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Hydrothermal synthesis, morphology and luminescent properties of $GdAlO_3:Eu^{3+}$ microcrystals

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ABSTRACT

Hydrothermal syntheses of $GdAlO_3$ and $GdAlO_3:Eu^{3+}$ microcrystals were reported, and the effects of reaction temperature and NaOH concentration on the formation of $GdAlO_3$ were discussed. The crystal structure, morphologies, composition and luminescent properties of the obtained samples were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive X-ray spectrometry (EDX) and photoluminescence (PL) spectra. XRD results indicate all X-ray diffraction patterns of the synthesized samples were indexed by an orthorhombic system with the space group of *Pbnm*(62#). SEM image exhibits the uniform rectangular shapes of the as-synthesized $GdAlO_3:0.05Eu^{3+}$ microcrystals with the sizes of about 3–6 μm. The PL spectrum shows that the main emissions of $GdAlO_3:Eu^{3+}$ are attributed to the $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+}. The host absorption of $GdAlO_3:Eu^{3+}$ in VUV region is weaker than that of the $O^{2-} \rightarrow Eu^{3+}$ charge transfer band.

1. Introduction

Rare earth aluminates, *RE*A1O_3 (*RE*:La···Lu,Y), are a kind of important inorganic functional materials, which can be used as the host matrices of luminescent materials, novel solid state laser and scintillator materials. Recently, the studies of rare earth aluminates used as luminescent host matrices have attracted considerable interest. For example, full color emission in single host $LaAlO_3$ was achieved by codoping Eu^{3+} and Eu^{2+} [1]. Nearly monodisperse $LaAlO_3$ hollow spheres were synthesized via a novel precursor thermal decomposition process [2]. Generally, rare earth aluminates, *RE*AlO_3, are synthesized by common solid state reaction at higher temperature (1400–1700 °C) for long time [3], so decreasing synthesis temperature of rare earth aluminates has attracted much attention. Recently, some new synthesis methods, such as sol–gel process [4], co-precipitation method [5], combustion synthesis [6] and precursor decomposition approach [2,7] have been employed to reduce the reaction temperature for obtaining *RE*AlO_3 samples. Although all methods mentioned above can decrease the synthesis temperature of *RE*AlO_3 after firing the precursors at different high temperatures, all as-prepared *RE*AlO_3 samples have the irregular shape. So the controlled synthesis of *RE*AlO_3 samples with uniform morphology and size remains a large challenge. Hydrothermal/solvothermal method is widely used to synthesize inorganic compounds as well as to control their microstructures [8]. Unfortunately, up to now, there are only a few reports on the preparation of *RE*AlO_3 powders by a hydrothermal process [9]. Kim and co-workers [10,11] reported the preparation of $GdAlO_3:Dy^{3+}/Tb^{3+}$ nanomaterials by a solvothermal treatment combined with high-temperature calcination. Wang and Yang [9] reported one-step hydrothermal synthesis of $LaAlO_3:Eu^{3+}$ microcrystals with uniform hexagonal shapes. Herein, the hydrothermal syntheses of $GdAlO_3$ and $GdAlO_3:Eu^{3+}$ powders are reported. Furthermore, the synthesis condition, morphologies and luminescent properties of the obtained samples are detailed discussed.

2. Experimental

2.1. Synthesis

$GdAlO_3$ and $GdAlO_3:xEu^{3+}$ samples were prepared by a hydrothermal method. Gd_2O_3, Eu_2O_3, $Al(OH)_3$ and NaOH were used as the starting materials. The well grinding mixtures of Gd_2O_3, Eu_2O_3 and $Al(OH)_3$ with the ratio of 1:5 of *RE*: Al were transferred into an autoclave with a volume of 25 mL, and then 18 mL distilled water or NaOH aqueous solution with different concentration was added into the autoclave. The autoclave sealed was placed in a temperature-controlled electric oven, heated at the aimed temperatures (300–380 °C) for 3 d and then cooled down

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to room temperature in the furnace. The products were collected from the solution, washed with dilute NaOH solution, distilled water and ethanol for several times, and dried at 80 °C for 1 h.

2.2. Chemicals and instruments

The purity of Gd_2O_3 and Eu_2O_3 is 99.99%. $Al(OH)_3$ (67.0%), NaOH and ethanol (95%) are all analytical pure (A.R.). XRD studies were carried out on a DX-2700 X-ray powder diffractometer using Cu Kα radiation. The morphologies of the as-prepared samples were characterized by FEI Quanta 200 scanning electron microscopy. The VUV data (excitation spectra) were collected through remote access on 4B8 VUV spectroscopy station at the Beijing Synchrotron Radiation Facilities (BSRF) under a dedicated synchrotron mode (2.5 GeV, 250–150 mA) [12], the emission spectra measurements were performed using a Hitachi F-4600 spectrofluorometer. The excitation and emission spectra were measured at room temperature.

3. Results and discussion

3.1. Phase formation

Fig. 1 shows the XRD patterns for the undoped samples synthesized by a hydrothermal reaction at different temperatures (300–380 °C) in distilled water for 3 d. When the hydrothermal reaction temperature is 300 °C, just only the diffraction peaks of $Gd(OH)_3$ (JCPDS No: 97-020-0093) and AlOOH (JCPDS No: 97-009-3732) are observed (Fig. 1a). As shown in Fig. 1a, no diffraction peaks of $GdAlO_3$ (JCPDS No: 97-015-0348) are detected, indicating only the following reactions occur:

$$Gd_2O_3 + 3H_2O = 2Gd(OH)_3 \quad (1)$$

$$Al(OH)_3 = AlO(OH) + H_2O \quad (2)$$

When the hydrothermal reaction temperature reaches to 350 °C, besides the diffraction peaks of $Gd(OH)_3$ and AlOOH, some weak characteristic diffraction peaks of $GdAlO_3$ are observed (Fig. 1b). When the reaction temperature increases to 380 °C, strong diffraction peaks of $GdAlO_3$ are found (Fig. 1c), indicating the formation of $GdAlO_3$ becomes easy with the increase of reaction temperature. The results showed that under the condition of above 300 °C in distilled water, the reactants are $Gd(OH)_3$ and AlOOH, thereby generation of $GdAlO_3$ can be expressed by following reaction:

$$Gd(OH)_3 + AlO(OH) = GdAlO_3 + 2H_2O \quad (3)$$

As reactants $Gd(OH)_3$ and AlOOH are both solid, so Eq. (3) is a typical solid state reaction, and its reaction rate is very slow. In order to increase the reaction rate of $GdAlO_3$ formation, dilute NaOH aqueous solution instead of distilled water was selected as the reaction medium. Because $Al(OH)_3$ is an amphoteric hydroxide, it is easily transferred into $Al(OH)_4^-$ in strong alkaline solution. Therefore the synthesis reaction of $GdAlO_3$ changes from solid–solid reaction into solid-solution reaction, resulting in the increasing contact area of the reactants and fast reaction rate. The synthesis reaction of $GdAlO_3$ is expressed as follows:

$$Gd(OH)_3 + Al(OH)_4^- = GdAlO_3 + 3H_2O + OH^- \quad (4)$$

Fig. 2 presents the XRD patterns of the undoped samples synthesized by a hydrothermal reaction at 380 °C for 3 d in NaOH aqueous solution with different concentrations. All diffraction peaks in Fig. 2 can be attributed to an orthorhombic perovskite crystal structure of $GdAlO_3$ (JCPDS No. 97-015-0348). Even in NaOH aqueous solution with 0.25 mol L^{-1}, the reactant $Al(OH)_3$ is easily transferred to $Al(OH)_4^-$, the reaction of Eq. (4) becomes faster than that of Eq. (3). The peaks and intensities of the as-synthesized $GdAlO_3$ powders are same as that of the standard $GdAlO_3$ in different alkaline solution. This indicates that the single phase $GdAlO_3$ was formed during the hydrothermal process at 380 °C for 3 d in 0.25 mol L^{-1} NaOH aqueous solution.

3.2. XRD analysis of $GdAlO_3$:xEu^{3+} (x = 0.005, 0.020, 0.035, 0.050, 0.075, 0.100) samples

A series of $GdAlO_3$:xEu^{3+} samples were obtained by a hydrothermal route at 380 °C for 3 d in 0.50 mol L^{-1} NaOH aqueous solution, and characterized by X-ray powder diffraction. Their X-ray diffraction patterns for a series of $GdAlO_3$:xEu^{3+} samples are in good agreement with the standard JCPDS file No. 97-015-0348. Based on the basis of the structural model of $GdAlO_3$ [13], the XRD data of $GdAlO_3$:xEu^{3+} samples were refined by the Rietveld method using the GSAS program [14]. All lattice parameters for the $GdAlO_3$:xEu^{3+} samples calculated from Rietveld refinement are shown in Fig. 3. The lattice parameters of $GdAlO_3$ and $EuAlO_3$ are taken from Refs. [13] and [15], respectively. As the ionic radii of Gd^{3+} (0.938 Å) and Eu^{3+} (0.947 Å) are almost the same, so the effect of the Eu^{3+} concentration on the lattice parameters is not obvious. The Rietveld profile fits of diffraction data of $Gd_{0.95}Eu_{0.05}AlO_3$ is presented in Fig. 4.

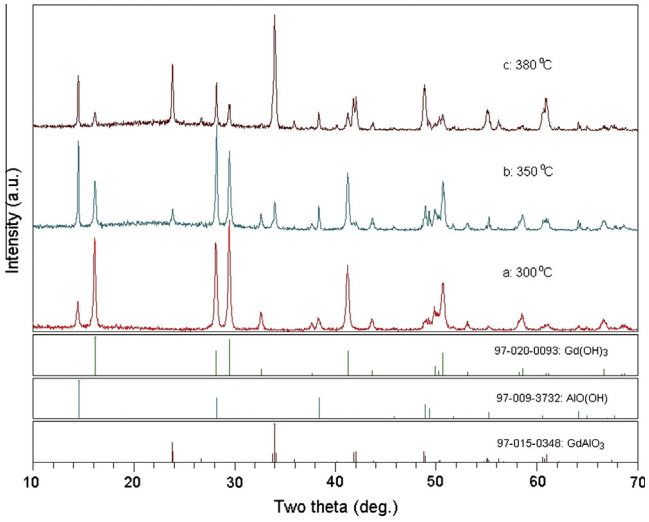

Fig. 1. XRD patterns of the undoped samples synthesized by hydrothermal reaction at different temperatures for 3 d in distilled water. t/°C: (a) 300; (b) 350; (c) 380.

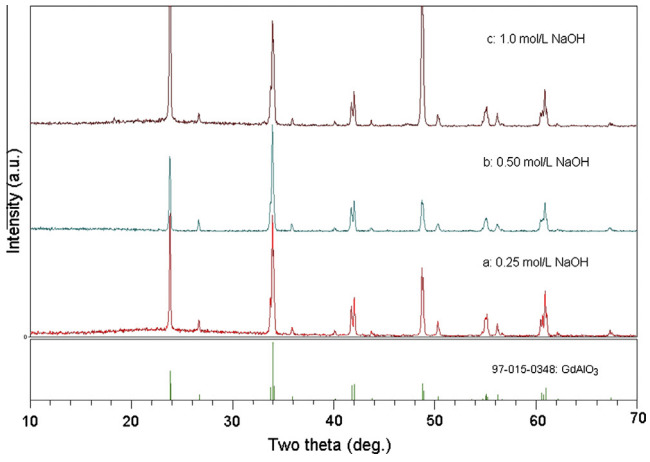

Fig. 2. XRD patterns of the undoped samples synthesized by hydrothermal reaction at 380 °C for 3 d in NaOH aqueous solution with different concentrations. c(NaOH)/(mol L^{-1}): (a) 0.25; (b) 0.50; (c) 1.0.