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# Melting salt assisted sol–gel synthesis of blue phosphor $Y_2SiO_5$:Ce

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**Abstract**

High brightness $Y_2SiO_5$:Ce phosphor powders with spherical shape and fine size were synthesized by melting salt assisted sol–gel method (MS&Sol–Gel). Commercial tetraethyl orthosilicate was used as the silica source and rare earth oxides were used as rare earth source. The prepared $Y_2SiO_5$:Ce powders were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), laser particle sizer, and fluorescentometer techniques. $Y_2SiO_5$:Ce powders were obtained at significantly lower temperature than that by conventional techniques. When sintered at 1200 °C for 2 h with 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes, particles with spherical shape and narrow particle distribution could be obtained. Moreover, the grain size of the powders prepared through this process was in the range of 2–7 μm, strongly depending on the thermal treatments and the species of fluxes. PL intensity of the prepared $Y_2SiO_5$:Ce phosphor using 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes was similar to that of commercial product.


*Keywords:* Sol–Gel method; Grain growth; Grain size; Powders-chemical preparation; $Y_2SiO_5$; Phosphors

## 1. Introduction

At the beginning of the 1990s, a new type of flat panel display device, field emission display (FED) was developed. In this device, the phosphors are excited by the cathode rays with low voltage (<5 kV) and high current density. Due to these excitation conditions, the general requirements for FED phosphors are more stringent than that for conventional cathode ray tube (CRT) phosphors. Besides good luminescent properties, perfect FED phosphors should have ideal particle morphology: spherical shape, small size (~3 μm), narrow size distribution and well dispersion.[1,2] The good particle morphology is important for obtaining dense screen coating, which may reduce light scattering, so that the emission efficiency and the resolution of the device would be improved. At present, $Y_2SiO_5$:Ce is selected as a blue phosphor candidate for this device.[3] However, it is very difficult to prepare phosphor satisfying the requirements of FED equipments until now.

Structural studies show that $Y_2SiO_5$ contains isolated $SiO_4$ tetrahedral and non-silicon-bonded oxygen. Two different monoclinic structures have been found, low temperature phase (X1) and high temperature phase (X2). The luminescence of $Y_2SiO_5$:Ce has been studied for several decades.[4–7] Previous studies found that the luminescent intensity of X1-$Y_2SiO_5$:Ce is much weaker than that of X2-$Y_2SiO_5$:Ce.[8] In this paper, luminescent properties for X2 phase are mainly considered, thus formula $Y_2SiO_5$:Ce is used for short to represent X2 phase phosphor.

$Y_2SiO_5$:Ce phosphor can be prepared by solid-state reaction between $Y_2O_3$, $SiO_2$ and $Ce(NO_3)_3$, but high temperature and long sintering duration are required.[9] When the reactants are heated below 1500 °C, a single phase cannot be obtained. It has disadvantages in controlling the morphology and maintaining uniformity after the sample is sintered at high temperature for a long time.[10] $Y_2SiO_5$:Ce also has been prepared by sol–gel method.[8] However, phosphor prepared by this method is blocked for its poor quality.

Melting salt synthesis (MSS) method has been reported to be one of the simplest techniques to prepare pure, stoichiometric oxide powders,[11–13] in which low melting, water-soluble salt

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or salt mixture is used as the reaction aid or medium.[14] To our knowledge, no research has been conducted on controlling the characteristics of melting salt synthesized phosphor powders.

In this work, a new kind of synthesis process named as melting salt assisted sol–gel method (MS&Sol–Gel) is proposed. Particle morphology and photoluminescent intensity can be controlled by adjusting species and ratio of fluxes. By this method, phosphor particles with spherical shape, fine size, narrow size distribution, nonaggregation, and high luminescent intensity can be prepared.

## 2. Experimental

$(Y_{0.995}Ce_{0.005})_2SiO_5$ phosphors were synthesized by melting salt assisted sol–gel method according to a scheme of the preparation method shown in Fig. 1. Rare earth oxides ($Y_2O_3$ and $CeO_2$, 99.99%) and tetraethylorthosilicate (TEOS) were used as raw materials. $Y(NO_3)_3$ and $Ce(NO_3)_3$ solutions were prepared by dissolving stoichiometric $Y_2O_3$ and $CeO_2$ into diluted $HNO_3$. When $Y(NO_3)_3$ and $Ce(NO_3)_3$ aqueous solutions were mixed with TEOS, homogenous solutions were obtained, and then their PHs were adjusted to neutral by adding $NH_4OH$ solution. When the solutions were heated at 70 °C overnight, $H_2O$ was evaporated and clear gels formed. After the gels were heated at 400 °C for 6 h, amorphous powders were obtained. Subsequently, the as-prepared powders were ground into fine particles and sintered at 700 °C for 6 h to remove organic components. Then suitable amount of fluxes were mixed with the powders homogeneously by grindings, and the mixtures were fired at 1200 °C for 2 h. All samples were fired in reductive atmospheres; spectrally pure carbon rods were used as reductive agent. Residual fluxes were removed by washing the powder samples in diluted hot $HNO_3$ solution and then in distilled water for several times.

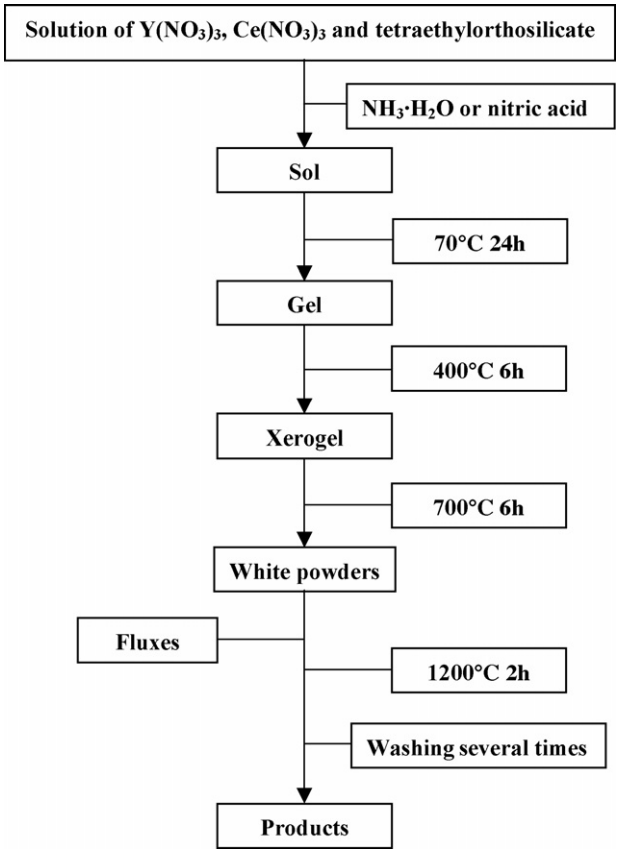


Fig. 1. Schematic representation of the synthesis process.

The X-ray diffraction (XRD) patterns of the samples were recorded using a Rigaku D/max 2000 X-ray powder diffractometer with a wavelength of Cu Kα (λ = 1.5406 Å). The scanning speed was 8°/min. The phases present were examined by analyzing the XRD patterns of the samples using PowderX software.[15]

The as-prepared phosphor powders were examined with a scanning electron microscope (SEM, KYKY-2800) to investigate the particle size, particle shape and surface morphology. The phosphor powders were further examined with a Laser Particle Sizer (Analysette 22, Fritsch) to evaluate the particle size distribution. The photoluminescence (PL) was measured using a Hitachi F-4500 Fluorescentometer, and energy correction was conducted for the spectrum data collection. The emission energy in visible light range was integrated to represent the luminescent intensity.

## 3. Results and discussion

Fig. 2 shows XRD patterns of $Y_2SiO_5:Ce^{3+}$ blue phosphors prepared by different sol–gel methods. Fig. 2(a) shows XRD patterns of samples sintered at 700 °C for 6 h and did not exhibit any Bragg lines, but a broad band centered at 31° (2$\theta$). Therefore, it was amorphous. Fig. 2(b) shows XRD pattern of $Y_2SiO_5$:Ce powders sintered at 1200 °C for 2 h with 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes, which matched well with JCPDS files of monoclinic X2-$Y_2SiO_5$ (Card number: 36–1476). This indicated that the sample was fully crystallized and contained $Y_2SiO_5$ as single phase. No other phases could be detected. Fig. 2(c) shows XRD pattern of $Y_2SiO_5$:Ce powders sintered at 1200 °C for 2 h without flux as comparison, most peaks matched with JCPDS files of monoclinic X1-$Y_2SiO_5$ (Card number: 52–1810). In addition to X1-$Y_2SiO_5$, $Y_2O_3$, X2-$Y_2SiO_5$, and $Y_2Si_2O_7$ can also be detected in this sample. It is a mixture. It could be deduced that the phase of the samples were decided by whether fluxes were used or not.

Most previous synthesis of $Y_2SiO_5$ resulted in mixed phases with the presence of X1-$Y_2SiO_5$, $Y_2O_3$, X2-$Y_2SiO_5$, or $Y_2Si_2O_7$ as impurities.[4] Ref. 16 reported that by sol–gel method sintering temperature should be up to 1500 °C in order to get high purity X2-$Y_2SiO_5$. In our work, the synthesis temperature in melting salt assisted sol–gel method was significantly lower than that required by solid-state reaction (>1500 °C) and sol–gel method. This indicated that the MS&Sol–Gel process was a suitable way to prepare X2-$Y_2SiO_5$:Ce. On the other hand, sintering duration was only 2 h, which was obviously shorter than that of other synthesis methods.

For the $Y_2SiO_5$:Ce phosphor fabricated by MS&Sol–Gel method, the grain nucleation and growth were associated with the fluxes at high temperatures. Species and ratio of fluxes decided particle morphology of $Y_2SiO_5$:Ce when other parameters such as temperature and sintering duration were fixed.

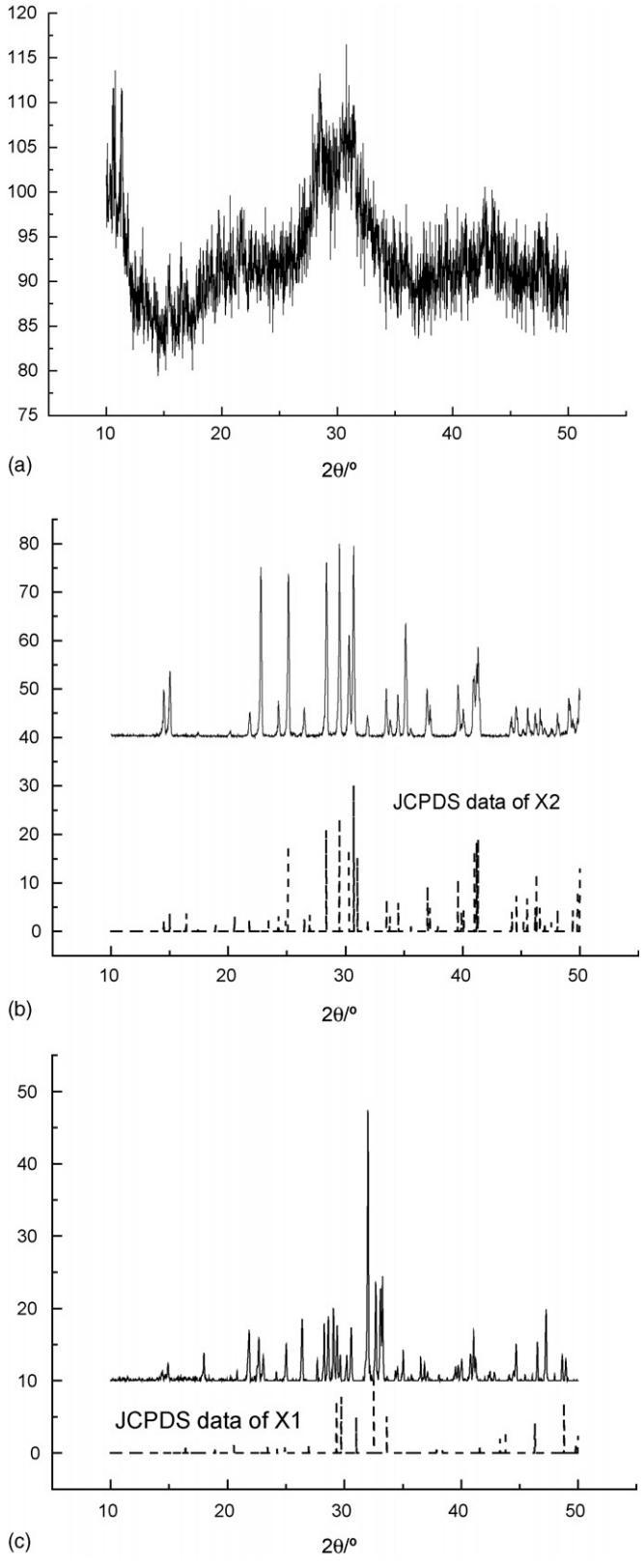


Fig. 2. XRD patterns of $Y_2SiO_5$:Ce sintered (a) at 700 °C for 6 h, (b) at 1200 °C for 2 h with 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes, and (c) at 1200 °C for 2 h without flux.

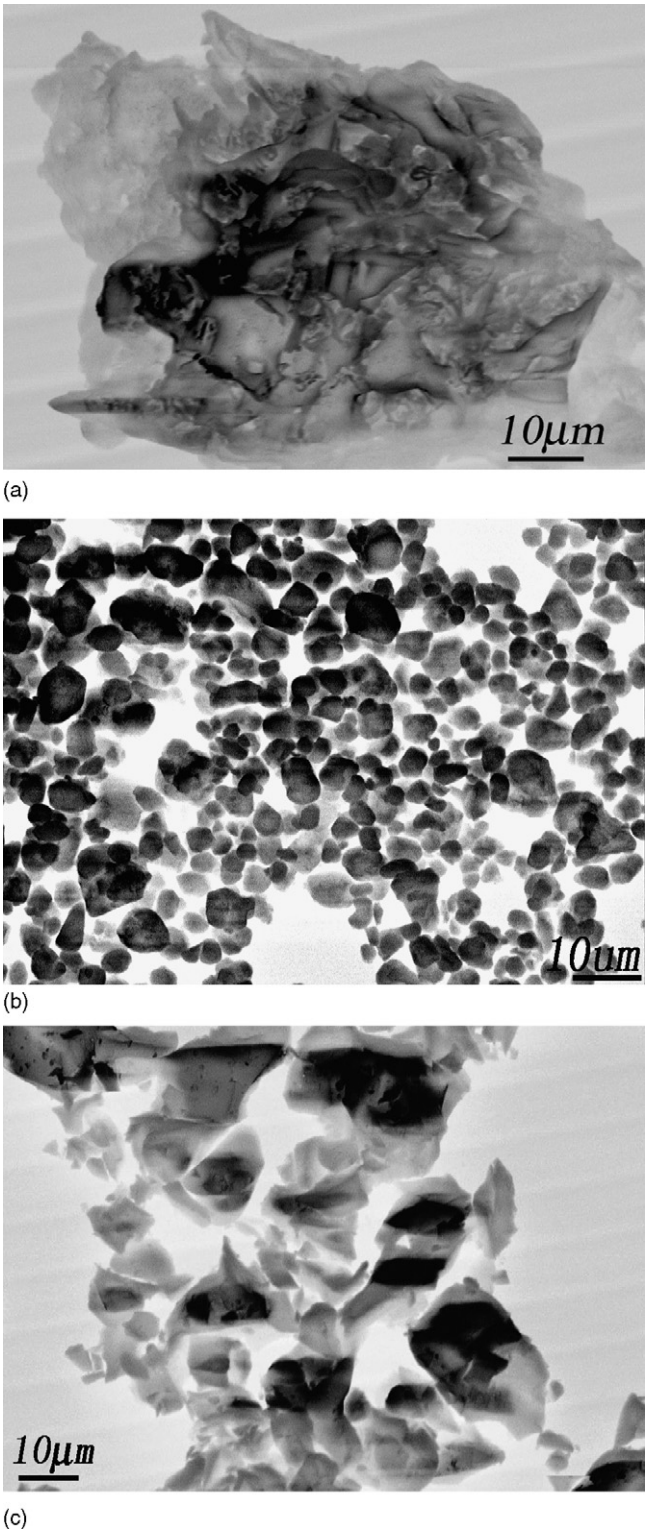


Fig. 3. Morphology of $Y_2SiO_5$:Ce particles with and without flux: (a) sample sintered at 700 °C for 6 h; (b) sample sintered at 1200 °C for 2 h using 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes; (c) sample sintered at 1200 °C for 2 h without flux.

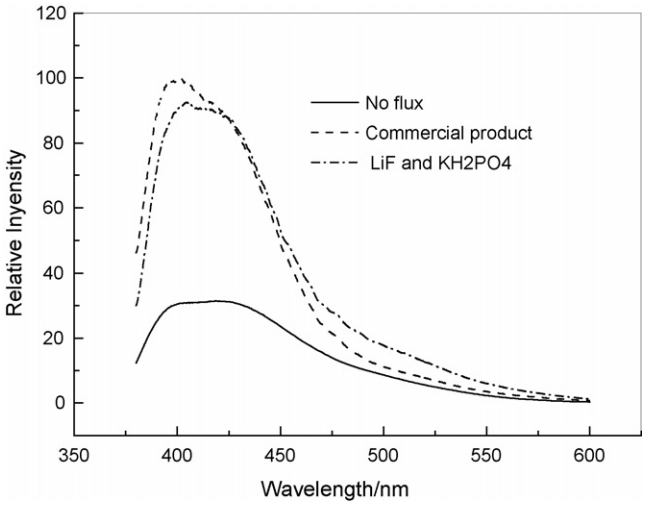


Fig. 4. PL spectra of samples prepared with and without flux.

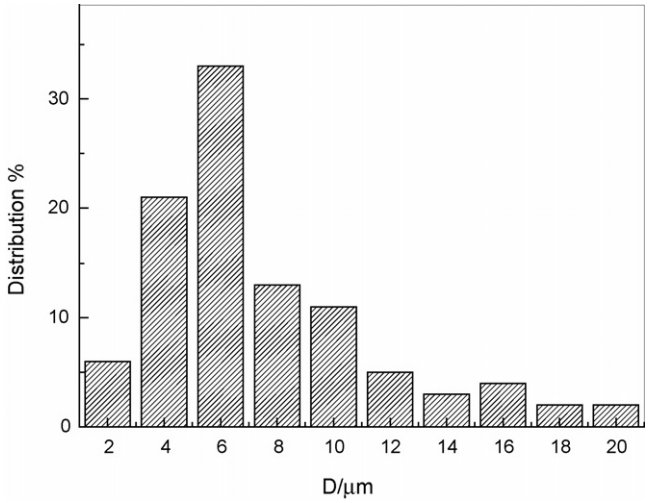


Fig. 5. Particle size distribution diagram of samples fired at 1200 °C for 2 h using 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes.

SEM was used to study the morphology of $Y_2SiO_5$:Ce powders. Fig. 3 shows the morphology of $Y_2SiO_5$:Ce phosphor sintered at different stages. Fig. 3(a) shows the morphology of the sample sintered at 700 °C. The particles were in irregular shape, with a flaky morphology. The particle size was in range of 10 μm. Fig. 3(b) shows the morphology of $Y_2SiO_5$:Ce phosphor particles sintered at 1200 °C for 2 h with 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes. As crystallization process had occurred and as a result, all particles were nearly spherical. The particles size was distributed in range of 2–7 μm. For sample sintered at 1200 °C for 2 h without flux, as shown in Fig. 3(c), the particles morphology was irregular, the grain size was larger than 10 μm. These results indicated that the morphology of the formed $Y_2SiO_5$ crystals strongly depended on the fluxes.

Fig. 4 shows the PL spectra of the phosphors prepared with and without flux. Here, commercial product $P_{47}$ ($Y_2SiO_5$:Ce) was also measured for comparison. The phosphor particles were excited by UV light of 365 nm for measurement of PL spectra. The spectral shape was not influenced by the fluxes, however, the PL intensity varied. The PL intensity of the sample sintered without flux was very low. However, the PL intensity of the sample sintered with 5 wt.% LiF and 2 wt.% $KH_2PO_4$ was several times higher than that of the sample sintered without flux. This result indicated that the fluxes can improve luminescent intensity. The PL intensity of the sample sintered with fluxes was about 90% to that of commercial product. More work was needed to optimize fluxes composition in order to obtain phosphor with high luminescent intensity and perfect morphology.

Fig. 5 shows the particle size distribution diagram of the samples sintered with 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes at 1200 °C for 2 h. The sample exhibited a narrow distribution with particle size ranging from 2 to 7 μm without agglomeration or aggregation. This indicated that using suitable species and ratio of fluxes in xerogel was an effective way to control particle size and particle distribution.

## 4. Conclusion

Different species and ratio of fluxes were used in sol–gel method to synthesis $Y_2SiO_5$:Ce powders, and melting salt assisted sol–gel method was proposed. The results can be summarized as follows:

1. A new kind of synthesis method, melting salt assisted sol–gel method was proposed, and high purity $Y_2SiO_5$:Ce phosphors were fabricated.
2. By MS&Sol–Gel method, the sintering temperature could be lowered for several hundred degrees.
3. By using 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes, particles with nearly spherical shape were obtained. The particle size distribution was in the range of 2–7 μm.
4. Photoluminescence properties of the as-prepared phosphor were measured. PL intensity of the prepared $Y_2SiO_5$:Ce phosphors using 5 wt.% LiF and 2 wt.% $KH_2PO_4$ as fluxes was similar to that of commercial product.

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