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Property of YAG: Ce phosphors powder prepared by mixed solvothermal method

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ABSTRACT

YAG: Ce phosphors were synthesized by a mixed solvothermal method. The effect of washing method of precursor, synthesis temperature, holding time and filling factor on the property of YAG: Ce had been researched by changing the synthetic conditions. The results show that as the increase of the synthesis temperature, the prolonging of the holding time and the rise of filling factor, the pressure of synthesis reaction system and the nucleation rate of grains increase, the rate of mass transfer and grain growth speed up. The degree of crystallization grows up, the crystal structure of YAG: Ce phase is improved. The particles are spherical and the distribution of particle size is uniform. The Ce^{3+} ions easily enter the YAG lattice and the distribution of Ce^{3+} ions is more homogeneous. The fluorescence property of YAG: Ce enhances. In this research, the YAG: Ce phosphor with good property can be obtained at 230–250 °C for 15–20 h with the filling factor 90%. The mean particle size is 1.4 μm. This synthetic method has good potential applications.

1. Introduction

Ce-doped yttrium aluminum garnet (YAG: Ce) has numerous applications such as a luminescent material in vacuum ultraviolet (VUV), plasma display panels (PDPs), solid-state lasers, and solid-state lighting, because it has a high luminescent efficiency and chemical stability [1,2]. YAG: Ce phosphors have been found to be suitable for converting the blue light emitting diode (LED) radiation into a very broad band yellow emission, which can be used as one of the most common methods for producing white light with a gallium nitride-based blue LED [3]. It is known that the combination of a white LED with a blue LED using YAG: Ce phosphors suffer from a red spectral deficiency, resulting in a relatively low value of color rendering index [4,5]. Attempts have been made in some work to increase the properties of the phosphor by co-doping trivalent Gd, Eu, Pr, or Sm [6–8]. YAG: Ce phosphors also have much potential in biological application [9]. The main properties of YAG: Ce are shown in Table 1 [10].

Recently, the study of fast YAG: Ce phosphors in X-ray digital imaging detectors has been presented [11–13]. YAG: Ce single crystal screens are used for X-ray micro-radiography, and are suitable for imaging with high spatial resolution. The material transparency decreases with increasing of the thickness of the imaging plate. And the detection efficiency decreases with scintillator thickness [11,12]. In the range of X-ray tube voltages (25–35 kVp) usually employed in mammography the thinner YAG: Ce of 33 mg/cm^2 and 42 mg/cm^2 shows the highest luminescence efficiency [13].

YAG powders are traditionally produced by solid-state reaction, which generally introduces impurities [14]. Other methods of producing YAG powders, such as co-precipitation [15], sol–gel method [16], spray pyrolysis [17], microwave-induced combustion process [18], and solvothermal method [19–21] have been developed in recent years. Zych et al. [15] prepared nanocrystalline powders of YAG: Ce using Pechini technique and precipitation with urea at 80–90 °C for 24 h. The powders heating at reducing atmosphere of nitrogen–hydrogen mixture at 1000 °C caused a red shift of the Ce^{3+} luminescence. The YAG: Ce powders were prepared by sol–gel combustion method at 540 °C [16]. The using of LiF in sol–gel process was helpful to decrease sintering temperature about 100–200 °C. The optimized doping amount of LiF was 4 wt.% to the precursor. Lee et al. [17] synthesized YAG: Ce powders by spray pyrolysis from the spray solutions with BaF_2 flux. The BaF_2 flux was added to the spray solution to prepare the YAG: Ce phosphor powders with regular morphology, fine size and high photoluminescence intensity under blue light. The maximum photoluminescence intensity of YAG: Ce phosphor powders prepared flux was 144% of that of the phosphor powders obtained from the spray solution without flux material. Wu et al. [19] prepared the submicronsized YAG: Ce phosphors with a relatively narrow grain size distribution, well-dispersed, and spherical by the solvo-thermal method under mild conditions with ethylenediamine solution as the solvent at the temperature of 200 °C for 5 h. The particles were not aggregated from

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Table 1
Main properties of YAG: Ce.

Properties	Chemical formula	Crystal structure	Density/g/cm^3	Conversion efficiency/$\eta_{x/v}$	Emission wavelength/nm	Melting point/°C	Afterglow (at% 6 ms)	Decay time/ns
	$Y_3Al_5O_{12}$	Cubic	4.55	4%	550	1970	<0.005	60–80

each other, which will be beneficial for phosphor applications, and the excitation and emission intensities enhanced with prolonging the holding time. The YAG: Ce phosphors nanoparticles of 5 nm size were prepared by thermal decomposition of metal carbonates-oleate complex solutions in an autoclave at 300 °C [21]. Nucleation of the phosphors nanoparticles was mediated by oleic acid and their formation was facilitated by the oleylamine (capping agent) which inhibited crystal growth. The electron-phonon coupling strength decreases with reducing phosphors size. Nyman et al. [20] prepared nano-YAG: Ce growth in 1,4-butatnediol. This study provided a mean to increase the quantum yield of nano-YAG: Ce from 39% to 56%. YAG: Ce prepared from neat 1,4-butanediol solutions that were surface-passivated with a layered alumina. The layered alumina was an insoluble intermediate in the reaction process, and nano-YAG: Ce nucleates were heterogeneously on its surface, forming a precipitate with high QY.

In this research, we attempt to synthesis YAG: Ce powders via a new method, mixed solvothermal method, and investigate the effect of synthesis conditions on property of YAG: Ce powders.

2. Experimental

The yttrium, aluminum and cerium sources for YAG: Ce synthesis were Y_2O_3 (99.99%), $Al(NO_3)_3{\cdot}9H_2O$ (99.99%) and $Ce(NO_3)_3{\cdot}6H_2O$ (99.99%), respectively. At first, $Y(NO_3)_3$ solution was obtained by dissolving Y_2O_3 in nitric acid, and adding distilled water to make $Y(NO_3)_3$ solution whose concentration was 0.2 mol/L. Then appropriate amount of $Al(NO_3)_3{\cdot}9H_2O$ and $Ce(NO_3)_3{\cdot}6H_2O$ were dissolved in the above solution, in which the mol ratio of the Y^{3+}, Ce^{3+} and Al^{3+} was maintained as $3-x$:x:5 ($x=0.06$). The ammonium hydrogen carbonate (AHC) solution was prepared by adding 10 g of NH_4HCO_3 into 100 ml of distilled water, and its pH value was 7.7. At last, the precursor precipitate was prepared by adding the mother salt solution at a speed of 0.5 ml/min into the above AHC mixture solution under vigorous agitation at room temperature. A part of precipitate was repeatedly washed with distilled water to remove the residual nitric and ammonia ions, and the rest of the precipitate was washed twice with ethanol. The precursor precipitate washed which was dispersed in mixed solvent of ethylenediamine–ethanol with the ratio of 20:1 was placed in an autoclave. The autoclave was heated between 180 °C and 250 °C at a heating rate of 2 °C/min and kept at that temperature between 5 h and 20 h. After cooling to room temperature, the products in the autoclave were washed and dried for further study. All experimental conditions are shown in Table 2.

The speed of adding the mother salt solution into the AHC solution was measured by electronic stopwatch. Phase development in the synthesis process was analyzed by X-ray diffraction (XRD, PAnalytical X'Pert PRO, Cu Kα, λ = 0.15418 nm). The particle shape, size and dispersion of powders were observed by a transmission electron microscope (TEM; Hitachi model H-800) and a scanning electron microscope (SEM; Quanta200ESEM FEIco-Holland). The crystal structure of grains was observed by high resolution transmission electron microscope (HRTEM, Philips Tecnai 20μ-TWIN microscope, 300 kV). The distribution of particles size of powders was detected by laser scattering particle size distribution analyzer (Model LA-950, Horiba). The samples for morphology study were pretreated by hand grinding in an agate mortar and the ultrasonic treatment with ethanol. Photoluminescence (PL) of powders was measured by WFY-28 fluorescence spectrometer at room temperature. The grain size was also calculated according to Scherer equation [22].

3. Results and discussion

3.1. Effect of washing method of the precursor on synthesis reaction and property of powders

Fig. 1A is the XRD patterns of powders prepared at 250 °C for 15 h with water washed and ethanol washed precursor. As shown in Fig. 1A, the powders prepared with water-washed precursor are composed of YAG and AlO (OH) phase, and the powders prepared with ethanol-washed precursor are composed of pure YAG phase without any impurity phase.

The TEM photograph of the powders prepared with water washed precursor is shown in Fig. 1B. According to the XRD pattern analysis, the spherical particles in micrometer scale are YAG phase and the sheets in nano-scale are AlO (OH) phase. As shown in Fig. 1C, powders prepared with ethanol washed precursor are of uniform particle size distribution, better dispersion and the diameter of particles is about 1.4 μm. The above results show that the presence of water in mixed solvent may result in the appearance of impurity phase in the powders. Therefore, using ethanol instead of distilled water to wash the precursor is beneficial to prepare pure YAG phase via mixed solvent-thermal method.

3.2. Effect of temperature on synthesis reaction and property of powders

Fig. 2A shows the XRD patterns of the powders prepared with ethanol washed precursor at different temperature for 15 h. As shown in Fig. 2A, the powders prepared at 180 °C are amorphous. Pure YAG phase is obtained at 210 °C, but the characteristic peak intensity of YAG phase is weak and the widening of diffraction line profile appears. The powder grain size calculated by the Scherer equation is about 20 nm. The diffraction peaks of YAG phase become sharp and the crystallinity of the YAG: Ce powders is enhanced as the synthesis temperature gets up to 230 °C. At 250 °C, the characteristic peak intensity and crystallinity of YAG: Ce powders are the largest. As shown in Fig. 2B and C, the particle size of YAG: Ce powders with slight agglomeration at 210 °C is about 160 nm and the particle size of powders prepared at 230 °C is in a range between 150 nm and 500 nm. The particle size distribution of the powders is wide, and the shape of particles is irregular. As shown in Figs. 2D and 5B, the particle size of powders prepared at 250 °C is about 1.4 μm, and the particle size distribution becomes narrow and the shape of particles is spherical. The HRTEM image in Fig. 5A reveals high crystallinity and perfect structure of grains of the powders prepared at 250 °C for 15 h. According to the above results, it

Table 2
All experimental conditions.

	Washing method	Temperature/°C	Holding time/h	Precursor/g	Mixed solvent/ml	Filling factor/%
S1	Water washed	250	15	4.5	18	90
S2	Ethanol washed	250	15	4.5	18	90
S3	Ethanol washed	230	15	4.5	18	90
S4	Ethanol washed	210	15	4.5	18	90
S5	Ethanol washed	180	5	4.5	18	90
S6	Ethanol washed	230	10	4.5	18	90
S8	Ethanol washed	230	20	4.5	18	90
S9	Ethanol washed	250	15	3.5	14	70
S10	Ethanol washed	250	15	2.5	10	50

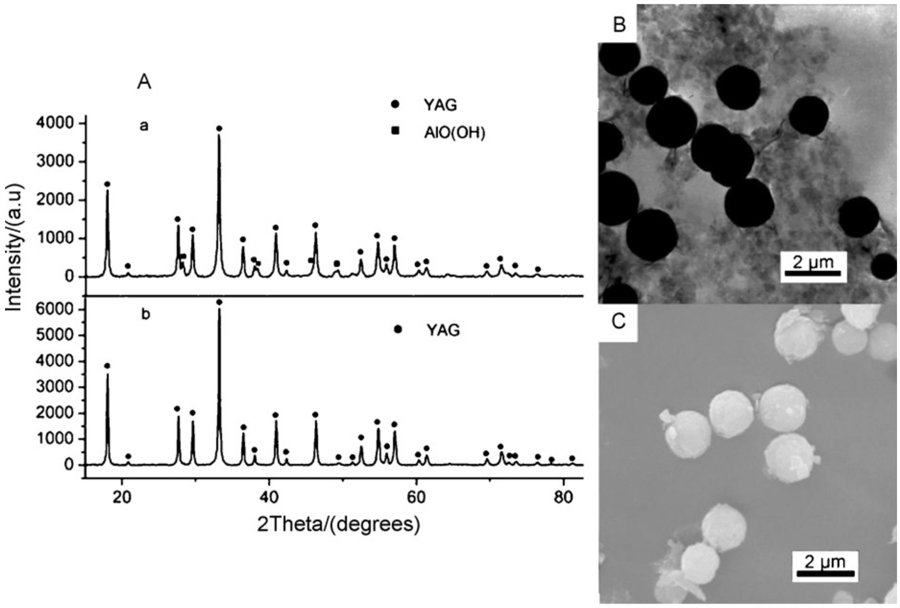

Fig. 1. (A) XRD patterns of synthetic powders prepared with (a) water washed and (b) ethanol washed precursor at 250 °C for 15 h. (B) TEM photographs of synthetic powders prepared with water washed precursor at 250 °C for 15 h. (C) SEM photograph of synthetic powders prepared with ethanol washed precursor at 250 °C for 15 h.

can be concluded that the crystallinity and particle size of YAG: Ce powders increase with temperature increasing, and the particles are in a high degree of regularity. The distribution of particle size is more uniform. This is because the pressure of reaction system rises with reaction temperature increasing, the driving force of grain nucleation and growth is enhanced, and the rate of grain nucleation and mass transfer speed up meanwhile. Hence, a large amount of grains with perfect crystal structure can uniformly grow to the large spherical particles under a relatively short period of time.

Fig. 2E shows the excitation and emission spectra of powders synthesized at different temperature for 15 h. The YAG: Ce powders prepared at 210 °C have no sign of fluorescence property, which is caused by the lower grain crystallinity and the lower concentration of Ce^{3+} ions in the YAG lattice. The YAG: Ce powders prepared at 230 °C produce the characteristic $^2F \rightarrow {}^2D$ transitions of Ce^{3+} with excitation in the blue region which center at 450 nm and a broad emission in the yellow region with a peak of 530 nm [15]. The emission band of GaN LED chips located in the range of 450–480 nm is in good match with the excitation band of YAG: Ce powders. The excitation and emission intensities are enhanced with increasing of synthesis temperature, and they reach maximum value at 250 °C. As the synthesis temperature rises, the energy of the reaction system increases. The rate of grain growth and grain crystallinity improves. The crystal defects decrease. The concentration of Ce^{3+} ions in the YAG lattice is higher, and the distribution of Ce^{3+} ions is more homogeneous. Therefore, the fluorescence spectra intensity of YAG: Ce powders gradually increases.

3.3. *Effect of holding time on synthesis reaction and property of powders*

Fig. 3A shows the XRD patterns of the powders prepared at 230 °C under different holding time. The powders held for 5 h are

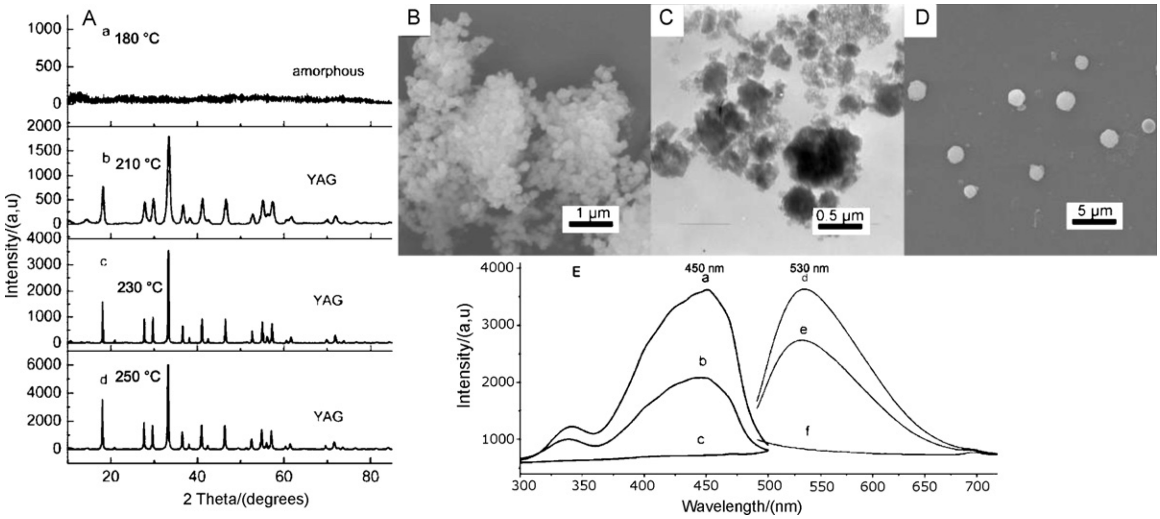

Fig. 2. (A) XRD patterns of synthetic powders prepared with ethanol washed precursor at 180 °C, 210 °C, 230 °C and 250 °C for 15 h. (B) SEM photograph of synthetic powders prepared at 210 °C for 15 h. (C) TEM photograph of synthetic powders prepared at 230 °C for 15 h. (D) SEM photograph of synthetic powders prepared at 250 °C for 15 h. (E) Room-temperature excitation and emission spectra of the YAG: Ce powders prepared for 15 h at (a, d) 250 °C, (b, e) 230 °C and (c, f) 210 °C.

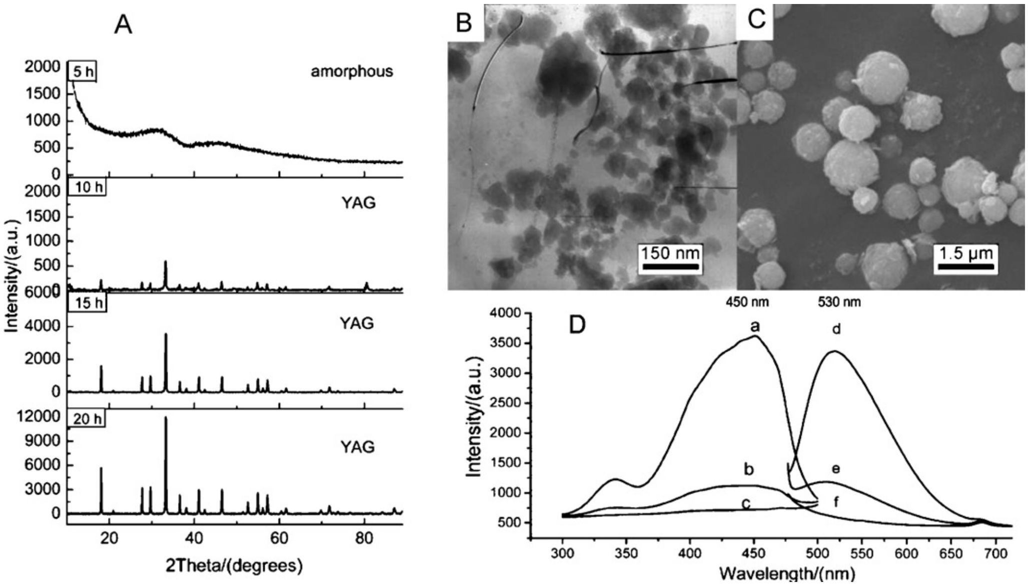

Fig. 3. (A) XRD patterns of synthetic powders prepared with ethanol washed precursor at 230 °C for 5 h, 10 h, 15 h and 20 h. (B) TEM photograph of YAG: Ce powders prepared at 210 °C for 10 h. (C) SEM photograph of synthetic powders of prepared at 230 °C for 20 h. (D) Room-temperature excitation and emission spectra of the YAG: Ce powders prepared at 230 °C for (a, d) 20 h, (b, e) 15 h and (c, f) 10 h.

amorphous. When the holding time is 10 h, YAG phase with low crystallinity appears, and the intensity of diffraction peak is weaker. The intensity of the characteristic peak of YAG phase increases with the prolongation of holding time. As the holding time is 20 h, the intensity of the characteristic peak of YAG phase with the high crystallinity is the largest. Fig. 3B shows that the particle size of powders held for 10 h is 40–200 nm. While the holding time prolongs to 15 h, the particle size of powders with slight agglomeration is in a range between 150 nm and 500 nm, as shown in Fig. 2C. The particles of YAG: Ce powders held for 20 h are regular spherical, as shown in Fig. 3C, the YAG: Ce particles with good dispersion have narrow size distribution. The range of particle size is 0.5–1.4 μm. According to the above results, the particle size and grain crystallinity increase with the prolongation of holding time.

Fig. 3D shows the excitation and emission spectra of YAG: Ce powders prepared at 230 °C under different holding time. As the holding time is 10 h, the YAG: Ce powders have no sign of fluorescence property. This is because the grain crystallinity of YAG: Ce powders is low and the Ce^{3+} ions cannot diffuse into the YAG crystal lattice homogenously in such a short time. The intensity of excitation and emission spectra of YAG: Ce powders gradually increases with the prolongation of holding time, which reach the maximum when the holding time prolongs to 20 h. It is because with the prolongation of holding time the grain crystallinity of YAG: Ce powders increases gradually, the Ce^{3+} ions are easy to distribute into YAG lattice homogenously and the particles of YAG: Ce powders with regular spherical particles grow up gradually. Hence, the fluorescence property of YAG: Ce powders enhances.

3.4. Effect of filling factor on synthesis reaction and property of powders

In this research, the effect of filling factor of the autoclave on phase composition, grain morphology and fluorescence property of YAG: Ce powders were also investigated. The filling factor of the autoclave has a great influence on the pressure of synthesis reaction system. Fig. 4A shows the XRD patterns of powders prepared with different filling factor at 250 °C for 15 h. The powders prepared with 50% of filling factor are amorphous. The YAG phase has obtained with the 70% of filling factor. But the crystallinity of YAG phase is low. And it increases markedly when the filling factor rises to 90%.

As shown in Fig. 4B and D, when the filling factor is 70%, the particle size of YAG: Ce powders with slight agglomeration is 0.5–1.4 μm, and the excitation and emission intensity are weak. When the filling factor reaches 90%, the YAG: Ce powders with good dispersion have narrow particle size distribution, the particles are regular spherical and the mean particle size is about 1.4 μm. The excitation and emission intensity of powders reach the maximum as shown in Fig. 4C and D. Due to the reaction system pressure rising with the increasing of the filling factor, the speed of the mass transfer, grain growth and grain crystallinity increase. At the same time, the diffusion rate of Ce^{3+} ions speeds up, a large mount of Ce^{3+} ions are doped into the YAG lattice, which can enhance the fluorescence property of YAG: Ce phosphors.

In conclusion, as the filling factor is 90%, the YAG: Ce powders with high crystallinity and perfect crystal structure can be obtained at 230–250 °C for 15–20 h, and the YAG: Ce powders have narrow particle size distribution, the range of particle size is 1.2–1.5 μm, as shown in Fig. 5A and B.

Compared with the emission spectra of YAG: Ce powders prepared at 1100 °C for 2 h via co-precipitation method, the YAG: Ce powders prepared at 250 °C and at 230 °C for 15 h by mixed solvothermal method have higher emission intensity, as shown in Fig. 5C. Therefore, this synthetic method has a good potential application.

In this research, a small amount of ethanol in the mixed solvent is a kind of auxiliary solvent, which can improve the dispersibility of precursor in the synthetic process. The formation of hydrogen bonds of non-bridging hydroxyls on the surface of the precursor particles reduces due to the ethanol radical group. Ethanol can lead to change of properties on the precursor particles surface, intensify space steric effect, and avoid hard agglomeration during the synthetic reaction. Ethylenediamine is a kind of strong polar solvent with high strong chelating ability. It chelates easily with Ce^{3+}, Y^{3+} and Al^{3+} ions and increases the solubility of precursor. Ethylenediamine can accelerate the diffusion of metal ions and promote the nucleation and growth of YAG: Ce grains.

The formation process of YAG: Ce grains includes three steps which are the dissolution of precursor, crystal nucleation and grain growth. The illusion of the reaction mechanism is shown in Fig. 6 [23]. With increasing of temperature, the precursor which contains Ce^{3+}, Y^{3+} and Al^{3+} in the mixed solvent is dissolved gradually.

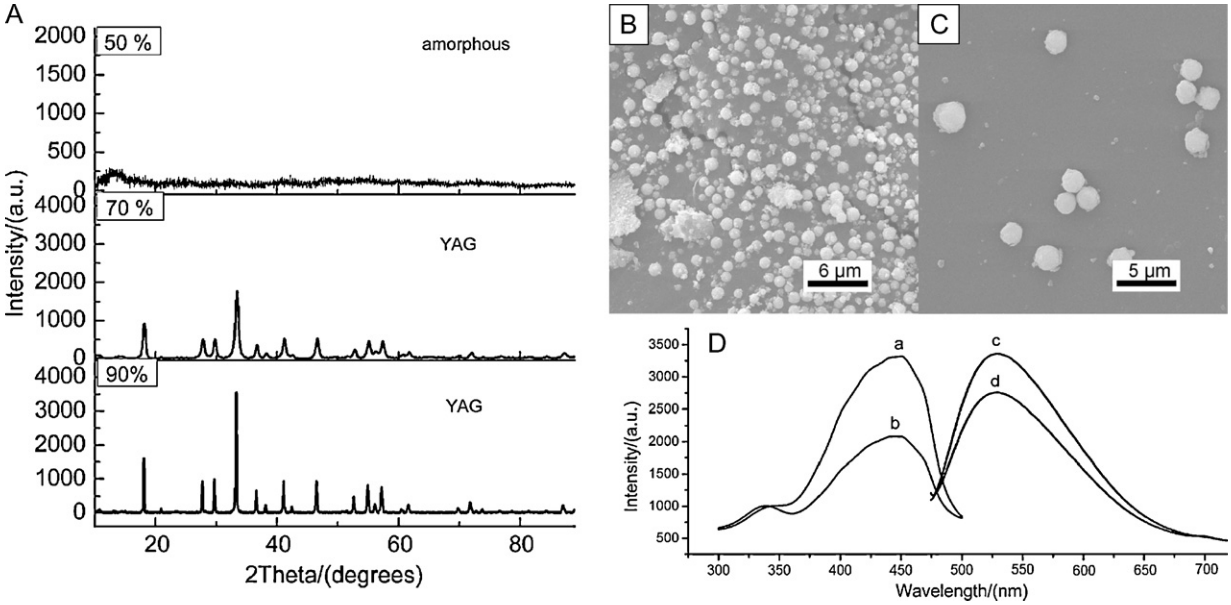

Fig. 4. (A) XRD patterns of synthetic powders prepared with ethanol washed precursor at 250 °C for 15 h with different filling factors. SEM photographs of YAG: Ce powders prepared at 250 °C for 15 h with filling factor (B) 70% and (C) 90%. (D) Room-temperature excitation and emission spectra of the YAG: Ce powders prepared at 250 °C for 15 h with filling factor (a, c) 90% and (b, d) 70%.

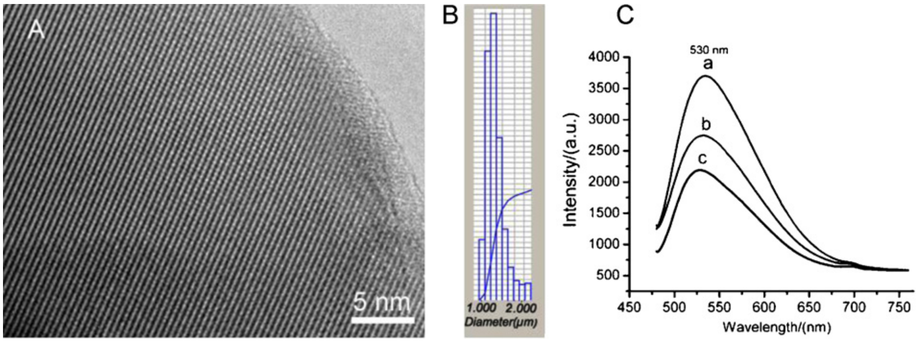

Fig. 5. (A) HRTEM picture of YAG: Ce powders prepared with ethanol washed precursor at 250 °C for 15 h, (B) Particle size distribution of YAG: Ce powder prepared at 250 °C for 15 h, (C) Room-temperature emission spectra of the YAG: Ce powders prepared at (a) 250 °C and (b) 230 °C for 15 h via mixed solvothermal method and at (c) 1100 °C for 2 h via co-precipitation method.

When the metal ions concentration reaches to the saturation state according to the stoichiometric ratio of YAG: Ce, the YAG: Ce grains begin to nucleate and grow gradually. With further rising of the temperature and prolongation of holding time, the grains grow bigger via growth-recrystallization process, and small grains constantly gather together and gradually become larger particles. The formation of the YAG: Ce particles is the interactional result of aggregation without alignment and oriented arrangement and growth as shown in Fig. 6.

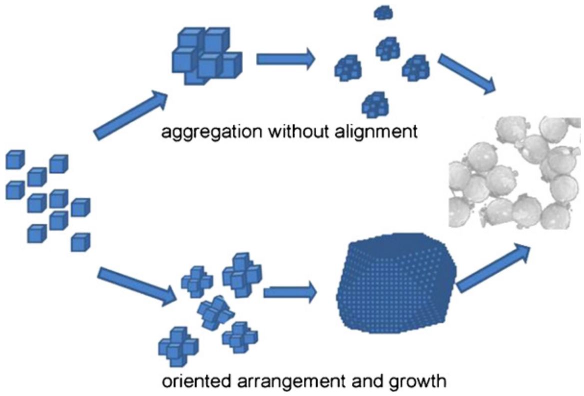

Fig. 6. The illustration of the reaction mechanism.

4. Conclusions

The YAG: Ce phosphors were prepared by the mixed solvothermal method, and the effect of synthesis conditions on the property of YAG: Ce phosphor was investigated. The results show that the water in the mixed solvent is not conductive to the formation of pure YAG phase. The synthesis temperature, holding time and filling factor have important influence on the property of YAG: Ce phosphor. With the increasing of the synthesis temperature, holding time and filling factor, the pressure of reaction system increases, then the crystal nucleation and mass transfer speed up, and rate of grain growths and grain crystallinity of YAG increase. The crystal structure of the YAG phase is prefect. The YAG: Ce particles are regular spherical and the powders have uniform distribution of particle size. The Ce^{3+} ions are easier to be doped into the YAG lattice and the distribution of Ce^{3+} ions is more homogeneous and the fluorescence property of YAG: Ce phosphors enhances. In summary, the optimal conditions of obtaining YAG particles of minimum particle size is at 210 °C for 15 h with the filling factor 90%.

The YAG: Ce phosphor powders with good property can be obtained at 230–250 °C for 15–20 h with 90% of filling factor.

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References

[1] W.H. Chao, R.J. Wu, T.B. Wu, J. Alloys Compd. 506 (2010) 98–102.
[2] G. Li, Q. Cao, Z. Li, Y. Huang, Y. Wei, J. Shi, J. Alloys Compd. 485 (2009) 561–564.
[3] M.L. Saladino, A. Zanotto, D.C. Martino, A. Spinella, G. Nasillo, E. Caponetti, Langmuir 26 (2010) 13442–13449.
[4] W. Ma, Z. Shi, R. Wang, J. Alloys Compd. 503 (2010) 118–121.
[5] P. Li, L. Pang, Z. Wang, Z. Yang, Q. Guo, X. Li, J. Alloys Compd. 478 (2009) 813–815.
[6] Y.X. Pan, W. Wang, G.K. Liu, S. Skanthakumar, R.A. Rosenberg, X.Z. Guo, et al., J. Alloys Compd. 488 (2009) 638–642.
[7] J.W. Lee, J.H. Lee, E.J. Woo, H. Ahn, J.S. Kim, C.H. Lee, Ind. Eng. Chem. Res. 47 (2008) 5994–6000.
[8] H.S. Jang, W.B. Im, D.C. Lee, D.Y. Jeon, S.S. Kim, J. Lumin. 126 (2007) 371–377.
[9] R. Asakura, T. Isobe, K. Kurokawa, H. Aizawa, M. Ohkubo, Bioanal. Chem. 386 (2006) 1641–1647.
[10] M. Stampanoni, G. Borchert, P. Wyss, R. Abel, B. Patterson, S. Hunt, D. Vermeulen, et al., Nucl. Instrum. Methods Phys. Res., Sect. A 491 (2002) 291–301.
[11] J. Touš, M. Horváth, L. Pína, K. Blažek, B. Sopko, Nucl. Instrum. Methods Phys. Res., Sect. A 591 (2008) 264–267.
[12] J. Touš, K. Blažek, L. Pína, B. Sopko, Appl. Radiat. Isot. 68 (2010) 651–653.
[13] S.L. David, C.M. Michail, M. Roussou, E. Nirgianaki, A.E. Toutountzis, I.G. Valais, et al., IEEE Trans. Nucl. Sci. 57 (2010) 951–957.
[14] S. Hong, Z. Fu, J. Zhang, S. Zhang, J. Lumin. 118 (2006) 179–185.
[15] E. Zych, A. Walasek, A.S. Hojniak, J. Alloys Compd. 451 (2008) 582–585.
[16] H. Jiao, Q. Ma, L. He, Z. Liu, Q. Wu, Powder Technol. 198 (2010) 229–232.
[17] S.H. Lee, D.S. Jung, J.M. Han, H.Y. Koo, Y.C. Kang, J. Alloys Compd. 477 (2009) 776–779.
[18] Y.P. Fu, J. Alloys Compd. 414 (2006) 181–185.
[19] Z. Wu, X. Zhang, W. He, Y. Du, N. Jia, G. Xu, J. Alloys Compd. 468 (2009) 571–574.
[20] M. Nyman, L.E.S. -Rohwer, J.E. Martin, P. Provencio, Chem. Mater. 21 (2009) 1536–1542.
[21] L.T. Su, A.I.Y. Tok, Y. Zhao, N. Ng, F.Y.C. Boey, J. Phys. Chem. C 113 (2009) 5974–5979.
[22] Y.P. Fu, S.B. Wen, C.S. Hsu, J. Alloys Compd. 458 (2008) 318–322.
[23] H.W. Zhang, E.W. Shi, Z.Z. Chen, X.C. Liu, B. Xiao, Solid State Commun. 137 (2006) 272–274.