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Tailoring the photoluminescence properties of lanthanum strontium aluminate phosphors by controlling crystal field environment with fluorine ions

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Abstract: A series of novel lanthanum strontium aluminate phosphors, Ce^{3+}-doped $LaSr_2AlO_{(5-0.5x)}F_x$(LSAF) phosphors were successfully synthesized using the high-temperature solid state synthesis procedure under reducing atmosphere (H_2/N_2=1/4). The X-ray diffraction pattern revealed that LSAF sample was a pure $LaSr_2AlO_5$ phase with a sintering temperature of 1250 °C. With the increasing amount of SrF_2, the particle size of powders increased and the shape of particles changed more regularly. Being an orange/red emitting phosphors for orange and white light emitting diodes, LSAF:Ce^{3+} could be effectively excited by blue lights with typical 4f→5d transitions of Ce^{3+} ions. PL and PLE spectra showed inhomogeneous enlargement effects with the increase of F/O ratios, which suggested that electronegativity effect was promoted when F/O ratio increased. This was further confirmed by a red shift of PL spectra peak when F/O was increased. It can be concluded that the LSAF:Ce phosphors have the potential to meet the development of white light-emitting diodes.

Keywords: photoluminescence; LSAF:Ce^{3+}; phosphors; lanthanum strontium aluminate; rare earths

Over the past decades, luminescence properties of phosphors with suitable host compound have been widely investigated. Especially, the unique electronic and optical characteristics of rare earth (RE) ions have received much more attentions arising from their 4f electrons. Doped with RE ions such as Ce^{3+}/Eu^{2+}, phosphors can be excited by blue LED chip and emit longer-wavelength light because of 4f→5d transitions which are mainly applied to white LED devices[1–3]. Nevertheless, $Y_3Al_5O_{12}$:Ce^{3+} phosphors can lead to the lower color rendering index (R_a) on account of weaker emission in the orange/red and the green spectral region[4–6].

In order to develop novel phosphors, more Ce^{3+}-ligand bonds and higher anions can lower the energy of 4f→5d transitions[7], which can result in the strong absorption in the UV and blue region of aluminate phosphors and give an efficient yellow emission. Recently, Ce^{3+}-doped $LaSr_2AlO_5$ (LSA) yellow phosphor has been studied by Won et al., which shows efficient orange emission for cerium under 450 nm excitation[8]. Using the LSA:Ce yellow phosphors, it is possible to fabricate white LEDs lamps with a good color rendering index (R_a=85) and high emission efficiency (higher than the YAG:Ce's)[9]. The LSA compound has a stable tetragonal structure with *I*4/*mcm* space group and can be doped with higher concentration of RE^{3+} ions because of the existence of La^{3+} ions. The LSA lattice is composed of alternating $LaSrO^{3+}$ layers (Z_{La}=Z_{Sr}=0 or 1/2) and $SrAlO_4^{3-}$ layers (Z_{Sr}=Z_{Al}=1/4 or 3/4) along the *c*-axis[10]. Surprisingly, these unconventional structures of the host lead to more desirable properties. The cations substitutions such as Gd/Tb for La, Ca/Ba for Sr, and B/Ga/Si for Al in LSA:Ce are widely studied to understand the influence of structural modifications on optical properties[11,12]. Even so, it still exists spare positive charges in each cell, and the problem of the charge balance is not mentioned yet in other reports. There are several ways to compensate the excessive positive charges such as increasing the fluorine-to-oxygen (F/O) ratio or cation vacancies, which can control crystal field environment of the host.

For $La_{1x-0.025}Ce_{0.025}Sr_{2+x}Al_{1-x}Si_xO_5$:$Ce^{3+}$ and $Sr_{2.475}La_{0.5}Ce_{0.025}AlO_{4.5}F_{0.5}$, two substitutions that occur across the solid solution series, both of anions (F^- for O^{2-}) and cations (Si^{4+} for Al^{3+}), show the superior phosphor properties[9–11]. In this paper, we attempted to prepare the $La_{0.99}Ce_{0.01}Sr_2AlO_{5-x}F_{2x}$ (LSAF:Ce) phosphors using high-temperature solid state synthesis method and tailor the band emission photoluminescence (PL) spectra by varying the F/O ratios to tune the color in this rare earth doped system. X-ray diffraction (XRD), scanning electron microscopy (SEM) and photoluminescence spectroscopy were employed to characterize the samples.

1 Experimental

The lanthanum strontium aluminate phosphors, LSAF:Ce

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(F/O=0.04, 0.08, 0.12, 0.16) were prepared from the high-temperature solid state reaction:

$$0.495La_2O_3+(2-x)SrCO_3+0.5Al_2O_3+xSrF_2+0.01CeO_2 \rightarrow La_{0.99}Ce_{0.01}Sr_2AlO_{5-x}F_{2x} \quad (1)$$

In accordance with Eq. (1), a stoichiometric mixture of La_2O_3 (AR, supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), Al_2O_3 (AR, supplied by Silian Chemical Industry, Shanghai, China), $SrCO_3$ (AR, supplied by Silian Chemical Industry, Shanghai, China), SrF_2 (99.99%, supplied by Alfa), CeO_2 (AR, supplied by Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) were weighed and ground in an agate mortar employing ethanol as a grinding media and then dried at 80 ℃ for 2 h in an oven. After that, the dried powders were pressed into tablets and sintered at 1250 ℃ for 4 h under reductive atmosphere (H_2/N_2=1/4).

The phase and crystal structures of LSAF:Ce phosphors were characterized by powder X-ray diffraction (Ultima IV, Rigaku, Japan, operated at 40 kV and 40 mA), which were obtained over the scattering angle of $20°\leq 2\theta \leq 70°$ with the step of 0.016° using Cu Kα radiation. The unit-cell parameters were obtained using a nonlinear least-squares cell refinement program (UnitCell)[13]. The morphology and structure of the phosphors are inspected using SEM (Hitachi-4500). For performing SEM, a layer of Au is deposited on the samples using a sputter deposition set up. This is necessary to get SEM images since the samples are insulating. The absorption spectra of the samples were recorded on a UV-spectrophotometer (Shimadzu UV-3600, Japan). The photoluminescence emission and excitation spectra were measured on a spectrofluorometer (VARIAN, Cary Eclipse, USA) equipped with an Xe lamp with the slit of 2.5 nm for excitation and emission source. The fluorescent decay curves were measured on an Edinburgh ELS920 fluorescence spectrometer. All of above-mentioned measurements were carried out at room temperature.

2 Results and discussion

2.1 Structural characterization

The X-ray powder diffraction (XRD) patterns of LSAF:Ce^{3+} (F/O=0.04, 0.08, 0.12 and 0.16) synthesized at 1250 ℃ for 4 h under 20% H_2/80% N_2 mixture gas are shown in Fig. 1. XRD patterns reveal that the LSAF phases have a tetragonal structure with an *I*4/*mcm* space group. Moreover, all the diffraction peaks of LSAF phases with different F/O ratios fit well with the expected structures of $EuSr_2AlO_5$ and $LaSr_2AlO_5$ calculated from the single crystal data[8]. It should be indicated that novel Ce^{3+}-active LSAF phosphor was successfully synthesized in this experiment. From the X-ray line broadening data, the unknown phase (2θ=24.9°, 26.7°, 28.3°, 44.5°) occurs as the F/O ratios go beyond 0.16, which

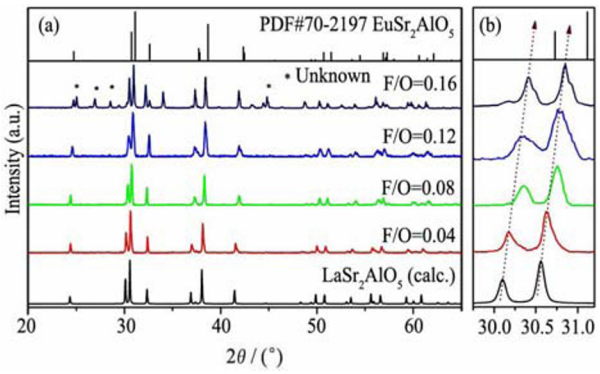

Fig. 1 XRD patterns of LSAF:Ce (F/O=0.04, 0.08, 0.12, 0.16) samples prepared in H_2/N_2 atmosphere (a) and angle shift to larger angles observed in the XRD signal profiles of the samples (b)

agree with previous work[14]. It is important to provide the sample in a "single phase" to ensure in each sample, only one crystalline contributes to the observed phenomena. In addition, Fig. 1(b) displays that an enlargement of the strongest diffraction peaks of (211) tends to be right-shifted as the ratio of F/O changes from 0.04 to 0.16, as for the lattice spacing of (211) decreases with the increase of the F/O ratio which is smaller than $EuSr_2AlO_5$.

Variation of the unit cell parameters (*a*, *b* and *c*) in LSAF:Ce with different F/O ratios can be seen in Fig. 2. The alteration of the unit-cell parameter *a*=*b* in the plane of the layer is small (from 6.731 to 6.719), compared with the larger increase in the unit-cell parameter *c* perpendicular to the plane of the layers in the LSAF (from 10.949 to 10.991), which reflects the rigidity of the LSA system. Both *a* and *c* unit cell parameters show a correlation with the fluorine ions content in the LSAF compounds. The *a* and *c* lattice parameters decrease from the replacement of the larger O^{2-} (r_O=0.138 nm) by the smaller F^- (r_F=0.131 nm)[15]. We can infer that the replacement of O^{2-} with fluorine ions in the LSA structure leads to the formation of a new host of LSAF.

2.2 Morphology characterization

The morphology (such as crystallite size, shape, defeat

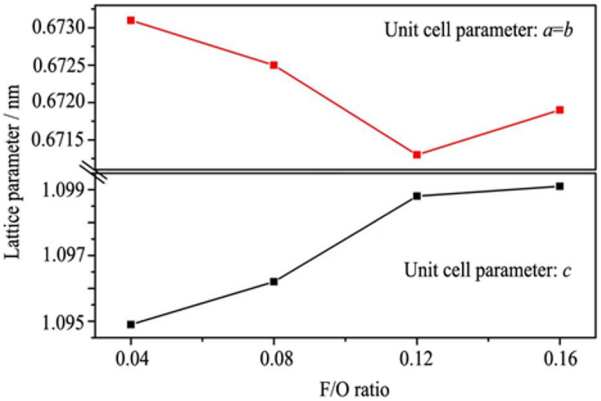

Fig. 2 Variation of the unit cell parameters (*a*, *b* and *c*) in LSAF:Ce with different F/O ratios