

Crystallization, morphology and luminescent properties of YAG:Ce³⁺ phosphor powder prepared by polyacrylamide gel method

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Abstract: A novel synthesis process, based on the polyacrylamide gel method, was used to prepare Ce-doped YAG phosphor powders. Effects of heat treatment parameters, temperature and holding time, the fluxes, and atmosphere on microstructure and particle morphology as well as luminescent properties of YAG:Ce³⁺ phosphor powders were studied by X-ray powder diffractometry, scanning electron microscopy, and fluorescence spectrophotometry. The results show that the formation temperature (1 000 °C) of pure YAG phase is significant low when being synthesized by the polyacrylamide gel method, compared with solid-state reaction. For luminescent properties, the intensity of emission of YAG:Ce³⁺ phosphor increases steadily with increasing temperature from 900 °C to 1 300 °C and prolonging holding time from 100 min to 400 min. But blue shift phenomenon is observed for 400 min calcination. Fluxes as BaF₂ and H₃BO₃ can enhance the intensity of emission of phosphor due to the improvement of crystallization of YAG and the stabilization of trivalence cerium ion in YAG host lattice at high temperature. Weak reduction atmosphere can contribute to improvement of the emission intensity of YAG:Ce³⁺ phosphor powders.

Key words: YAG phosphor; polyacrylamide gel; crystallization; morphology; luminescent properties

1 Introduction

YAG (Y₃Al₅O₁₂, the cubic garnet structure[1–2] based phosphor) has been widely used as solid-state laser material in luminescence fields. As known as an efficient phosphor, cerium-activated yttrium aluminum garnet (YAG:Ce³⁺) has strong yellow luminescence excited by blue light diode, and its broad emission band from 4f to 5d levels extends from 500 to 650 nm. So YAG:Ce³⁺ phosphor has extensive application in white light emitting diode(WLED). To obtain properties of higher power and brightness, there are many technologies used for preparation of YAG powder with high crystallinity, small particle size and regular morphology. Although the traditional solid state method is easy to form pure YAG phase, it normally needs a high temperature near 1 600 °C using yttria (Y₂O₃) and aluminum (Al₂O₃) compounds [3–4]. Generally, several stable phases of yttrium aluminum perovskite YAlO₃ (YAP) and yttrium aluminum monoclinic Y₄Al₂O₉ (YAM) are formed as intermediate products during the solid-state reaction. As

a result, the particulates are nonuniform and large in size, and have irregular shape, which brings negative influence to luminescent properties. In recent years, several wet chemical techniques such as co-precipitation method[5–6], sol-gel[7–8], combustion[9–10] hydrothermal synthesis[11], glycothermal method[12], and spray-pyrolysis synthesis[13–14] were used to prepare the YAG precursor. Although YAG phosphor particles synthesized by chemical methods have many advantages, i.e. high purity, homogenous composition and fine grains, they require additional heat treatment at higher temperatures (>1 000 °C) to get well crystallized products. Thus, hard aggregation of resulting powder is easily caused during the post heat treatment.

The polyacrylamide gel method was reported firstly by DOUY and ODIER[15] to prepare YBa₂Cu₃O_{7-x} powder. This process is fast and easy to scale-up method for obtaining fine powders of complex compounds. However, so far, no individual study has been published on the YAG:Ce³⁺ phosphors prepared by the polyacrylamide gel method. In this study, the polyacrylamide gel method was used to form an organic

three-dimension(3D) tangled network, where a solution of Y^{3+} , Ce^{3+} and Al^{3+} was soaked. The polyacrylamide gel reduces the diffusion path (up to nano-metric scale) for obtaining the desired material. The effects of the fluxes and atmosphere on luminescent properties (PL excitation and emission spectra) of YAG: Ce^{3+} phosphor powders was also discussed.

2 Experimental

2.1 Raw materials

High-purity Y_2O_3 (99.99%), $Al(NO_3)_3 \cdot 9H_2O$ (99.99%) and $Ce(NO_3)_3 \cdot 6H_2O$ (99.99%) were used as the starting chemicals. Acrylamide ($CH_2=CHCONH_2$, 99%), N', N-methylene-bis-acrylamide ($CH_2=CHCO-NHCH_2NHCOCH=CH_2$, 99%) and ammonium persulfate($(NH_4)_2S_2O_8$, 98%) were used as polymerization agents.

2.2 Preparation of phosphor powders

The processing steps for the polyacrylamide gel method are shown in Fig.1. The monomers, acrylamide and N', N-methylene-bis-acrylamide were dissolved in YAG:0.06Ce transparent solution. The polymerization was initiated by ammonium persulfate, and a gel was obtained for 2 h at 80 °C. The gel was constituted by the

auxiliary 3D network, immobilizing the precursor solution of Y^{3+} , Al^{3+} and Ce^{3+} . The gels were dried and pretreated to remove the water and organic species. The calcination was conducted by a heating rate of 10 °C/min up to the holding temperature (800–1 300 °C) for different holding time (100–400 min), under weak reduction atmosphere in the presence of acetylene black powder or in air.

2.3 Characterization of phosphor powders

Phase analysis of as-received samples was accomplished with a X-ray diffractometer using Cu K_α radiation (PANalytical X'Pert Pro, Philips, Netherlands). Micrographs of as-received samples were observed by scanning electron microscopy (SEM, LEO 1530, Germany) under a working voltage of 20 kV. The PL excitation and emission spectra of polycrystalline YAG: Ce^{3+} phosphors (particle size: 30–50 μm) were measured by a fluorescence spectrophotometer (F-4500, Hitachi, Tokyo, Japan, wavelength range: 310–650 nm, scan speed: 1 200 nm/min, excitation slit: 5.0 nm, emission slit: 2.5 nm, PMT voltage: 400 V) with a 150 W Xenon short-arc lamp as an excitation source (Ushio, Tokyo, Japan). The container for depositing YAG:Ce phosphors was columniform, and a undersurface area of about 0.2 cm^2 was illuminated. All the measurements were carried out at room temperature.

3 Results and discussion

3.1 Effect of calcining temperature and holding time on crystallization and morphology of phosphor powder

The XRD patterns of Ce-doped YAG powders calcined for 300 min at different temperatures between 700 °C and 1 300 °C are shown in Fig.2. The patterns of the powder obtained at 700 °C (pretreatment step) exhibit broad bands indicative of incipient crystallization and the presence of short-range ordering, and the powder remains in amorphous state. At 800 °C, the diffraction pattern shows small bands of YAG. At 900 °C, however, a minor band (indicated by *) is observed due to YAP as an impurity together with formation of partial YAG phase. Moreover, at higher temperature, the intensity of emission of YAG phase increases and intensity of YAP phase decreases. At 1 000 °C, YAG is the only crystalline component, showing a complete conversion process from YAP to YAG. The temperature (1 000 °C) in our experiment is significantly lower than the crystallinity temperature of the sample prepared by the conventional solid-state reaction ($>1\ 600\ ^\circ C$ [4]). It is reported[16] that there are two basic routes for the

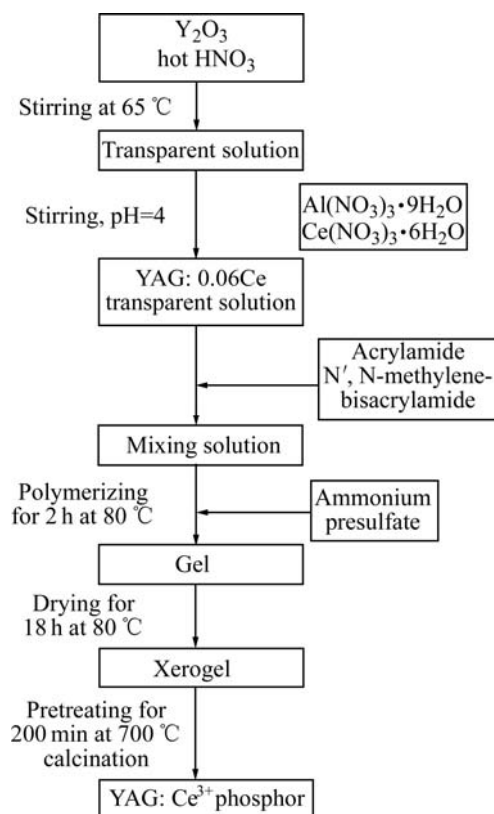


Fig.1 Flow chart of YAG: Ce^{3+} phosphor prepared by polyacrylamide gel method

formation of YAG phase. One is the direct formation of YAG from amorphous Y_2O_3 and Al_2O_3 mixture at 800 °C; the other is the indirect transformation through intermediates phases of YAP. In order to obtain pure YAG at lower temperature, it is necessary to avoid the formation of intermediate phase. As shown on XRD pattern, moreover, further calcining at higher temperatures leads to an increase in the YAG diffraction band intensity and decrease in the full-width at half-maximum due to the improvement of crystallinity and growth. The XRD patterns of Ce-doped YAG powders calcined at 1 100 °C for different holding time are shown in Fig.3. From this figure, it can be seen that the fine YAG phase can be obtained for holding time of 100 min. For the longer holding time, however, the change of diffraction band intensity and the full-width at half-maximum is not significant. Compared with other

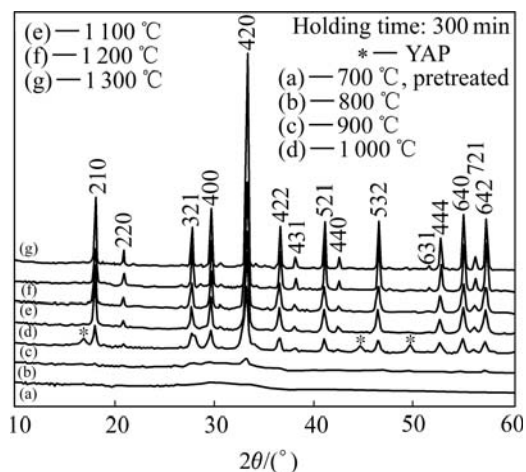


Fig.2 XRD patterns of Ce-doped YAG powders calcined for 300 min at different temperatures

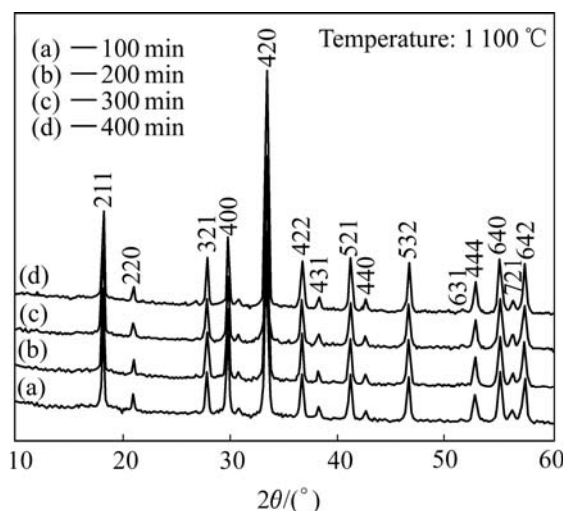


Fig.3 XRD patterns of Ce-doped YAG powders calcined at 1 100 °C for different holding time

methods[17–19], a pure YAG phase is produced for Ce-doped YAG prepared by polyacrylamide gel method at lower calcining temperature for shorter holding time in the present work. The reasons may be attributed to the loose and ultra-fine powder in this experiment.

Fig.4 shows the SEM images of Ce-doped YAG powders calcined for 300 min at different temperatures (1 000–1 300 °C). It is clear that uniform and spherical particles of $YAG:Ce^{3+}$ with homogeneous microstructure are obtained at 1 000 °C. With the calcining temperature increasing to 1 300 °C, the grain size grow gradually from 80 nm to 120 nm. In polyacrylamide gel method, polyacrylamide 3D network inhibits the movement of metal ions and metal atoms are distributed homogeneously. However, the aggregation of the uniform particles appears at 1 000 °C and 1 100 °C. On the other hand, as shown in Fig.4(d), sintering phenomenon appears among particles at 1 300 °C and particles connect with “sintering necks”.

Fig.5 shows the SEM images of Ce-doped YAG powders calcined at 1 100 °C for different holding time (100–400 min). It can be seen that the difference of particulate morphology is not significant in four samples: 1) the particles grow completely and connect together; 2) the particles have regular shape; 3) the length of particle is about 100 nm and the diameter is less than 50 nm.

3.2 Effect of calcining temperature and holding time on luminescent characteristics of phosphor powder

Fig.6 shows the PL excitation and emission spectra of Ce-doped YAG powders prepared with polyacrylamide gel method for 300 min at different calcining temperatures between 900 °C and 1 300 °C. Calcining temperature profoundly affects the intensity of emission. With the calcining temperature increasing, the intensity of emission increases steadily. As mentioned earlier, the band intensity of XRD increases and the homogeneous microstructure is obtained at the higher calcining temperature, and the intensity of emission increases. Compared with that at 1 200 °C, however, the increment is not significant at 1 300 °C. This can be attributed to sintering of phosphor powders at higher calcining temperature.

The PL excitation and emission spectra of Ce-doped YAG powders at 1 100 °C for different holding time is shown in Fig.7. The intensity of emission increases with holding time prolonging below 400 min. But the intensity of emission does not increase significantly for 400 min. Moreover, there is a blue shift phenomenon compared with 300 min. The wavelength of peak is about 526.0 nm for 300 min calcined at 1 100 °C, and it is about 525.4 nm when holding time increases to 400

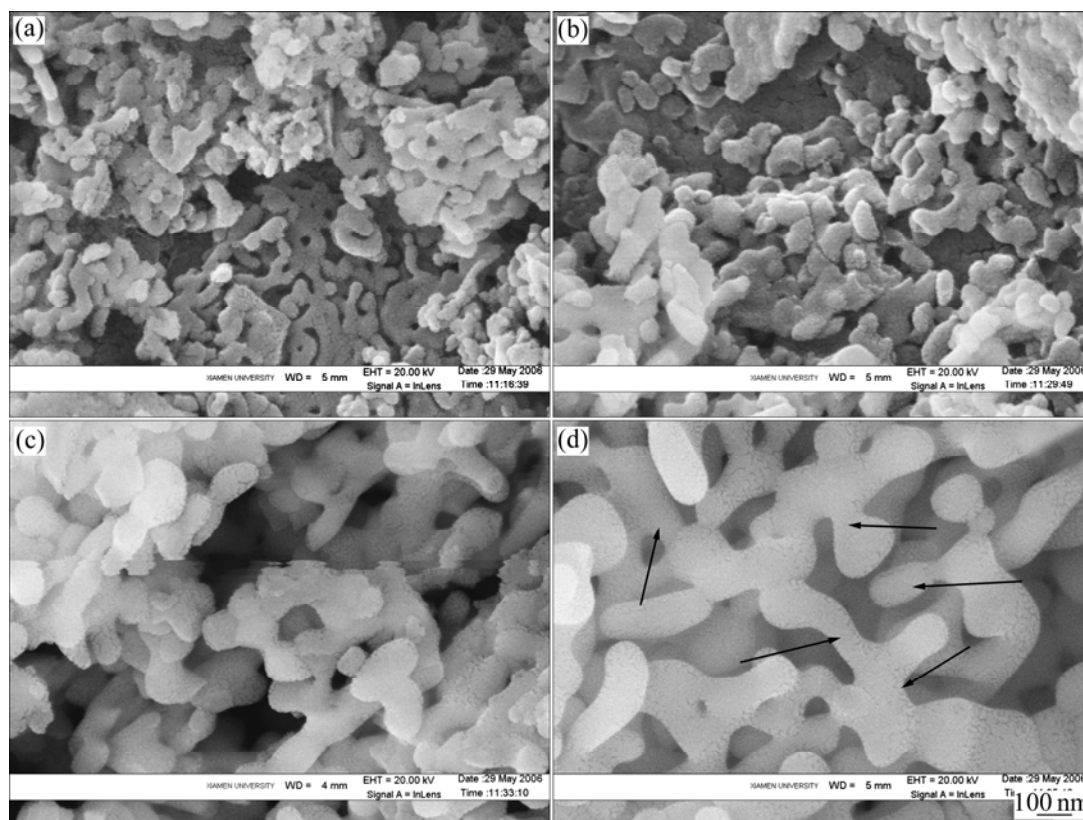


Fig.4 SEM images of Ce-doped YAG powders calcined for 300 min at different temperatures: (a) 1 000 °C; (b) 1 100 °C; (c) 1 200 °C; (d) 1 300 °C (Arrows remark “sintering necks”)

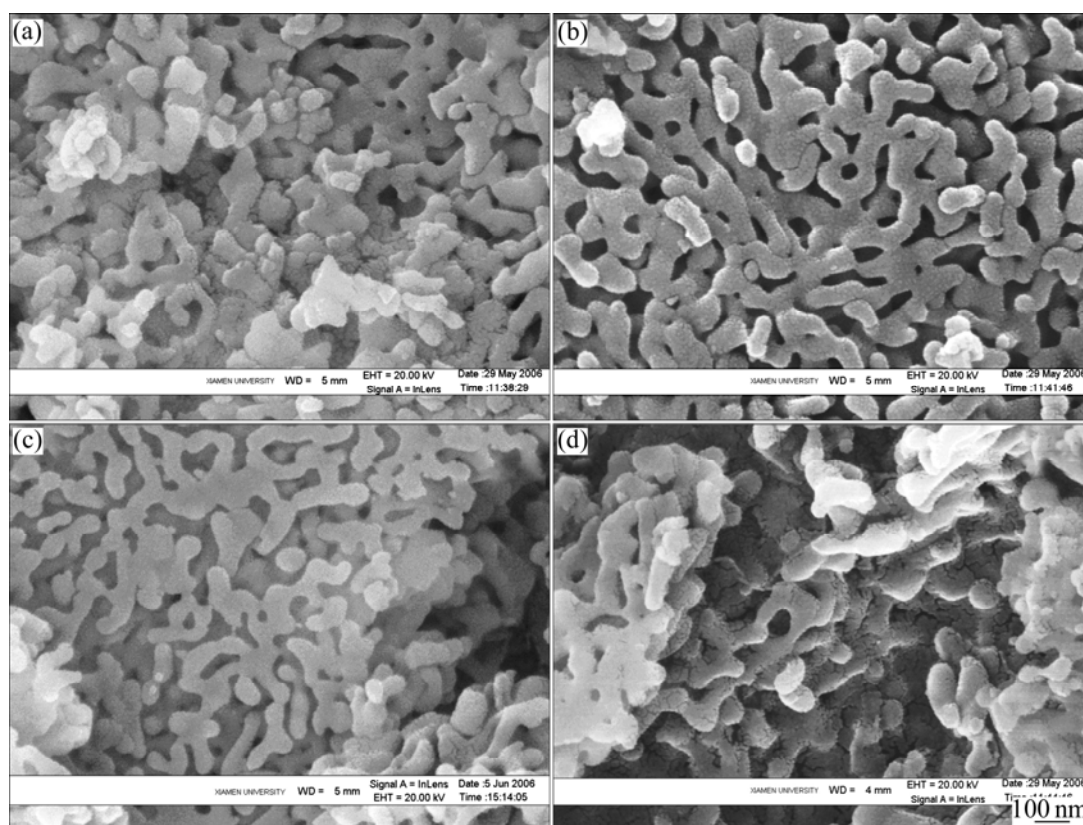


Fig.5 SEM images of Ce-doped YAG powders calcined at 1 100 °C for different holding time: (a) 100 min; (b) 200 min; (c) 300 min; (d) 400 min

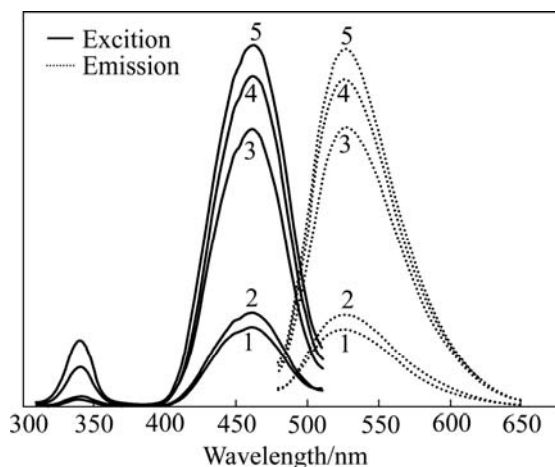


Fig.6 Photoluminescence spectra of Ce-doped YAG calcined for 300 min at different temperatures: 1—900 °C; 2—1 000 °C; 3—1 100 °C; 4—1 200 °C; 5—1 300 °C (Excitation spectrum $\lambda_{em}=528\text{nm}$ and emission spectrum $\lambda_{ex}=461\text{ nm}$)

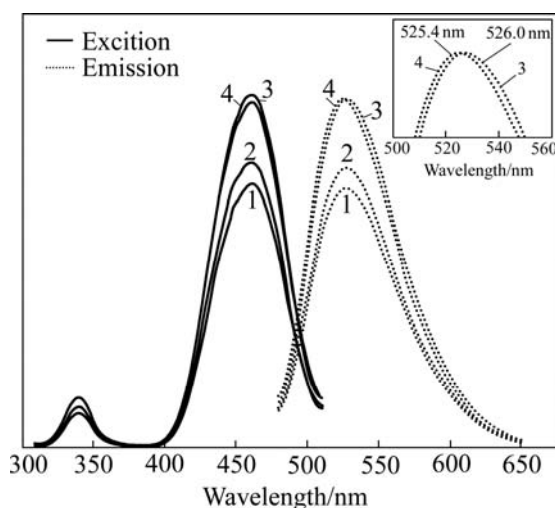


Fig.7 Photoluminescence spectra of Ce-doped YAG calcined at 1 100 °C for different holding time: 1—100 min; 2—200 min; 3—300 min; 4—400 min (Excitation spectrum $\lambda_{em}=528\text{nm}$ and emission spectrum $\lambda_{ex}=461\text{ nm}$)

min at 1 100 °C. The blue shift phenomenon in Ce-doped YAG phosphor has also been found in the samples prepared by citrate gel and polyacrylamide methods [20–21]. It is reported that the change of unit cell affects the crystal field around Ce^{3+} , and causes the blue-shift phenomena of spectra[21]. As shown in Fig.3, the lattice parameter of $\text{YAG}:\text{Ce}^{3+}$ powders decreases from 1.202 3 nm (for 300 min) to 1.201 4 nm (for 400 min) calculated by JADE software. The reason may be attributed to the transform of $\text{Ce}^{3+} \rightarrow \text{Ce}^{4+}$. The weak reduction atmosphere (provided by acetylene black) is exhausted with the holding time prolonging, and Ce^{3+} is oxygenated to Ce^{4+} . Ce^{4+} occupies the position of Ce^{3+} , in which Y^{3+}

is substituted by Ce^{3+} in YAG unit cell. The radius of Ce^{4+} is less than that of Ce^{3+} . So the original unit cell will be changed, affecting the crystal field around Ce^{3+} , and the blue-shift phenomena of spectra are observed.

3.3 Effect of fluxes and atmosphere on characteristics of cerium doped YAG phosphor

Fig.8 shows that the PL excitation and emission spectra of cerium doped YAG phosphors synthesized at 1 100 °C for 300 min by polyacrylamide gel method without flux (1) and followed by the same heat treatment process with flux of BaF_2 (2) and $\text{BaF}_2+\text{H}_3\text{BO}_3$ (3) in weak reduction atmosphere, as well as that followed by a heat treatment at 1 100 °C for 300 min in air (4). All the emission peaks are wide with the maximum at 528 nm, which corresponds to the transition emission of Ce^{3+} 5d-4f. It can be seen from curve 4 that the intensity of emission of phosphors in air declines in comparison with other phosphor at 1 100 °C for 300 min. As shown in Fig.9, calculated by JADE software, the lattice parameter of as-calcined $\text{YAG}:\text{Ce}^{3+}$ powders is 1.202 0 nm in air without flux, which is less than that of as-calcined $\text{YAG}:\text{Ce}^{3+}$ powders in weak reduction atmosphere without flux (1.202 3 nm). The reason is that Ce^{3+} is partially oxidized into Ce^{4+} . Curve 2 and curve 3 show the PL spectra of phosphor prepared by calcining with 1% flux of BaF_2 and with 1% flux of $\text{BaF}_2+\text{H}_3\text{BO}_3$ (1:1), whose intensity is higher in comparison with that of without flux. This enhancement is attributed to both the improvement of crystallization processes of YAG particles and the stabilization of trivalence cerium ion at high temperature[3, 22]. When two fluxes are used, the intensity of emission is higher than that of one flux, which

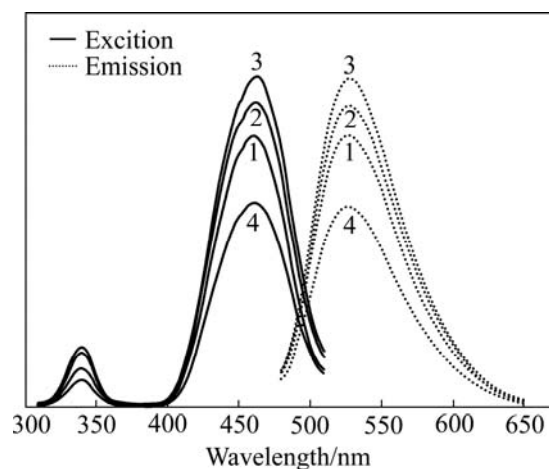


Fig.8 Photoluminescence spectra of Ce-doped YAG phosphors synthesized at 1 100 °C for 300 min: 1 Without flux; 2 With flux of BaF_2 ; 3 With flux of $\text{BaF}_2+\text{H}_3\text{BO}_3$ in weak reduction atmosphere; 4 In air without flux (Excitation spectrum $\lambda_{em}=528\text{ nm}$ and emission spectrum $\lambda_{ex}=461\text{ nm}$)

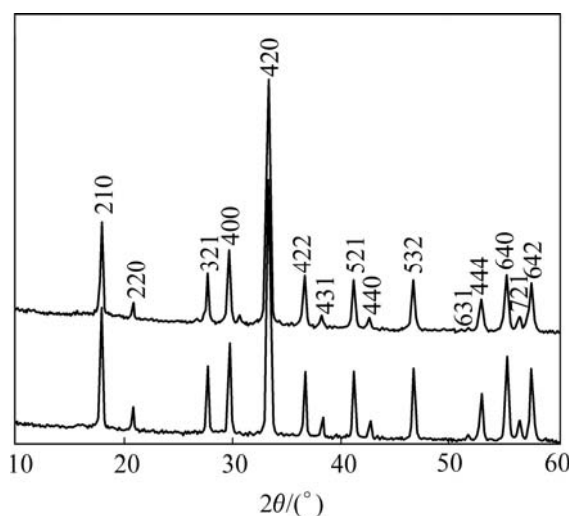


Fig.9 XRD patterns of Ce-doped YAG powders calcined for 300 min at 1 100 °C without flux in weak reduction atmosphere (a) and in air (b)

which indicates that two fluxes can stabilize trivalent Ce ion more efficiently.

Fig.10 shows the SEM images of Ce-doped YAG powders calcined at 1 100 °C for 300 min without flux Fig.10(a) and followed by the same heat treatment process with flux of BaF_2 Fig.10(b) and $\text{BaF}_2+\text{H}_3\text{BO}_3$ Fig.10(c) in weak reduction atmosphere, as well as that

followed by a heat treatment at 1 100 °C for 300 min in air Fig.10(d). The sample without flux in weak reduction atmosphere shows small particles in Fig.10(a). On the other hand, the samples with BaF_2 and $\text{BaF}_2+\text{H}_3\text{BO}_3$ present regular particles in Fig.10(b) and Fig.10(c), respectively. But the aggregation is serious with only BaF_2 compared with $\text{BaF}_2+\text{H}_3\text{BO}_3$, that is to say, the good decentrality between particles appears by using H_3BO_3 . From Fig.10(d), the borders of particles are not clear, and the shapes of particles are irregular in air without flux.

4 Conclusions

1) Polymer network formed by polyacrylamide gel inhibits the aggregate of ions in mixed solutions, pure YAG phase is obtained by calcining at 1 000 °C. The temperature (1 000 °C) is lower than general calcining temperature (over 1 600 °C).

2) With the calcining temperature increasing, the intensity of emission increases. But the increment is not significant at 1 300 °C compared with that at 1 200 °C due to “sintering” of phosphor powders at higher calcining temperature. With holding time prolonging, the intensity of emission increases below 400 min. However the intensity of emission does not increase significantly for 400 min, moreover, there is a blue shift phenomenon

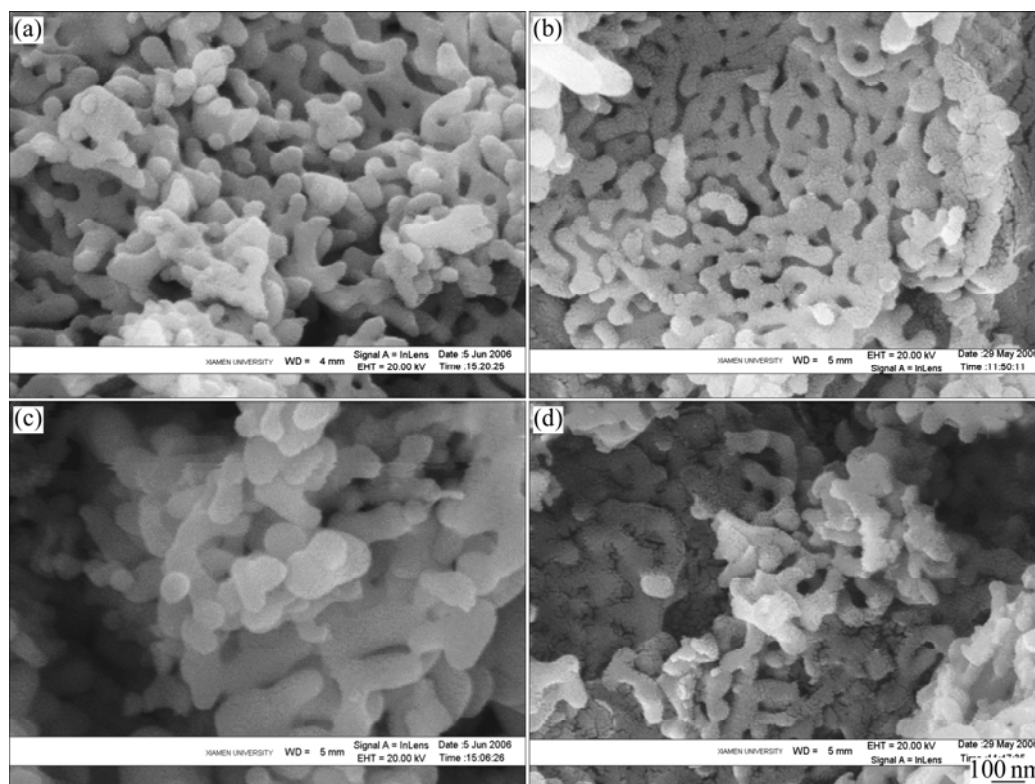


Fig.10 SEM images of Ce-doped YAG powders calcined at 1 100 °C for 300 min: (a) Without flux; (b) With flux of BaF_2 ; (c) With flux of $\text{BaF}_2+\text{H}_3\text{BO}_3$ in weak reduction atmosphere; (d) In air without flux

compared with that for 300 min.

3) Fluxes as BaF_2 and H_3BO_3 can enhance the intensity of emission of phosphor due to the improvement of crystallization processes of YAG and the stabilization of trivalence cerium ion in YAG:Ce^{3+} at high temperature. And two fluxes can increase emission efficiently than only one flux in this experiments.

4) Weak reduction atmosphere is useful to prevent the oxidation of trivalence cerium ion.

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