Synthesis and luminescent properties of Ce$^{3+}$ doped LuAG nano-sized powders by mixed solvo-thermal method

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Abstract: Polycrystalline LuAG: Ce$^{3+}$ (cerium$^{3+}$-doped lutetium aluminum garnet) powders were prepared by mixed solvo-thermal method. Fourier-transform IR spectroscopy (FTIR) and X-ray diffraction (XRD) measurements showed that the precursors were ethanol derivatives AlO(OH) crystal with hydroxyl and carbonate group. XRD results showed that phase of Lu$_2$O$_3$ disappeared with the precursors were annealed at 400 °C, cubic phase Lu$_2$O$_3$:Ce$^{3+}$ appeared but only one diffraction peaks of Lu$_3$O$_5$ (Lu$_3$AlO$_5$) at calcination temperature to 700 °C, and the purified crystalline phase of Lu$_3$O$_5$:Ce$^{3+}$ was obtained at 1000 °C. The scanning electron microscopy (SEM) analysis revealed that the synthesized Lu$_3$O$_5$:Ce$^{3+}$ powders were uniform and had good dispersivity with an average particle size about 100 nm. Excitation and emission spectra of Ce$^{3+}$ doped LuAG phosphors were measured. Many factors of affecting the intensity of emission spectra were discussed.

Keywords: LuAG: Ce$^{3+}$ phosphors; hydrothermal; mixed solvo-thermal method; photoluminescence; rare earths

An inorganic scintillator plays an important role in radiation detection in many sectors of research concerning almost all medical diagnostic imaging modalities that use X-ray or gamma rays, dosimetry, nuclear medicine, high energy physics and also in many industrial measuring systems$^{[4,5]}$. For these different applications, scintillator is the primary radiation sensor, and scintillator material can absorb high-energy photons and then emit different energy photons$^{[3]}$.

Recently, lutetium aluminum garnet (Lu$_3$Al$_5$O$_{12}$), because of its high density (6.73 g/cm$^3$, 94% of BGO), high luminescent efficiency, and good chemical radiation stability, has been known to be one of the promising host crystals for scintillating materials. In rare earth ions doped Lu$_3$Al$_5$O$_{12}$ host lattice, cerium (Ce$^{3+}$) as luminescent activators can yield fast decay with 5d-4f allowed transitions of the Ce$^{3+}$ ion, so Lu$_3$O$_5$:Ce$^{3+}$ is a fast efficient response scintillator materials$^{[4–6]}$. However, the growth of high optical quality Lu$_3$O$_5$:Ce$^{3+}$ single crystal is an arduous process with high costs and long production cycle$^{[7,8]}$. Instead of this goal, for achieving the luminescent properties, synthesizing high density, fine dispersive and less agglomerative Lu$_3$O$_5$:Ce$^{3+}$ powder is required. Many methods have been used to synthesize rare earth (RE)-doped LuAG such as combustion method$^{[9]}$, high temperature solid-state method$^{[9,10]}$, sol-gel method$^{[11]}$, and precipitation method$^{[12,13]}$. However, hydrothermal method is scarcely used to synthesize Lu$_3$O$_5$:RE phosphors. In this paper, Lu$_3$O$_5$:Ce$^{3+}$ nano-phosphors were synthesized by mixed solvo-thermal method. The structures and photoluminescent properties of Lu$_3$O$_5$:Ce$^{3+}$ phosphors were investigated.

1 Experimental

1.1 Preparation

Fig. 1 shows the schematic flow chart for the synthesis of Lu$_3$O$_5$:Ce$^{3+}$ nano-sized powders. The synthesis procedure of Lu$_3$O$_5$:Ce$^{3+}$ phosphors can be divided into three steps. Firstly, lutetium oxide (Lu$_2$O$_3$, 99.99%) dissolved in dilute nitric acid (HNO$_3$) under continuously stirring and heating. Aluminium nitrate (Al(NO$_3$)$_3$·9H$_2$O, 99.99%) and cerium nitrate (Ce(NO$_3$)$_3$·6H$_2$O, 99.99%) were dissolved in deionized water. Then the solutions of Lu(NO$_3$)$_3$, Al(NO$_3$)$_3$, and Ce(NO$_3$)$_3$ were mixed to yield a composition with general formula (Lu$_{1–x}$Ce$_x$)$_3$Al$_5$O$_{12}$ (x mol.% Ce$^{3+}$), and then proper ethanol was added as dispersant. The mixture was stirred for hours at room temperature. Mixed solution was dripped into the precipitation agent solution at a titration speed of 2 ml/min, and stirred continuously. Three precipitants, AHC$^+$ AW (ammonium hydrogen carbonate and ammonia water), AW (ammonia water) and urea were used respectively. After the titration finished, proper amount of ammonium was dripped into the mixture to adjust the pH value (pH=8–9) of suspension. After continuously stirring and aging for hours, the white precipitation was washed four times with distilled water and collected by filtrating. Proper amount of the resultant

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precipitate, mixed with a certain proportion of alcohol and water, was sealed in a 50 ml autoclave, and then put into an oven at 250 °C for 20 h. The precursor powder was obtained by filtering and drying at 100 °C, and was annealed at a higher temperature ranging from 400 to 1100 °C in a muffle furnace for 2 h in air. In addition, for the sake of contrast, the part of the above mentioned white precipitation was respectively washed four times with distilled water and anhydrous ethanol, without hydrothermal treatment, and then dried at 100 °C. The obtained powders were crushed and directly calcined at 800 °C for 2 h in air.

1.2 Characterization

The phase evolution of the product was identified by X-ray diffraction (XRD, MAC Science Co. Ltd. MXP18AHF) with Cu Kα radiation in the range of 2θ= 10°–70°. FTIR spectra were measured with Magra-IR 750 (Nicolet Instrument Co. U.S.A) Fourier transform infrared spectrometer. The microstructure and morphology of precursor and calcined powders were examined by scanning electron microscope (SEM, Sirion200, FEI Co., Ltd., Holland). The excitation and emission spectra of the samples were measured by a HITACHI (JAPAN) M850 fluorospectrophotometer using an Xe lamp as the excitation source. All the measurements were carried out at room temperature.

2 Results and discussions

2.1 FTIR analysis

The FT-IR spectra of the precursor (1) and powders (2) calcined at 1000 °C for 2 h are shown in Fig. 2. In precursor (1), the peaks at 488, 618, 737 cm⁻¹ are corresponding to the Lu–OH, Al–OH and the Al–O vibration absorption [13–16]. As characteristic peaks of ethanol, the strong absorption peak at 3090 is assigned to the stretching and bending mode of O–H bands in pseudoboehmite [15,17,18], which refer to the poorly crystallized Al³⁺ compound of composition Al₂O₃·nH₂O (1.0<n<2.0) [15,19]. In addition, there are some weak peaks, such as the peak at about 840 cm⁻¹, which is associated with the out-of-plane bending of CO₂⁻ [16], the peak at about 1630 cm⁻¹ from the bending of H–O–H, which overlaps the O–C–O stretching band [20,21], the absorption peaks of CO₂ at 2350 cm⁻¹ [22], and the weak peaks at 2850 and 2925 cm⁻¹ corresponding to the vibrations of –CH₃ and –CH₂–, respectively [23]. As temperature increases, all the above peaks become weaker or finally disappear because of the decomposition of the precursor. As shown in the sample (2), at 1000 °C, the characteristic peaks of organic ingredients disappear and are replaced by the fingerprint vibrations of the isolated [AlO₄] tetrahedral and [AlO₆] octahedral at 809, 742, 708, 575, 519 and 460 cm⁻¹ [14,15], which indicates that pure LuAG phase is formed [15]. This result well coincides with the XRD patterns in Fig. 3.
at 400 °C for 2 h, phase of Lu$_2$O$_3$ (JCPDS card 86-2475) appears. At 600 °C, diffraction peak intensities of Lu$_2$O$_3$ become stronger. Until calcined temperature reaches 700 °C, cubic phase LuAG appears and the data are all in good agreement with those of JCPDS card (73-1368), but only one peak at 2θ = 34.59° is characteristic diffraction peaks of LuAP (LuAlO$_3$). With the calcined temperature increasing, the intensity of LuAP diffraction peaks decreases. At calcined temperature of 1000 °C, pure cubic phase LuAG is obtained. At calcined temperature from 1000 to 1100 °C, the phase of LuAG has no change, but the width of diffraction peaks becomes narrower. It indicates that the particle diameter grows.

2.3 SEM images

Fig. 4 shows SEM micrograph of the precursor (a), powders calcined at 1000 °C (b) and 1100 °C (c), respectively. SEM result showed that the precursors (a) are crystal with octahedral structure, which is consistent with the XRD results seen in Fig. 3. In Fig. 4(b), the morphology of LuAG:Ce powders calcined at 1000 °C is uniform and near spherical, with an average particle size of about 100 nm and good dispersivity, which is generally beneficial to improving the powers luminescence efficiency and producing transparent polycrystalline ceramics. When the calcined temperature reaches 1100 °C, agglomeration of particles becomes serious, and the average particle size of a polycrystalline material grows up, which are consistent with analysis results of XRD.

2.4 Formation mechanisms analysis of LuAG:Ce

In the experimental process, we found that pure LuAG was relatively easy to obtain only in volume ratio from 3 to 5 for alcohol and water in the same hydrothermal condition. When mixed ethanol was too much or too little, pure LuAG was difficult to get in the same condition.

Through infrared spectra, we can obtain qualitative analysis of the chemical composition and molecular structure. Based on the above analysis, the formation mechanism of LuAG crystals and the effect of hydrothermal on synthesis of LuAG are as follows. The first, in the hydrothermal condition, suspensions dissolve and generate Lu$^{3+}$, Al$^{3+}$ ions, and then Lu$^{3+}$, Al$^{3+}$ and OH$^{-}$ will form anion coordination polyhedron [Al-(OH)$_6$]$^{3-}$, [Lu-(OH)$_6$]$^{3-}$, [Lu-(OH)$_9$]$^{6-}$, that is crystal growth units$^{[24,25]}$. At the same time, hydroxyl oxygen atoms of ethanol molecule have higher electronegativity, easily connect with above mentioned growth units, and form relevant alcohol derivatives with low stability. The alcohol derivatives and ethanol prevent OH$^-$ intervention and avoid the formation of the Boehm mine$^{[25]}$. With the temperature increase, alcohol derivatives molecules can be easily separated from derivatives$^{[26,27]}$ and the part of the OH$^-$ is replaced by oxygen atoms. OH$^-$, O and Al$^{3+}$ will constitute a hexa-coordinate octahedral AlO$_3$(OH)$_3$[20,24,25], which is in agreement with analysis results of XRD patterns for precursor. It indicates that weak crystallization has existed in the precursor. When the precursor powders are calcined at high temperature, and the weak bond Al-OH leads to dehydration of Al-(OH)$_6$ octahedral until O and Al$^{3+}$ form isolated [AlO$_4$] tetrahedral and [AlO$_6$] octahedral. Meanwhile Lu$^{3+}$ will be located in dodecahedron consisted of aluminum oxygen tetrahedron and aluminum oxygen octahedron which indicate that pure cubic phase lutetium aluminum garnet is generated$^{[14,24,25]}$.

2.5 Luminescence properties of LuAG:Ce

Fig. 5 shows the excitation spectrum and emission spectrum of LuAG: Ce$^{3+}$ powders calcined at 1100 °C for 2 h. It
can be seen that excitation spectrum of Ce$^{3+}$ contains two bands, a weak band with maximum peak at 347 nm and a strong broad band with a maximum at 450 nm. These excitation bands result from the absorption of the incident radiation by Ce$^{3+}$ ions, which lead to the excitation of electrons from the 4f ground state ($^2F_{5/2}$, $^2F_{7/2}$) to the excited 5d level ($^2D$). The emission spectra display an apparent broad band covering from 450 to 650 nm with a maximum at 510 nm, which is well in agreement with the room temperature spectra of the LuAG:Ce single crystal films.$^{[11,30,31]}$ According to the Gaussian fitted curves for emission spectra for $\lambda_{ex}=450$ nm, the photoluminescence spectra consist of two bands of Ce$^{3+}$ emission centered at about 500 and 534 nm, respectively, which is also observed in the luminescence spectrum of the LuAG:Ce$^{3+}$ single crystal films at 9 K.$^{[30]}$. This emission is ascribed to the electron transitions from the lowest crystal-splitting component of the 5d level ($^2D$) to the ground state of Ce$^{3+}$ ($^2F_{5/2}$, $^2F_{7/2}$). At room temperature, two emission bands overlap.

Fig. 6 shows intensity dependence of 5d$\rightarrow$4f emission on concentration of Ce$^{3+}$ for LuAG phosphors. As shown in Fig. 6, the maximum intensity of 5d$\rightarrow$4f emission was obtained at 1% Ce$^{3+}$ doped LuAG phosphors. With doped concentration of Ce$^{3+}$ gradually increase, the emission intensity of Ce$^{3+}$ reduced.

Fig. 7 shows the emission spectrum of 1% Ce$^{3+}$ doped LuAG using different precipitator. In this experiment, the mixture of NH$_4$HCO$_3$ and NH$_3$·H$_2$O, NH$_3$·H$_2$O or urea respectively as precipitator, it is found that using mixture precipitator of NH$_4$HCO$_3$ and NH$_3$·H$_2$O, the emission spectrum intensity of Ce$^{3+}$ is stronger compared with using other two precipitator, and the obtained powders using mixture precipitator of NH$_4$HCO$_3$ and NH$_3$·H$_2$O are more loosely agglomerated and uniform. The relative large values of the solubility constants of NH$_3$·H$_2$O or urea may cause rapid and thorough reaction of the precipitation, resulting in a fast growing rate and uncontrolled severe agglomeration of the resultant crystallites.$^{[32,33]}$. It can be concluded that precipitant plays an important role in the morphology of the final powders. Thereby, the particle size distribution and agglomeration will further affect luminescent properties of powders.$^{[32]}$.

The emission spectra of 1% Ce$^{3+}$-doped LuAG phosphors sintered at different temperatures were obtained as shown in Fig. 8. The emission intensity increases with increasing sintering temperature below 1000 °C. The crystallite growth and the defects which decrease with temperature were probably the reason for the above-mentioned factor.$^{[4]}$, while the sintered temperature reaches 1100 °C, the emission intensity of Ce$^{3+}$ is weakened, and this may be ascribed to the oxygenation of certain Ce$^{3+}$ ions at this temperature.

According to the above analysis, there are many factors that could affect the emission intensity of rare earth ion,
such as the concentration of the solution, pH values of the solution, the speed of titration, the different precipitation agent and effect of titration sequence. In this study, the experiments have been repeated several times under strictly controlled conditions, although the results of each experiment come out a bit different. The detailed mechanism deserves to be further investigated.

Additionally, the emission spectra match well with the sensitivity curve of Si photodiode and CCD arrays that may be a good candidate as scintillation sensors in digital application under X-ray or blue-green light excitation.

3 Conclusions

The Polycrystalline LuAG:Ce powders with an average particle size of about 100 nm were synthesized by mixed solvo-thermal method. FTIR, XRD measurements showed that the precursors were hexa-coordurate octahedral structure ethanol derivatives crystal with hydroxyl and carbonate group. The purified crystalline phase of LuAG:Ce was formed from the precursors materials calcined at 1000 °C for 2 h. Intensity dependence of 5d→4f emission on concentration of Ce, different precipitation agent and sintering temperature was measured. It was found that the emission intensity reached the maximum for 1%Ce3+-doped LuAG using the mixture precipitator of NH4HCO3 and NH3·H2O at calcined temperature to 1000 °C by mixed solvo-thermal method. The emission spectra of Ce3+ doped LuAG phosphors were located in the range of 450–650 nm consisting of two emission bands, because of transition from the lowest 5d excited state (2D) to the 4f ground state of Ce3+, which matched well with the sensitivity curve of the Si-photodiode.

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WANG Linxiang et al., Synthesis and luminescent properties of Ce$^{3+}$ doped LuAG nano-sized powders by mixed solvo-thermal ... 21

58(19): 2377.


