^{3+} -doped LaAlO_3 and GdAlO_3

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ABSTRACT

Eu^{3+} -doped trigonal LaAlO_3 and orthorhombic GdAlO_3 phosphors have been successfully synthesized by sol–gel method. The crystallization processes of the phosphors have been characterized by X-ray diffraction (XRD) and thermogravimetry-differential scanning calorimetry (TG–DSC). The optical properties of these phosphors were investigated using the photoluminescence (PL) and photoluminescence excitation (PLE) spectra. The influences of the different structures and bonding of the hosts on the luminescence performance of Eu^{3+} ion-doped LaAlO_3 and GdAlO_3 were investigated in detail based on chemical bond theory. Under appropriate UV-radiation, the reddish orange light emitted from $\text{GdAlO}_3:\text{Eu}^{3+}$ was brighter than that from $\text{LaAlO}_3:\text{Eu}^{3+}$. Such a brightly luminescent phosphor could be considered as an ideal optical material for the development of new optical display systems.

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1. Introduction

Perovskite crystals interest scientists in many domains. SrTiO_3 and LaAlO_3 , grown in laboratories, are well known as superconductive substrates [1]. The manganese perovskite $\text{R}_{1-x}\text{A}_x\text{MnO}_3$ (R =rare earth ion, A =Ca, Sr, Ba, Pb) characterize strong interaction of structural, electronic and magnetic properties [2]. Recently, an amount of research has indicated that RAIO_3 are a great potential class of host materials for rare-earth ions to give color light emission [3–7]. Both LaAlO_3 and GdAlO_3 are typical RAIO_3 as optical materials with great research significance. In 2009, Lin et al. reported that $\text{LaAlO}_3:\text{Sm}^{3+}$ was one of the promising yellow phosphor for Field Emission Displays (FED) [3], and $\text{LaAlO}_3:\text{Re}^{3+}$ (Re =Tm, Tb) had potential applications in FED, Cathode Ray Tube (CRT), and Vacuum Fluorescent Display (VFD) [4]. $\text{GdAlO}_3:\text{Pr}^{3+}/\text{Dy}^{3+}/\text{Tb}^{3+}$ nanophosphors have been prepared by solvothermal reaction method for optical display systems [7–9]. Among various RE^{3+} ions, less information is available concerning the optical properties of Eu^{3+} ions in the two kinds of hosts as an ideal optical material for the development of new optical display systems [10–14]. For the Eu^{3+} -doped phosphors, the charge transfer (CT) transition from ligand anions to Eu ions is electric-

dipole allowed and has a transition probability of 3 or 4 orders of magnitude stronger than $4f$ intraconfiguration transitions. Therefore, in the exploration of new phosphors, a selection of proper hosts to make the CT transition of Eu^{3+} located in a proper spectral range of UV is a major concern [15,16]. However, upon going through the literature, there have been no studies concerning the influence of the different structures and bonding of the hosts on the luminescence performance of Eu^{3+} ion-doped LaAlO_3 and GdAlO_3 so far. So we have undertaken this work.

In general, phosphors are prepared by traditional solid-state reaction method. Due to insufficient mixing and low reactivity of raw materials, several impurity phases easily co-exist in the product. Similarly, the solid state synthesis of LaAlO_3 and GdAlO_3 also calls extensive mixing followed by lengthy heat treatments in relatively high temperatures ($>1400^\circ\text{C}$) [17,18]. However, in recent years, several wet chemical techniques such as co-precipitation method, sol–gel, combustion, hydrothermal synthesis, solvothermal synthesis and spray-pyrolysis synthesis were used to prepare the phosphor precursor [19–26]. Phosphor materials synthesized by these wet chemical methods have many advantages, i.e. high purity, homogenous composition and fine grains in nanometer range.

In this paper, we successfully synthesized Eu^{3+} -doped trigonal LaAlO_3 and orthorhombic GdAlO_3 phosphors through sol–gel process. Our interest is primarily concerned with the studies on luminescent properties of Eu^{3+} in the two different host materials. The influences of the different structures and bonding of the hosts

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on the luminescence performance of Eu^{3+} ion-doped LaAlO_3 and GdAlO_3 were investigated in detail based on chemical bond theory. The optimal doping concentrations in the trigonal LaAlO_3 and orthorhombic GdAlO_3 were determined to be about 4.0 and 8.0 mol%, respectively. Furthermore, the CT band energy of $\text{Eu}^{3+}-\text{O}^{2-}$ in Eu^{3+} -doped LaAlO_3 and GdAlO_3 were also quantitatively calculated by the empirical formula. The calculated values are basically in good agreement with our experimental results. The results are important as far as increasing our understanding of the luminescence of doped rare earth ions and developing their future applications are concerned.

2. Experimental

2.1. Synthesis

$\text{Ln}_{1-x}\text{Eu}_x\text{AlO}_3$ ($\text{Ln} = \text{La}, \text{Gd}$) ($x = 0.02, 0.04, 0.06, 0.08, 0.10, 0.12$) was prepared by sol-gel method. According to the chemical formulas stated above, stoichiometric amounts of La_2O_3 , Gd_2O_3 and Eu_2O_3 (99.9%, analytical reagent, AR) were dissolved in dilute HNO_3 (AR, Beijing Chemical Company) under stirring and heating, and the excess HNO_3 were removed at high temperature. The solutions of $\text{Eu}(\text{NO}_3)_3$ and $\text{La}(\text{NO}_3)_3$ [or $\text{Gd}(\text{NO}_3)_3$] were mixed together followed by the addition of the stoichiometric amounts of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR, Beijing Chemical Company) under stirring. Then the citric acid (AR, Beijing Chemical Company) was added to the solution as chelating agent for metal ions. The molar ratio of total metal ions to citric acid was 1:2. The highly transparent solution was obtained after stirring for a few minutes. Then the resultant mixtures were heated in 80°C water bath to get transparent light-brown gels, promote the temperature to 90°C to get dark-brown gels, and the gels were further dried at 120°C for 24 h to obtain the dried gels. After an intermediate grinding in an agate mortar, the gels were finally annealed at desired temperatures in air.

2.2. Characterization

Thermogravimetry-differential scanning calorimetry (TG-DSC) of the corresponding citrate precursor of $\text{LaAlO}_3:\text{Eu}^{3+}$ and $\text{GdAlO}_3:\text{Eu}^{3+}$ powders were carried out at a heating rate of $10^\circ\text{C}/\text{min}$ and the samples were heated from room temperature to 1100°C . The chemical purity of these products was checked by X-ray powder diffraction (XRD) pattern using a Rigaku-Dmax 2500 diffractometer with $\text{Cu K}\alpha$ ($\lambda = 0.15405 \text{ nm}$) radiation. The ultraviolet-visible PL and PLE spectra were recorded with a Hitachi F-7000 fluorescence spectrophotometer equipped with xenon lamp as the excitation source. All the measurements were performed at room temperature.

3. Results and discussion

3.1. TG-DSC analysis

Fig. 1 shows TG-DSC diagram of lanthanum aluminate citrate precursor, the decomposition starts below 100°C with a weight loss corresponds to the removal of adsorbed and chemisorbed water which is confirmed by the appearance of endothermic peak in DSC curve. In the temperature range of $160\text{--}560^\circ\text{C}$, the main decomposition with a weight loss occurs. The final weight loss on TG curve in the temperature range of $800\text{--}900^\circ\text{C}$ is due to the removal of residual organics. The exothermic peak between 300°C and 600°C in DSC curve is due to the decomposition of citric acid. The exothermic peak at 880°C is assignable to LaAlO_3 crystallization.

The TG-DSC curves of gadolinium aluminate citrate precursor are shown in Fig. 2, the decomposition of Gd-Al-nitrate-citrate

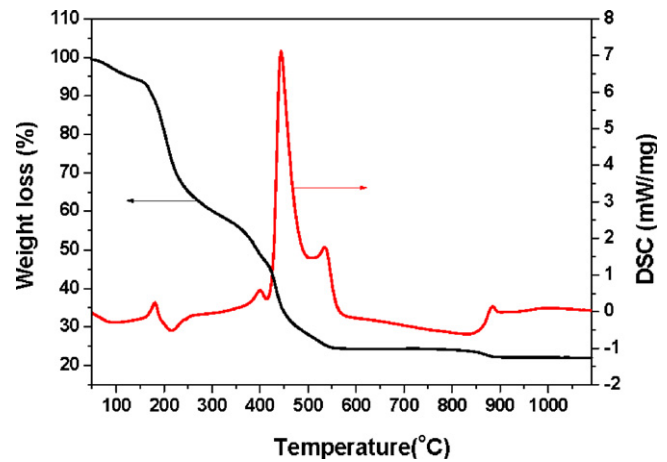


Fig. 1. TG-DSC curves of lanthanum aluminate citrate precursor.

precursor was found to be three step processes. In the first step, the weight loss below 100°C in the TG graph can be attributed to the removal of adsorbed and chemisorbed water which is indicated by the appearance of endothermic peak in DSC curve. In the second step, a major weight loss takes place in the temperature range of $160\text{--}560^\circ\text{C}$, which is similar to the TG curve of LaAlO_3 . The final weight loss on TG curve in the temperature range of $760\text{--}950^\circ\text{C}$ is due to the removal of residual organics. The exothermic peak between 300°C and 650°C in DSC curve is due to the decomposition of citric acid. The exothermic peak at 1041°C is assignable to GdAlO_3 crystallization.

3.2. X-ray diffraction analysis

Fig. 3(1) shows the X-ray diffraction (XRD) patterns for $\text{La}_{1-x}\text{Eu}_x\text{AlO}_3$ ($x = 0.02$) powders as a function of heating temperature for 3 h, which are in good agreement with the standard JCPDS file 31-0022. With the increase of heating temperature from 800°C to 1000°C , the diffraction pattern becomes stronger and sharper, reflecting greater crystallization, which is consistent with the TG-DSC result of lanthanum aluminate citrate precursor.

The XRD patterns of the $\text{Gd}_{1-x}\text{Eu}_x\text{AlO}_3$ ($x = 0.02$) samples annealed at various temperatures are shown in Fig. 4(1). The pure orthorhombic phase GdAlO_3 can be obtained from 1000°C to 1200°C , which is also consistent with the TG-DSC result of gadolinium aluminate citrate precursor. It can be seen that all diffraction peaks of the three samples can be well-assigned to the

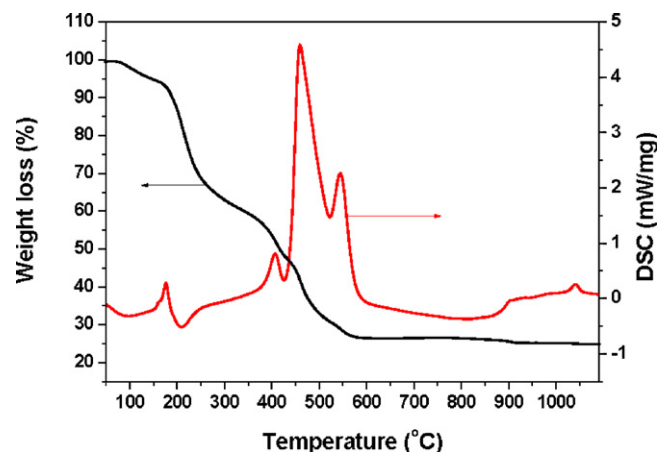


Fig. 2. TG-DSC curves of gadolinium aluminate citrate precursor.

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