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A novel charge transfer blue-emitting phosphor: $BaY_2Si_3O_{10}$

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Abstract

A novel charge transfer blue-emitting phosphor $BaY_2Si_3O_{10}$ has been synthesized by the conventional solid state reaction method. The results of XDR patterns demonstrate that the single-phase $BaY_2Si_3O_{10}$ was formed with $P2_1/m$ symmetry. The excitation spectrum of $BaY_2Si_3O_{10}$ consists of two bands centered at 294 and 333 nm, which are associated with the $^1A_1 \rightarrow {}^1T_2$ and $^1A_1 \rightarrow {}^1T_1$ charge transfer between oxygen 2*p* orbital and the 3*d* orbital of Si^{4+} ions, respectively. Strong emission with the peak position at 426 nm and with the decay time in ns range is revealed. The blue emission is corresponding to the superposition of $^3T_2 \rightarrow {}^1A_1$ and $^3T_1 \rightarrow {}^1A_1$ charge transfer under the near-ultraviolet excitation of 333 nm. The enhancement of the blue luminescence calcining in different atmospheres suggests that a reductive atmosphere is better to form $BaY_2Si_3O_{10}$ particles with a better light yield. The CIE chromaticity coordinates of as-prepared $BaY_2Si_3O_{10}$ are (0.181, 0.148) for air-calcined sample and (0.161, 0.090) for H_2-N_2 calcined one, respectively.

Keywords: C. Optical properties; D. silicate; Phosphors

1. Introduction

Nowadays, rare earth luminescent materials have attracted increasing attentions due to the advantages of high luminous efficiency, energy savings, environmental friendliness, small volume, long persistence and reliability [1,2]. As far as host materials are concerned, a variety of silicates have been developed to be as the host materials for phosphor because of their various crystal structures and high physical-chemical stability [3,4]. Among them, $BaY_2Si_3O_{10}$ is a new trisilicate which was first reported by Kolitsch et al. in 2006 [5]. Until recently, Liu et al. [6] have synthesized rare earth doped versatile phosphors $BaY_2Si_3O_{10}$:RE (RE=Ce^{3+}, Tb^{3+} or Eu^{3+}) and also investigated the photoluminescence properties and applications in VUV and UV LEDs. Nevertheless, the photoluminescence phenomenon of the $BaY_2Si_3O_{10}$ host was not discussed in the literature. It is well known that tungstate [7] with $[WO_4]^{2-}$, molybdate [8,9] with $[MoO_4]^{2-}$ and vanadate [10,11] with isolated tetrahedral $[VO_4]^{3-}$ are efficient hosts with intrinsic emission due to the charge transfer between the oxygen and transition metals. However, to the best of our knowledge, there is no report about the photoluminescence originated from un-doped silicates. Therefore, the emission stemmed from un-doped silicates host is reported for the first time in this article.

In this work, a novel charge transfer blue-emitting phosphor $BaY_2Si_3O_{10}$ has been prepared via solid state reaction method. And the photoluminescence properties and mechanism were studied.

2. Experimental

The $BaY_2Si_3O_{10}$ phosphors were synthesized by the conventional solid state reaction method. $BaCO_3$ (99.99%), Y_2O_3 (99.99%), SiO_2 (A.R) were used as the raw materials. The stoichiometric amounts of starting materials were weighted and mixed in an agate mortar, 5 mol% BaF_2 (A.R) were added as the flux. After adequately grinding, the powders were transferred into two aluminate crucibles

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and calcined at 1350 °C for 4 h in air and a reductive atmosphere of 10% H_2 and 90% N_2, respectively.

The crystal structure of $BaY_2Si_3O_{10}$ phosphors was characterized by X-ray powder diffractmeter (XRD) (Bruker D8 Focus) with Cu-kα ($\lambda = 1.540598$ Å) radiation at 40 kV and 40 mA. Excitation and emission spectra were measured by fluorescence spectrometer (FLUOROMAX-4) with a 150W xenon lamp as excitation source. The lifetime was recorded on a spectro-fluorometer (HORIBA, JOBIN YVON FL3-21), and the 333 nm pulse laser radiation (nano-LED) was used as the excitation source. All the measurements were carried out at room temperature.

3. Results and discussion

The structure of $BaY_2Si_3O_{10}$ is based on zigzag chains, parallel to [010], of edge-sharing distorted YO_6 octahedra, linked by horseshoe-shaped trisilicate groups and Ba atoms in irregular eight-coordination[5,12]. The two symmetry equivalent terminal SiO_4 tetrahedra in the Si_3O_{10} unit adopt an eclipsed conformation with respect to the central SiO_4 tetrahedron as shown in Fig. 1.

Fig. 2 shows the XRD patterns of $BaY_2Si_3O_{10}$ phosphors and the ICSD standard pattern. It can be seen that the as-prepared phosphors are consistent with the $BaY_2Si_3O_{10}$ ICSD standard pattern, indicating that a single-phase $BaY_2Si_3O_{10}$ which belongs to the monoclinic structure was formed [5]. Furthermore, the lattice parameters of the selected $BaY_2Si_3O_{10}$ samples were calculated by the *Celref* program in the monoclinic system based on the given XRD data in Fig. 2, and the corresponding lattice constants are presented in Table 1.

The photoluminescence spectra of $BaY_2Si_3O_{10}$ phosphors are shown in Fig. 3. Line 1 and 2 denote the excitation and emission spectra of air-calcined $BaY_2Si_3O_{10}$, respectively. It can be observed form Fig. 3 that the phosphor shows a broad blue emission band. Obviously, this is an interesting and unique phenomenon because no previous researches of un-doped silicate report such photoluminescence. Specifically, the excitation band monitored at 426 nm is made up of an intense band centered at 333 nm and a weak one peaked at 294 nm. Under the excitation of 333 nm, the emission spectrum exhibits a broad change transfer band range from 370 nm to 600 nm located at 426 nm, as shown in Fig. 3 (line 2). A slight emission peak at about 564 nm also can be found on the longer wavelength tail of the blue emission, which is interpreted as being due to impurities or Schottky defects [13].

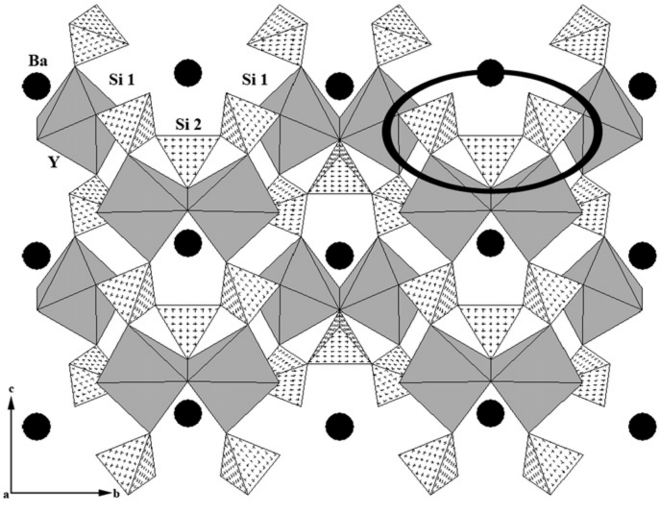

Fig. 1. The crystal structure of $BaY_2Si_3O_{10}$ (originate from Reference [5]).

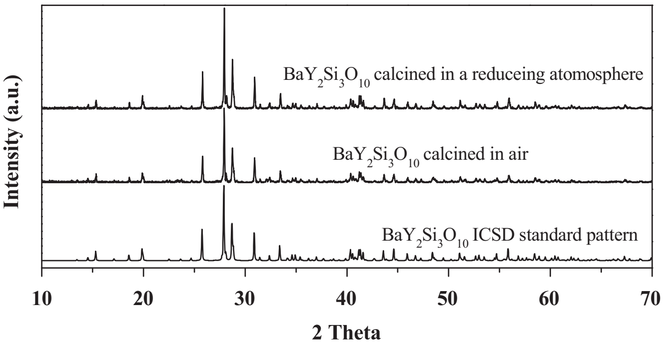

Fig. 2. XRD patterns of $BaY_2Si_3O_{10}$ phosphors and the ICSD standard pattern.

The photoluminescence of $BaY_2Si_3O_{10}$ host can be explained similarly to the luminescence phenomenon corresponding to MnO_4^-, MoO_4^{2-}, WO_4^{2-} and VO_4^{3-} by the model of the MO_4^{n-} complex due to the common closed-shell electronic configurations of those compounds [13]. In this case, Si^{4+} ion is sp^3 orbital hybridization, and shares eight electrons with four oxygen ions. Therefore, the Si^{4+} ion has a closed-shell electronic configurations with no 3*d* electrons. Using a one-electron transition scheme, it can be considered that a one-electron charge transfer process from the oxygen 2*p* orbital (t_1 symmetry in T_d) to the 3*d* orbital (*e* and t_2 symmetry) of Si^{4+} ions. A molecular orbital calculation lead to *e* and t_1 states for the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO), respectively [13]. By taking the $e \rightarrow t_1$ transition into account, the excited electronic states of t_1^5e electronic configuration in T_d symmetry are found to consist of $^3T_1$, $^3T_2$, $^1T_1$ and $^1T_2$ ($^3T_1 \leq {}^3T_2 < {}^1T_1 < {}^1T_2$) in order to increase energies, the ground state being a $^1A_1$ state. The energy level configuration is illustrated in Fig. 3.

According to the above discussion, the two excitation bands centered at 333 nm and 294 nm can be associated with the $^1A_1 \rightarrow {}^1T_1$ and $^1A_1 \rightarrow {}^1T_2$ change transfer of SiO_4^{4-}, respectively. The broad emission band can be fitted into two Gaussian components, presented as the dotted line in Fig. 3. The higher-energy component (line a) centered at 422 nm and the lower-energy component (line b) centered at 472 nm are attributed to the $^3T_2 \rightarrow {}^1A_1$ and $^3T_1 \rightarrow {}^1A_1$ charge transfer of SiO_4^{4-}, respectively.

We compared the photoluminescence properties of the $BaY_2Si_3O_{10}$ samples calcined in a reducing atmosphere

Table 1
Lattice parameters of the selected $BaY_2Si_3O_{10}$ samples.

Samples $BaY_2Si_3O_{10}$	Lattice Parameters				
	a (Å)	***b*** **(Å)**	***c*** **(Å)**	***β*** **(°)**	***V*** **(Å^3)**
Reference[5]	5.399	12.179	6.852	106.37	432.28
air-calcined	5.390	12.174	6.844	106.40	430.83
calcined in reducing atmospheres	5.391	12.178	6.846	106.38	431.18

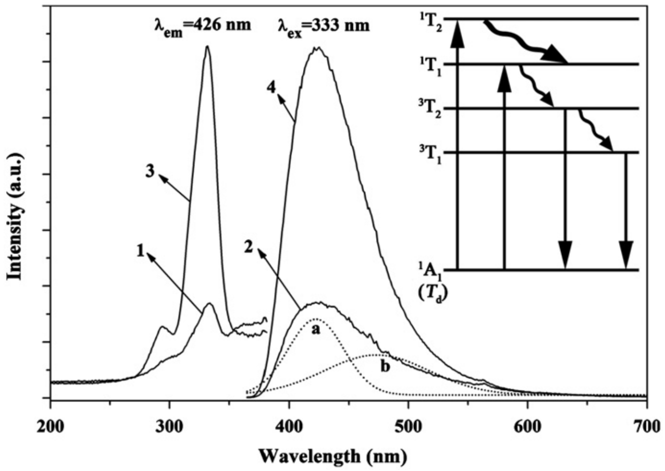

Fig. 3. The photoluminescence spectra of $BaY_2Si_3O_{10}$ phosphors, the insert displays the excitation and emission processes in SiO_4 tetrahedron.

with that of air-calcined samples to show that the calcined atmosphere is also one effect on the photoluminescence properties of phosphors. The excitation and emission spectra of $BaY_2Si_3O_{10}$ calcined in a reducing atmosphere are demonstrated as line 3 and 4 in Fig. 3, respectively. The spectra are consistent with that of air-calcined $BaY_2Si_3O_{10}$ phosphor except for the peak intensity. It can be noted from Fig. 3 that the photoluminescence intensity at 426 nm of air-calcined phosphor is relatively low. However, it is enhanced by 262% while calcined in a reductive atmosphere. Here, the oxygen vacancy deficiency is considered to be responsible for the enhancement of photoluminescence intensity [14–16]. In fact, the calcining in air atmosphere induces the diffusion of oxygen ions into the $BaY_2Si_3O_{10}$ particle thus lowering the oxygen vacancy concentration. Such a process can effectively increase the O^- center concentration [17]. Calcining in a reductive atmosphere induces the reverse process-oxygen diffusion out of the sample, increase of oxygen vacancy and decrease of O^- center concentrations. Based on the above results, calcining atmosphere in the synthesis of phosphors will be possible to get $BaY_2Si_3O_{10}$ particle with a better light yield.

Fig. 4 shows the photoluminescence decay curve of the $BaY_2Si_3O_{10}$ sample. The decay curve can be fitted to single exponential functions as [18,19]

$$I = I_0 \exp(-t/\tau) \qquad (1)$$

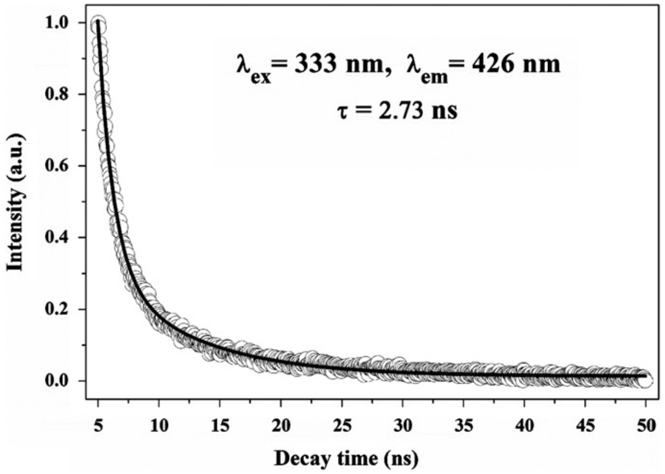

Fig. 4. Photoluminescence decay curve of $BaY_2Si_3O_{10}$ phosphor (excited at 370 nm, monitored at 426 nm).

Where t is the time, I_0 is the initial intensity at $t=0$, τ is the lifetime. Based on the above equation, the lifetime of the $BaY_2Si_3O_{10}$ phosphor is determined to be 2.73 ns.

The CIE 1931 chromaticity coordinates of the phosphors which are calculated based on the corresponding emission spectra are represented in Fig. 5. The chromaticity coordinates of air-calcined $BaY_2Si_3O_{10}$ phosphor are (0.181, 0.148), indicating that the emission color locates in the blue area. However, the chromaticity coordinates of the phosphor calcined in a reductive atmosphere move to (0.161, 0.090), and the emission color change from blue to the purplish blue, as shown in the chromaticity diagram.

4. Conclusions

The bright blue emitting phosphors $BaY_2Si_3O_{10}$ were synthesized by the conventional solid state reaction at 1350 °C. The excitation spectrum presents two bands centered at 294 nm and 333 nm, which are assigned to the $^1A_1 \rightarrow {}^1T_2$ and $^1A_1 \rightarrow {}^1T_1$ charge transfer of SiO_4^{4-}. The phosphors exhibit a strong emission band centered at 426 nm under the excitation of 333 nm. The emission spectrum is attributed to the $^3T_2 \rightarrow {}^1A_1$ and $^3T_1 \rightarrow {}^1A_1$ charge transfer of SiO_4^{4-}. Additionally, the production of the oxygen vacancy deficiency is quite effective to enhance the photoluminescence intensities of $BaY_2Si_3O_{10}$ phosphors. The CIE coordinates of $BaY_2Si_3O_{10}$ calcined in

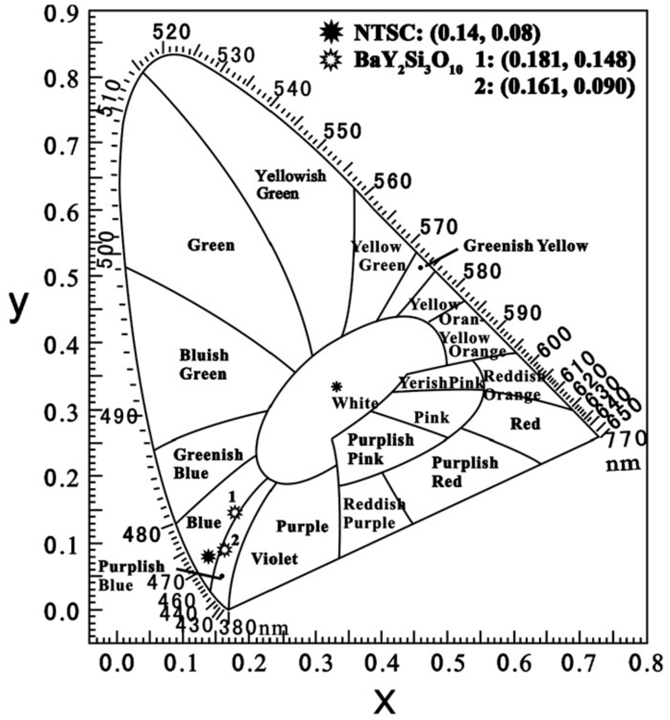

Fig. 5. The CIE 1931 chromaticity coordinates of $BaY_2Si_3O_{10}$ phosphors.

the present and absent of oxygen atmospheres are situated in blue and purplish blue area, respectively. The results indicate that the trisilicate $BaY_2Si_3O_{10}$ without dopant would be a potential blue-emitting phosphor in fluorescent lamps and field emission displays.

Acknowledgments

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