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Crystal structure and luminescence properties of novel $Sr_{10-x}(SiO_4)_3(SO_4)_3O{:}xEu^{2+}$ phosphor with apatite structure

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ABSTRACT

In this paper, a series of novel luminescent $Sr_{10-x}(SiO_4)_3(SO_4)_3O{:}xEu^{2+}$ phosphors with apatite structure were synthesized by a high temperature solid-state reaction. The phase structure, photoluminescence (PL) properties, as well as the PL thermal stability were investigated. $Sr_{9.92}(SiO_4)_3(SO_4)_3O{:}0.08Eu^{2+}$ phosphor exhibits better thermal quenching resistance, retaining the luminance of 66.55% at 150 °C compared with that at 25 °C. The quenching concentration of Eu^{2+} in $Sr_{10}(SiO_4)_3(SO_4)_3O$ was about 0.08 (mol) with the dipole–quadrupole interaction. The $Sr_{10-x}(SiO_4)_3(SO_4)_3O{:}xEu^{2+}$ phosphors exhibited a broad-band green emission at 538 nm upon excitation at 396 nm. The results indicate that $Sr_{10-x}(SiO_4)_3(SO_4)_3O{:}xEu^{2+}$ phosphors have potential applications as near UV-convertible phosphors for white-light UV LEDs.

1. Introduction

As we know, white light emitting diodes (*w*-LEDs) solid-state lighting technology has been widely used and attracted lots of research interests due to their promising features, such as low power consumption, high efficiency, as well as environmental friendliness characteristics [1–4]. In general, the typical *w*-LEDs can be obtained by a combination of a yellow-emitting $Y_3Al_5O_{12}{:}Ce^{3+}$ phosphor and a blue InGaN chip [5]. However, these phosphors are suffering from some disadvantages such as poor color-rendering index and high correlated color temperature caused by the weak red emission. Therefore, it is necessary to introduce bright tricolor (red, green, and blue) phosphors for the development of tricolor emission phosphors upon *n*-UV light (350–420 nm) [6,7]. It is known to us that the rare earth ions plays an important and irreplaceable role in lighting and display fields for their $4f\rightarrow4f$ or $5d\rightarrow4f$ transitions. As a highly efficient activator, Eu^{2+} has a wide range of emission ascribed to the allowed $4f^65d^1\rightarrow4f^7$ transitions, which has been widely investigated in many compounds, such as $Sr_5(PO_4)_3Cl{:}Eu^{2+}$ [8], $BaMgAl_{10}O_{17}{:}Eu^{2+}$ [9], $Ca_3Si_2O_7{:}Eu^{2+}$ [10]. Thus, it is necessary to find new hosts with a specific crystal field to accommodate Eu^{2+} ions.

Alternatively, compounds with apatite structure have attracted many attentions due to their excellent stability and compatibility with efficient luminescent in *n*-UV LEDs. Therefore, many apatite structure type phosphors for *w*-LEDs application have been widely developed, such as $Ca_9Mg(PO_4)_6F_2{:}Eu^{2+}$, Mn^{2+} [11], $Ca_2Gd_8(SiO4)_6O_2{:}Eu^{3+}$ [12], $Ca_4Y_6(SiO_4)_6O{:}Ce^{3+}/Mn^{2+}/Tb^{3+}$, [13], and $Na_6(SO_4)_2FCl{:}RE$ [14]. To the best of our knowledge, the $Sr_{10}(SiO_4)_3(SO_4)_3O{:}Eu^{2+}$ phosphor has not been reported up to now.

In the present work, we successfully synthesized $Sr_{10-x}(SiO_4)_3(SO_4)_3O{:}xEu^{2+}$ phosphors with apatite structure for the first time. The relationship between the crystal structure and the luminescence properties of Eu^{2+} in $Sr_{10}(SiO_4)_3(SO_4)_3O$ (SSSO) host was investigated in detail. Results show that the SSSO:Eu^{2+} phosphors can be potentially applied as the green-emitting component in *w*-LEDs.

2. Experimental procedure

2.1. Materials and synthesis

SSSO:xEu^{2+} phosphors were synthesized by a traditional high temperature solid-state reaction method. Stoichiometric amounts of raw materials $SrCO_3$ (Aldrich, 99.9%), SiO_2 (Aldrich, 99.9%), SrSO4 (Aldrich, 99.9%)and Eu_2O_3 (A.R.) were weighed and mixed by grinding in an agate mortar. The mixture was firstly pre-heated at 650 °C for 3 h in air atmosphere in alumina crucibles. After the preliminary products were ground thoroughly in an agate mortar

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after cooling to room temperature, they were placed into alumina crucibles and annealed at 1150 °C in a reducing atmosphere in flowing gas (10% H_2+90% N_2) for 5 h. After firing, the samples were gradually cooled to room temperature in the furnace. The products were crushed and finally obtained for measurements.

2.2. Characterization methods

The phase structures of the as-prepared samples were checked by X-ray powder diffractometer (D/max-rA 12kw, Japan) with Cu Kα radiation (λ=1.5418 Å) from 4° to 70° (2θ). The step scanning rate (2θ values ranging from 10 to 120°) used for Rietveld analysis was 2 s/step with a step size of 0.02°. Rietveld refinement of the structure of the select $Sr_{9.92}(SiO_4)_3(SO_4)_3O:0.08Eu^{2+}$ was performed by using the computer software TOPAS [15]. Room temperature photoluminescence excitation (PLE) and emission (PL) spectra were measured on a fluorescence spectrophotometer (F-4600, HITACHI, Japan) with a photomultiplier tube operating at 400 V, and a 150 W Xe lamp was used as the excitation lamp. Besides, the temperature-dependence luminescence properties were measured on the same spectrophotometer combined with a self-made heating attachment and a computer-controlled electric furnace.

3. Results and discussion

3.1. Phase purity and structure

The XRD patterns of the standard $Sr_{10}(PO_4)_6O$ (ICSD no. 168209) [16] and $Sr_{10-x}(SiO_4)_3(SO_4)_3O:xEu^{2+}$ (x=0.002, 0.04, 0.06, 0.08, and 0.10) samples are shown in Fig. 1. It is obvious that the XRD patterns of all the $Sr_{10-x}(SiO_4)_3(SO_4)_3O:xEu^{2+}$ phosphors can be exactly assigned to the phase of $Sr_{10}(PO_4)_6O$ (ICSD no. 168209), belonging to hexagonal structure with the group space $P6_3/m$, and no second phases is observed. Thus, doping of Eu^{2+} does not cause any detectable change in the crystal lattice. As we know, Sr^{2+} ions have two different coordination numbers (CN) in the structure of SSSO. Sr1 is defined as being nine-fold coordinated, and Sr2 is defined as being seven-fold coordinated. The effective ionic radii of Eu^{2+} (r=1.20 Å for CN=7 and r=1.30 Å for CN=9) is the close to that of Sr^{2+} (r=1.21 Å for CN=7 and r=1.31 Å for CN=9) [17]. Therefore, we suggest that the activators Eu^{2+} ions are expected to occupy the Sr^{2+} sites randomly in the SSSO host. To better understand the crystallographic sites of Eu^{2+} in SSSO, the powder diffraction data of $Sr_{9.92}(SiO_4)_3(SO_4)_3O:0.08Eu^{2+}$ was collected at room temperature for Rietveld analysis. Rietveld refinement was performed by using TOPAS 4.2. Almost all peaks were indexed by hexagonal cell ($P6_3/m$) with parameters close to $Sr_{10}(PO_4)_6O$ (apatite-type structure). Therefore crystal structure of $Sr_{10}(PO_4)_6O$ was taken as starting model for Rietveld refinement. The inset of Fig. 2 illustrates the structure of SSSO compound. As given in the inset of Fig. 2, The P atoms are tetrahedrally coordinated forming [SiO_4] or [SO_4] groups, which are isolated from each other. There are two independent sites for Sr^{2+} ions in the structure and both of them were occupied by Eu^{2+} ion with fixed occupancy p=0.08 and Sr ion with p=0.992. One P site in an asymmetric unit was occupied by Si and S ions with p=0.5, respectively, according to suggested formula. Refinement was stable and gives low R-factors (Table 1, Fig. 2). The reliability parameters of refinement are R_{wp}=9.37%, R_p=7.04%, and GOF=2.42, which can verify the phase purity of the as-prepared sample. Fractional atomic coordinates and isotropic displacement parameters (Å^2) of $Sr_{9.92}(SiO_4)_3(SO_4)_3O:0.08Eu^{2+}$ is shown in Table 2. Besides, the small refined residual factors indicate that Eu^{2+} can occupy both types of Sr^{2+} sites with seven- or nine-fold coordination randomly.

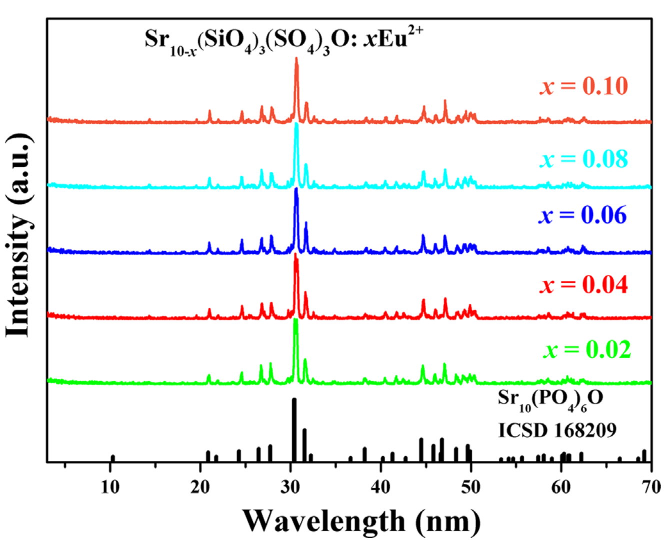

Fig. 1. The XRD patterns of $Sr_{10-x}(SiO_4)_3(SO_4)_3O:xEu^{2+}$ (x=0.002, 0.04, 0.06, 0.08, and 0.10), and the standard data for $Sr_{10}(PO_4)_6O$ (ICSD card no. 168209) is shown as a reference.

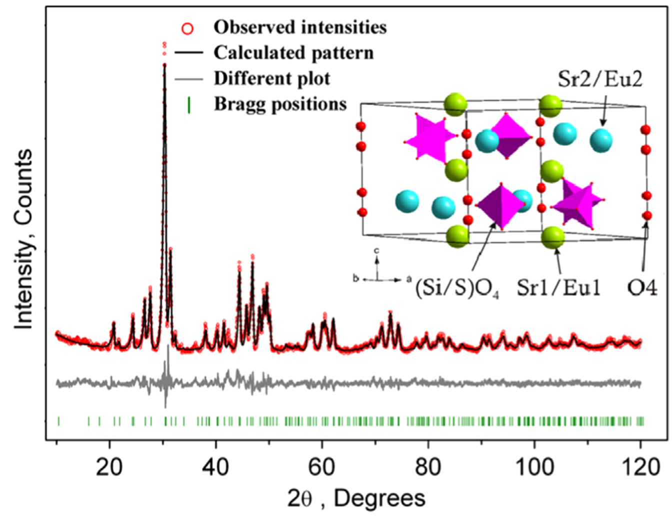

Fig. 2. Rietveld analysis patterns for X-ray powder diffraction data of $Sr_{9.92}(SiO_4)_3(SO_4)_3O:0.08Eu^{2+}$. The solid black lines are calculated intensities, and the red dots are the observed intensities. The gray solid lines below the profiles stand for the difference between the observed and calculated intensities. The short green vertical lines show the position of Bragg reflections of the calculated pattern, and the inset of this figure shows the crystal Structure of $Sr_{10}(SiO_4)_3(SO_4)_3O$ compound. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1
Main parameters of processing and refinement of the $Sr_{9.92}(SiO_4)_3(SO_4)_3O:0.08Eu^{2+}$.

Compound	$Sr_{9.92}(SiO_4)_3(SO_4)_3O:0.08Eu^{2+}$
Space group	$P6_3/m$
a, Å	9.8103(7)
c, Å	7.2593(6)
V, Å^3	605.0(1)
2θ-interval, °	10–120
No. of reflections	332
No. of refined parameters	46
R_{wp}, %	9.37
R_p, %	7.04
R_{exp}, %	3.88
$\chi 2$	2.42
R_B, %	2.85