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Structure and photoluminescence properties of $Ba_{2-x}Si_4O_{10}:2xSm^{3+}$

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ABSTRACT

We investigated the structure and photoluminescence properties of novel $Ba_{2-x}Si_4O_{10}:2xSm^{3+}$ phosphor prepared by the solid state reaction method. In the prepared phosphor the high temperature monoclinic phase was dominant over the low temperature orthorhombic phase. The shifting of the X-ray diffraction peaks with the Sm^{3+} ion addition was explained on the basis of the refinement results. The photoluminescence study showed that on excitation with 402 nm the phosphor emitted at 560 nm, 600 nm and 645 nm which corresponds to the $^4G_{5/2}\rightarrow{}^4H_{5/2}$, $^4G_{5/2}\rightarrow{}^4H_{7/2}$ and $^4G_{5/2}\rightarrow{}^4H_{9/2}$ transitions, respectively. Concentration quenching effect was also observed in the prepared phosphor. CIE chromaticity coordinates showed that the phosphor can be further developed for display applications.

1. Introduction

In the modern society the luminescence based materials are very useful in everyday life. Commercialization of phosphor materials in the field of light emitting diode (LEDs), liquid plasma display (LCD), infrared detectors and scintillation materials increases in the past few decades [1]. For the advancement in these fields there is a need of phosphors with high efficiency, easy preparation method, low cost and environmental friendliness [2]. For the display application two or more different phosphor were used to meet the specific criteria. But the use of multi phosphor lead to colour aberration and the change in luminous efficiency due to re-absorption in the different phosphors [2]. This problem is more serious with the red emitting phosphors. Therefore it is necessary to find new phosphors to resolve these problems.

Compare to other available rare earth dopant samarium ions are very popular because of its reddish orange emission in the visible region. Sm^{3+} ions belongs to the $^4f_5$ configuration and in any crystal field perturbation it is doubly generated [3]. The excitation spectra of Sm^{3+} ions doped materials covers the UV, blue and bluish-green spectral range Therefore it is possible to get the reddish orange emission by excitation in this region [4–7]. The emission profile of Sm^{3+} ions is narrow and it shows longer life times, similar to Eu^{3+} ions. Sm^{3+} ions doped materials are a better alternative.

As most of the silicate materials has a high melting point, silicate based phosphor are well known in phosphor research because of its chemical and thermal stability [8–10]. The present study deals with exploration of a new silicate based phosphor to find the possibility of its use in the WLEDs. In the present study novel $Ba_{2-x}Si_4O_{10}:2xSm^{3+}$ was prepared by the solid state reaction method and an attempt has been made to understand its structure as this phosphor has a low temperature and high temperature phase. We also studied the emission properties along with the compositional behavior of the Sm^{3+} ion in the novel host.

2. Experimental

The $Ba_{2-x}Si_4O_{10}:2xSm^{3+}$ (were x= 1, 2, 3 and 4 mol%) phosphors were prepared by the simple solid state reaction method. The stoichiometric quantities of high purity $BaCO_3$ (99.99%), SiO_2 (99.99%), and Sm_2O_3 (99.99%) were mixed in an agate mortar with acetone. The obtained mixture were heated in a furnace at 800 °C for 5 h for pre-sintering. After pre-sintering the mixture again was grounded for 1 h and sintered at 1250 °C for 8 h. The mixture was again grounded after final sintering for further characterization.

Powder X-ray diffraction patterns (XRD) were measured using a Bruker D8 advanced instrument with a Cu target radiation (λ=0.154056 nm). The diffraction data were refined by the FULLPROF software. Parameters refined are scale factor, background, overall factor, cell position, shape parameters and Wycoff positions. The JEOL JSM-7800 F field emission scanning electron microscope (FE-SEM) was used to analyze the surface morphology. The Oxford instruments AzTEC energy dispersive X-ray spectroscopy (EDS) was used for the composition analysis. The excitation and emission spectra of the prepared phosphor were recorded by a Varian Cary eclipse fluorescence spectrophotometer.

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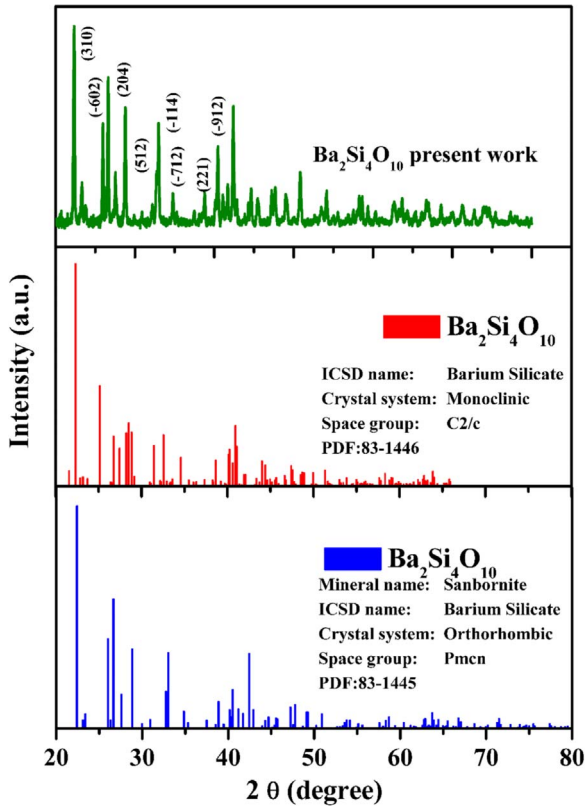

Fig. 1. XRD pattern of the base undoped $Ba_2Si_4O_{10}$: Sm^{3+}sample with the ICSD standards.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction pattern for the $Ba_2Si_4O_{10}$ prepared by the solid state reaction method. The prepared phosphor consisted of two phases which are the high temperature monoclinic phase and the low temperature orthorhombic phase. The quantitative analysis shows that the monoclinic phase was dominant over the orthorhombic phase. The monoclinic phase of $Ba_2Si_4O_{10}$ belongs to the space group C 2/c and the lattice parameter values are a= 23.195 (Å), b= 4.658 (Å), c= 13.613 (Å) with β= 97.57 (°) and V=1457.96 (Å^3) (JCPDS Card No. 83–1446). On the other hand orthorhombic phase of $Ba_2Si_4O_{10}$ (Sanbornite) has the space group Pmcn and lattice parameter are a= 7.688 (Å), b= 4.629 (Å), c= 13.523 (Å) and V=481.25 (Å^3) (JCPDS Card No. 83–1445). The XRD pattern was indexed with the monoclinic phase indexes.

Fig. 2(a) shows the XRD patterns for the $Ba_2Si_4O_{10}$ with different mol% of Sm^{3+} ions. Fig. 2(b) is the magnified view for the comparison of the 310 peak for the different concentrations. This figure indicates that the main 310 peaks shifted slightly towards the higher angle with the addition of the activator Sm^{3+} ions in the crystal structure. This indicates that the activator Sm^{3+} ions have strong influence on the crystal structure of the $Ba_2Si_4O_{10}$ host. When the Sm^{3+} (cn=8, 1.08 nm)ions enters in the crystal structure as a substitution for the Ba^{2+} (cn=8, 1.42 nm)ions it decreased the volume of the unit cell which results in the shifting of the XRD peaks to the higher angle [10].

To get the information about the lattice parameters of monoclinic and orthorhombic phases present in the $Ba_2Si_4O_{10}$ phosphors Rietveld analysis were implemented [11]. As seen from the refinement results showed in Fig. 3. In this figure the black dots and red line represent the measured and calculated pattern which are in good agreement with each other. The obtained values for the monoclinic phase are a= 23.112 (Å), b= 4.531 (Å) and c= 13.216 (Å) and orthorhombic phase are a= 7.631 (Å), b= 4.581 (Å) and c= 13.391 (Å). The obtained volume from the Rietveld analysis for the monoclinic phase is V=1451.07 (Å^3) and for the orthorhombic phase is V=480.36 (Å^3) which are in accordance with previous argument that the XRD peaks shift to the higher angle with an increase in Sm^{3+} concentration [10].

It has been previously reported that the increase in the high temperature monoclinic phase was responsible for the increase in the emission intensity of the Eu^{3+} in the $Ba_2Si_4O_{10}$ phosphor [10]. This may be due to the fact that the crystal symmetry for the monoclinic phase is lower than the orthorhombic phase [12]. Both the phases have SiO_4 tetrahedra which share corners to form a chain with two other tetrahedra to make a layer. In the orthorhombic phase these layers are strongly folded. In the monoclinic phase the SiO_4 tetrahedral layers are less corrugated [13]. This less corrugated levels may provide the sites for the Sm^{3+} ion. This argument is supported by experimental results. Fig. 4 shows the quantitative analysis of the monoclinic and orthorhombic phase for the $Ba_2Si_4O_{10}$ phosphor prepared at 1200 °C and 1250 °C. As the temperature increased there was a significant increase in the high temperature monoclinic phase. By comparing the emission spectra of Sm^{3+} containing $Ba_2Si_4O_{10}$ phosphor it is observed that, phosphor with higher percentage of monoclinic phase shows improved luminescence. Hsiao et al. [14] investigated the luminescence properties of $LaNbO_4$ synthesized by the citric gel process. They found that a mixture of crystallized orthorhombic and monoclinic biphasic structures formed at temperatures below 1100 °C and well-crystallized monoclinic $LaNbO_4$ was obtained by heat treatment at a temperature of 1200 °C. The monoclinic phase also has the highest luminescence intensity. Cheng et al. [15] also found that a change in crystal field was mainly responsible for the increase in intensity of Dy^{3+}-doped $Gd_2(MoO_4)_3$.. This spectral difference is caused by the different crystal fields in monoclinic and orthorhombic $Gd_2(MoO_4)_3$, since the spectral properties of rare earth doped materials are decided by crystal field environments surrounding rare earth ions.

Fig. 5 shows the SEM images of the $Ba_2Si_4O_{10}$ (a) and $Ba_2Si_4O_{10}$ with 3 mol% Sm^{3+} ions (b) phosphor. This figure shows the agglomerated, porous, irregular shaped particles. This may be due to the preparation method of the present phosphor. EDS data for the doped and un-doped phosphor is presented in Fig. 5c and d. this data confirms that the samples were composed of Ba, Si, O and Sm. The elemental mapping of the $Ba_2Si_4O_{10}$:Sm (Fig. 6) shows the uniform distribution of the Ba, Si, O and Sm ions in the prepared phosphor.

Fig. 7 shows the excitation spectra of the 3 mol% Sm^{3+} ions containing phosphor. The observed excitation transition are at 345 nm, 362 nm, 374 nm, 402 nm, 417 nm and 476 nm. These transition belongs to $^4H_{9/2}$, $^4D_{3/2}$, $^4L_{15/2}$, $^4F_{7/2}$, $^6P_{5/2}$ and $^4I_{11/2}$. Similar excitation peaks were observed for other samples and concentration of Sm^{3+} ions. The transition at 402 nm ($^4F_{7/2}$) was the most prominent one and was used for the emission studies.

On excitation with 402 nm, the emission spectrum shows three prominent peaks situated at 560 nm, 600 nm and 645 nm in Fig. 8. These emission bands correspond to $^4G_{5/2}\rightarrow{}^4H_{5/2}$, $^4G_{5/2}\rightarrow{}^4H_{7/2}$ and $^4G_{5/2}\rightarrow{}^4H_{9/2}$. When the phosphor was excited with 402 nm electrons in the ground state $^6H_{5/2}$ of the Sm^{3+} ions go to the $^4F_{7/2}$ excited energy state. Electrons in the $^4F_{7/2}$ get populated in the metastable $^4G_{7/2}$ energy state by non-radiative transitions. The electrons in the metastable state get relaxed by emitting the photon of $^4H_{5/2,\ 7/2\ \text{and}\ 9/2}$. Fig. 7 describes the possible pathway for the emission phenomenon observed in the present system. $^4G_{5/2}\rightarrow{}^4H_{7/2}$ transition peak