Journal of Luminescence 192 (2017) 626–633

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Effect of single and composite fluxes on the morphology and luminescence properties of layered perovskite $Sr_{1.95}TiO_4$:$0.05Sm^{3+}$ phosphor

Xiulan Wu, Yehui Jiao*, Ou Hai, Qiang Ren, Fei Lin, Huanhuan Li

School of Materials Science and Engineering, Shaanxi University of Science and Technology, Xi'an 710021, China

ARTICLE INFO

Keywords:
$Sr_{1.95}TiO_4$:$0.05Sm^{3+}$
Phosphor
Flux
Layered perovskite

ABSTRACT

$Sr_{1.95}TiO_4$:$0.05Sm^{3+}$ phosphors with various fluxes were synthesized. The influence of these fluxes on the crystallization behavior, morphology, and luminescence properties of $Sr_{1.95}TiO_4$:$0.05Sm^{3+}$ phosphor was systematically investigated. The results showed that the luminescence properties and morphology of the phosphor were improved by adding fluxes. The emission intensity of the phosphor was enhanced about 39–94% with the addition of single fluxes, while, it was enhanced about 200% when $H_3BO_3 + NH_4HF_2$ was used as composite flux. The synthesis temperature of the $Sr_{1.95}TiO_4$:$0.05Sm^{3+}$ phosphor was decreased but the emission intensity was increased when $H_3BO_3 + NH_4HF_2$ was used as composite flux. The luminescence spectrum mainly showed three intense emission bands at 568, 603 and 649 nm. Its luminescence lifetime was 716.77 μs. All these indicated that the addition of $H_3BO_3 + NH_4HF_2$ was greatly useful to lower the sintering temperature, improve the crystallization and morphology, and enhance the luminescence properties of layered perovskite $Sr_{1.95}TiO_4$:$0.05Sm^{3+}$ phosphor.

1. Introduction

In recent years, the rare earth doped luminescence materials are intensively investigated and play an important role in the field of semiconductor lighting [1–4]. As the fourth generation of illumination technology, the white light-emitting diodes (WLEDs) have many advantages, such as low power consumption, high light efficiency, long serving time and environmental friendliness, and it is proved that the rare earth doped phosphors conversion is the most common approach for obtaining white lights emission at present [4–7]. The currently commercial WLEDs are obtained by GaN-based LED chip which emitting blue light (~465 nm) and yellow phosphor ($Y_3Al_5O_{12}$:Ce^{3+}) [8]. However, such kind of white light has the poor color rendering index (CRI < 80), and high correlated color temperature (CCT ≈ 7750 K) due to the lack of red-emitting component, which restricts its further application [9,10]. In order to solve these problems, exploring a desirable red phosphor to compensate the red-emitting component is found to be an effective way to enhance the performance of WLEDs.

Titanate compounds have been considered as promising and alternative host materials of phosphors due to its properties of low cost, easy preparation, and excellent physical and chemical stabilities [11,12]. As one kind of titanate phosphor, Sr_2TiO_4 has two dimensionals layered perovskite-like crystal structure [13]. This layered perovskite compound has longer distance between layers, which induce it has bigger doping concentration [14]. Therefore, Sr_2TiO_4 is an attractive candidate for the host material of phosphors. Nevertheless, it is very difficult to obtain Sr_2TiO_4 host material with high purity due to the high temperature and long sintering time is needed during the sintering process. Hence, it is of great significance to lower the sintering temperature of Sr_2TiO_4. As is well known to all, the ceramics can be sintered at lower temperature mainly using liquid phase sintering mechanism. The liquid phase would appear in a low temperature with addition of fluxes. There are many fluxes that used in the preparation of phosphors have been reported, such as Li_2CO_3, NH_4Cl, NaF, H_3BO_3 and so on, which have a significant effect on lowering the sintering temperature, controlling the morphology of phosphors, improving the crystallization and luminescence intensity of the phosphors [15–17].

The action of fluxes on phosphor particles can be seen as a liquid phase sintering mechanism which includes three steps: (1) generation of a liquid phase; (2) dissolution of some raw materials of Sr_2TiO_4 in the liquid phase and precipitation of Sr_2TiO_4; (3) Ostwald ripening [16]. Table 1 shows a few basic properties of five kinds of fluxes. The melting points of H_3BO_3 and NH_4HF_2 are relatively lower. H_3BO_3 can be decomposed into B_2O_3 that has the characters of low melting point, low viscosity and difficult to volatile in low temperature (below 800 °C), which indicates that the liquid phase could exist for a relatively long time [18–20]. Likewise, NH_4HF_2 has similar characters with H_3BO_3, it can be decomposed as NH_4F and HF. The liquid phase NH_4F can

---

* Corresponding author.
E-mail address: 13700275836@163.com (Y. Jiao).

http://dx.doi.org/10.1016/j.jlumin.2017.07.054
Received 18 February 2017; Received in revised form 5 July 2017; Accepted 27 July 2017

Table 1
The basic properties of five kinds of fluxes.

Basic properties	$AlF_3·3H_2O$	NH_4HF_2	H_3BO_3	B_2O_3	NaCl	Na_2CO_3
Melting point (°C)	1040	125	185	445	801	851
Boiling point (°C)	1537	230	300	1860	1465	1600
Solubility in water	Insoluble	Soluble	Soluble	Slightly soluble	Soluble	Soluble

degrade the decomposition temperature of carbonates and accelerate the phase formation as the flux [21]. What's more, Ostwald ripening is an essential factor for the formation of morphology of the samples. During the solid-state reaction, there are many particles with different sizes formed. Meanwhile, the liquid phase can be produced by flux. Because of a higher solubility and energy of smaller particles than that of the larger ones, the smaller particles would gradually dissolve into the liquid phase, and redeposit on the surface of the larger particles. Therefore, the smaller particles shrink, while the larger ones grow, this process would result in the smaller particles gradually become uniform near-spherical particles [22,23].

In this paper, we used five different flux materials (H_3BO_3, $AlF_3·3H_2O$, NH_4HF_2, NaCl and Na_2CO_3) as single flux and H_3BO_3 with four other fluxes as composite flux respectively to synthesize the $Sr_{1.95}TiO_4:0.05Sm^{3+}$ phosphor. Effects of fluxes on crystal formation, morphology and luminescence properties of $Sr_{1.95}TiO_4:0.05Sm^{3+}$ phosphors were researched. Finally, the luminescence lifetimes of $Sr_{1.95}TiO_4:0.05Sm^{3+}$ phosphors prepared with 1 mol% (it's the amount of Sr_2TiO_4 molar) $H_3BO_3+NH_4HF_2$ as flux were systematically investigated.

2. Experimental sections

2.1. Solid state synthesis of phosphor powders

$Sr_{1.95}TiO_4:0.05Sm^{3+}$ samples with different kinds of fluxes were prepared by high-temperature solid-state method. $SrCO_3$ (99.0%) and TiO_2 (99.0%) and Sm_2O_3 (99.99%) were served as the raw materials. H_3BO_3 (99.5%), $AlF_3·3H_2O$ (98.0%), NH_4HF_2 (98.0%), NaCl (99.5%) and Na_2CO_3 (99.8%) were used as single flux, and H_3BO_3 couple with one of others as composite flux. At first, weighted raw materials and fluxes according to the stoichiometric ratio. Then, the starting materials were sufficiently grinded and mixed in an agate mortar. After that, placed it in a corundum crucible and annealed at 1200 °C −1400 °C in air for 6 h. The calcinations were controlled at a heating rate of 5 °C/min until reach the target temperature. The phosphors $Sr_{2-x}TiO_4$:xSm were synthesized via the reaction as follows:

$$(2-x)SrCO_3 + TiO_2 + \frac{x}{2}Sm_2O_3 \rightarrow Sr_{2-x}TiO_4\text{: } xSm + CO_2\uparrow \tag{1}$$

Finally, the phosphors were obtained in the form of powders.

2.2. Characterization

The phase composition and crystal structure of the $Sr_{1.95}TiO_4:0.05Sm^{3+}$ phosphors were characterized by X-ray diffraction (XRD-D/max2200pc, Japan) technique with Cu k_α radiation (λ = 0.154 nm) of wavelength. The morphologies and particle size of the phosphors were observed by field-emission scanning electron microscope FE-SEM (Hitachi S-4800). The photoluminescence intensity of the $Sr_{1.95}TiO_4:0.05Sm^{3+}$ phosphors were researched by Hitachi F-4600 fluorescence spectrophotometer equipped with a 150 W Xe lamp as the excitation light source. The photoluminescence decay curves were measured by Edinburgh Instruments FS5 spectrofluorimeter equipped with a 150 W Xe lamp as an excitation source. All of the measurements were performed at room temperature.

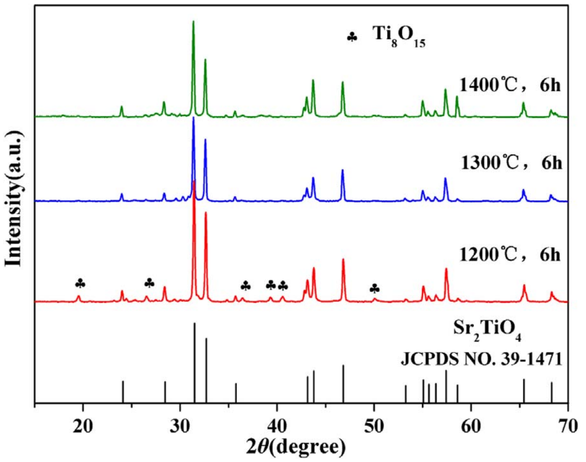

Fig. 1. X-ray diffraction (XRD) patterns of the $Sr_{1.95}TiO_4:0.05Sm^{3+}$ phosphors annealed at different temperature for 6 h in air and JCPDS NO. 39-1471.

3. Results and discussion

3.1. Phase identification

The XRD patterns of the $Sr_{1.95}TiO_4:0.05Sm^{3+}$ phosphors annealed at different temperatures in air for 6 h are shown in Fig. 1. It shows that when the calcination temperature is above 1300 °C, the phosphor exhibits the pure Sr_2TiO_4 crystal phase. However, when the firing temperature reduced to 1200 °C, the Ti_8O_{15} phase appears. The lower sintering temperature increase the possibilities of the generation of impurity. At the same time, the melting point of raw materials should be considered into the high-temperature solid-state reaction. As one of the raw materials, TiO_2 has a relatively high melting temperature (1850 °C), it is difficult to gain highly purified Sr_2TiO_4 crystal phase when the sintering temperature is reduced. With the increase of the sintering temperature, the chemical activity and the diffusion coefficient of solids increased, which lead to the solid-state reaction become more active, so the raw material TiO_2 can more effectively participate in the solid-state reaction. Therefore, the impurity phase Ti_8O_{15} disappears when the sintering temperature reach 1300 °C. However, it is of great value to prepare Sr_2TiO_4 host material with high purity but lower sintering temperature. It was reported that adding the flux can achieve this objective.

The XRD patterns of $Sr_{1.95}TiO_4:0.05Sm^{3+}$ phosphors prepared at 1200 °C with different fluxes are shown in Fig. 2(a). All of the peaks match well with the JCPDS No. 39-1471 when two different compounds are used as flux. However, the impurity peaks of $Sr_2Ti_6O_{13}$ are clearly observed in Fig. 2(a) when NaCl and Na_2CO_3 are used as single flux respectively. The addition of H_3BO_3 as composite flux has a great significance in improving the crystal purity of Sr_2TiO_4. Obviously, the impurity peaks disappear when H_3BO_3 + NaCl and $H_3BO_3+Na_2CO_3$ are used as composite flux. Therefore, the composite flux is more beneficial to the formation of Sr_2TiO_4 crystalline phase. It is worth noting that the high purified Sr_2TiO_4 crystalline phase can be obtained at lower sintering temperature (1200 °C) when the composite flux is used. From another point of view, the accommodation of Sm^{3+} in the Sr_2TiO_4 host requires charge compensation and that the addition of a flux (such as NaCl or Na_2CO_3) can significantly influence this process and then the emission performance. By comparing the XRD patterns of the samples prepared without flux and with NaCl or Na_2CO_3 as flux at 1200 °C, we find that the number of impurity peaks obviously decreased with the addition of NaCl and Na_2CO_3, which indicates their emission performance would be improved. But, since the molar amount of NaCl or