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Effect of doping Gd^{3+} on crystal structure and luminescent properties of $Sr_2SiO_4:Eu^{2+}$ phosphor

ZHAO Cong (赵 聪)[1,2,3], ZHU Dachuan (朱达川)[1,*], GAO Wei (高 唯)[2], HAN Tao (韩 涛)[3], PENG Lingling (彭玲玲)[3], TU Mingjing (涂铭旌)[1]

(1. College of Materials Science and Engineering, Sichuan University, Chengdu 610065, China; 2. Department of Chemical & Materials Engineering, The University of Auckland, Auckland 1142, New Zealand; 3. Research Center for Material Interdisciplinary Science, Chongqing University of Arts and Science, Chongqing Engineering Research Center for Optoelectronic Materials and Devices, Chongqing 402168, China)

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Abstract: $Sr_{1.995-1.5x}Gd_xSiO_4:0.005Eu^{2+}$ phosphor series with x=0–0.08 mol for near-ultraviolet white light-emitting diodes (NUV w-LEDs) were synthesized via solid-state reaction method. XRD profile pattern and refinement results demonstrated that doping Gd^{3+} ions resulted in the phase transformation (β-Sr_2SiO_4→α'-Sr_2SiO_4). The photoluminescence spectrum of the sample with x=0 mol displayed two emission peaks centered at 470 and 525 nm. The two-peak spectra became one-peak spectra with the Gd^{3+} concentration increasing. Actually, the fitting results demonstrated that the one-peak spectra were still composed of two single emission spectra. The photoluminescence intensity was improved and the CIE chromaticity coordinates were adjusted via doping Gd^{3+}.

Keywords: doping; solid-state reaction; photoluminescence; Sr_2SiO_4; phosphors; rare earths

Since Nakamura in Nichia Company[1] invented the white light-emitting diodes (w-LEDs) which are regarded as a potential light source for replacing the traditional light sources, because of their higher energy efficiency, longer life, higher reliability and safety. As the important building blocks of w-LEDs, phosphors have been developed into many kinds of host, such as silicates, aluminates, sulfides, phosphates, nitrogen-oxides, nitrides and so on[2–15]. However, the properties of above mentioned phosphors cannot meet the demand of w-LEDs' development due to some disadvantages more or less—the sulfides have poor physical and chemical stabilities, the production cost of nitrogen-oxides and nitrides is too high[16–18].

Among the above phosphors, silicate phosphor is regarded as a potential luminescent material due to many advantages, such as abundant crystal structure, excellent thermal stability, and low sintering temperature[19–21]. Currently, more and more researchers pay their attention to the field of M_2SiO_4-based phosphors. Kalaji et al.[22] have synthesized a novel yellow emitting γ-Ca_2SiO_4:Ce phosphor. Li et al.[23] have researched the photoionization behavior of Eu^{2+}-doped $BaMgSiO_4$ long-persisting phosphor. Denault et al.[24] have studied the luminescence properties of $BaSiO_4:Eu^{2+}$ orthosilicate phosphors via doping Sr^{2+} into the host of this phosphor. Yang et al.[25] have researched the effects of the concentration of activators on microstructure and photoluminescence of $Sr_2SiO_4:Eu^{3+}$ phosphor. Actually, many researchers are investigating how to improve the luminescent properties of the $Sr_2SiO_4:Eu^{2+}$ phosphors via developing synthesis method and doping alkaline earth ions[26–35].

To our best knowledge, few researchers have studied the effect of co-doping trace amount of rare earth ions on the properties of $Sr_2SiO_4:Eu^{2+}$ phosphors. In addition, many researchers have improved the luminescence properties of some phosphors via doping Gd^{3+} ions. In this work, we mainly focused on improving the properties of $Sr_2SiO_4:Eu^{2+}$ phosphors via doping Gd^{3+} ions into the host lattice of this phosphor. We synthesized the $Sr_{1.995-1.5x}Gd_xSiO_4:0.005Eu^{2+}$ phosphor series via conventional solid-state reaction method. The effects of doping Gd^{3+} ions on the crystal structures and luminescent properties of $Sr_2SiO_4:Eu^{2+}$ phosphors were studied via XRD and spectrophotometer.

1 Experimental

1.1 Preparation

$Sr_{1.995-1.5x}Gd_xSiO_4:0.005Eu^{2+}$ (x=0–0.08 mol) were synthesized by conventional solid-state reaction method using high-purity oxides and carbonates as starting materials: $SrCO_3$ (99.5%), SiO_2 (99.99%, nano-particles),

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[*] **Corresponding author:** ZHU Dachuan (**E-mail:** zhudachuan@scu.edu.cn; **Tel.:** +86-28-85460830)

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Gd_2O_3 (99.99%) and Eu_2O_3 (99.99%). Stoichiometric amounts of these materials were mixed in an agate jar with agate balls and ethanol for 24 h. After being mixed thoroughly, the mixture was dried and ground in an agate mortar. And then, the as-obtained mixture was pre-heated in an alumina crucible at 800 ºC for 1 h in air, finally, sintered at 1300 ºC for 4 h under a reducing atmosphere (10%H_2+90%N_2) in a high-temperature furnace.

1.2 Characterization

The crystal structures of the samples were investigated by X-ray diffraction (XRD) (XRD-6000, SHIMADZU, Japan) with Cu Kα radiation (λ=0.154056 nm). The overall measurement time was about 55 min per pattern in order to obtain good statistics over the 2θ range of 25º–60º with a step size of 0.01º. Photoluminescence (PL) excitation and emission spectra of the phosphors were recorded on a Hitachi F-7000 spectrophotometer equipped with a 150 W xenon lamp (scanning rate=1200 nm/s, slit width=5 nm, and PMT voltage=400 V) as the excitation source. The colorimetric coordinates (x_c, y_c) of the samples were calculated by the equidistant wavelength method.

2 Results and discussion

2.1 Crystal structure transformation of $Sr_{1.995-1.5x}Gd_xSiO_4$:$0.005Eu^{2+}$

Fig. 1 shows the XRD patterns of $Sr_{1.995-1.5x}Gd_xSiO_4$:$0.005Eu^{2+}$ phosphor series with x=0–0.08 mol. It can be deduced from the XRD pattern of the sample (x=0 mol) that the sample is a mixture of dominant phase β and secondary phase α’. With the Gd^{3+} content increasing, the β phase decreased. When x=0.04 mol, the β phase has disappeared and almost all of the diffraction peaks are consistent with those of α’-Sr_2SiO_4 phase (JCPDS#39-1256) except the peak at 2θ=28°, which is consistent with the diffraction peak (222) of Gd_2O_3 phase (JCPDS#86-2477). The diffraction peak (222) has become more apparent with the continuing increase of Gd^{3+} ions. Obviously, the doping of Gd^{3+} ions has resulted in the phase transformation (β→α’).

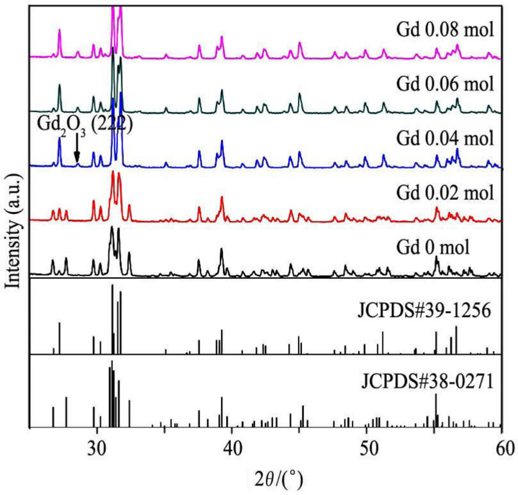

Fig. 1 XRD patterns of $Sr_{1.995-1.5x}Gd_xSiO_4$:$0.005Eu^{2+}$ phosphors (x=0–0.08 mol)

In order to prove that the dopant has been doped into the Sr_2SiO_4 lattice and analyze the mechanism of the above phase transformation, the XRD patterns of sample (x=0–0.08 mol) have been refined. Considering the similarity of β and α’ phase, here we just give the lattice parameters of α’ phase, as seen in Fig. 2. The lattice parameter a and c decrease while the lattice parameter b increases sharply first, and then settles to stable values with the increasing of Gd^{3+} concentration. Obviously, the critical concentration of lattice parameter variation is the same as that of phase transformation, which suggests that the dopant has been doped into the Sr_2SiO_4 lattice. There are two different Sr^{2+} sites (Sr_I and Sr_{II}) in the Sr_2SiO_4 lattice. The Sr_I site is ten-coordinated by oxygen atoms and Sr_{II} site is nine-coordinated by oxygen atoms, as shown in Fig. 3(d, e). The corresponding Sr–O distances (d) of the two Sr_I and Sr_{II} sites in the above two phases are summarized in Table 1. As the above mentioned that the β and α’ phases belong to different space groups, it can be seen from Fig. 3(b, c) that the Sr_I site connects with silica tetrahedron end-to-end via sharing silica tetrahedron vertex (oxygen atom), forming a liner along b-axis in α’ phase. In addition, Fig. 3(c) also shows that the projection of Sr_I site along b-axis is almost located in the geometric center of the bottom triangle of right silica tetrahedron and overlapped on the left silica tetrahedron vertex (oxygen atom). The Sr_{II} atoms form two straight parallel lines along b-axis located in the center of the hexagonal cylinder formed by six silica tetrahedrons on the a-c-plane (see in Fig. 3(b)). However, the situation in β phase is different from that in α’ phase. Firstly, the projection of Sr_I site along b-axis deviates from the geometric center of the bottom triangle of right silica

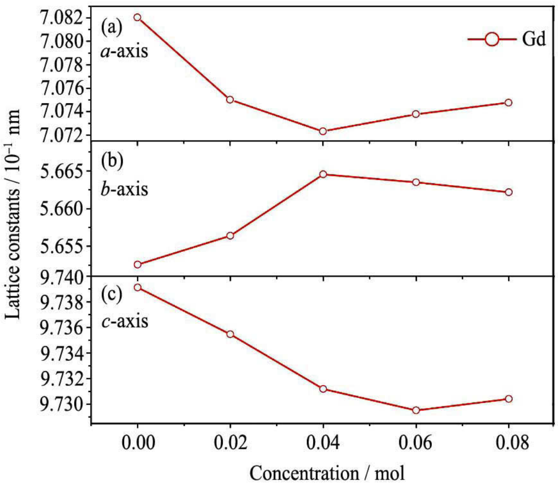

Fig. 2 Lattice parameters of α’-$Sr_{1.995-1.5x}Gd_xSiO_4$:$0.005Eu^{2+}$ phosphors (x=0–0.08 mol)