

Solution – combustion synthesis and photoluminescence property of (Gd,Y)BO₃:Tb³⁺ phosphor powders

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Abstract. GdYBO₃:Tb³⁺ nanocrystalline were successfully deposited by a solution–combustion method, using rare-earth nitrates, urea and boric acid as starting materials. The crystal structure, morphology, chemical composition and photoluminescence property of the films were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM). The results of SEM, XRD and revealed that the powders were composed of spherical GdYBO₃:Tb³⁺ nanocrystals with average grain size of between 50 and 100 nm. EDS (electron diffraction spectroscopy) confirm the presence of the Gd, Y, B, O, and C. XRD measurements revealed GdBO₃:Tb structure when annealed at 1000°C for two hours. The GdYBO₃:Tb³⁺ powders exhibited emissions at 490, 545 and 585 nm, which were assigned to the 5D₄–7F₆, 5D₄–7F₅ and 5D₄–7F₄ transitions of Tb³⁺, respectively. Among them, the green emission at 545 nm (5D₄–7F₅) was dominant.

1. Introduction

Traditional fluorescent lamp is mainly filled with mixture of He and Xe noble gases containing a little amount of mercury vapour [1]. When broken it releases mercury vapour which is not environmentally friendly. Large band gap materials incorporated with small concentrations of metal ions meet the demand for phosphor to be excited by vacuum ultraviolet (VUV) produced by Xe discharge for plasma display panels and mercury free fluorescent lamps [2, 3, 4]. In recent years, rare-earth-doped nanocrystalline phosphors have attracted great interest. Good glass host is very important for efficient luminescence of rare-earth ions. Borate glass is a suitable optical material with high transparency, low melting point, high thermal stability and good rare-earth ions solubility [5, 6]. Among them, (Gd,Y)BO₃ is one of the best candidates for the desired host materials of phosphors, and (Gd,Y)BO₃:Eu as a red phosphor is used extensively today in plasma display panels. However, the current phosphor is far from satisfying, because of colour and efficiency problems. As the vapour pressure of boron oxide at 800 °C is relatively high since boron oxide is known as high volatile material. Therefore, lack of boron may occur by evaporation or annealing of boron during the firing process. To prevent this phenomenon, excess amounts of boron is generally added to the sample during the preparation. Different methods have been used to prepare (Gd,Y)BO₃ such as high temperature solid state method [7,8], spray pyrolysis technique [9], etc.

In this study, GdYBO₃:Tb phosphor powder was obtained by the solution-combustion process, formed by a solution of metal nitrate, urea and boric acid. The properties of morphology, crystallization behaviour, metal composition and photoluminescence of resulting GdYBO₃:Tb powder were described and discussed.

2. Experimental procedure

GdYBO₃:Tb³⁺ phosphor powders were prepared by the solutions combustion method without any flux material. To investigate the effect of annealing temperature as prepared samples are annealed at 1000°C and the properties of the two compared. The solutions were prepared by dissolving various amounts of the nitrate precursors of each component into distilled water. The resulting solution was transferred into a crucible, which was then introduced into a muffle furnace maintained at 500°C for 5-6 minutes. The voluminous and foamy combustion ash was easily milled to obtain the final GdYBO₃:Tb³⁺ phosphor powder. XRD patterns of the as-synthesized samples were recorded on an x-ray diffractometer with Cu K_α = 1.5406 Å, which was operated at 40 kV voltage and 40 mA anode current. Data were collected in 2θ values from 20° to 80°. The morphologies and size of particles were examined using a PHI 700 Nanoprobe and a Shimadzu model ZU SSX – 550 Superscan scanning electron microscope (SEM), coupled with an energy dispersive x-ray spectrometer (EDS).

Photoluminescence measurement was performed at room temperature on a Cary Eclipse fluorescence spectrophotometer (Model: LS 55) with a built-in 150 W xenon lamp as the excitation source and a grating to select a suitable wavelength for excitation.

3. Results and discussion

3.1 Thermogravimetric analysis

The TGA curves of the as prepared and 1000 °C annealed GdYBO₃:Tb nanophosphors are studied as displayed in Fig. 1(a), to understand its pyrolysis and crystallization process. Fig. 1 indicate that the weight loss of the as prepared phosphor occur in the TGA curves with the increase of temperature from room to 750 °C, and the decomposition can roughly be divided into three regions. The first weight loss step occurred bellow 200 °C in the TGA curve, which was attributed to removal of surface adsorbed water or the residual water molecules. The second gentle weight loss step occurs between 200 and around 680°C, which were attributed to burning of organic compound ligands and the decomposition of metallic nitrates. The last sharp significant weight loss step around 700 °C is ascribed to the phase transition and crystallization process. Therefore samples annealed above this temperature will not show any degradation.

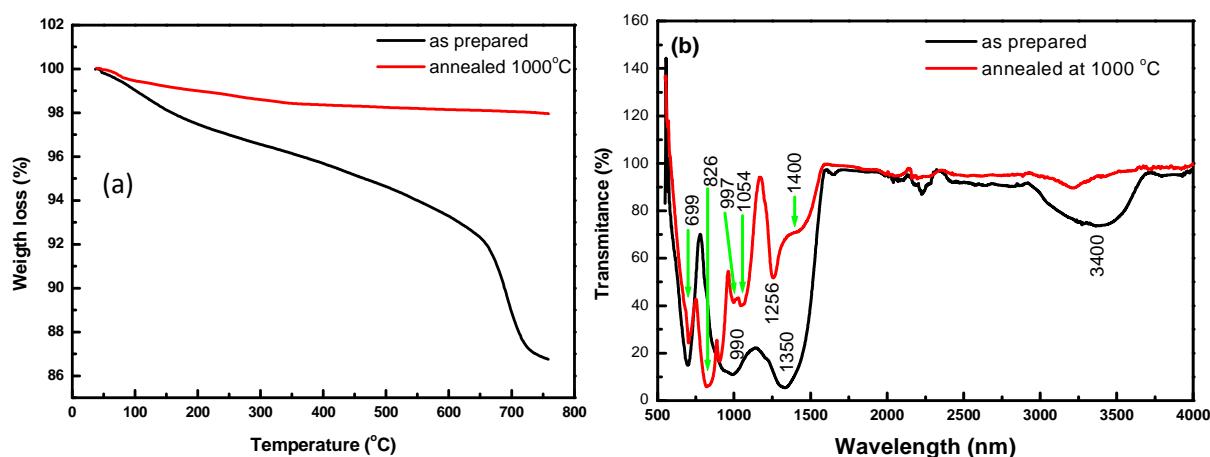


Fig. 1: (a) TGA and (b) FTIR curves for GdYBO₃:Tb as prepared and annealed phosphor powders.

FTIR spectra of as prepared and annealed at 1000 °C are shown in Fig. 1(a). A broad peak at around 3346 cm⁻¹ is originated from O-H stretching in hydroxyl groups. Absorption bands of as prepared samples at around 1350 and 990 cm⁻¹ might originate from C-H bend and C-C stretching. C-O stretching (E) was observed at around 1023 cm⁻¹. The intensity of these bands decreases for samples annealed at 1000 °C. The absorption peaks resulting from bonding to metal ions usually appear at short wave numbers [34]. The band at ~1400 cm⁻¹ was assigned to B-O stretching vibrations of trigonal (BO₃) units in metaborate, pyroborate and ortoborate groups [10]. The absorption band at ~1256 cm⁻¹ was assigned to B-O stretching vibrations of trigonal (BO₃) units in boroxol rings [11]. The weak bands evidenced at ~1054 cm⁻¹, at ~997 cm⁻¹ and at ~990 cm⁻¹ was assigned to stretching vibrations of B-O bonds of BO₄ units from tri-, tetra- and penta- borate groups [11-12].

3.2 Morphological and structural analysis

The results of SEM micrograph as shown if Fig. 1(a) revealed that the powders were composed of spherical GdYBO₃:Tb³⁺ nanocrystals with average grain size of between 50 and

100 nm. They exhibit identical grains and tend to aggregate. EDS (electron diffraction spectroscopy) confirm (see Fig. 1b) the presence of the Gd, Y, B, O, and C.

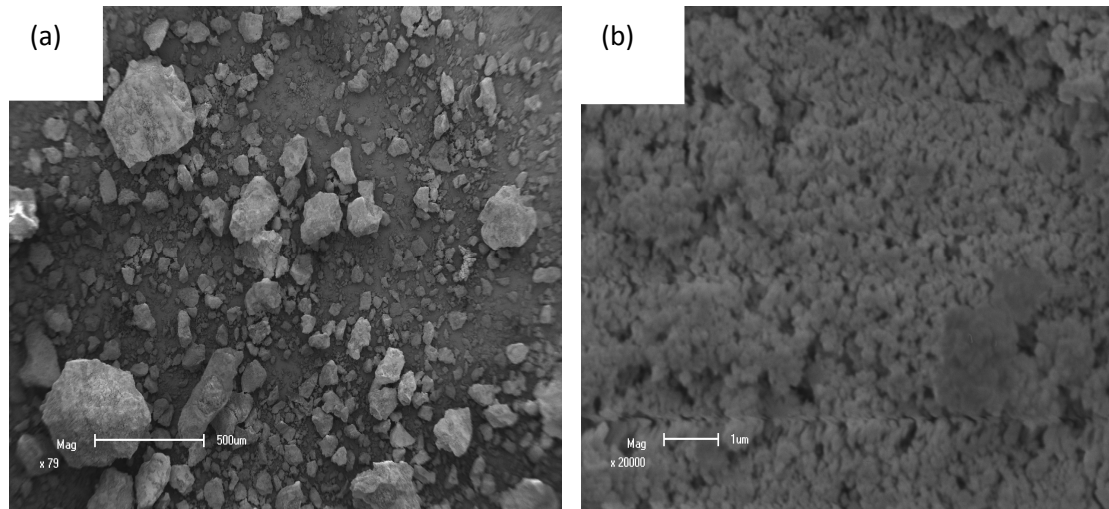


Fig. 2 SEM Micrographs of Gd,YBO₃:Tb³⁺ nano phosphors at (a) low and (b) high magnifications.

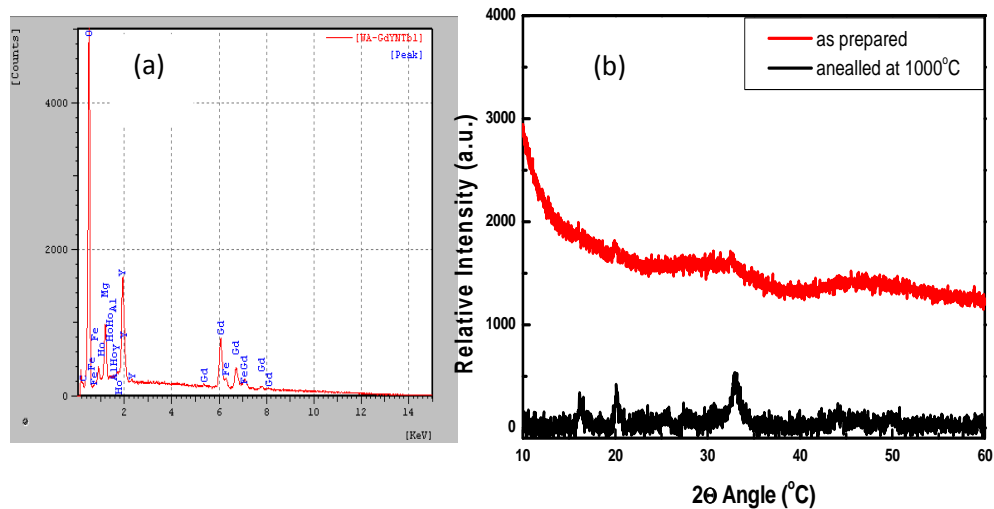


Fig. 3 (a) EDS Micrographs and (b) XRD spectra of Gd,YBO₃:Tb³⁺ nano phosphors.

The XRD patterns of as prepared and annealed at 1000°C GdYBO₃:Tb³⁺ phosphor powders are shown in Fig. 3(b). It is known that its difficulty to precisely defining the crystal structure of these borates compounds, mainly originates from the weak scattering power of boron and oxygen atoms for X-rays. However the spectrum shows the expected orthoborate crystalline phase for the nanopowders. The position and the intensity of diffraction peaks of annealed samples are consistent with that of standard powder diffraction file (JCPDS:83-1205), which indicated that the samples prepared at 1000 °C were pure phase while as prepared samples are amorphous. The main diffraction peaks index well with the card file (JCPDS:83-1205) in agreement with other reports [2]. All the patterns are similar with the respect of strongest six peaks and the presence of diffraction peak of GdYBO₃ at around 16° confirms the P6c2 space group. The crystallite size estimation based on the Scherrer equation analysis confirmed the size obtained using SEM micrograph.

3.3 Optical analysis

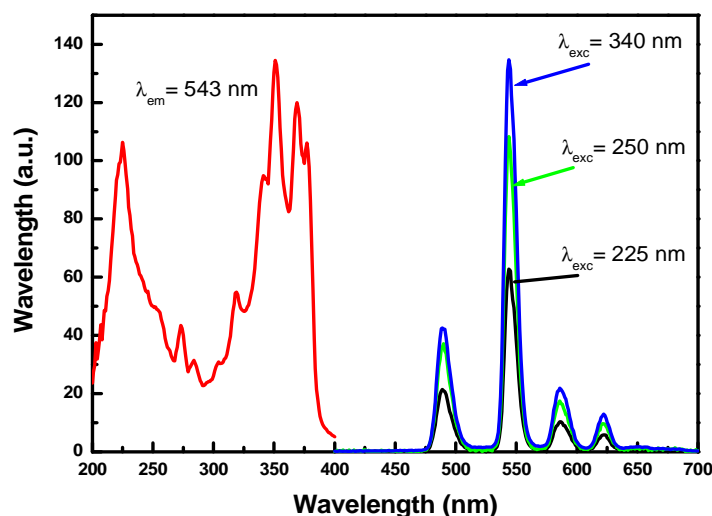


Figure 4 Representative PL excitation and emission spectra of GdYBO₃:Tb³⁺ phosphors.

Fig. 4 gives the excitation and emission spectra of Tb³⁺ green emission in Tb³⁺ doped GdYBO₃. The excitation spectra show two broad bands from 200 to 400 nm with peaks around 224, 340, 368 and 375 nm. The 340, 368 and 375 nm bands are associated with the crystal field splitting of the Tb d-orbital transitions from the ground level ⁷F₆ to ⁵D₁, ⁵D₂ and ⁵D₃ levels, respectively. The second broad band at higher energy is owing to host or the charge transfer state. The prepared phosphor compositions exhibit emission in the blue-green region. The GdYBO₃:Tb³⁺ powders exhibited emissions at 490, 545 and 585 nm, which were assigned to the ⁵D₄→⁷F₆, ⁵D₄→⁷F₅ and ⁵D₄→⁷F₄ transitions of Tb³⁺, respectively. Among them, the green emission at 545 nm (⁵D₄→⁷F₅) was dominant and the emission intensities are greatly dependent on the excitation wavelength. The emission bands at 383, 419 and 438 nm that usually originate from the ⁵D₃→⁷F_J transitions are not observed may be due to non radiative transitions through cross relaxation process. Local crystal field symmetry around the Tb³⁺ cations can have a significant effect on electric dipole transitions [1]. For example, bulk-scale single crystals have high local symmetry around the Tb³⁺ cations, which diminishes the intensity of the green emission. However, when the crystal size is decreased to the nano regime, surface defects decrease the local symmetry around the Tb³⁺ cations, increasing the intensity of the green emission. For use in plasma displays, it is important that the GdYBO₃:Tb have a strong red emission component. The comparison of emissions using various excitation wavelengths indicates that emissions are significantly influenced for efficient practical applications of these phosphors. Fig. 5 shows the persistent luminescence intensity (I) vs time (t) plot of the phosphor powders. The GdYBO₃:Tb persistent luminescence is due to existence of suitable charge carrier traps in the crystal due to the presence of the defects ions. It was observed that annealing the samples at 1000 enhances the initial luminescent intensity and after glow time.

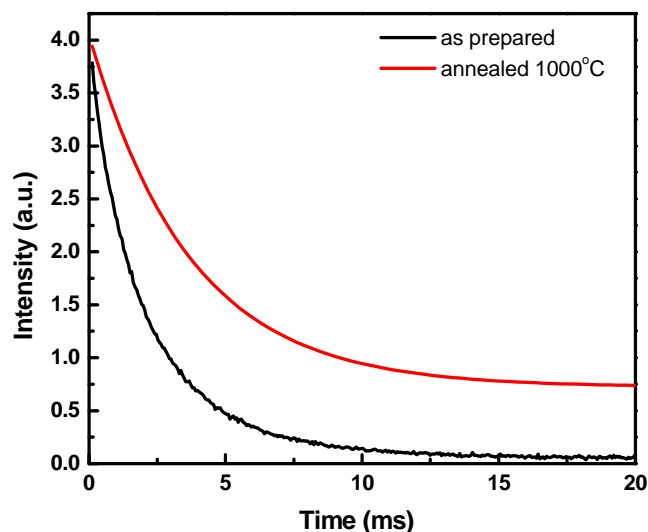


Figure 5 Decay curve of as prepared and annealed GdYBO₃:Tb phosphors.

4. Conclusions

Tb³⁺ doped borate glasses have been synthesized and characterized. In doped glasses, Tb³⁺ emit intense green lights under UV light excitation. Enhancement of Tb³⁺ green emission is observed when the phosphor is excited at 340nm. The excitation wavelength range for Tb³⁺ emission is broadened due to the energy transfer from host to Tb³⁺.

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