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Photoluminescence properties of Bi^{3+}-doped $YInGe_2O_7$ phosphors under an ultraviolet irradiation

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ABSTRACT

Yttrium indium germanate ($YInGe_2O_7$) doped with different concentrations of Bi^{3+} ion was synthesized using a vibrating milled solid-sate reaction. The compound was characterized and its optical properties were investigated. The precursor powders were heated at 1300 °C for 10 h to obtain good crystallinity with better luminescence. The XRD results show that all peaks can be attributed to the monoclinic $YInGe_2O_7$ phase when the Bi^{3+} ion concentration is increased up to 5 mol%. Furthermore, the 0.5 mol% of Bi^{3+} ion doping lead to obvious improvements in the surface morphology of the $YInGe_2O_7$ powder, because the Bi_2O_3 also acts as a flux reagent. In the PL studies, excitation under an ultraviolet (302 nm) irradiation shows that the $(Y_{1-x}Bi_x)InGe_2O_7$ phosphors display luminescence belonging to the $^3P_1 \rightarrow {}^1S_0$ transition from 457 to 496 nm, and the CIE color coordinates changed from a blue to blueish region as the Bi^{3+} ion concentration increased from 0.2 mol% to 5 mol%. The time-resolved of the $^3P_1 \rightarrow {}^1S_0$ transition presents a non-single exponential decay behavior, and the decay time decreases from 8 ms to 1 ms.

1. Introduction

Luminescent materials have many common applications, such as in fluorescent lamps [1], cold cathode fluorescent lamps (CCFL) [2], cathode-ray tube displays (CRT) [3], and light emitting diodes (LED) [4]. It is thus highly desirable to develop novel low-voltage phosphors with high efficiency and chemical stability under electron beam bombardment in a high-vacuum system for the next generation field-emission displays [5,6].

Oxide phosphors have recently gained a lot of attention for applications such as display devices and lighting, because of their higher chemical stability compared to sulfide phosphors. Many studies have been conducted to develop new oxide phosphors in powder form to improve luminescent performance, including color purity, emission intensity, and quantum efficiency [7,8].

Yttrium indium germanate ($YInGe_2O_7$) has a thortveitite structure with a symmetry described by space group C2/m (No. 12), and this crystallizes in the monoclinic system, with unit cell parameters of $a = 6.8286$ Å, $b = 8.8836$ Å and $c = 4.9045$ Å. The In^{3+} and Y^{3+} cations occupy the same octahedral site, forming a hexagonal arrangement on the ab planes. The hexagonal arrangements of InO_6/YO_6 octahedral layers are held together by sheets of isolated diorthogroups comprising a double tetrahedral that shares a common vertex [9].

Research results show that Bi^{3+} ions are superior as not only an activator but also a sensitizer of luminescence. In addition, recent work has demonstrated that compounds containing Bi^{3+} have great potential with regard to the discovery of new intrinsically luminescent materials. The ground state of the Bi^{3+} ion is $^1S_0$, whereas the 6s6p excited states give rise to the triplets levels [$^3P_0$,$^3P_1$,$^3P_2$] and the $^1P_1$ singlet state. The $^1S_0 \rightarrow {}^3P_1$ transition (A-band) becomes allowed as a result of spin–orbit interaction, whereas the $^1S_0 \rightarrow {}^3P_2$ transition (B-band) is forbidden but can be induced by coupling with asymmetrical lattice vibration modes. The $^1S_0 \rightarrow {}^1P_1$ transition (C-band) is an allowed transition but the $^1S_0 \rightarrow {}^3P_0$ is strongly forbidden [10,11]. To date, the optical properties of the rare earth Bi^{3+} ion doped yttrium indium germanate have not been reported. Therefore, $YInGe_2O_7$ doped with different Bi^{3+} ion concentrations were synthesized using a vibrating milled solid-sate reaction in this investigation. The phases, morphologies, and optical properties of the $YInGe_2O_7$:Bi^{3+} phosphors thus produced were then investigated.

2. Experimental procedure

2.1. Powder preparation

The Bi^{3+}-doped $YInGe_2O_7$ phosphors were prepared using a planetary ball mill solid-state reaction with yttrium oxide (Y_2O_3), indium oxide (In_2O_3), germanium oxide (GeO_2) and Bismuth oxide

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(Bi_2O_3). The starting materials, with the purity of 99.99%, were obtained from Alfa Aesar company, Inc. The materials were weighed according to the stoichiometric ratios and mixed by a mechanically activated high energy vibro-mill for 20 min with zirconia balls in a polyethylene jar. After mechanically mixing, the mixtures were calcined at 1300 °C in air for 10 h in a programmable furnace. The vibrating ball milling method can produce unique and metastable materials via a self-sustaining reaction of highly exothermic powder mixtures. The characteristics of vibrating ball milling method include material destruction, formation of a new surface, fine grinding, and transformation into a new material with a completely different structure [12].

2.2. Characterization

The obtained powders were analyzed for crystal structure using an X-ray diffractometer (XRD, Rigaku Dmax-33 X-ray diffractometer) with Cu Kα radiation to identify the possible phases formed after heat treatment. The surface morphology of powders was examined using high-resolution scanning electron microscopy (HR-SEM, S-4200, Hitachi). In order to determine the absorption behavior of $(Y_{1-x}Bi_x)InGe_2O_7$ phosphor, the powders were placed inside a black stainless holder capped with a quartz glass, and measured from 200 to 700 nm at room temperature using a Hitachi U-3010 UV–visible spectrophotometer. Both the excitation and luminescence spectra of these phosphors were analyzed with a Hitachi F-4500 fluorescence spectrophotometer using a 150 W xenon arc lamp as the excitation source at room temperature.

3. Results and discussion

3.1. Phases in the samples

Fig. 1 shows the X-ray powder diffraction pattern of $YInGe_2O_7$ doped with various Bi^{3+} ion concentrations calcined at 1300 °C in air for 10 h. In general, it is difficult to obtain a high Bi^{3+}-doped concentration phosphor because the Bi_2O_3 will evaporate at a high temperature [13]. In the current study, all the peaks are attributed to the monoclinic $YInGe_2O_7$ phase [JCPD No. 65–3170], even the Bi^{3+} ion concentration were increased up to 5 mol%. When the trivalent bismuth ions (1.03 Å) [14] were introduced to substitute the trivalent yttrium ions (0.9 Å) [15] in the $(Y_{1-x}Bi_x)InGe_2O_7$ system, the variations were almost the same as for the Bi^{3+} and Y^{3+} ion radii, and there were no charge compensation issues, since both have the same valence, and thus they can form a solid solution easily. In addition, the diffraction angle of the diffraction peaks shifted to a small angle as the Bi^{3+} ion concentration increased. Because cationic Bi^{3+} have larger radii than the Y^{3+} ions, the lattice distorted and intra-stress occurred when increasing the concentration of Bi^{3+} ions to substitute the Y^{3+} ions in the $YInGe_2O_7$ crystal.

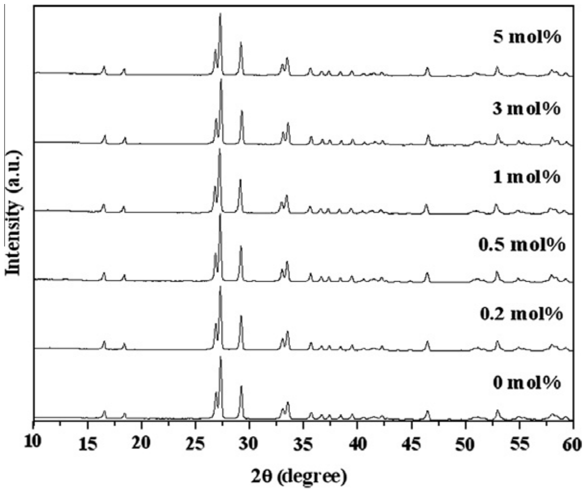

Fig. 1. The X-ray diffraction patterns of $YInGe_2O_7$ doped with different Bi^{3+} ion concentrations calcined at 1300 °C for 10 h in air.

3.2. Microstructures

Fig. 2 shows the SEM micrographs of $YInGe_2O_7$ doped with 0.2, 0.5, 1, 3 and 5 mol% Bi^{3+} ions calcined at 1300 °C in air for 10 h. The particles aggregated and had irregular shapes when the Bi^{3+} ion concentration increased from 0.2 mol% to 5 mol%. At low Bi^{3+}-doped concentrations (Fig. 2a and b) the particle size seems to be increased obviously. A flux is a material that melts lower than the solid-state reaction temperature, dissolves one or more of the components, and allows material transport to the reaction zone without entering into the solid-state reaction [16]. Bi_2O_3 has a low melting point of about 825 °C, and it was used as a flux reagent in this study to reduce the calcination temperature and increase the crystallinity [17]. The self-flux was effective when the Bi^{3+}-doped concentration rose from 0.2 to 0.5 mol%, with the greatest effect achieved of 0.5 mol%. When the Bi^{3+} concentration was higher than this, the particles seemed to decrease as the Bi^{3+} concentration continued to rise. When the Bi^{3+} ions entered the $YInGe_2O_7$ crystal, the distinct difference in ion radius between the lattice atoms and substitution atoms caused the lattice to be distorted and induced a local non-uniform strain in the vicinity of the Bi^{3+} ions, resulting in the decreased particle size [18].

3.3. Absorption and excitation spectrum

Fig. 3 is the optical absorption spectra for pure $YInGe_2O_7$ and $YInGe_2O_7$ doped with various Bi^{3+} ion concentrations calcined at 1300 °C for 10 h measured at room temperature. The series of sharp absorption bands between 200 and 280 nm correspond to the charge transfer (CTS) between the In^{3+} and O^{2-} ions of the InO_6 anionic group in the host lattice. According to previous studies [19–22], metal ions with a d^{10} configuration, such as In^{3+}, show a strong absorption peak in the ultraviolet region. Another peak appears near 300 nm corresponding to the $^1S_0 \rightarrow {}^3P_1$ transition (A-band), and this is allowed due to the spin–orbit interaction.

Fig. 4 shows the excitation spectra of $YInGe_2O_7$ doped with various Bi^{3+} ion concentrations calcined at 1300 °C for 10 h. The emission wavelength is detected at 457 nm for the $^3P_1 \rightarrow {}^1S_0$ transition of Bi^{3+} ions. Two excitation peaks appeared like a shoulder in the excitation spectra. Blasse and Grabmaier [23] indicated that ions with an s^2 electronic configuration will cause significant optical absorption in the UV region. Therefore, a broad absorption band around 300 nm is due to the $^1S_0 \rightarrow {}^3P_1$ transition of the Bi^{3+} ions which have the $6s^2$ electronic configuration. Another peak appears around 260 nm is due to the CTS of $YInGe_2O_7$ host and this supports the observation in the absorption spectrum. In addition, the intensity of the $^1S_0 \rightarrow {}^3P_1$ transition increased along with increasing the Bi^{3+} ion concentration, and reached maximum value for at 0.5 mol%, but then decreased as the Bi^{3+} ion concentration continued to rise.

3.4. Emission spectrum

Fig. 5 is the luminescence spectra for different Bi^{3+}-doped $YInGe_2O_7$ phosphors calcined at 1300 °C for 10 h under ultraviolet excitation (302 nm). A wide emission band between 330 and 650 nm centered at 457 nm is observed that corresponds to the $^3P_1 \rightarrow S_0$ transition for the Bi^{3+} ion. Just as seen with the excitation spectra, the maximum intensities for the $^3P_1 \rightarrow {}^1S_0$ transition