Crystal structure and luminescence properties of novel Sr$_{10-x}$(SiO$_4$)$_3$(SO$_4$)$_3$O:xEu$^{2+}$ phosphor with apatite structure

Qingfeng Gua, Bin Ma a, Libing Liaoa, Maxim S. Molokeevb,c, Lefu Meia, Haikun Liua

a Beijing Key Laboratory of Materials Utilization of Nonmetallic Minerals and Solid Wastes, National Laboratory of Mineral Materials, School of Materials Sciences and Technology, China University of Geosciences, Beijing 100083, China
b Laboratory of Crystal Physics, Institute of Physics, SB RAS, Krasnoyarsk 660036, Russia
c Department of Physics, Far Eastern State Transport University, Khabarovsk 680021, Russia

A R T I C L E   I N F O
Article history:
Received 28 December 2015
Received in revised form 15 April 2016
Accepted 15 April 2016
Available online 16 April 2016

Keywords:
Crystal structure
Apatite
Phosphor

A B S T R A C T
In this paper, a series of novel luminescent Sr$_{10-x}$(SiO$_4$)$_3$(SO$_4$)$_3$O: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$_4$)$_3$O: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$_{9.92}$(SiO$_4$)$_3$(SO$_4$)$_3$O was about 0.08 mol with the dipole–quadrupole interaction. The Sr$_{10-x}$(SiO$_4$)$_3$(SO$_4$)$_3$O: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$_4$)$_3$O:xEu$^{2+}$ phosphors have potential applications as near UV-convertible phosphors for white-light UV LEDs.

© 2016 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

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$_3$Al$_5$O$_{12}$: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 4$f$→4$f$ or 5$d$→4$f$ transitions. As a highly efficient activator, Eu$^{2+}$ has a wide range of emission ascribed to the allowed 4$f$→5$d$,→4$f$ transitions, which has been widely investigated in many compounds, such as Sr$_2$(PO$_4$)$_3$:Cl:Eu$^{2+}$ [8], BaMgAl$_2$O$_4$:Eu$^{2+}$ [9], Ca$_3$Si$_2$O$_5$: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$_{9.5}$Mg$_{0.5}$(PO$_4$)$_3$:F$_2$-Eu$^{2+}$, Mn$^{2+}$ [11], Ca$_{9}$Gd$_{1}$SiO$_4$:O$_2$:Eu$^{3+}$ [12], Ca$_{4}$Y$_{6}$(SiO$_4$)$_2$:O$_2$:Ce$^{3+}$/Mn$^{2+}$/Tb$^{3+}$ [13], and Na$_{6}$(SO$_4$)$_2$:FCl:RE [14]. To the best of our knowledge, the Sr$_{10}$(SiO$_4$)$_3$(SO$_4$)$_3$O:Eu$^{2+}$ phosphor has not been reported up to now.

In the present work, we successfully synthesized Sr$_{10-x}$(SiO$_4$)$_3$(SO$_4$)$_3$O: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$_4$)$_3$O (SSSO) host was investigated in detail. Results show that the SSSO:Eu$^{2+}$ phosphors can be potentially applied as the green-emanating 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%), SrSO$_4$ (Aldrich, 99.9%) and Eu$_2$O$_3$ (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...
after cooling to room temperature, they were placed into alumina crucibles and annealed at 1150 °C in a reducing atmosphere in flowing gas (10% H2 + 90% N2) 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°/step with a step size of 0.02°. Rietveld refinement of the structure of the select Sr10(SiO4)3(SO4)3O·0.08Eu2+ 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 Sr10(P2O7)O (ICSD no. 168209) [16] and Sr10–x(SiO4)x(SO4)3O·xEu2+ (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 Sr10–x(SiO4)x(SO4)3O·xEu2+ phosphors can be exactly assigned to the phase of Sr10(P2O7)O (ICSD no. 168209), belonging to hexagonal structure with the group space P63/m, and no second phases is observed. Thus, doping of Eu2+ does not cause any detectable change in the crystal lattice. As we know, Sr2+ 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 Eu2+ (r = 1.20 Å for CN = 7 and r = 1.30 Å for CN = 9) is the close to that of Sr2+ (r = 1.21 Å for CN = 7 and r = 1.31 Å for CN = 9) [17]. Therefore, we suggest that the activators Eu2+ ions are expected to occupy the Sr2+ sites randomly in the SSSO host. To better understand the crystallographic sites of Eu2+ in SSSO, the powder diffraction data of Sr10(SiO4)x(SO4)3O·0.08Eu2+ 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 (P63/m) with parameters close to Sr10(P2O7)O (apatite-type structure). Therefore crystal structure of Sr10(P2O7)O 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 [SiO4] or [SO4] groups, which are isolated from each other. There are two independent sites for Sr2+ ions in the structure and both of them were occupied by Eu2+ ion with fixed occupancy x = 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 Rwp = 9.37%, Rp = 7.04%, and GOF = 2.42, which can verify the phase purity of the as-prepared sample. Fractional atomic coordinates and isotropic displacement parameters (Å2) of Sr10(SiO4)x(SO4)3O·0.08Eu2+ is shown in Table 2. Besides, the small refined residual factors indicate that Eu2+ can occupy both types of Sr2+ sites with seven- or nine-fold coordination randomly.

![Fig. 1. The XRD patterns of Sr10–x(SiO4)x(SO4)3O·xEu2+ (x = 0.002, 0.04, 0.06, 0.08, and 0.10), and the standard data for Sr10(P2O7)O (ICSD no. 168209) is shown as a reference.](image)

![Fig. 2. Rietveld analysis patterns for X-ray powder diffraction data of Sr10(SiO4)x(SO4)3O·0.08Eu2+. 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 Sr10(SiO4)x(SO4)3O compound. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image)

| Table 1 | Main parameters of processing and refinement of the Sr10(SiO4)x(SO4)3O·0.08Eu2+.
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>Sr10(SiO4)x(SO4)3O·0.08Eu2+</td>
</tr>
<tr>
<td>Space group</td>
<td>P63/m</td>
</tr>
<tr>
<td>a, Å</td>
<td>9.103(7)</td>
</tr>
<tr>
<td>c, Å</td>
<td>7.5939(6)</td>
</tr>
<tr>
<td>V, Å³</td>
<td>605.0(1)</td>
</tr>
<tr>
<td>2θ-interval, °</td>
<td>10–120</td>
</tr>
<tr>
<td>No. of reflections</td>
<td>332</td>
</tr>
<tr>
<td>No. of refined parameters</td>
<td>46</td>
</tr>
<tr>
<td>Rwp, %</td>
<td>9.37</td>
</tr>
<tr>
<td>Rp, %</td>
<td>7.04</td>
</tr>
<tr>
<td>Rwp, %</td>
<td>3.88</td>
</tr>
<tr>
<td>J2</td>
<td>2.42</td>
</tr>
<tr>
<td>Rp, %</td>
<td>2.85</td>
</tr>
</tbody>
</table>
earlier discussion by Van Uitert, the emission position of Eu

The effective ionic radius of Sr$_2$

ions (34,000 cm$^{-1}$) to obey the following equation:

$$E = Q - \left( \frac{V}{4} \right) 10^{n-x_{E-80}}$$

(1)

Where $E$ represents the position of the rare-earth ion emission peak (cm$^{-1}$), $Q$ is the energy position of the lower d-band edge for the free ions (34,000 cm$^{-1}$ for Eu$^{2+}$), $V$ stands for the valence of the active cation $V_{\text{active}}$ for Eu$^{2+}$, $n$ is the number of ions in the immediate shell around the active cation, $r$ is the effective radius of the host cations (Sr$^{2+}$) replaced by the Eu$^{2+}$ ion ($\bar{A}$), and $E$ is the electron affinity of the atoms that form anions, which is constant in the same host.

The effective ionic radius of Sr$^{2+}$ with nine-coordination is bigger than that with seven-coordination. Thus, we proposed that the emission peaks centered at 529 and 555 nm are attributed to Eu$^{2+}$ ions with nine-coordination and seven-coordination, respectively.

3.2. Luminescence properties

The representative photoluminescence excitation (PLE) and photoluminescence (PL) spectra of the as-prepared Sr$_{0.92}$(SiO$_4$)$_3$(SO$_4$)$_3$:0.08Eu$^{2+}$ phosphor are presented in Fig. 2. The PLE spectrum of the phosphor shows a broad absorption centered at 396 nm ranging from 250 to 525 nm, which is attributed to the 4f-5d transitions of the doped Eu$^{2+}$ ions. Under the excitation at 396 nm, the PL spectrum exhibits a green emission band peaked at 538 nm. In addition, the PL spectrum can be divided into two dotted bands centered at about 529 and 555 nm by using Gaussian fitting, as shown in Fig. 3. Based on the earlier discussion by Van Uitert, the emission position of Eu$^{2+}$ ions is strongly dependent on its local crystal environment, which is suggested to obey the following equation: [18,19]

$$E = Q - \left( \frac{V}{4} \right) 10^{n-x_{E-80}}$$

(1)

Where $E$ represents the position of the rare-earth ion emission peak (cm$^{-1}$), $Q$ is the energy position of the lower d-band edge for the free ions (34,000 cm$^{-1}$ for Eu$^{2+}$), $V$ stands for the valence of the active cation (V$_{\text{active}}$), $n$ is the number of ions in the immediate shell around the active cation, $r$ is the effective radius of the host cations (Sr$^{2+}$) replaced by the Eu$^{2+}$ ion (Å), and $E$ is the electron affinity of the atoms that form anions, which is constant in the same host. The effective ionic radius of Sr$^{2+}$ with nine-coordination is bigger than that with seven-coordination. Thus, we proposed that the emission peaks centered at 529 and 555 nm are attributed to Eu$^{2+}$ ions with nine-coordination and seven-coordination, respectively.

**Table 2**

| Fractional atomic coordinates and isotropic displacement parameters (Å$^2$) of Sr$_{0.92}$(SiO$_4$)$_3$(SO$_4$)$_3$:0.08Eu$^{2+}$. |
|---|---|---|---|---|
| x | y | z | Biso |
| Sr1 | 1/3 | 2/3 | $-0.0009$ (9) | 0.9 (2) | 0.992 |
| Eu1 | 1/3 | 2/3 | $-0.0009$ (9) | 0.9 (2) | 0.008 |
| Sr2 | 0.0112 (5) | 0.2488 (3) | 0.25 | 1.1 (1) | 0.992 |
| Eu2 | 0.0112 (5) | 0.2488 (3) | 0.25 | 1.1 (1) | 0.008 |
| Si | 0.4090 (9) | 0.3753 (8) | 0.25 | 0.4 (2) | 0.5 |
| S | 0.4090 (9) | 0.3753 (8) | 0.25 | 0.4 (2) | 0.5 |
| O1 | 0.326 (2) | 0.490 (2) | 0.25 | 1.5 (3) | 1 |
| O2 | 0.398 (2) | 0.475 (2) | 0.25 | 1.5 (3) | 1 |
| O3 | 0.250 (1) | 0.278 (1) | 0.25 | 1.5 (3) | 1 |
| O4 | 0 | 0 | 0.170 (6) | 1.5 (3) | 0.25 |

Fig. 3. PLE (left) and PL (right) spectrum of the selected Sr$_{0.92}$(SiO$_4$)$_3$(SO$_4$)$_3$:0.08Eu$^{2+}$ fitted by Gaussian.

**Fig. 4.** The PL spectra of Sr$_{10-x}$(SiO$_4$)$_3$(SO$_4$)$_3$:O:xEu$^{2+}$ ($x=0.002, 0.04, 0.06, 0.08$, and $0.10$) phosphors under 396 nm excitation, and the inset of Fig. 4 shows the Eu$^{2+}$ doping concentration dependent PL intensity. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

**Fig. 4** displays the PL spectra of Sr$_{10-x}$(SiO$_4$)$_3$(SO$_4$)$_3$:O:xEu$^{2+}$ phosphors ($x=0.002, 0.04, 0.06, 0.08$, and $0.10$) under 396 nm light excitation, and the inset of Fig. 4 shows the Eu$^{2+}$ doping concentration dependent PL intensity. The result displayed that the optimal doping concentration of Eu$^{2+}$ in SSSO host was 0.08 mol. It can be easily seen that the PL intensity would decrease when the concentration exceeds the critical concentration, which is caused by the concentration quenching effect. Moreover, the critical energy transfer distance $R_c$ between Eu$^{2+}$ ions can be estimated by using concentration quench equation proposed by Blasse: [20,21]

$$R_c \approx 2\left[\frac{3V}{4\varepsilon\chi N}\right]^{1/3}$$

(2)

Where $V$ stands for the volume of the unit cell, $\chi_x$ is the atom fraction of activator at which the quenching occurs, and $N$ represents the number of host cations in the unit cell. For the SSSO host, $N=10$, $V$ is estimated to be 605.01 Å$^3$, $\chi_x$ is 0.08 for emission peak at 538 nm. The critical distances $R_c$ of energy transfer can be estimated to be about 10.41 Å ($x_e=0.08$) using Eq. (2). Furthermore, the non-radiative transitions between Eu$^{2+}$ ions took place via electric multipolar interactions with $R_c$ more than 5 Å according to the Dexter theory. Moreover, the interaction type between sensitizers or between sensitizer and activator can be calculated by the following equation: [22,23]

$$I = k \left[1 + \beta x \theta\right]^{-1}$$

(3)

where $I$ is the emission intensity, $x$ stands for the activator concentration, $K$ and $\beta$ are constants for each type of interaction for a given host lattice, and $\theta$ is an indication of electric multipolar character. In general, $\theta=6, 8, 10$ can be assigned to dipole–dipole (d–d), dipole–quadrupole (d–q), quadrupole–quadrupole (q–q) interactions, respectively. **Fig. 5** illustrates the fitting line of log($I$) vs. log($x$) in Sr$_{10-x}$(SiO$_4$)$_3$(SO$_4$)$_3$:O:xEu$^{2+}$ phosphors for the emission peak of 538 nm beyond the quenching concentration. The fitting line was found to be relatively linear with a slope equal to $-\theta/3$, and the slope was determined to be $-1.447$. Therefore, the value of $\theta$ can be calculated to be 4.341. In this case, dipole–dipole interactions play the dominant role for concentration quenching of Eu$^{2+}$ ions in Sr$_{10-x}$(SiO$_4$)$_3$(SO$_4$)$_3$:O:xEu$^{2+}$ phosphors.
The thermally stable luminescence properties of Sr$_{9.92}$(SiO$_4$)$_3$(SO$_4$)$_3$O:0.08Eu$^{2+}$ phosphor has been monitored by 396 nm from 25 °C to 250 °C, and the temperature dependence PL spectra of Sr$_{9.92}$(SiO$_4$)$_3$(SO$_4$)$_3$O:0.08Eu$^{2+}$ sample are shown in Fig. 6(a) and (b), respectively. The emission intensities of the sample decrease gradually with the temperature increases, and Sr$_{9.92}$(SiO$_4$)$_3$(SO$_4$)$_3$O:0.08Eu$^{2+}$ phosphor seems to possess good thermal stability. Besides, the emission wavelength shows slight blue shift from 538 to 530 nm with raising temperature, which was caused by the thermally active phonon-assisted excitation from the lower-energy emission band to the higher-energy emission band in the excited states of Eu$^{2+}$ [24]. The PL intensity of Sr$_{9.97}$(PO$_4$)$_6$O:0.03Eu$^{2+}$ drops to 66.55% when the temperature is raised to 150 °C compared with that of 25 °C.

In order to give a quantitative analysis on the thermal stable luminescence behavior of Sr$_{9.92}$(SiO$_4$)$_3$(SO$_4$)$_3$O:0.08Eu$^{2+}$ phosphor, the Arrhenius equation were employed to calculate the activation energy as following: [25,26]

$$I_T = \frac{I_0}{1 + c \exp \left( \frac{-E}{kT} \right)}$$

Where $I_0$ is the initial intensity, $I_T$ is the intensity at a given temperature $T$, $c$ is a constant, $E$ is the activation energy for thermal quenching, and $k$ is the Boltzmann’s constant (8.617 × 10$^{-5}$ eV K$^{-1}$). Based on the equation, the activation energy $E$ can be calculated via a linear fitting of ln[$(I_0/I_T)-1$] against 1/kT, where a straight slope equals $-E$. Therefore, $E$ was intended to be 0.168 eV for Sr$_{9.92}$(SiO$_4$)$_3$(SO$_4$)$_3$O:0.08Eu$^{2+}$ phosphor shown in Fig. 7.

CIE chromaticity coordinates $(x, y)$ of the Sr$_{9.92}$(SiO$_4$)$_3$(SO$_4$)$_3$O:0.08Eu$^{2+}$ phosphor calculated through its PL spectrum and the digital image of the sample under 365 nm UV lamp excitation are shown in Fig. 8. The color coordinate is calculated to be (0.3246, 0.6243), and the phosphor shows intense green emission shown in the inset of Fig. 8. Therefore, this phosphor can be used as a green-emitting phosphor for $n$-UV w-LEDs.
the concentration quenching of Eu$^{2+}$ coordination. Moreover, the dipole citation band locates in the 250–300 nm broad absorption in the near UV regions and the optimum excitation at 396 nm. In addition, SSSO:Eu$^{2+}$ phosphor exhibits a broad-band green emission at 538 nm under excitation at 365 nm.

4. Conclusions

In summary, a novel apatite structure phosphor SSSO:Eu$^{2+}$ has been synthesized and investigated in this paper. The SSSO:Eu$^{2+}$ phosphor exhibits a broad-band green emission at 538 nm under the excitation at 396 nm. In addition, SSSO:Eu$^{2+}$ shows strong and broad absorption in the near UV regions and the optimum excitation band locates in the 250–525 nm region. Eu$^{2+}$ can occupy both the Sr1 site with nine-coordination and Sr2 site with seven-coordination. Moreover, the dipole–dipole interactions results in the concentration quenching of Eu$^{2+}$ in SSSO:Eu$^{2+}$. The Sr$_{9.92}$(SiO$_4$)$_3$(SO$_4$)$_3$O:0.08Eu$^{2+}$ phosphor shows high thermal quenching temperature (66.55% of the initial intensity at 150 °C). The above results demonstrate the SSSO:Eu$^{2+}$ phosphor can be used as green emitting phosphor in the w-LEDs.

Acknowledgments

This present work is supported by the National Natural Science Foundation of China (Grant no. 41172053).

References

[3] Q.F. Guo, L.B. Liao, Z.G. Xia, Luminescence properties and energy transfer in La$_{6}$Ba$_{4}$Si$_{3}$O$_{8}$F$_{x}$:Ce$^{3+}$/Tb$^{3+}$ phosphors, J. Lumin. 145 (2014) 65–70.