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Thermochromic material $Sr_2SiO_4:Eu^{2+}$ based on displacive transformation

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ABSTRACT

Strontium silicate Sr_2SiO_4 undergoes a displacive phase transformation around 85 °C. However, the steady state spectra involved in the process lacks investigation. In this paper, two kinds of $Sr_2SiO_4:Eu^{2+}$ with and without Ba ions are synthesized. They are tested for XRD patterns and luminescent spectra at varying temperatures. The results show that Ba ions could effectively suppress the phase transition. For sample without Ba, temperature-dependent XRD patterns confirm the occurrence of phase transition and the emission peak positions at varying temperatures demonstrate a hysteresis behavior. The color of sample heated to 100 °C under UV illumination is distinguishable from that unheated. This structure-sensitive behavior make $Sr_2SiO_4:Eu^{2+}$ as potential thermochromic material.

1. Introduction

The luminescence of Eu^{2+} doped Sr_2SiO_4 has been widely explored. Most researchers focus mainly on the peak shift caused by different Eu concentration [1] or Sr/Ba ratio [2]. Therefore, $Sr_2SiO_4:Eu^{2+}$ is commonly treated as potential WLED phosphor and fabricated with LED chips to obtain white light [1,3–5]. However, there exists a displacive phase transformation for Sr_2SiO_4 which occurs around 85 °C [6]. It will be shown in this work that this transformation has a negative effect on the spectra distribution of $Sr_2SiO_4:Eu^{2+}$ phosphors. Since the working temperature of common LED devices will easily exceed the transition point, for those devices fabricated with $Sr_2SiO_4:Eu^{2+}$ phosphor, the light generated will inevitably change by time. In a word, Eu doped $Sr_2SiO_4:Eu^{2+}$ is not appropriate for LED fabrication. Conversely, the low temperature phase transition entitles $Sr_2SiO_4:Eu^{2+}$ as potential thermochromic materials.

Thermochromic materials change color when the ambient temperature changes. In modern societies, they have extensive applications, such as temperature-sensitive coatings and pigments [7,8]. Most of the thermochromic materials are composed of organic substances [9]. In harsh environments where corrosion or extreme temperatures exist, inorganic thermochromic materials are greatly needed. Only a few inorganic materials have thermochromic properties [10,11]. Luminescent materials present different colors and have the potential to detect temperature by color. Generally, as temperature changes, the emission spectra of luminescent material differ in intensity, while the wavelength distribution maintains almost the same. This will not give an easily perceivable difference in color at different temperatures.

In this work, the XRD patterns and emission spectra of $Sr_2SiO_4:Eu^{2+}$ with varying temperatures are investigated. The results reveal the impediment of Ba ions to phase transition and the thermal hysteresis behavior of peak positions for sample without Ba. This work provides a further understanding of dynamic process in displacive phase transition.

2. Experimental

Two samples with nominal composition $(Sr_{0.97}Ba_{0.02}Eu_{0.01})_2SiO_4$ and $(Sr_{0.99}Eu_{0.01})_2SiO_4$ are synthesized by solid state reactions. The starting materials are $SrCO_3$, $BaCO_3$, SiO_2, and Eu_2O_3 (Sinopharm Chemical Reagent Beijing Co., Ltd, regent grade). The reagents are then weighted stoichiometrically and thoroughly ground in an agate mortar. The sintering condition for both samples is 1400 °C under reducing atmosphere, $90\%N_2+10\%H_2$, for 4 h. After cooling to ambient temperature, the samples were taken out and pulverized into fine powders for measurement.

XRD patterns are checked by Philips X' Pert diffractometer. It works at 45 kV, 40 mA, with Cu $K\alpha1$ radiation. Non-ambient testes employ Anton Paar HTK-1200N Oven sample stage. Temperatures increase from 300 to 400 K, and then decrease to 300 K, with 20 K interval. At each temperature point, the sample is kept for 5 min before test.

The steady state spectra are measured on FLSP920 spectrometer, Edinburgh Instruments. A 450 W Xenon arc lamp working in continuous mode is employed as light source for steady state measurement. The samples are mounted into the expander chamber of closed cycle liquid helium cryostat DE202, Advanced Research Systems, which provides varying temperatures from 10 to 400 K, with temperature controller Model 331, Lake Shore Cryotronics, Inc. The measurement commence about 5 min after the panel temperature is stabilized at some fixed value. The photomultiplier used is

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Hamamatsu R928P which provides very low dark noise level. The emission and excitation spectra are all corrected according to the spectral instrumental response and the spectral output of the light source, respectively.

3. Results and discussion

The phase transformation of strontium silicate Sr_2SiO_4 was first reported by Pieper et al. to occur at about 358 K (85 °C) [6]. Then Catti et al. determined structures of α and β phases at 383 and 298 K [12–14]. Phase transition of Sr_2SiO_4 is a second order displacive phase transformation with a short-range structure rearrangement without breaking any coordination bonds [12,13]. It occurs without nucleation and growth. The atoms are observed to move in a concerted fashion such as to rotate SiO4 tetrahedra [14]. Therefore, the symmetry changes from Pmnb of α phase to its subgroup $P2_1/n$ of β phase (Fig. 1). The high-temperature α phase cannot be quenched completely [12], so the two phases always coexist. Doping a small amount of 2.5% Ba [6] or 2% Eu [15] could effectively stabilize α phase. In this work, XRD pattern of Ba doped sample $(Sr_{0.97}Ba_{0.02}Eu_{0.01})_2SiO_4$ confirms a majority of α phase, with a minority SiO_2 phase; meanwhile, an obvious mixture of α+β phase is obtained for $(Sr_{0.99}Eu_{0.01})_2SiO_4$. What is more, it is reported that the transition demonstrates a hysteresis behavior. As mentioned above, Pieper et al. determined the transition temperature as 358 K by DTA measurements [6]. Catti et al. studied the single crystal diffraction and found that the phase change occurred at 364 and 355 K for β to α and α to β, respectively [13]. Considering the similarity in crystal structure of α and β phases, their XRD patterns resemble each other. Despite this, the two phases can be distinguished by existence or not of diffraction peaks at 27.16° (α phase) and 27.67°, 32.35° (β phase), as indicated by the temperature-dependent XRD patterns in Fig. 2. For $(Sr_{0.97}Ba_{0.02}Eu_{0.01})_2SiO_4$, the structure is stable against temperatures. No diffraction peaks appear or disappear throughout the whole test. The stability derives from dopant Ba ions. However, for $(Sr_{0.99}Eu_{0.01})_2SiO_4$, from 300 to 400 K, diffraction peaks of α phase strengthen while those of β phase weaken. This indicates a transformation from β to α phases. During the cooling process, β phase reemerges with the 27.67°, 32.35° peaks strengthening. When temperature goes down to 300 K, the sample returns to mixture of α and β phase. It should be noted that the XRD pattern at 300 K in the end of cooling process is not exactly the same compared with that in the beginning of heating process. This minor difference indicates a hysteresis behavior for displacive transition of Sr_2SiO_4.

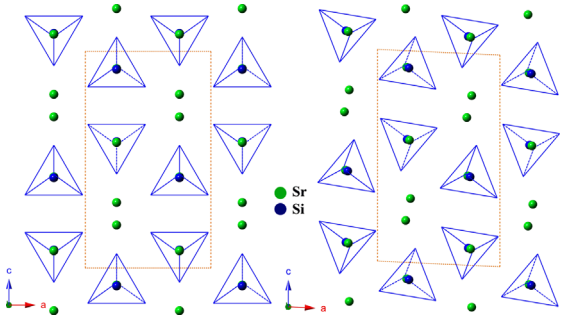

Fig. 1. Crystal structure projection along [0 1 0] of α (Left) and β (Right) phase, respectively. The blue polyhedrons stand for Si–O tetrahedrons, with Si atoms in the center and O atoms (they are not plotted) at the vertices. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Doping Eu^{2+} into the Sr_2SiO_4 lattice gives a composite emission originating from the two coexisting phases, and the emission spectra vary with different α/β amount [3,16]. This dependence on phase amount leads to the fact that the emission spectra are sensitive to different excitation wavelengths, as shown in Fig. 3. The emission spectra of $(Sr_{0.97}Ba_{0.02}Eu_{0.01})_2SiO_4$ are tested during a heating and cooling cycle, in which the temperatures first rise from 50 to 380 K and then return to 50 K gradually. It can be shown from Figs. 4 and 5

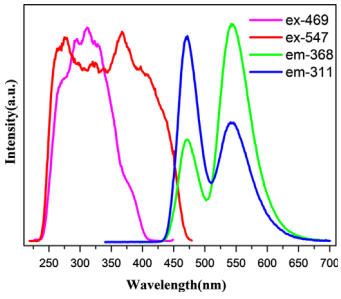

Fig. 3. Typical PL and PLE spectra of $(Sr_{0.99}Eu_{0.01})_2SiO_4$ measured at 50 K.

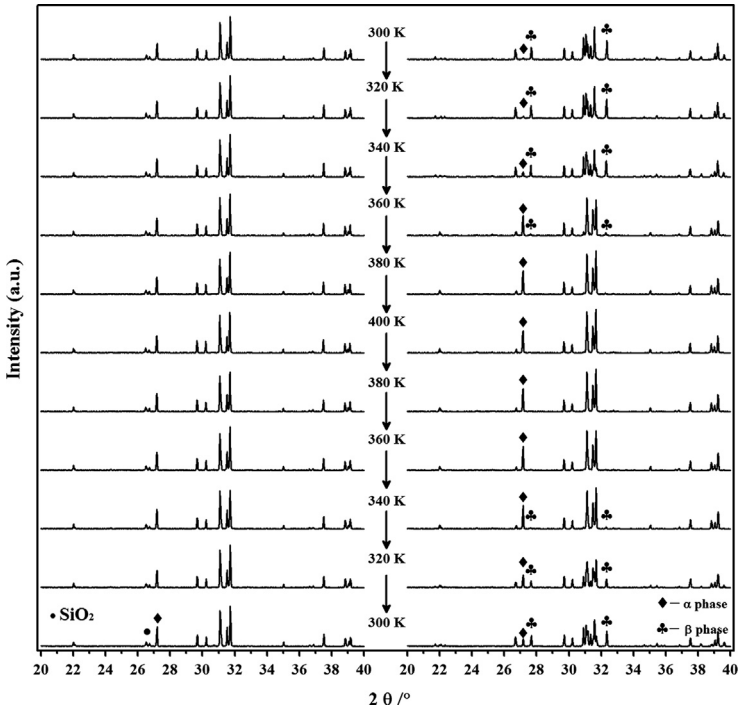

Fig. 2. XRD patterns of $(Sr_{0.97}Ba_{0.02}Eu_{0.01})_2SiO_4$ (Left) and $(Sr_{0.99}Eu_{0.01})_2SiO_4$ (Right) at varying temperatures, which first increase from 300 to 400 K, and then decrease to 300 K.