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Effect of Si–N substituting for Al–O bonds on luminescence properties of $Sr_3AlO_4F:Ce^{3+}$ phosphor

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Abstract: Cerium-doped $Sr_3(Al_{1-x},Si_x)O_{4-x}N_xF$ oxynitride phosphors with different x values were synthesized by solid-state reaction. The structure and optical properties of these phosphors were investigated by X-ray diffraction (XRD), energy dispersive spectroscopy (EDS) and photoluminescence (PL) spectra. The XRD results showed that Si–N substitution for Al–O did not change the structure of Sr_3AlO_4F host and there was no impurity for $x<0.6$. With the increasing of x values, the absorption of phosphors at the blue region was enhanced and the emitting band varied from 519 to 529 nm under the 460 nm blue light excitation. The red shift of the emission band was associated with an increase in the crystal-field splitting and the covalence, which arose from the incorporation of N. Moreover, the incorporation of N also improved the thermal quenching properties and the external quantum efficiency with a maximum value up to 43.3%, indicating that this phosphor is a promising candidate for white LEDs application.

Keywords: oxynitride phosphor; red shift; external quantum efficiency; rare earths

White light emitting diodes (LEDs) have attracted a great deal of attention in solid-state lighting applications for the next-generation general illumination due to the favorable advantages of high luminous efficiency, long lifetime, environment friendly and so on[1–5]. It is well known that phosphor-converted white LEDs are the most common commercial white LEDs because of the simple preparation method and the low cost. Herein, phosphors play a critical role in white LEDs, which determine color temperature, chromaticity coordinate, luminous efficiency and lifetime, etc[6].

Among these LED phosphors, nitride and oxynitride phosphors have attracted particular attention and been extensively investigated due to advantages of high luminous efficiency and thermal stability[7–10]. It had been reported that oxynitride phosphor could be obtained by two substitution approaches, starting from nitride and oxide compounds[11–13]. Particularly, the formation of oxynitride phosphors from oxides was confirmed to be a highly promising approach for obtaining novel properties. For example, Wang's group obtained a series of red-emitting oxynitride phosphors $Sr_2SiN_zO_{4-1.5z}:Eu^{2+}$ by incorporating N into Sr_2SiO_4 lattice[13]. Li[12] investigated the structure and optical properties of $Sr_2Al_{2-x}Si_{1+x}O_{7-x}N_x:Eu^{2+}$ by partial Si–N substituting for Al–O bond. It was found that the blue absorption was enhanced and the emission spectra had a red-shift. Recently, air-stable and highly efficient $Sr_3AlO_4F:Ce^{3+}$-based phosphor had been reported[14,15], showing outstanding luminescence properties that are suitable for white LEDs. However, the absorption in blue region of these phosphors was very weak. Theoretically, the incorporation of N into Sr_3AlO_4F host could enhance the blue excitation and thermal stability. Unfortunately, there is very limited knowledge about the influence of the incorporation of N on the structure and luminescence properties of $Sr_3AlO_4F:Ce^{3+}$ phosphor. In this work, oxynitride phosphors $Sr_3(Al_{1-x},Si_x)O_{4-x}N_xF:Ce^{3+}$ were successfully prepared from Sr_3AlO_4F oxyfluoride by partial Si–N replacing Al–O bond. The crystal structure, luminescence and thermal quenching properties were estimated in order to understand the influence of Si–N incorporating Al–O on the $Sr_3AlO_4F:Ce^{3+}$ phosphor.

1 Experimental

1.1 Preparation

Powder samples of $Sr_3(Al_{1-x},Si_x)O_{4-x}N_xF:Ce^{3+}$ were synthesized by high temperature solid-state reaction from $SrCO_3$ (99.995%), Al_2O_3 (99.9%), SrF_2 (99.9%), Si_3N_4 (99.9%), CeO_2 (99.99%). First, the powder reagents were mixed in an agate mortar and adequately triturated for a

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good mixing. Then each mixed powder with the same quality was put into the alumina crucible, and then heated at 1000 ºC in a reducing atmosphere of N_2/H_2 (25%/75%) for 6 h. After that, the temperature was raised to 1350–1400 ºC with different x values and kept for 12 h to generate the final products.

1.2 Characterization

Phase purity and crystal structure of the prepared products were analyzed by X-ray diffraction (XRD, PANalytical X'Pert PRO) with Cu Kα radiation (λ= 0.15406 nm). The photoluminescence (PL) and PL excitation (PLE) spectra were measured at room temperature with Fluoromax-4 spectrofluorimeter (Horiba Jobin Yvon) equipped with a 150 W xenon lamp as the excitation source and the wavelength range of 200–800 nm. The absorption and quantum efficiencies of the phosphors were determined on a quantum yield measurement system (QE-2100, Hamamatsu Photonics K.K., Japan) under the excitation of 460 nm and a white plate $BaSO_4$ was used as a reference material. The local compositions of the powders were identified by energy dispersive spectrometry system (EDS) in transform electron microscopy (TEM, Hitachi SU-1510).

2 Results and discussion

2.1 X-ray diffraction analysis

Fig. 1 shows the XRD patterns of $Sr_3(Al_{1-x},Si_x)O_{4-x}N_xF$ doped Ce^{3+} with different x values. When x=0.2, the diffraction peaks of as-prepared sample are consistent with those of Sr_3AlO_4F (JCPDS No. 89-4485), having tetragonal crystal system. *I*4/*mcm* (No. 140) space group. No other diffraction peaks of impurity phase are found when $x\leq0.4$, which indicates that Si–N bond is effectively doped into the host lattice. The sample with $x\geq0.6$ shows the weak diffraction peaks characteristic of Sr_2SiO_4 phase, suggesting that solubility limit of Si–N substituting for Al–O is less than 0.6. The formation of Sr_2SiO_4 may be attributed to the increase of Si/Sr ratio[16]. With the increase of x values, it is obviously seen that the (004) diffraction peak shifts to large angle, while the (114)/(220) and (204)/(310) diffraction peaks shift to small angle. It is because that the structure of all the samples is between that of Sr_3AlO_4F and Sr_3SiO_5 and the structure of samples goes to that of Sr_3SiO_5 with the increase of Si/Al ratio. Accordingly, all the diffraction peaks of samples correspondingly shift to those of Sr_3SiO_5.

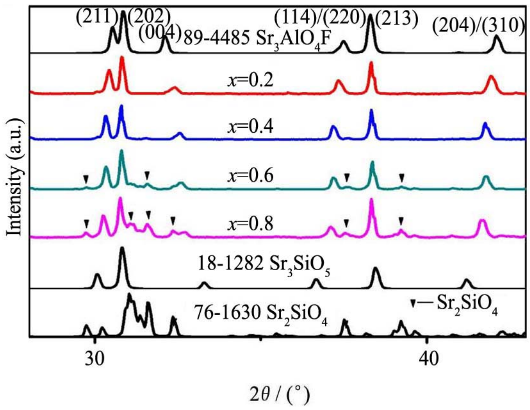

Fig. 1 XRD patterns of $Sr_3(Al_{1-x},Si_x)O_{4-x}N_xF:Ce^{3+}$ (x=0.2, 0.4, 0.6, 0.8)

2.2 Si/Al and N/O contents for $Sr_3(Al_{1-x},Si_x)O_{4-x}N_xF$ as a function of x

The Si/Al and N/O ratios were measured by energy dispersive spectrometry system (EDS). The experimental and theoretical calculation of Si/Al and N/O ratios are shown in Table 1. With the increase of x from 0.2 to 0.6, the Si/Al ratio increases from 0.295 to 1.435, Si content increases from 1.554% to 4.700%, and Al contents decreases from 5.259% to 3.276; the N/O ratio increases from 0.059 to 0.144, N content increases from 1.008% to 2.100%, and O content decreases from 16.995% to 14.550%, which is in accordance with the theoretical calculation values. While x=0.8 the Si/Al and N/O ratio is not in accordance with the theoretical calculation values due to the existing of large amounts of Sr_3SiO_4. Thus, the results of EDS showed an agreement with the compositions of $Sr_3(Al_{1-x},Si_x)O_{4-x}N_xF$ ($0.2\leq x\leq0.6$) as designed.

2.3 Spectra analysis

It is reported that the Sr_3AlO_4F and Sr_3SiO_5 host lattice involve two Sr^{2+} sites marked as Sr(1) and Sr(2): Sr(1) is coordinated by eight oxygen and two fluorine; Sr(2) is coordinated by six oxygen and two fluorine[17–22], which would result in two different sites for the Ce^{3+} ions when Sr^{2+} ions are substituted by Ce^{3+} ions. As seen there are four major excitation bands at about 296 and 366 nm from 4f→5d transition of $Ce(1)^{3+}$, 308 and 393 nm from 4f→5d transition of $Ce(2)^{3+}$ (Fig. 2(b)). With the replacement of Si–N for Al–O bond, the excitation band of

Table 1 Comparison of Si/Al and N/O content between experimental values and theoretical calculation values

x	Experimental values						Theoretical calculation values					
	Si/wt.%	Al/wt.%	Si/Al	N/wt.%	O/wt.%	N/O	Si/wt.%	Al/wt.%	Si/Al	N/wt.%	O/wt.%	N/O
0.2	1.554	5.259	0.295	0.748	16.995	0.044	1.507	5.379	0.280	0.752	16.315	0.046
0.4	2.908	4.659	0.624	1.518	15.566	0.096	3.016	4.346	0.694	1.504	15.463	0.097
0.6	4.700	3.276	1.435	2.100	14.550	0.144	4.526	2.899	1.561	2.257	14.611	0.154
0.8	6.029	1.063	5.672	2.335	13.542	0.172	6.038	1.450	4.164	3.011	13.758	0.218