

Characteristics and synthesis mechanism of Gd₂O₂S:Tb phosphors prepared by vacuum firing method

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ABSTRACT

Characteristics and synthesis mechanism of Gd₂O₂S:Tb phosphors prepared by vacuum firing were investigated by photoluminescence (PL) spectra, X-ray diffraction (XRD), scanning electronic microscopy (SEM) and transmission electron microscopy (TEM). The mixtures of raw materials were tested by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). The firing temperature was reduced to about 725 °C by the vacuum firing method. The particle size decreased. Meanwhile the particle size distribution and morphology were improved and the luminescence of Gd₂O₂S:Tb phosphors was also enhanced as the degree of vacuum decreases. With the decrease of the degree of vacuum, the intensity of the excitation spectrum was strengthened and the band was widened being the particle size of the host lattice decreased to nano scales. The peak with high intensity around 272 nm in the excitation spectra ($\lambda_{Em} = 545$ nm) of Gd₂O₂S:Tb nanophosphor may be attributed to the 4d–5f transitions of Gd atoms, which may play a significant role in the energy transfer between Tb³⁺ and Gd³⁺ ions. ³D₄–⁷F_J transitions of Tb³⁺ ion were mainly concentrated in the narrow green emission spectrum (535–555 nm) with its sharp peak at 545 nm. The synthesis mechanism of Gd₂O₂S:Tb phosphors prepared by vacuum firing was also studied.

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1. Introduction

Lanthanide oxysulfides with high chemical stability and high thermal stability are known as wide-gap (4.6–4.8 eV) materials suitable for doping ion activation [1], and have been considered for its brilliant properties as an efficient luminescent emitting material [2]. In recent years, lanthanide-doped luminescent nano-sized materials have received much attention for their wide applications on high-resolution displays, integrated optical systems, substitute for organic dyes, solid-state lasers, and especially biological labels [3]. But most of them were mainly micro-scale particles to date which may restrict the application in many aspects. Therefore, in order to further improve the resolution of display devices and to enhance the level of detection, the phosphors with smaller particle and higher luminescent quality are required [4]. Nanophosphors have been extensively investigated during the last decade due to their application potential for various high-performance displays and devices. But the early research of

the nanophosphors focused on the preparation and optical properties of the nano-semiconductor materials such as CdS, ZnS, GaS and SiN. It was first reported by Bhargava et al. [5,6] in 1994 that the life time was shortened by five orders of magnitude and the quantum efficiency was up to 18%, so that great attention was given to the nanophosphors and is of significance to investigate the full potential of nanophosphor materials.

Although some rare earth oxysulfide (M₂O₂S) nano-materials have been produced, the synthesis of mono-disperse M₂O₂S nanocrystals still remains a challenge for researchers to date because of the great difficulty in finding an effective synthetic route. The synthesis of the oxysulfide nanophosphors such as coprecipitation method [7,8], homogeneous precipitation method [4,9], combustion method [10], hydrothermal method [3,11], microemulsion liquid method [12], vapor-phase sulfuration method [13] and decomposition method [14], etc were reported according to the literature. But most of them are of high cost, difficult control of operation and environmental pollution. The conventional way to synthesize bulk lanthanide oxysulfide is the solid-state reaction in which lanthanide oxides are added with elementary sulfur and fluxes at high temperature (about 1200 °C) [15]. This method has been widely applied due to the high stability,

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low cost and high luminescence efficiency. This traditional phosphor synthesis techniques could be improved by elimination of time-consuming multiple steps and the need for high temperatures. Therefore, investigation on the synthesis of this material is extremely urgent for practical applications. Compared to the preparation methods of the oxysulfide luminescent materials abovementioned, vacuum method not only has the advantages of simple process, friendly environment and low production cost, but also can prepare uniform and small-sized spherical particles. Unlike conventional solid-state reaction methods, nanocrystalline oxysulfide phosphors can be prepared by vacuum method at a relatively low temperature (about 700 °C) and short firing time (2–3 h) using simple equipments. The synthesis of terbium-activated gadolinium oxysulfide nanophosphor using vacuum method has not been published before. The studies on synthesis mechanisms of vacuum method were summarized and the luminescent characteristics of $\text{Gd}_2\text{O}_2\text{S:Tb}^{3+}$ nanophosphors were also studied in this work. It might be feasible for scale-up industrial mass production and we believe this technique will be readily adopted in realizing other forms of nanophosphors.

2. Experiment

The phosphor raw materials $\text{Gd}_2\text{O}_3(4\text{N})$, $\text{Tb}_4\text{O}_7(4\text{N})$, $\text{Dy}_2\text{O}_3(4\text{N})$ were added by sulfur, $\text{Na}_2\text{S}_2\text{O}_3$ and various fluxes (Na_2CO_3 , K_2CO_3 , Li_3PO_4 and Li_2CO_3) with high pressure pre-treatment on the thoroughly mixed raw materials, followed by heating the mixture in a covered crucible at the temperature (about 725 °C) for a sufficient time under vacuum to prepare $\text{Gd}_2\text{O}_2\text{S:Tb}$. Then wash the $\text{Gd}_2\text{O}_2\text{S:Tb}$ with deionized water and diluted hydrochloric acid solution to remove essentially any water-soluble impurities.

The solid-state reaction process was determined by METTLER TOLEDO TGA/DSC1 thermal analyzer in vacuum and atmosphere respectively. Phosphor samples were characterized by X-ray diffractions (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and fluorescence spectroscopy. The phase and crystal structure of the samples were identified by means of Rigaku D/Max 2200 Automatic X-ray diffractometer with a wavelength of $\text{Cu K}\alpha$ ($\lambda = 0.154 \text{ nm}$). The morphology and particle size of the phosphors were observed by XL30ESEM scanning electron microscope (SEM) and JEM-2100 transmission electron microscope (TEM). The emission spectrum and excitation spectrum were recorded by F-7000 FL-type spectrophotometer.

3. Results and discussion

To understand the formation mechanism of $\text{Gd}_2\text{O}_2\text{S:Tb}$ and find out the optimal firing temperature for the raw materials, the solid state reaction process was tested by heating the mixture of Gd_2O_3 , Tb_4O_7 , S, Na_2CO_3 , K_2CO_3 , Li_2CO_3 and Li_3PO_4 at atmosphere and vacuum condition respectively as were shown in Fig. 1 and Fig. 2. $\text{Na}_2\text{S}_2\text{O}_3$ was also added in the mixture in Fig. 3. The TG curve shows a continuous weight loss between room temperature and end temperature. It is obvious that the first two endothermic peaks mean the loss of the physical adsorbent water and chemical adsorbent water, which are correspond to the weight loss steps in TG curves. As the temperature increases, the chemical reaction between sulfur and sodium carbonate proceeded at 259.99 °C (see Fig. 1). Because the melting point of sulfur is 119.3 °C, above which sulfur starts to react with sodium carbonate to produce Na_2S_x and CO_2 . The escape of CO_2 leads to the massive weight loss. An exothermal peak was seen in DSC curve in Fig. 2 because of the melting of sulfur. At vacuum condition, the melting point and boiling point of sulfur decrease considerably, which leads to the weight loss (−10.77%). The reaction is shown in Eq. (1)

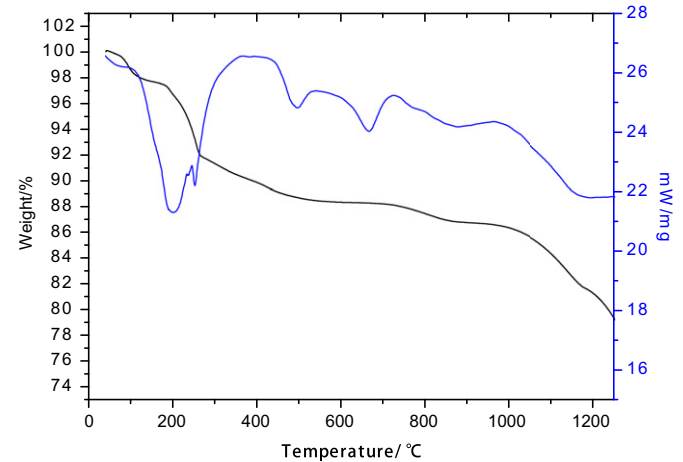
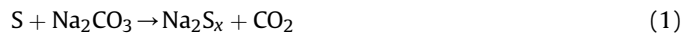
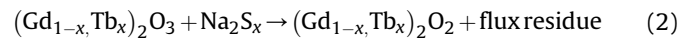


Fig. 1. TG–DSC curves of raw materials mixture at atmosphere.



To compare Fig. 1 and Fig. 2, it is easy to determine the temperature of the main reaction (see Eq. (2)) in DSC curves that the vacuum firing temperature is about 725 °C which is much lower than that of traditional SSR method.



There is also an endothermic peak at 462.4 °C in DSC curves in Fig. 2. It is indicated that the oxysulfide began to be produced from this temperature. In practice, the $\text{Gd}_2\text{O}_2\text{S:Tb}$ phosphor was prepared at about 525 °C by vacuum method. To decrease the weight loss of sulfur, $\text{Na}_2\text{S}_2\text{O}_3$ was also added to replace a part of sulfur. It also helps to flux and react with $(\text{Gd}_{1-x}\text{Tb}_x)_2\text{O}_3$ directly with the reaction temperature decreased to 707 °C (see Fig. 3).

XRD patterns of the $\text{Gd}_2\text{O}_2\text{S:Tb}$ phosphors prepared by vacuum firing under different vacuum degree are shown in Fig. 4(a–c). All the main peaks can be perfectly indexed as the pure hexagonal phase and they are in good agreement with standard $\text{Gd}_2\text{O}_2\text{S:Tb}$ data (JCPDS# 26-1422). Fig. 4 (a) shows the pure $\text{Gd}_2\text{O}_2\text{S}$ phases with the hexagonal structure, and there is no any other phase. In Fig. 4(a) single-phase gadolinium oxysulfide ($\text{Gd}_2\text{O}_2\text{S}$) is observed without Gd_2O_3 as obtained under the pressure with 15 Pa (see Fig. 4(b)) and 30 Pa (see Fig. 4(c)). The higher the vacuum degree increased, the more impurities were produced, which may be

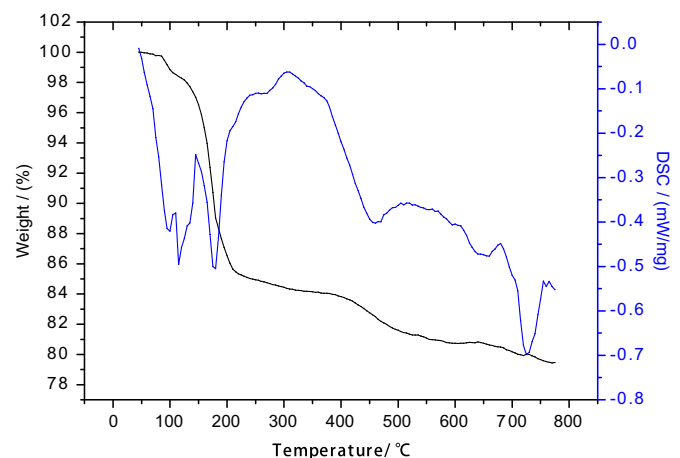


Fig. 2. TG–DSC curves of raw materials mixture in vacuum.

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