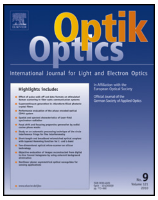
Optik 127 (2016) 1126–1129

Contents lists available at ScienceDirect

Optik

journal homepage: www.elsevier.de/ijleo



# Synthesis and luminescence properties of $BaSO_4$ phosphor activated with Sm

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ARTICLE INFO

*Article history:*
Received 9 February 2015
Accepted 29 October 2015

*Keywords:*
$Sm^{2+/3+}$ ion
Luminescence
Phosphor
Solid state reaction method

ABSTRACT

$BaSO_4$ phosphor activated with Sm are prepared by the high temperature solid state reaction method in air, and its crystal structure, morphology, and luminescence properties are investigated. Broadband PLE spectrum are observed within the range 250–580 nm owing to mainly the 4f–5d transitions of $Sm^{2+}$ ions, and PL spectrum consists seven emission bands in the range of 550–780 nm owing to mainly $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0, 1, 2, and 3) transitions of $Sm^{2+}$ ion and $^4G_{5/2} \rightarrow {}^6H_J$ ($J$ = 5/2, 7/2, and 9/2) transitions of $Sm^{3+}$ ions. $Sm^{2+}$ ions can exist steadily in $BaSO_4$:Sm phosphor sintered at different temperature and time in air. The optimum $Sm^{2+/3+}$ doping concentration, sintering temperature and time are about 2 mol%, 800 °C and 30 min, respectively. The luminous mechanisms are discussed by the schematic energy level diagrams of $Sm^{3+}$ and $Sm^{2+}$ ions.

## 1. Introduction

The number of phosphors suitable for thermoluminescence (TL) dosimetry phosphors has been reported widely owing to their very high TL sensitivity to ionizing radiations and negligible fading, and alkaline-earth sulfates are one of the useful host materials [1,2]. Calcium and barium sulfate phosphors activated with Dy, Tm, Tb, Sm, and Eu have been researched and used widely in the TL dosimetry of γ-rays, X-rays, β-rays, neutrons and high-energy cosmic rays, etc. [3–5], and barium sulfate as the host phosphors can usually give extremely bright TL and high efficiency comparable to the other sensitive phosphors [6]. Therefore, $BaSO_4$ is selected as the research object in the paper.

Divalent samarium is a particularly interesting ion for the investigation of spectral hole burning, laser properties, and excited state absorption, and its luminescence properties in single crystals and glasses has attracted much attention [7–10]. Luminescence from $Sm^{2+}$ ion has also been reported widely, such as BaFCl:Sm, $SrSO_4$:Sm, $SrB_4O_7$:Sm, $BaCl_2$:Sm, $CaF_2$:Sm, etc. [11–14]. However, photoluminescence (PL) property of $BaSO_4$:Sm has seldom been reported except its TL and cathodoluminescence (CL) properties. $Sm^{2+}$ doped materials are usually prepared in the reducing atmosphere or high energy radiation [15,16], and there are few reports on their synthesis by the high temperature solid state reaction method in air.

In the paper, $BaSO_4$ phosphors activated with Sm are prepared by using the high temperature solid state reaction method in air, and its crystal structure, morphology, and luminescence properties are investigated, respectively. To analyze luminescence properties of $BaSO_4$:Sm phosphors, $Sr_{0.96}MoO_4$:$0.04Sm^{3+}$ phosphor is also synthesized by solid state reaction method at 900 °C in air. The origins of emission bands from $BaSO_4$:Sm phosphors are discussed. The relation between emission intensity and Sm ions doping concentration is discussed and the luminous mechanism is explained.

## 2. Experiments

All the chemicals are analytical grade, purchased from the Aladdin Chemical Reagent Company, and used as received without further purification, such as $BaCl_2$ (A.R. 99.9%), $NH_4HSO_4$ (A.R. 99.9%), $MoO_3$ (A.R. 99.9%), $SrCO_3$ (A.R. 99.9%), and $Sm_2O_3$ (99.99%). A series of $Ba_{1-x}SO_4$:$x$Sm ($x$ = 0–6 mol%) phosphors are synthesized by solid state reaction method in air. The stoichiometric raw materials are weighed and well grounded in an agate mortar, then sintered 800 °C for 30 min in air. To analyze luminescence properties of $BaSO_4$:Sm phosphor, $Sr_{0.96}MoO_4$:$0.04Sm^{3+}$ phosphors is synthesized by solid state reaction method at 900 °C in air. All samples are obtained after natural cooling to room temperature in the

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http://dx.doi.org/10.1016/j.ijleo.2015.10.220
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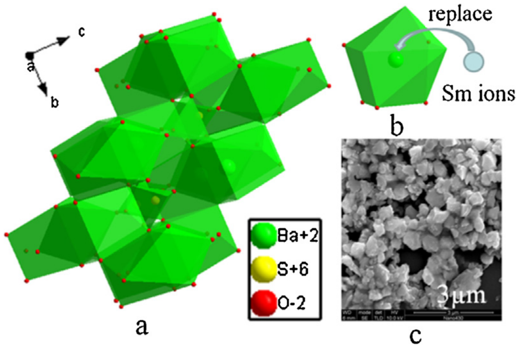

**Fig. 1.** (a) Unit cell of $BaSO_4$ drawn on the basis of ICSD #154286, (b) the coordination polyhedral around Ba atom, and (c) SEM image of $Ba_{0.98}SO_4$:2%Sm phosphor sintered at 800 °C.

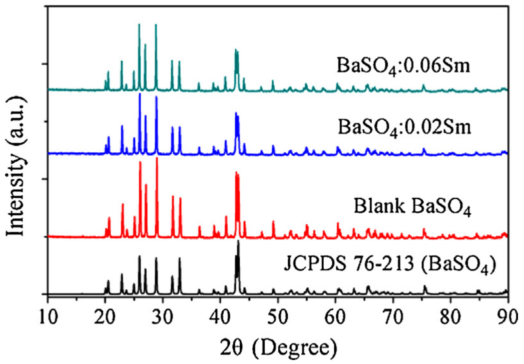

**Fig. 2.** XRD patterns of JCPDS card no. 76-213 ($BaSO_4$), Blank $BaSO_4$, $Ba_{0.98}SO_4$:2%Sm, and $Ba_{0.94}SO_4$:6%Sm phosphors sintered at 800 °C.

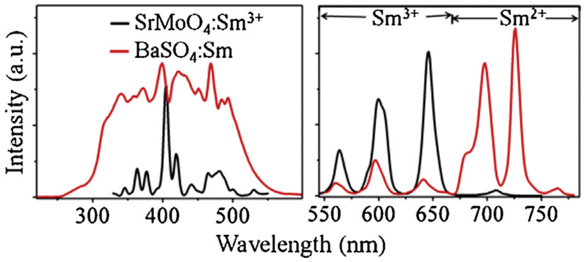

**Fig. 3.** PL and PLE spectra of $Ba_{0.98}SO_4$:0.02Sm phosphor sintered at 800 °C ($\lambda_{ex}$ = 400 nm, $\lambda_{em}$ = 697 nm) and $Sr_{0.96}MoO_4$:0.04$Sm^{3+}$ phosphor sintered at 900 °C ($\lambda_{ex}$ = 405 nm, $\lambda_{em}$ = 611 nm) at room temperature.

furnace. Sintered specimens are sieved to classify the powder size within the range 200–400 nm by using the sieve for fluorescence and chromaticity measurements.

The crystal structures of the phosphors are characterized by X-ray diffractometer (XRD) (Philips Model PW1830) with Cu-Kα radiation at 40 kV and 40 mA. The XRD data are collected in the range $2\theta = 10–90°$ in 0.02° steps at room temperature. The morphologies of the phosphors are inspected using SEM (ZEISS, EVO18) operating at an accelerating voltage of 15 kV. The luminescence properties of the powder phosphors are measured using a FLS920 spectrofluorimeter (Edinburgh) with a high spectral resolution (signal to noise >6000:1) at room temperature, respectively. A 450 W ozone free xenon lamp is used for steady-state measurements.

## 3. Results and discussion

Fig. 1 shows unit cell of $BaSO_4$ drawn on the basis of the Inorganic Crystal Structure Database (ICSD) #154286, the coordination polyhedral around Ba atom and SEM image of $Ba_{0.98}SO_4$:2%Sm phosphor sintered at 800 °C. $BaSO_4$ is isomorphic and crystallize, the isolated [$SO_4$] tetrahedral groups are linked via common edges and corners by the irregular coordination polyhedra of Ba, and the polyhedral around central atom S is tetrahedral structure [17]. According to ICSD # 154286, $BaSO_4$ is described in the orthorhombic crystal system with space-group Pnma (62), and their lattice parameters $a = 8.896(1)$ Å, $b = 5.462(1)$ Å, $c = 7.171(1)$ Å, $v = 348.44(9)$ Å$^3$, $z = 4$ [18]. These $Sm^{2+/3+}$ ions occupy the $Ba^{2+}$ ions site in the host owing to their similar ionic radii ($Sm^{3+}$: ~0.964 Å, $Sm^{2+}$: ~1.11 Å, and $Ba^{2+}$: ~1.35 Å). The morphology of $Ba_{0.98}SO_4$:2%Sm phosphor sintered at 800 °C is irregular particle within the size range 300–500 nm.

XRD patterns of Joint Committee on Powder Diffraction Standards (JCPDS) card no. 76-213 ($BaSO_4$), Blank $BaSO_4$, $Ba_{0.98}SO_4$:2%Sm, and $Ba_{0.94}SO_4$:6%Sm phosphors sintered at 800 °C are shown in Fig. 2. The XRD patterns of these samples match well with the standard data of JCPDS card no. 76-213 ($BaSO_4$). The XRD patterns of other $Ba_{1-x}SO_4$:$x$Sm ($0 \le x \le 0.06$) phosphors are not displayed in Fig. 2, but those patterns are also in line with those of JCPDS card no. 76-213 ($BaSO_4$). No other crystalline phase is formed, and doping of Sm ions does not cause any significant structure changes.

PL and photoluminescence excitation (PLE) spectra of $Ba_{0.98}SO_4$:0.02Sm phosphor sintered at 800 °C ($\lambda_{ex}$ = 400 nm, $\lambda_{em}$ = 697 nm) and $Sr_{0.96}MoO_4$:0.04$Sm^{3+}$ phosphor sintered at 900 °C ($\lambda_{ex}$ = 405 nm, $\lambda_{em}$ = 611 nm) at room temperature are shown in Fig. 3. Broad PLE band of $BaSO_4$:Sm phosphor is observed within the range 250–580 nm owing to the 4f–5d transitions of $Sm^{2+}$ ions [19], and some narrow PLE band peaks located at ~340, 371, 400, 412, and 478 nm are also shown due to $^6H_{5/2} \rightarrow (^4H_{9/2}$, $^6P_{7/2}$, $^4F_{7/2}$, $^6P_{5/2}$, and $^4I_{11/2})$ transition of $Sm^{3+}$ ion, respectively [20]. PL spectrum $BaSO_4$:Sm phosphor consists seven emission bands in the range of 550–780 nm. According to the comparison with $SrMoO_4$:$Sm^{3+}$, PL bands peaking at ~565, 590, and 635 nm are assigned to the intra-4f-shell transitions of $Sm^{3+}$ ion from the excited state $^4G_{5/2}$ to ground levels $^6H_J$ ($J$ = 5/2, 7/2, and 9/2), respectively [21]. The emission of $Sm^{2+}$ results from transitions between levels of the $4f^6$ electron configuration. The ground state levels of $Sm^{2+}$ arise from the $^7F_J$ ($J$ = 0–6) multiplet at successively higher energies, the lowest excited state is $^5D_0$, and the emission is the result of the $^5D_0 \rightarrow {}^7F_J$ transitions. Therefore, The stronger PL bands peaking at ~680, 697, 730, and 765 nm are corresponding to the $^5D_0 \rightarrow {}^7F_J$ ($J$ = 0, 1, 2, and 3) transitions of $Sm^{2+}$ ion, respectively [22,23], and these PL bands of $Sm^{2+}$ in $BaSO_4$:Sm phosphor are broad, which are differ from those sharp line PL bands of $Sm^{2+}$ in other host, such as, $SrB_4O_7$, BaFCl, $BaCl_2$, $SrF_2$, $Sr_4Al_{14}O_{25}$, etc. [8–13,15,16,19]. When $Sm^{3+}$ ion dopes the $Ba^{2+}$ ion in the host, negatively charged Ba vacancy defect ($V_{Ba}^{''}$) can be occur in order to maintain charge balance. The $Sm^{3+}$ ion can be reduced to the $Sm^{2+}$ ion by the negative charge, and $Sm^{2+}$ ion replaces the $Ba^{2+}$ ion position in the host. According to PL and PLE spectra of $Ba_{0.98}SO_4$:0.02Sm phosphor, luminescence center in $BaSO_4$:Sm phosphor are from $Sm^{2+/3+}$ ions, $Sm^{2+}$ ion is main part.

PL spectra of $Ba_{0.98}SO_4$:002Sm phosphors sintered at 800 °C with excitation different wavelength lights at room temperature are shown in Fig. 4. It can be seen that all PL spectra shape are same except changing of the PL intensity, the PL intensity of $Sm^{2+}$ ion in $BaSO_4$:Sm is stronger than those of $Sm^{3+}$ ion, and the PL spectrum of $Sm^{3+}$ ion with excitation different wavelength lights except 400 nm are weak. These results indicate that luminescence center source in $BaSO_4$:Sm phosphor are from $Sm^{2+/3+}$ ions, $Sm^{2+}$ ion is main luminescence center source, and PL intensity of $Sm^{3+}$ can be decreased by electing excitation wavelength light.

PL spectra of $Ba_{1-x}SO_4$:$x$Sm ($0 \le x \le 0.06$) phosphors at 800 °C ($\lambda_{ex}$ = 400 nm) at room temperature and the relation between PL intensity and Sm doping concentration are shown in Fig. 5. PL spectrum of $BaSO_4$ host is not observed. PL spectra shapes and