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Hydrothermal synthesis and photoluminescent properties of $Li_2Sr_{0.996}SiO_4:Pr^{3+}_{0.004}$ phosphors for white-LED lightings

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Abstract: Red phosphors, $Li_2Sr_{0.996}SiO_4$: $Pr^{3+}_{0.004}$, with different hydrothermal conditions were prepared via hydrothermal synthesis and then heat-treatment. The chemical structures of the phosphors were identified with X-ray diffraction (XRD). Surface morphological features were observed by scanning electron microscopic (SEM) investigation. Spectra of excitation and emission for the phosphors were also obtained by a spectrophotometer. Results showed that the optimum conditions were as follows: pH value of solution was 1–2, reaction temperature was at 180 ºC for 24 h. The as-prepared phosphors exhibited two excitation dominant peaks at 451 and 486 nm, attributed to transitions of $^3H_4 \rightarrow {}^3P_2$ and $^3H_4 \rightarrow {}^3P_0$ of Pr^{3+}, respectively. A narrow emission peak at 610 nm corresponded to the energy level transition of $^3P_0 \rightarrow {}^3H_6$ of Pr^{3+} under excitation of light at 451 nm, which indicated promising candidate red phosphors for blue LED chips.

Keywords: phosphor; hydrothermal synthesis; $Li_2Sr_{0.996}SiO_4:Pr^{3+}_{0.004}$; white-LEDs; rare earths

During the past decades, rare-earth ion doped luminescent materials have emerged as the potential choice in various kinds of modern lighting and displays, such as field emission displays (FED), plasma display panels (PDP), vacuum fluorescent displays (VFDs) and fabrication of white light emitting diodes (WLEDs)[1–4]. Hence, the increasing demands in WLEDs have motivated researchers to develop novel inorganic phosphor materials. These phosphors have received much attention due to their advantageous luminescent characteristics, such as brightness, efficiency, chemical stability, color richness and industrial processing ability[5–7]. Basically, there are two strategies of creating white light from LEDs: (a) mixing different red, green, and blue components from LED chips; (b) down converting the emission from a blue or ultraviolet LED to a longer wavelength using phosphors[8,9]. At present, $Y_3Al_5O_{12}$ phosphor has already been used as an excellent yellow phosphor for white LEDs[10,11]. Unfortunately, blue LEDs pumped white LEDs with $YAG:Ce^{3+}$ phosphor have low color-rendering index (CRI) due to the deficiency in the red region[12]. It is necessary to find proper red phosphor host materials, including borates, phosphates, aluminates, silicates, molybdates, tungstates, sulfides, oxynitrides or nitrides[13–21].

However, white LED devices fabricated from sulfide phosphors show a strong temperature dependence of chromaticity as well as the degradation in efficiency due to the lower thermal or chemical stability in humidity. Some of the nitride and oxynitride phosphors show promise, such as $M_2Si_5N_8$ (M=Ca, Sr, Ba) and $SrAlSiN_3$. While some special preparative conditions are required, high-pressure or carbothermal reactions and chemical stability in the ambient atmosphere is also a matter of concern[22,23].

Silicate phosphors have attracted wide attentions because of their excellent thermal and chemical stability[24,25]. Rao had explored $Li_2Sr_{1-1.5x}SiO_4:xPr^{3+}$ red phosphors by conventional solid state reaction, which indicated the potential red phosphors for blue LED chips[26]. However, the synthesis of uniform and well-dispersed $Li_2SrSiO_4:Pr^{3+}$ phosphors has been rarely studied via hydrothermal synthesis.

The objectives of this work were to synthesize red phosphors, $Li_2Sr_{0.996}SiO_4:Pr^{3+}_{0.004}$, by a facile hydrothermal method and processed with heat-treated at 850 ºC for 4 h. In particular, different conditions of pH values, temperature and soaking time in hydrothermal reaction were investigated in this paper. The results of XRD, microstructure and PL of the phosphors were reported in details.

1 Experimental

Red phosphors, $Li_2Sr_{0.996}SiO_4:Pr^{3+}_{0.004}$, i.e., LSSO, were prepared via hydrothermal synthesis route. The chemical reactants of $SrCO_3$ (AR), Li_2O_3 (AR), Pr_6O_{11} (99.99%) and tetraethyl orthosilicate (TEOS) were used.

The reagents were firstly weighed in a nominal

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chemical composition of $SrCO_3$, Li_2O_3 and Pr_6O_{11} and then certain amount of nitric acid was added to obtain nitrate solutions. Moreover, TEOS, ethanol and de-ionized water were weighed as molecular ratio of 1:5:5 and mixed with each other. After vigorous stirring for 60 min, certain amounts of metal nitrate solutions were then added and stirred for 30 min. Aqueous diluted ammonia or nitric acid was put in under stirring to adjust the pH value of the solution, which was measured by a digital pH meter (PHS-3C). Then the solution was transferred into a Teflon bottle which was held in a stainless steel autoclave and subsequently soaked at 160–200 ºC for 12–72 h. After the reaction was completed and cooled down to room temperature naturally, the samples collected at the bottom of the vessel were filtered, washed with distilled water several times and then dried in air at 80 ºC for 5 h. The precipitates were then heat-treated at 850 ºC for 4 h under a reducing atmosphere with a mixture of 5%H_2 and 95%N_2 and then cooled down to room temperature.

The samples were identified by an X-ray powder diffraction (XRD) (Philips X'pert PRO, Holland) using Cu Kα radiation. The microstructures of the samples were observed by a scanning electron microscope (Hitachi TM3000, Japan). Photoluminescence properties were recorded on a Hitachi F-7000 fluorescence spectrometer equipped with a Xenon lamp under a working voltage of 700 V. The excitation and emission slits were set at 2.5 nm. All the measurements were performed at room temperature.

2 Results and discussion

Pr^{3+}-doped Li_2SrSiO_4 phosphors could be obtained from aqueous solutions in the temperature range from 160 to 200 ºC and pH range from 1 to 12 with then heat treatment. As reported in the next few paragraphs, it was observed that the composition and property significantly varied for the different conditions in this study.

2.1 pH influence on the samples

The influence of pH value on the crystalline phase of the samples with and without heat treatment is demonstrated as XRD patterns in Figs. 1 and 2, respectively. In the hydrothermal process, the pH value of initial solution had a great influence on the crystal structure of LSSO precursors as shown in Fig. 1. Through the XRD patterns presented in Fig. 2, all peaks corresponding to that of Li_2SrSiO_4 matched well with the standard data (JCPDS No. 47-0120) when pH value was below 7. It was implied that appropriate hydrothermal precursor with sintering had no obvious influence on the crystal structure. For the samples, prepared from the solution with low pH value from 1 to 7, the metal ions in solution easily tended to complex with TEOS to form the unshaped three-dimensional network structure corresponding to the wide peaks of 20º–30º in XRD patterns. Observed from the original morphology of the samples, the solution was translucently gelatinous when pH value was below 7, while the solution milky turbid when pH value was above 7.

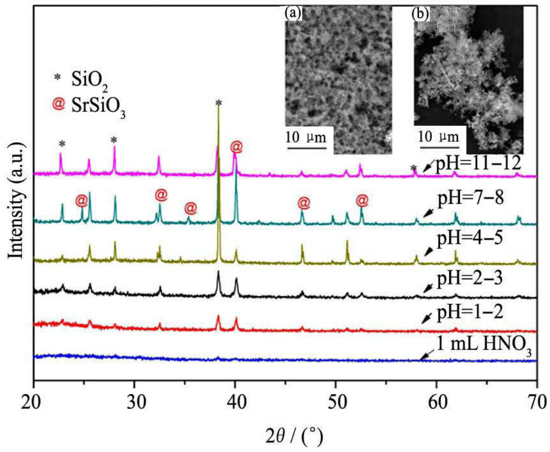

Fig. 1 XRD patterns of LSSO precursors with different pH values (Insets: SEM images at pH=1–2 (a) and pH=11–12 (b))

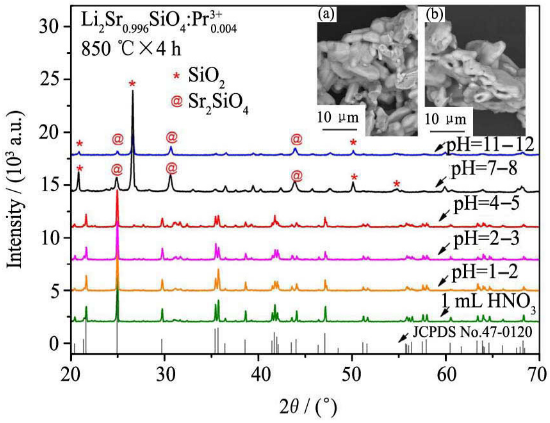

Fig. 2 XRD patterns of LSSO samples with different pH values annealing at 850 ºC for 4 h (Insets: SEM images at pH=1–2 (a) and pH=11–12 (b))

The impurities like SiO_2 and $SrSiO_3$ probably resulted from the hydrolysis-condensation mechanism of TEOS in the hydrothermal system. When the pH value of solvent was above 7, the hydrolysis of TEOS which the Si–OC_2H_5 bond transfer to Si–OH bond was limited, while the polycondensation of hydrolyzed TEOS was improved which resulted in the generation of impurities SiO_2. In addition, the formation of obvious impurities $SrSiO_3$ was due to the reaction between Sr^{2+} ions and large amount of OH^- ions in solution. However, when the pH value of solvent was below 7, the hydrolysis of TEOS was improved, the polycondensation of TEOS and reaction leading to the insoluble $SrSiO_3$ were inhibited because of the increasing concentration of H^+, so the decreasing of impurities like SiO_2 and $SrSiO_3$ is reasonable.

SEM images showed various morphologies of the