Journal of Metals, Materials and Minerals, Vol.23 No.1 pp.9-12, 2013

Upconversion Luminescence of Yttrium Oxysulfide Co-doped with Rare Earth Elements

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Abstract

Rare earth ions doped upconversion phosphors have been used in many applications such as infrared laser detecting, anti-counterfeit protection and solid state display. In this study, yttrium oxysulfide (Y_2O_2S) compounds co-doped with rare earth elements, ytterbium (Yb), and one of the following elements, erbium (Er), thulium (Tm), europium (Eu) or holmium (Ho) were synthesized from doped rare earth oxides using sulfide fusion method with pelletization pretreatment. The doping was carried out with the mixing of yttrium nitrate and rare earth nitrate solutions to obtain homogeneous mixture. The mixed nitrate solution was precipitated with oxalic acid and calcined to doped oxide precursors. Doping of Yb was 2.5 mol% and the other minor doping was 0.10 and 0.25 mol%. The structure and the morphology of the oxysulfide samples were examined by X-ray diffractometer (XRD) and scanning electron microscope (SEM). The upconversion luminescent characteristic of the synthesis phosphors was investigated with spectrofluorometer and IR laser pen. It was found that, under 980 nm excitation radiation, most of the phosphors exhibited green emission band of 541-552 nm wavelengths except the phosphor co-doped with Yb and Tm (Y_2O_2S:Yb,Tm) exhibited infrared emission band of 787-810 nm wavelength and slight blue color. Yttrium oxysulfide co-doped with Yb and Ho (Y_2O_2S:Yb,Ho) showed the highest brightness upconversion luminescence. The luminescence efficiency was seen to increase with the increasing of the dopants.

Key words : Upconversion, Yttrium oxysulfide, Rare earth, Phosphor

Introduction

Upconversion luminescence is a process that materials convert different invisible infrared light into visible light which is also known as Anti-Stokes shift. Upconversion material is a very rare class of inorganic crystal that can absorb multiple photons of a lower energy level and emit one photon of a higher energy level which is an inherently inefficient process. In contrast, the downconversion luminescence process occurs with the absorption of a high energy photon (UV) and emission of a lower energy photon which is more efficient and the materials are more available.[1-2]

Yttrium oxides and oxysulfides doped with trivalent rare earth elements have been reported to possess the upconversion property with promising upconversion luminescence efficiency. These materials have generated considerable interest for many applications such as infrared laser detecting, anti-counterfeit protection and phosphors for solid state display and fluorescent lighting as they have favorable physical properties such as high chemical durability and excellent thermal stability.[3-5]

The traditional solid-state reaction method called sulfide fusion method is widely employed for the preparation of rare earth oxysulfide materials because of the high reliability and cost efficiency. In this method, rare earth oxides are mixed with sulfur (S) and flux materials such as Na_2CO_3, K_2CO_3 or K_3PO_4 to assist and promote the reaction of oxide compounds and sulfur without entering into the solid-state reaction. The doping of minor elements is normally carried out by solution mixing before converting to oxide precursor to obtain homogeneous doping in crystal structure. The isostatic press pretreatment of starting raw materials was reported to enhance the yield of oxysulfide products.[6-7]

In this work, yttrium oxsysulfide doped with ytterbium (Yb) and one of the rare earth elements namely, erbium (Er), thulium (Tm), europium (Eu) or holmium (Ho) were prepared from the rare earth

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oxide precursors using modified sulfide fusion method with pelletization pretreatment and their luminescence properties were investigated.

Materials and Experimental Procedures

Materials

The rare earth oxides used in this experiment were Y_2O_3, Yb_2O_3, Eu_2O_3 and Ho_2O_3 from Merck, Er_2O_3 from Aldrich and Tm_2O_3 from Fluka. Sulfur was supplied from Panreac. The flux materials, Na_2CO_3 was from Merck and K_2CO_3 was from Unilab. Nitric acid and oxalic acid were obtained from Merck. All reagents were laboratory grade and used as received.

Preparation of Doped Yttrium Oxides

Yttrium oxides doped with rare earth elements were prepared by dissolving each rare earth oxide with HNO_3 at the concentration of 0.1M for Y and 0.01M for the other rare earth elements. The calculated amounts of rare earth nitrate solution were added into yttrium nitrate solution to obtain the required doping composition. Yb was doped at 2.5 mol% as the main dopant and one of the rare earth elements was co-doped at 0.10 and 0.25 mol%. The mixed nitrate solution was precipitated with oxalic acid. The oxalate precipitates were filtered and dried before being calcined at 800°C for 2 hours to obtain oxide compounds.

Synthesis of Doped Yttrium Oxysulfides

In the modified sulfide fusion with pelletization pretreatment method, doped yttrium oxide was mixed with S, Na_2CO_3 and K_2CO_3 at the weight ratio of 1 : 1.5 : 0.5 : 0.5. The materials were well mixed in mortar before pelletization in a 10-ton hydraulic press at 10 minutes holding time. The pellets were heated at 900°C in helium atmosphere for 2 hours. The sintered samples were washed with dilute hydrochloric acid and distilled water several times to remove the flux materials from the oxysulfide products. The dried samples were examined and characterized by scanning electron microscope (SEM) model JSM-5800LV from JEOL and X-ray diffractometer (XRD) model D8 Advance from Bruker. Their upconversion luminescence properties were determined by spectrofluorometer (Fluorolog-3, Horiba) and 980 nm IR laser pen of 100 mW.

Results and Discussion

The formula of some doped yttrium oxysulfide samples prepared in this study was listed in Table 1. The doping of Yb as the major dopant is 2.5 mol% and the rare earth co-dopant is 0.25 mol%. Yttrium oxysulfides with 2.5 mol% Yb doping and 0.1 mol% rare earth co-doping were also prepared. All of them appear as white powder.

Table 1. Formula of the synthesized yttrium oxysulfide samples co-doped with rare earth elements.

Sample code	Formula
YB195-05	$(Y_{1.95}Yb_{0.05})O_2S$
YBE195-005	$(Y_{1.945}Yb_{0.05}Er_{0.005})O_2S$
YBT195-005	$(Y_{1.945}Yb_{0.05}Tm_{0.005})O_2S$
YBU195-005	$(Y_{1.945}Yb_{0.05}Eu_{0.005})O_2S$
YBH195-005	$(Y_{1.945}Yb_{0.05}Ho_{0.005})O_2S$

The XRD patterns of the doped yttrium oxysulfide samples displayed in Figure 1 show that all of them have the hexagonal structure of Y_2O_2S according to Inorganic Crystal Structure Database (ICSD) pattern 00-24-1404. Sample YBH195-05 reveal the existence of Y_2O_3 (pattern 01-071-5970, cubic structure) remained in the sample. This indicates the incomplete conversion of oxide to oxysulfide in that sample. However, the Y_2O_3 content in the sample seems to be small.

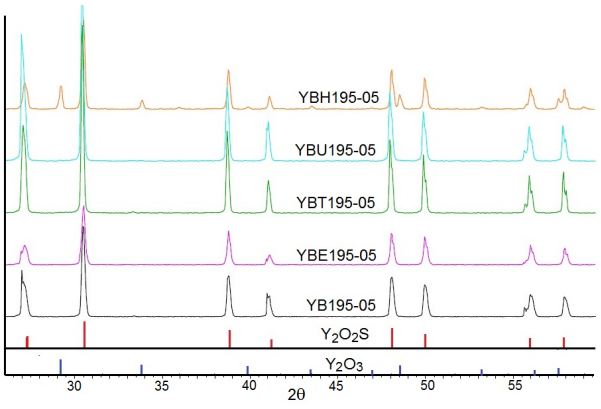

Figure 1. XRD patterns of the synthesized yttrium oxysulfide samples.

The morphology of two doped Y_2O_2S samples were shown by SEM images in Figure 2. It is seen that most particles have the similar hexagonal shapes with the size varying from around 2 to 10 μm.

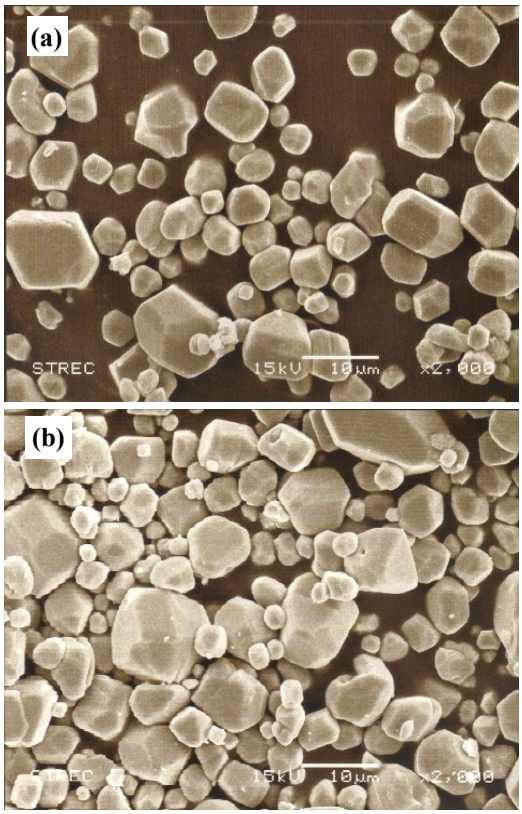

Figure 2. SEM images of doped yttrium oxysulfide powder (a) YB195-05 (b) YBU195-005.

The emission spectra of the synthesis Y_2O_2S samples when excited with 980 nm wavelength in spectrofluorometer are shown in Figure 3. Most of the samples exhibit emission peaks in the range of 541-552 nm wavelengths which are the green spectra except the sample co-doped with Yb and Tm (Y_2O_2S:Yb,Tm) exhibits infrared emission peaks in the range of 787-810 nm wavelengths and some small peaks in blue and green spectra (475-553 nm). It is seen that at the similar doping concentration, yttrium oxysulfide co-doped with Yb and Ho (Y_2O_2S:Yb,Ho) has the highest luminescence intensity about 1,000,000 cps/microAmp while the oxysulfide sample co-doped with Yb and Eu (Y_2O_2S:Yb,Ho) has the lowest luminescence intensity nearly 25,000 cps/microAmp. The single dope Y_2O_2S:Yb sample also has a low luminescence intensity.

The emission intensity of these upconversion phosphors were found to increase with the increasing of the minor doping. For the Ho doping of 0.10 mol% ($(Y_{1.945}Yb_{0.05}Ho_{0.002})O_2S$) and 0.25 mol% ($(Y_{1.945}Yb_{0.05}Ho_{0.005})O_2S$), their luminescence intensities are 596,600 and 1,003,950 cps/microAmp respectively at 542 nm peak. For the Tm doping of 0.10 and 0.25 mol%, the luminescence intensities at 798 nm peak are 101,800 and 205,065 cps/microAmp respectively.

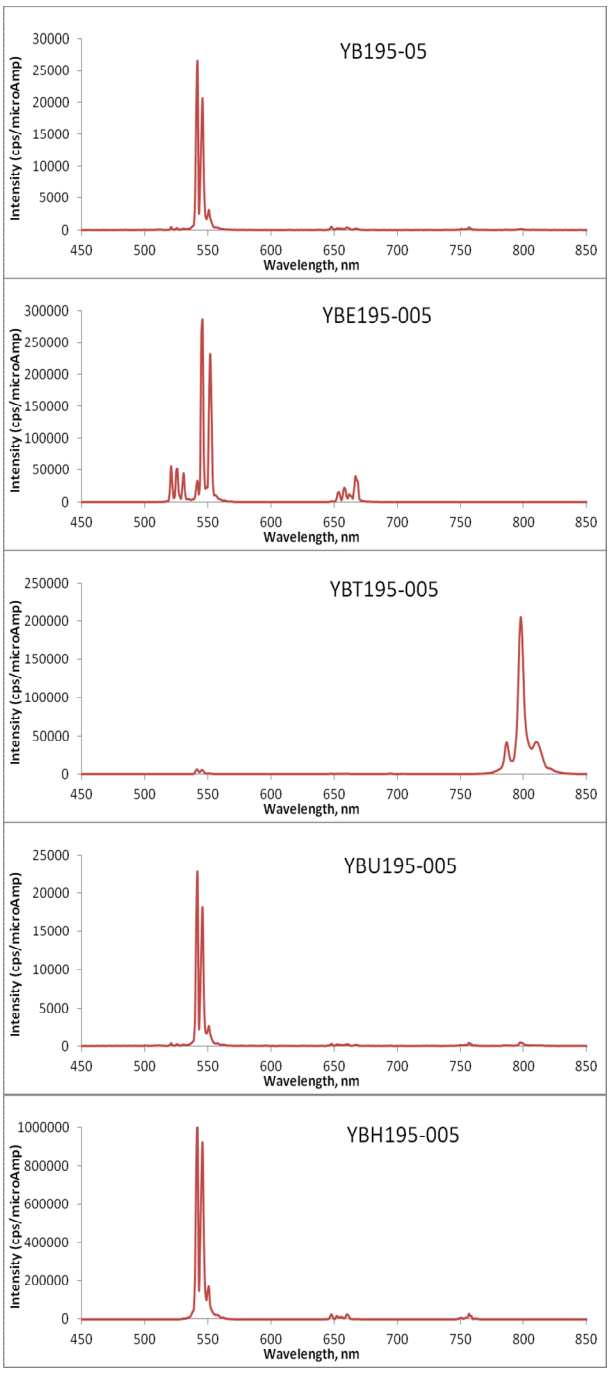

Figure 3. The upconversion spectra of doped Y_2O_2S samples excited by 980 nm wavelength.

The activation of the doped oxysulfide samples by 980 nm IR laser pen shown in Figure 4 confirms the green emission of Y_2O_2S:Yb,Ho sample while Y_2O_2S:Yb,Tm sample shows slight blue emission color from its minor emission peaks as its major emission peaks are in IR region which is invisible to the naked eyes.

Figure 4. The upconversion luminescence of co-doped Y_2O_2S samples excited by 980 nm laser pen.

Conclusions

Yttrium oxysulfide co-doped with rare earth elements namely Yb, Er, Tm, Eu and Ho were prepared by sulfide fusion method with pelletization pretreatment for the upconversion phosphors. Most of the samples exhibited major green emission wavelengths except the phosphor co-doped with Yb and Tm (Y_2O_2S:Yb,Tm) exhibited major infrared emission wavelengths and slight blue color. The oxysulfide sample co-doped with Yb and Ho (Y_2O_2S:Yb,Ho) showed the highest emission intensity. The luminescence efficiency was seen to increase with the increasing of the minor doping concentration. However, the optimal doping for the maximum luminescent intensity requires further study.

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