Short Communication

Facile combustion synthesis and photoluminescence properties of Ce\(^{3+}\) doped Sr\(_2\)La\(_8\)(SiO\(_4\))\(_6\)O\(_2\) phosphors

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The Sr\(_2\)La\(_8\)(SiO\(_4\))\(_6\)O\(_2\):Ce\(^{3+}\) powder phosphor with apatite structure has been successfully synthesized via a facile route of sol-combustion technique. X-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM), and photoluminescence (PL) spectroscopy were used to characterize the as-prepared samples. Sr\(_2\)La\(_8\)(SiO\(_4\))\(_6\)O\(_2\):Ce\(^{3+}\) phosphor was composed of particles with average sizes range about 300 nm. The phosphor exhibited an absorption ranging from 220 to 390 nm in ultraviolet range and a broad blue-violet emission band peaked at 403 nm with a CIE coordinates of (0.167, 0.028). The concentration quenching mechanism was also determined to be dipole–dipole interaction.

1. Introduction

As an important activator for luminescent materials, the broad band emitting rare earth ion Ce\(^{3+}\) has attracted great attention owing to many favorable advantages, such as unique emission properties, short decay time, and small stokes shift [1–3]. The Ce\(^{3+}\) ion shows allowed optical transitions in absorption and emission due to transition between the 4\(^f\) ground state and the crystal field components of the 5d excited state configuration. It is well-known that the 4\(^f\) ground state of Ce\(^{3+}\) shows a spin orbit splitting into two levels (\(^2\)\(^F\)\(_{5/2}\) and \(^2\)\(^F\)\(_{7/2}\)) and the theoretical energy difference of this splitting between \(^2\)\(^F\)\(_{5/2}\) and \(^2\)\(^F\)\(_{7/2}\) level is about 2000 cm\(^{-1}\) [4]. As the 4\(^f\)–5d transitions are parity allowed, the 4\(^f\)–5d transition of Ce\(^{3+}\) ions can usually show superior absorption in the spectral region of 200–450 nm, therefore, many Ce\(^{3+}\) ion doped phosphors for w-LEDs application have been developed [5–9].

Silicate oxyapatites with a general chemical formula as A\(_2\)RE\(_8\)(SiO\(_4\))\(_6\)O\(_2\) (A = Ca\(^{2+}\), Sr\(^{2+}\), Ba\(^{2+}\), Mg\(^{2+}\), etc. and RE = La\(^{3+}\), Y\(^{3+}\), Gd\(^{3+}\), Lu\(^{3+}\), etc.) are rigid and stable materials with variety of compositional substitutions for rare-earth activators, as they possess the capability of substituting by versatile ions and forming solid solution [10–12]. Recently, several groups focus on the investigation of the oxyapatite structure of the Ba\(_2\)Gd\(_8\)(SiO\(_4\))\(_6\)O\(_2\):Eu\(^{3+}\) [13], and Mg\(_2\)Y\(_8\)(SiO\(_4\))\(_6\)O\(_2\):Ce\(^{3+}\)/Tb\(^{3+}\)/Mn\(^{2+}\) [14]. However, the synthetic temperature is too high. In the present work, we report the synthesis of Sr\(_2\)La\(_8\)(SiO\(_4\))\(_6\)O\(_2\):Ce\(^{3+}\) phosphor with apatite structure by a facile route of sol-combustion technique for the first time. Additional, we carry out concentration quenching of Ce\(^{3+}\) in Sr\(_2\)La\(_8\)(SiO\(_4\))\(_6\)O\(_2\), and the corresponding luminescence mechanisms have been proposed.

2. Experimental

A series of Sr\(_2\)La\(_8\)\(_{x}\)(SiO\(_4\))\(_6\)O\(_2\):xCe\(^{3+}\) phosphors with different compositions were synthesized via sol-combustion method. At first, stoichiometric amounts of raw materials Sr(NO\(_3\))\(_2\), La(NO\(_3\))\(_3\), Ce(NO\(_3\))\(_3\) with analytic grade purity and Tetraethoxysilane (TEOS), citric acid, as well as urea were all weighed and dissolved in anhydrous ethanol. Then the mixture was stirred on magnetic stirring apparatus for half an hour at 60 °C to form a stable gel in ambient pressure. Next, the gel was transferred to an oven and dried at 80 °C for 12 h to obtain a xerogel, and then the xerogel was placed in an alumina crucible and calcined at 700 °C in furnace in the air atmosphere to gain the precursor. Subsequently, the precursor was annealed at 1200 °C for 5 h in a reducing atmosphere (5% H\(_2\) + 95% N\(_2\)). After that, the samples were cooled down to room temperature and ground to powders for the measurement.

X-ray diffraction (XRD) patterns were recorded using an X-ray powder diffractometer (XD-3, PGENERAL, China) with Cu K\(_\alpha\) radiation (\(\lambda = 0.15406 \) nm) operated at 40 kV and 30 mA. The morphology of the as-prepared samples was characterized by a field emission scanning electron microscopy (FESEM, JSM-7001F). Room
temperature excitation and emission spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer PL system equipped with a xenon lamp (400 V, 150 W) as excitation source. A 400 nm cutoff filter was used in the measurement to eliminate the second-order emission of source radiation. All the measurements were carried out at room temperature.

3. Results and discussion

The phase structures were checked by XRD measurements. Fig. 1 shows the comparison results of the as-prepared samples including the $\text{Sr}_2\text{La}_{7.9}(\text{SiO}_4)_6\text{O}_2:0.1\text{Ce}^{3+}$ and the $\text{Sr}_2\text{La}_{7.8}(\text{SiO}_4)_6\text{O}_2:0.2\text{Ce}^{3+}$ phosphor. It can be seen that all of the diffraction peaks are matched well with the standard data of Sr$_2$La$_8$(SiO$_4$)$_6$O$_2$ (ICSD No. 15-5625) indicating the introduction of Ce$^{3+}$ ion into the Sr$_2$La$_8$(SiO$_4$)$_6$O$_2$ lattice does not cause any significant change to the crystal structure of the host matrix. Based on the effective ionic radii [15] and charge balance of cations with different coordination number (CN) as shown in Table 1, the rare-earth Ce$^{3+}$ is expected to occupy the La$^{3+}$ sites randomly in the Sr$_2$La$_8$(SiO$_4$)$_6$O$_2$ host. An obvious phenomenon was observed that the diffraction peaks of the as-prepared samples shift toward the larger 2$h$ diffraction angle owing to the decrease of the cell volume with the substitution of Ce$^{3+}$ for La$^{3+}$ ions. Fig. 2a and b show the SEM micrographs of the typical Sr$_2$La$_7.9$(SiO$_4$)$_6$O$_2:0.1$Ce$^{3+}$ phosphor prepared by the low temperature combustion method shows relatively regular and rigid columnar micro-sheets particle morphology. The well-crystallized and columnar shaped Sr$_2$La$_7.9$(SiO$_4$)$_6$O$_2:0.1$Ce$^{3+}$ phosphors are with an average size of about 30 nm.

Fig. 3 gives the photoluminescence excitation (PLE) and photoluminescence (PL) spectra of Sr$_2$La$_7.9$(SiO$_4$)$_6$O$_2:0.1$Ce$^{3+}$. It could be seen that the excitation spectrum monitoring by 403 nm is composed of one strong absorption peak at 282 nm and a weak absorption peak located around 330 nm in the spectral range from 200 to 390 nm, which corresponds to the 4$f$–5$d$ transitions of the doped Ce$^{3+}$ ions. The PL spectrum of Sr$_2$La$_7.9$(SiO$_4$)$_6$O$_2:0.1$Ce$^{3+}$ exhibits an intense broad band centered at 403 nm under the excitation of 365 nm, which is ascribed to the 5$d$–4$f$ transition of the Ce$^{3+}$ ions. The CIE chromaticity diagram for the Sr$_2$La$_7.9$(SiO$_4$)$_6$O$_2:0.1$Ce$^{3+}$ phosphor under 365 nm UV excitation is shown in the inset.

![Fig. 1. XRD patterns of as-prepared Sr$_2$La$_7.9$(SiO$_4$)$_6$O$_2:0.10$Ce$^{3+}$ (a) and Sr$_2$La$_7.8$(SiO$_4$)$_6$O$_2:0.20$Ce$^{3+}$ (b). The standard data for Sr$_2$La$_8$(SiO$_4$)$_6$O$_2$ (ICSD card No. 15-5625) is shown as a reference.](image)

![Fig. 2. SEM images of Sr$_2$La$_7.9$(SiO$_4$)$_6$O$_2:0.10$Ce$^{3+}$ phosphor particles: (a) plotting scale × 4000 and (b) plotting scale × 10,000.](image)

![Fig. 3. PLE and PL spectra of as-prepared Sr$_2$La$_7.9$(SiO$_4$)$_6$O$_2:0.10$Ce$^{3+}$ phosphor. The inset shows that the CIE chromaticity diagram for Sr$_2$La$_7.9$(SiO$_4$)$_6$O$_2:0.1$Ce$^{3+}$ phosphor excited at 365 nm.](image)

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Meanwhile, the typical digital photo of the Sr$_2$La$_{7.9}$Ce$_{0.1}$O$_{20.5}$ exhibits a blue-violet emission band at 403 nm with a CIE coordinates of (0.167, 0.208), which could be assigned to the 4f–5d transition of Ce$^{3+}$. It was further determined that the dipole–dipole interactions results in the concentration quenching of Ce$^{3+}$ in Sr$_2$La$_8$(SiO$_4$)$_6$O$_2$:Ce$^{3+}$ phosphors.

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