Morphology and photoluminescence of $BaAl_{12}O_{19}$:Mn^{2+} green phosphor prepared by flux method*

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This paper reports that the green phosphor $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ is prepared by a flux assisted solid state reaction method. The effect of flux systems on the crystal structure, morphology and luminescent properties of the phosphor are studied in detail. The samples are characterized by the application of x-ray diffraction patterns, scanning electron microscopy patterns, luminescent spectra and decay curves. The results show that a pure phase $BaAl_{12}O_{19}$ can be achieved at the firing temperature above 1300 °C by adding the proper flux system, the firing temperature is reduced at least 200 °C in comparison with the conventional solid state reaction method. Maximum photoluminescence emission intensity is observed at 517 nm for (AlF_3+Li_2CO_3) flux system under vacuum ultraviolet region (147 nm) excitation. The photoluminescence emission intensity and the decay time of these phosphor is found to be more superior to that of the corresponding sample prepared by the conventional solid state reaction method implying the suitability of this route for the preparation of display device worthy phosphor materials.

Keywords: flux, $BaAl_{12}O_{19}$, green phosphor, vaccum ultraviolet

PACC: 7855H, 8250, 6150J

1. Introduction

The Mn^{2+}-doped alkaline earth aluminates have been well known for the phosphor materials due to the excellent luminescent properties.[1,2] The Mn^{2+}-doped phosphors generally show intense broad-band emissions generated from the electronic transitions between $6A^1$ ground state and $4T^1$ excited state of Mn^{2+}. Luminescence from Mn^{2+} plays an important role in several inorganic compounds including silicates, aluminates and sulfides where it emits in the visible region. The emission can be either in green or red region depending on the host matrix because of the sensitivity of the d–d transition in Mn^{2+} to the crystal field.[3] The Mn^{2+} activated $BaAl_{12}O_{19}$ (BHA) has been widely applied for its high luminous efficiency and good stability adaptable for plasma display panels (PDPs), field emission displays and a possible new generation of Hg-free lamps.[4] Recently, Sohn *et al.*[5] have studied the photo physical properties of $BaAl_{12}O_{19}$:$Mn^{2+}$and their study shows that the phosphor can serve as an alternative to the well-known green emitting phosphor material Zn_2SiO_4:Mn^{2+}. Recently, the studies of BHA mainly focus on enhancing the emission intensity and improving the synthesis method.

For the application in displays and lamps, it is desirable to have controlled morphology, a fine size and narrow size distribution for high resolution.[6] There are various methods for the preparation of $BaAl_{12}O_{19}$:Mn^{2+} phosphors, such as conventional solid state reaction method,[7] sol–gel,[8] combustion,[9] reverse microemulsion,[10] combinatorial chemistry method,[5] and so on. Solid state reaction method is a conventional method, but has some disadvantages of high firing temperature, long duration time, low chemical uniformity, and large average particle size. To get over these disadvantages, sol–gel, combustion, reverse microemulsion, combinatorial chemistry methods were suggested, which enabled low sintering temperatures and fine particle sizes. But they also have some disadvantages of a large energy loss for the removal of organic elements during calcining process and difficulties in powder morphology controlling. So far, flux assisted solid state reaction method (also flux method) is a potential synthesis which will be widely used for mass production.

This method was very simple and easy to obtain phosphor powders with desirable phases and proper-

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ties. Moreover, it is quite energy saving and economic. The flux also played an important role in the control of mean size, size distribution and shape of phosphors' particles.[11] In the process of phosphor production, flux materials were used to improve the brightness of regular shape phosphor particles with micrometer size. Fine particles can improve aging characteristics by forming a densely packed phosphor layer, and it has been reported that the particle of the range of 3–5 μm showed the best luminescence characteristics.[12] Regular morphology is also required for high brightness and high resolution in PDPs, because if the phosphor particles are regular, scattering of the light from the phosphor particle decreases. Additionally, high packing densities can be obtained by using regular phosphors. At the same time, the effect of flux on synthetic techniques and luminescent properties has become one of the hotspot in the aluminate luminescent materials.[13,14] As is known, the selection of flux generally follows two principles.

(i) The melting point of flux is lower than the reaction temperature;

(ii) Impurity ions would not be introduced or could be beneficial to the luminescent properties.

However, a single type of flux is not useful enough for the reaction. A multifold flux system would give more assistance. In this paper, the $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ phosphors with various flux systems (H_3BO_3+AlF_3, H_3BO_3+BaF_2, H_3BO_3+NH_4Cl, AlF_3+Li_2CO_3, BaF_2+Li_2CO_3) were prepared by flux assisted solid state reaction method, the influences of different flux systems on the structure, morphology and luminescent properties of $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ phosphor were studied in detail.

2. Experimental

The $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ phosphors were successfully prepared by a flux assisted solid state reaction method. The starting materials were $BaCO_3$ (99.0%), Al_2O_3 (99.99%), $MnCO_3$ (99.0%). The $BaCO_3$, Al_2O_3 and $MnCO_3$ were thoroughly mixed together in stoichiometric ratios. The fluxes were introduced from H_3BO_3 (99.9%), BaF_2 (99.9%), AlF_3 (99.9%), NH_4Cl (99.0%) and Li_2CO_3 (99.99%). Appropriate quantities of the raw materials were mixed according to the formula $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ and the concentration of each flux system was 7.0 wt% relative to the total amounts of raw materials. The concentration of each flux type was 50% per one flux system. Only one type of flux system was used in each sample. Starting materials were mixed and ground by using agate mortar and pestle. The powders were transferred into alumina boats, and sintered in a tube furnace at 1300 °C for 4 h in a reducing atmosphere, followed by milling and washing. The reducing atmosphere was obtained by a flow of 5% H_2/95% N_2 so that the desired activator ions (Mn^{2+}) could be attained.

The phases of the samples were identified by a Rigaku D/max-2400 x-ray diffractometer (XRD). The scanning electron microscope (SEM) analysis was conducted on (JEOL-5600) SEM. The photoluminescence (PL) properties were measured by a FLS920T spectrophotometer equipped with a VM504 vacuum monochromator (Acton Research Corporation). The vaccum ultraviolet (VUV) excitation spectra were corrected by sodium salicylate at the same conditions. All spectra were recorded at room temperature.

3. Results and discussion

The Ba hexa-aluminate $BaAl_{12}O_{19}$ is a kind of Ba hexaaluminate with space group $P6_3/mmc$.[15] Figure 1 shows the x-ray diffraction (XRD) patterns of as-prepared samples with respect to the calcination temperature at 1300 °C for 4 h with various flux systems. All samples appear to be white in body. The XRD patterns of the compounds were compared with the joint committee for powder diffraction standards (JCPDS) (26-0135) values. In Fig. 1(a), without flux, significantly weak XRD peaks of $BaAl_{12}O_{19}$ phase as well as peaks of $BaAl_2O_4$ phase were observed. When added fluxes, only a single $BaAl_{12}O_{19}$ phase is obtained and no extraneous phase is found. Figures 1(b) and 1(c) are similar to each other for whatever flux system type is. It is revealed that the BHA phase has been successfully synthesized in our preparation conditions. Compared with conventional solid state method (1500 °C), the much lower calcination temperature is needed in the flux assisted solid state reaction method.

Figure 2 represents the variation of the unit cell parameters of $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ phosphors with different flux systems. From the figure, it is found that there is a similar tendency in (a) and (c) with the varied types of flux systems. Moreover, there is no abrupt change in (a) and (c), which reveals that the addition of flux system could not alter the structure of BHA phase.

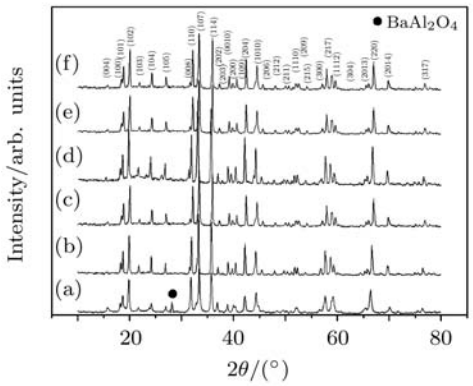


Fig. 1. The XRD patterns of $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ fired at 1300 °C with different flux systems: (a) without flux; (b) H_3BO_3+AlF_3; (c) H_3BO_3+BaF_2; (d) H_3BO_3+NH_4CL; (e) AlF_3+Li_2CO_3; and (f) BaF_2+Li_2CO_3.

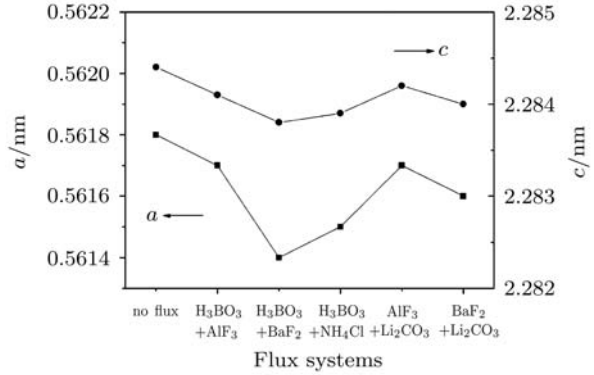
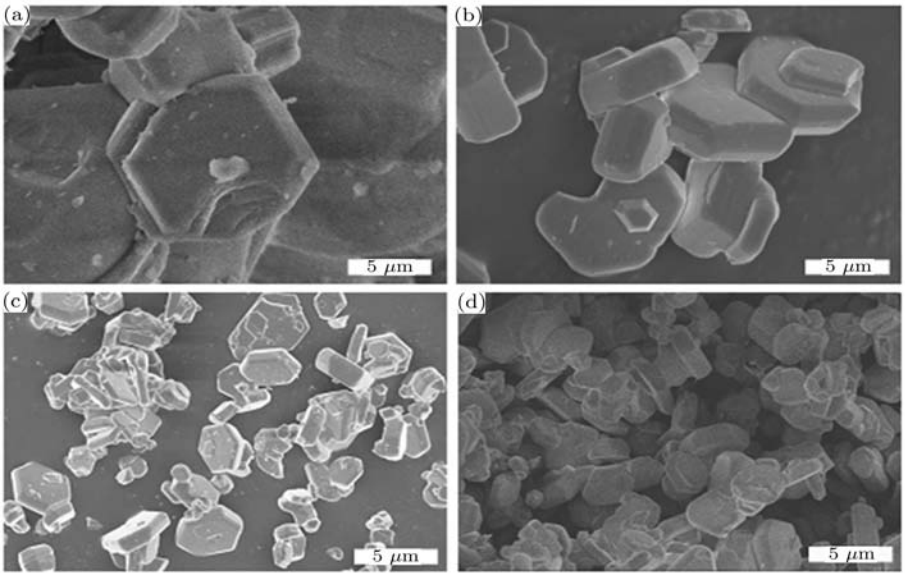


Fig. 2. Flux system types dependence of unit cell parameters of $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ powder samples.

Generally, fluxes are some compounds of alkali or alkaline earth metals with low melting points. When the fluxes heated and melt, the surface tension of liquid helps particles to coagulate. The liquid phase also makes it easier for particles to slide and rotate, provides more chances of particle contacts, and promotes particle growth.[16] Figures 3(a)–3(f) are the SEM images of $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ with different flux systems. Obviously, irregular and agglomerate grains (about 8∼10 μm) (Fig. 3(a)) are observed in the sample without flux. With an addition of flux system particles were crystallized to form regular and fine grains and showed a size around 2–4 μm (Figs. 3(b)–3(f)). The results indicate that a liquid phase caused a fluxing action can prompt the process of flexibility and accelerate the reaction via the addition of flux system. Moreover, it is well known that the phosphor with regular morphology can improve the slurry properties, packing density and improve the luminescence of phosphor in PDPs.[17]

The PL excitation spectra of the phosphors with various flux systems in Fig. 4 show that the position of excitation peaks did not change evidently when the phosphor was synthesized with varied flux systems. Three excitation peaks were observed at 157, 173 and 191 nm. According to previous reports, the band at 157 nm could be assigned to the optical absorption of spinel blocks, the excitation at around 173 nm occurred at mirror layers (i.e. Ba–O groups), and the band at 191 nm was due to the $3d^5 \rightarrow 3d^4 4s$ transition of Mn^{2+}.[18−20] It could be concluded that there is an effective energy transfer process from host material to Mn^{2+} via exchanging interaction under VUV excitation.



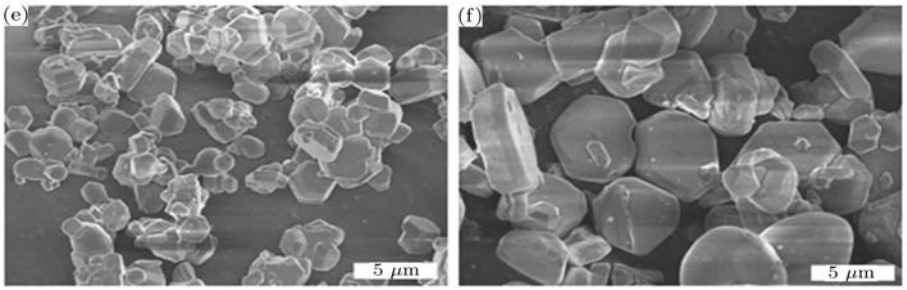


Fig. 3. The SEM images of $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ fired at 1300 °C with different flux systems: (a) without flux, (b) H_3BO_3+AlF_3, (c) H_3BO_3+BaF_2, (d) H_3BO_3+NH_4CL, (e) AlF_3+Li_2CO_3, and (f) BaF_2+Li_2CO_3.

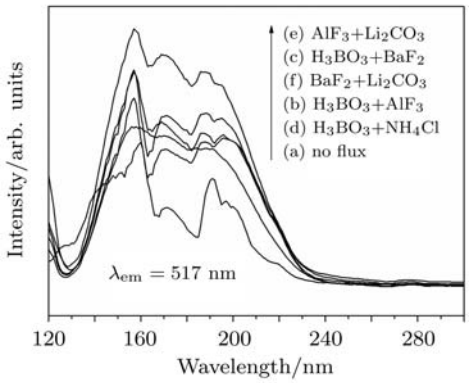


Fig. 4. The excitation spectra of $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ fired at 1300 °C with different flux systems.

Figure 5 demonstrates the PL spectra of the phosphors prepared with different flux systems. Generally, the luminescence properties are closely related with the crystalline structure of host materials and the energy transfer is efficient between activated ions and host matrix. The emission band shapes and peak positions of all samples are similar. The green emission of Mn^{2+} doped $BaAl_{12}O_{19}$ phosphor under VUV excitation has been assigned to an electronic transition of $^4T_1(G)$–$^6A_1(S)$ of Mn^{2+} peaking at 517 nm, which is a parity forbidden emission transition.[21] The Mn^{2+} ion substitutes for Al^{3+} in the $BaAl_{12}O_{19}$ lattice due to similar ionicity. The emission intensity of fluxes added samples are higher than the one without flux. If the crystal field of Mn^{2+} is weak, the splitting of the excited state d energy levels will be small, resulting in Mn^{2+} emission with higher energy.[22] Generally, tetrahedrally coordinated Mn^{2+} (weak crystal field) generates a green light, however, octahedrally coordinated Mn^{2+} (strong crystal field) gives an orange to red emission.[3] As is known, there are three different kinds of tetrahedrally coordinated Al^{3+} sites in $BaAl_{12}O_{19}$ which are adoptable for Mn^{2+} emitting green light, but Mn^{2+} preferentially enters tetrahedral Al(2) sites of $BaAl_{12}O_{19}$which has two Al(2) sites with a distance about 0.34 nm between them.[23] The Mn^{2+} ion in $BaAl_{12}O_{19}$ has fourfold coordination since it replaces Al^{3+} in the host and hence the green emission occurs.

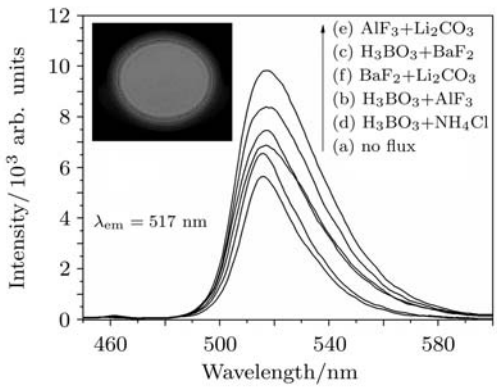


Fig. 5. The emission spectra of $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ fired at 1300 °C with different flux systems.

The PL spectra of $BaAl_{11.9}O_{19}$:$0.1Mn^{2+}$ for various flux systems were studied to check the effect of the flux system. The PL emission brightness of phosphor is strongly affected by the types of the flux systems. The flux systems dependence of the emission intensity is shown in Fig. 5. The PL spectra show a broadband emission peak (at 517 nm) from Mn^{2+}, which is due to the transition of Mn^{2+} that originates from $4T^1$ excitation state to $6A^1$ ground state. The PL intensities of samples added flux systems are all higher than that of the one prepared by conventional solid state reaction method at 1500 °C. The maximum PL intensity is attained for adding AlF_3+Li_2CO_3, which increased about 128% in comparison with the sample without flux. At this point, the results are in good agreement with the SEM analysis, described formerly. The relative emission intensity exhibits in Table 1.

Table 1. Relative emission intensity for $BaAl_{11.9}O_{19}$:0.1Mn^{2+} phosphors with various flux systems (λ_{ex} = 147 nm).

flux system	no flux	H_3BO_3+AlF_3	H_3BO_3+BaF_2	H_3BO_3+NH_4Cl	AlF_3+Li_2CO_3	BaF_2+Li_2CO_3
relative intensity	100	112	124	107	128	118

The PL process of the $BaAl_{11.9}O_{19}$:0.1Mn^{2+} phosphor has been characterized by the transition of $3d^5$ electrons in the Mn^{2+} ion acting as an activating centre. Particularly, the transition from the $^4T_1$–$^6A_1$ transition is directly responsible for the green light emission.[24–26] This transition is doubly forbidden in terms of spin and parity selection rules so that a relatively slow decay process could be expected. The decay behaviour is substantially governed by the energy migration between the Mn^{2+} centres associated with the quenching to defect impurities.[27–29] It is well known that $BaAl_{12}O_{19}$:Mn^{2+} has a relatively long decay time, which is a disadvantage for use as a green source for PDPs.[4] In order to investigate the effect of the decay time for $BaAl_{12}O_{19}$:Mn^{2+} phosphors with various flux system, the decay curves were examined and represented the results (the inset of Fig. 6) which were fitted by using the following equation:

$$I = A \exp\left(\frac{-t}{\tau}\right), \tag{1}$$

where I is the phosphorescence intensity at any time 't' after switching off the excitation illumination, A is a constant, τ is the decay time for the exponential component. The result illustrates that all samples with fluxes have shorter decay time than that of the one without flux. Moreover, a relatively short decay time is beneficial to obtain high colour purity for PDPs. This phenomenon implies that some kind of radiationless process occurs after adding fluxes, additional studies such as electron paramagnetic resonance spectra and time-resolved luminescent spectroscopy are presently underway and will be summarized in our next study.

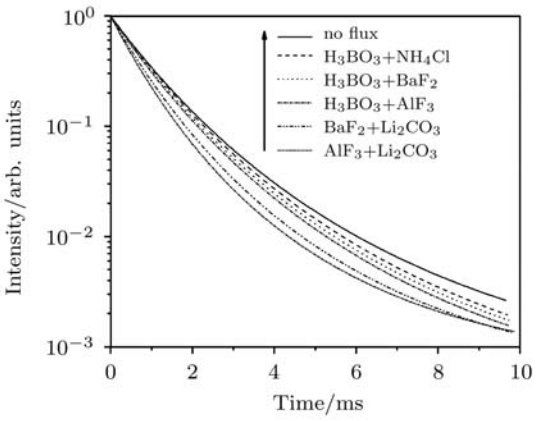


Fig. 6. The decay curves of Mn^{2+} emission (517 nm) in $BaAl_{11.9}O_{19}$:0.1Mn^{2+} excited by 147 nm.

4. Conclusions

The $BaAl_{11.9}O_{19}$:0.1Mn^{2+} green colour emitting phosphors were prepared by the flux method and conventional solid state reaction method, and their crystallinity and the PL properties were compared respectively. The results showed that the sintering temperature is reduced and the morphology of the phosphor is improved. The PL emission intensity was optimized and the maximum green emission intensity was obtained as (AlF_3+Li_2CO_3) a flux system. Occupation of Mn in tetrahedraylly coordinated site of $BaAl_{12}O_{19}$ is seen to be responsible for green emission. A shorter decay time is observed due to the addition of flux, possibly due to the improvement of morphology. The phosphor prepared by flux assisted solid state reaction method results in an enhancement in spectra properties suitable for display applications.

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