

Fabrication and properties of transparent Eu:Lu₂O₃ scintillation ceramics

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Abstract: The Eu:Lu₂O₃ ceramic precursor was synthesized by wet chemical method, and the morphologies, microstructures and phases of both Eu:Lu₂O₃ ceramic precursor and the calcined Eu:Lu₂O₃ ceramic powders were studied by SEM and XRD. The results showed that the powders are spherical, well-dispersed and good crystalline. The particle size is calculated to be about 68.5 nm. Using the powders calcined at 1100°C for 4 h as raw material, the highly transparent Eu:Lu₂O₃ ceramics were successfully fabricated by vacuum sintering at 1650°C for 30 h. The grain size is calculated to be about 46 μm, and in-line transmittance of the Eu:Lu₂O₃ ceramics reaches 66.7% at 611 nm. What's more, the absorption curve, the excitation spectrum, the emission spectrum and the X-ray excited emission spectrum of the Eu:Lu₂O₃ ceramics were studied. It can be observed that the absorption curve of Eu:Lu₂O₃ ceramics is consisted of the matrical absorption and active ion absorption. It can be seen from the photo-luminescence emission spectrum and X-ray excited emission spectrum of the Eu:Lu₂O₃ ceramics that an extremely strong peak is located at 611 nm, corresponding to the 5D₀?7F₂ transition of Eu³⁺ ions. By comparison with the BGO crystal, the light output of the Eu:Lu₂O₃ ceramics is estimated to be about ~85000 ph/MeV. Eu:Lu₂O₃ ceramics have an excellent X-ray stopping power due to its high density and effective atomic number. It is indicated that Eu:Lu₂O₃ ceramics are a potential ceramic scintillator for the application of X-ray detection imaging.

Keywords: transparent Eu:Lu₂O₃ scintillation ceramics; vacuum sintering; photo-luminescence; X-ray excited emission spectrum; light output

Lu₂O₃ is a sesquioxide that has received widespread attention. It has a stable cubic structure at room temperature, which is beneficial to the preparation of Lu₂O₃ transparent materials. Lu₂O₃ can be used as a matrix material, including high-performance scintillation detectors, laser media and other functional materials^[1-2]. The most prominent physical and chemical properties of Lu₂O₃ are its extremely high density (9.4 g/cm³) and atomic number (69), which gives Lu₂O₃ materials excellent X-ray and other high-energy particle blocking ability. Eu-doped Lu₂O₃ materials have been reported to have potential applications in the field of X-ray imaging^[3]. After that, the preparation of Eu:Lu₂O₃ materials has become a research focus^[4-7]. However because of its very high melting point (2490°C), it is difficult to prepare single crystal and requires strict requirements for crystal growth devices. Recently transparent ceramic preparation

technology including nano ceramic powder preparation and advanced densification technology effectively provide a way to overcome shortcomings and limitations of traditional single crystal growth methods. Ceramic preparation technology can produce crystal material at lower temperature (less than 700!) than melting point, compared with single crystal fabrication. Lempicki^[8] reported that Eu:Lu₂O₃ powder prepared by the oxalic acid precipitation method combined with hot-press sintering technology is the earliest way to prepare Eu:Lu₂O₃ ceramics. Through X-ray testing, it is found that Eu:Lu₂O₃ ceramics have high-intensity radioluminescence. After that, a variety of methods to prepare Eu:Lu₂O₃ ceramics were reported^[9]. Generally speaking can be divided into two categories, one is mixing metal ion oxide by ball milling and then ceramic preparation technology is used to prepare transparent ceramics; Moreover ceramic powders were synthesized by wet chemical method and ceramic sintering technology was prepared. Under normal conditions sintering temperature under wet chemical pathway was lower than that of sintered ceramics as raw materials. Mixing metal ions oxides can hardly be uniform on atomic scales when mixing metal ions with ball milling mixing. Chemical methods have advantages in mixing homogeneous particles^[10-11]. On preparation methods earlier researchers tried to use pressure during sintering because pressure could provide additional impetus to reduce residual porosity. However hot pressing process increases carbon pollution caused by graphite mold while samples are produced oxygen vacancies in reductive atmosphere which is unfavorable to transparency of ceramics. Vacuum sintering is an alternative method which can not only reduce pollution effectively but also promote mass transfer and reduce densification time.

Nano ceramic powders synthesized by wet chemical method combined with vacuum sintering technology were used to prepare Eu:Lu₂O₃ transparent ceramics. Ammonium bicarbonate (NH₃HCO₃) was used as a precipitant to prepare Eu:Lu₂O₃ ceramic powders. Powders were calcined at 1100! for 4 h. High transparent ceramic samples were prepared by vacuum sintering process. Microstructure and spectral properties were investigated.

1. Experimental materials and methods

1.1 Materials

Oxidation of lutetium (Lu₂O₃) is provided by Sinopharm Chemical Reagent Co., Ltd., Europium oxide (5N) is provided by EFAiSuo (China) Chemical Co., Ltd. HNO₃ is supplied by Sinopharm Chemical Reagent Co., Ltd., Ammonium bicarbonate (NH₃HCO₃) is provided by Sinopharm Chemical Reagent Co., Ltd., Ammonium sulfate (NH₄)₂SO₄ is provided by Sinopharm Chemical Reagent Co., Ltd. Alcohol (C₂H₅OH) is provided by Sinopharm Chemical Reagent Co., Ltd.

1.2 Experimental instruments

Precision electronic balance model is PL602-L, from Sedorius Scientific Instruments Co., Ltd. Muffle furnace is provided by Shanghai Yifeng Electric Furnace Co., Ltd. The model

SKY12D48, is used for calcining powder. The small tabletop electric pressing machine is provided by Tianji Shike High-tech Co., Ltd., model DY 20. The cold isostatic press is provided by Taiyuan Chenshengyuan Technology Co., Ltd., model DJY 100max 300-300. The vacuum tungsten wire furnace is provided by Shanghai Chenrong Electric Furnace Factory, the type of FD-1500K, box resistance furnace is provided by Shanghai Yifeng Electric Furnace Co., Ltd., and the model SSX-1600, is used for annealing and hot corrosion treatment of ceramic samples after vacuum sintering. Sample polishing equipment is provided by Alpha Instruments and equipment Co., Ltd. and AlphaBeta&Vector semi-automatic grinding and polishing machine and Shenyang Kejing Automation equipment Co., Ltd., model Un ipol-802.

The model of scanning electron microscope is field emission scanning electron microscope of Hitachi Company of Japan, and the instrument model is SU8220. The type of XRD instrument is Ultima IV X-ray diffractometer made by Rigaku Company of Japan. The test conditions are as follows: Cu-K α -ray, $\lambda = 1.5406$, scanning range is $10^\circ \sim 80^\circ$ (2θ), scanning rate is $8^\circ/\text{min}$. The BET testing instrument is a fully automatic four-station specific surface area and aperture analyzer made by American Kangta Instruments Co., Ltd., and the instrument model is Quadrasorb SI. The spectrophotometer is the Cary-5000 UV-VIS-NIR spectrophotometer produced by Varian Company in the United States. Photo-excited excitation and emission spectra are measured by Edinburgh FLS920 steady-state fluorescence spectrometer. The X-ray excitation emission spectrum is characterized by the self-built X-ray excitation emission meter, and the working current and voltage are 1.5 mA and 70 kV. The detector uses fiber optic CCD (American Ocean Optics Company, model QE65000).

1.3 Experimental process

Nitrate solution of lutetium (Lu) and europium (Eu) ions dissolved in slightly excess nitric acid with corresponding oxides. According to suitable proportion, Lu:Eu=0.95:0.05. cation concentration 0.2 mol / L, mother liquor containing 500 g/mol, containing $(\text{NH}_4)_2\text{SO}_4$ in mother liquor, and the amount of substance was equal to that of mother liquor cation substance. Ammonium bicarbonate solution was used as precipitant with volume of 400 mL. The experiment process was to add 500 ml precipitant solution at the speed of 3 mL/min to mother liquor and stir gently with magnetic stirrer to produce precursor precipitate after reaction ending 3 hours; After aging, the supernatant was filtered by filtering the supernatant liquid, washing 4 times respectively with deionized water, 2 times ethanol; settling precipitation after washing in 70% over 24 h; The dried blocks were screened over 200 meshes; the sifted powders were calcined at 1100°C for 4 h; After calcination, the powders were molded by dry pressing, sizes $\varnothing 18 \text{ mm} \times 2 \text{ mm}$ and then treated with cold isostatic pressing 200 MPa after calcination. Sintering temperature was 1650°C and time was 30 h; After annealing at 1450°C for 10 hours, ceramic ceramics were annealed at annealing temperature for 10 hours, respectively, which were used to remove oxygen vacancies and color centers formed during vacuum sintering process.

2. Experimental results and discussions

2.1 SEM characterization of precursor and calcined powders

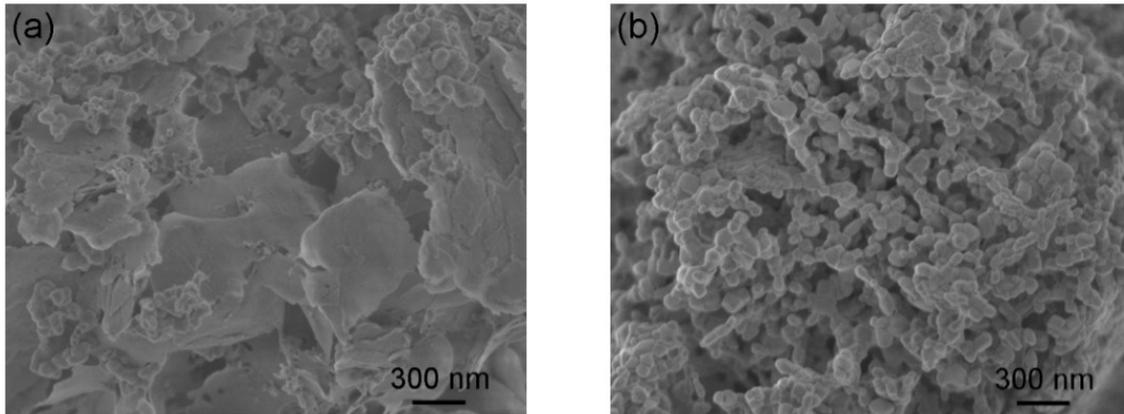


Fig. 1 SEM diagram of synthesized (a) precursors and (b) powders calcined at 1100°C for 4 h

Figure 1 shows the SEM surface morphology pictures of the synthesized precursor and the powder obtained after calcination at 1100°C for 4 h. From Figure 1(a), it can be seen that precursor consists of flaky layer material and agglomerated granular substance. From Figure 1(b), precursor is amorphous shape; calcination treatment, precursor transformation into granular powder, powder is spherical, good dispersion. The specific surface area (S_{BET}) of powders was 9.4 m²/g through BET surface area measurement. The Brunauer-Emmett-Teller formula can be used to calculate the particle size (DBET) of the powder as 68.5 nm.

$$D_{\text{BET}} = 6 / \rho S_{\text{BET}} \quad (1)$$

Here \tilde{n} is 5at%Eu: Lu₂O₃ theoretical density (9.3004 g/cm³).

2.2 XRD characterization of precursor and calcined powder

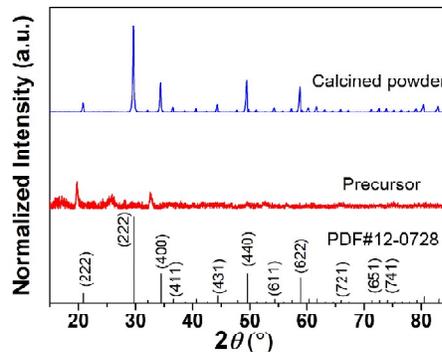


Fig. 2 XRD patterns of the synthesized precursor and the powder calcined at 1100°C for 4 h

Figure 2 shows the XRD patterns of the synthesized precursor and the powder calcined at 1100°C for 4 hours. It can be seen from the spectrum that the calcined powder has good crystallinity. Compared with the standard PDF card (12-0728) of cubic Lu₂O₃ crystal phase, it can be seen that the diffraction peak of the powder moves to a small angle. This is because the radius of Eu³⁺ (0.95Å) is larger than that of Lu³⁺ (0.848Å). After replacing the Lu³⁺ lattice position, the interlayer spacing increases, causing the diffraction peak to move to a small angle; There is no second phase in the XRD result of the powder; according to the refined XRD data, the crystal grain size of the powder can be calculated from the Scherrer formula to be 66.7 nm, which is similar to the particle size of the above powder, indicating that the calcined powder is small, and the primary particles of the powder shown in Figure 1(b) are basically single crystals.

2.3 Characterization of ceramic transmittance

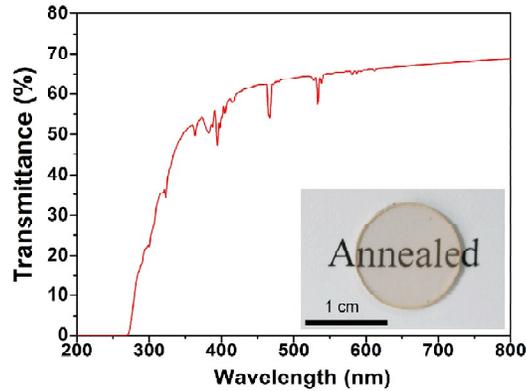


Fig. 3 The linear transmittance curve of 5at%Eu:Lu₂O₃ ceramics, the illustration is the actual picture of the sample (1 mm thickness)

The Eu:Lu₂O₃ ceramic prepared by the above powder combined with vacuum sintering was used. The sample was annealed at 1450°C in air for 10 h, and both sides were polished to a thickness of 1mm. Figure 3 is a graph of the linear transmittance curve of Eu:Lu₂O₃ ceramics, and the inset is a real picture of the sample. The sample is pink, which is the characteristic color of Eu³⁺; It can be seen from the transmittance curve that there are characteristic absorption peaks of Eu³⁺, which are the 5D⁰!7F² transitions at 394 nm, 467 nm and 533 nm, respectively. The transmittance of the main emission peak at 611 nm can reach 66.3%, and the scattering coefficient of the ceramic at the wavelength of 611 nm can be calculated as 5.07 cm⁻¹ by formula (2).

$$\alpha = \{-\ln T * 1 / (1 - R(\lambda))^2\} / l \quad (2)$$

Here T is the linear transmittance, R is the refractive index, λ is the wavelength, l is the thickness of the ceramic (the linear distance through which light passes), and α is the scattering coefficient.

2.4 Characterization of the absorption curve of ceramics

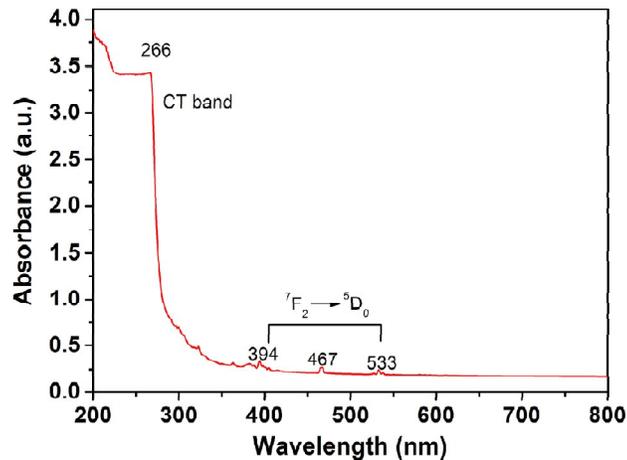


Fig.4 Absorption spectrum of 5at%Eu:Lu₂O₃ ceramic

Figure 4 shows the absorption spectrum of ceramics. It can be seen from the figure that the absorption curve of ceramic consists of two parts, the CT absorption edge at about 266 nm and the absorption peak at 270-550 nm; the position of the CT absorption edge is related to the band gap of the material, and the absorption peak is Eu³⁺ Characteristic absorption peak. In the wavelength range of 270-550 nm, the absorption of the substrate is not zero. This is because there are many light absorption factors inside the ceramic, which cause a certain intensity of light absorption except for ions.

2.5 Ceramic hot corrosion surface, fracture section and ceramic internal characterization

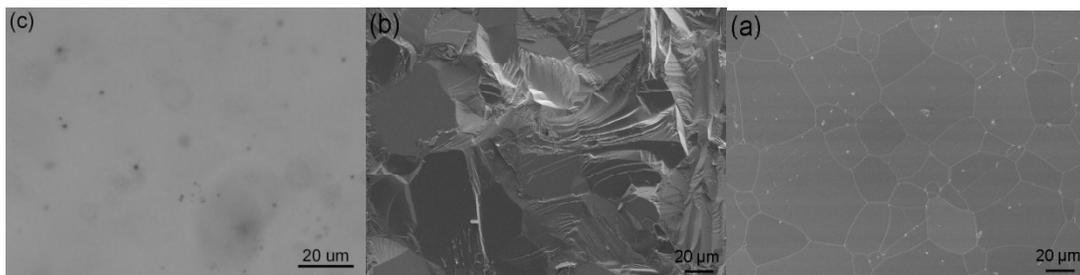


Fig.5 5at%Eu:Lu₂O₃ ceramic sample (a) polished hot corrosion surface and (b) SEM image of fracture section, (c) optical microscope image of ceramic interior

The ceramic samples are polished and hot-etched, and the 400 grains are statistically obtained by the line-cutting method (D_{lim}), and then the ceramic grain size (D_{ags}) is calculated as 46 μ m by formula (3)^[12].

$$D_{\text{ags}} = 1.56 D_{\text{lim}} \quad (3)$$

The existence of second phase and pores were not observed from the hot corrosion surface and fractured section; the optical microscope observation of the ceramics revealed that there were pores or impurities (black spots) in the ceramics. These impurities are small in size. The number is small, and it is difficult to see it in the hot corrosion surface and fracture section. However, these trace impurities will greatly reduce the transmittance of the ceramic and affect the scintillation performance of the ceramic.

2.6 Characterization of the spectral properties of ceramics

2.6.1 The photoexcitation and emission spectra characterization of ceramics

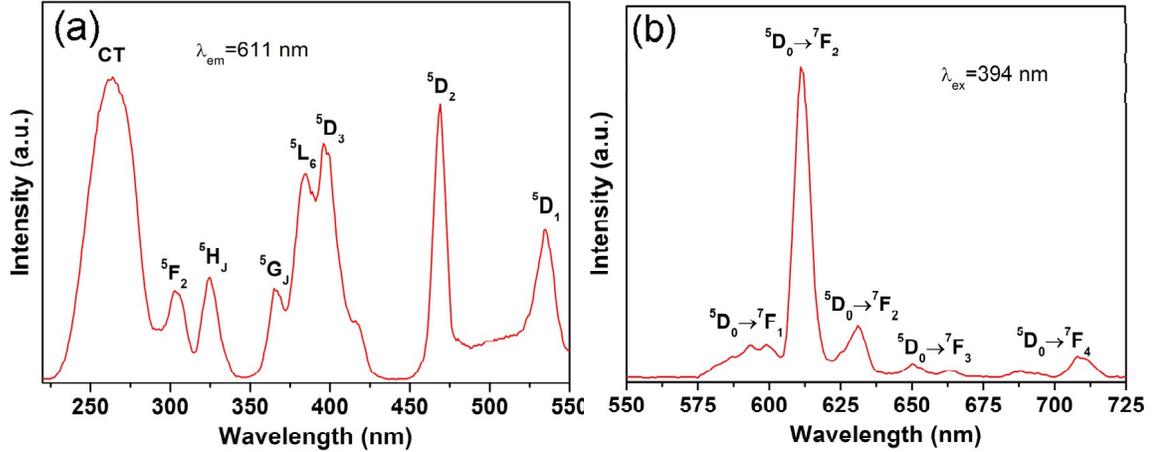


Fig.6 5at%Eu:Lu₂O₃ ceramics (a) photoexcitation spectroscopy and (b) emission spectrum

Set the detection wavelength to 611 nm to obtain the photoexcitation spectrum of the ceramic, See Figure 6(a), it can be seen that the excitation spectrum is composed of CT absorption peak and Eu³⁺ absorption peak. The CT absorption peak is located at 266 nm, which originates from the electronic transition from the 2p orbital electron of O²⁻ to the 4f orbital of Eu³⁺[13]; The absorption peaks of Eu³⁺ are derived from 4f-4f transitions, which are ⁷F_{0,1}!⁵H_{3,6}, ⁷F_{0,1}!⁵G_J, ⁷F_{0,1}!⁵L₆, ⁷F_{0,1}!⁵D₃, ⁷F_{0,1}!⁵D₂ transitions, respectively, located at 321, 380, 393, 414 and 465 nm. Using 394 nm as the excitation wavelength, the photoexcitation emission spectrum is obtained; it can be seen that there is a strong emission peak in the photoemission curve, which is derived from the ⁵D₀!⁷F₂ transition, and the other emission peaks are derived from the ⁵D₀!⁷F₁ transition. 587, 595 and 599 nm; ⁵D₀!⁷F₂ transition at 631 nm; ⁵D₀!⁷F₃ transition at 650 nm; ⁵D₀!⁷F₄ transition at 708 nm.

2.6.2 X-ray excitation emission spectrum characterization of ceramics

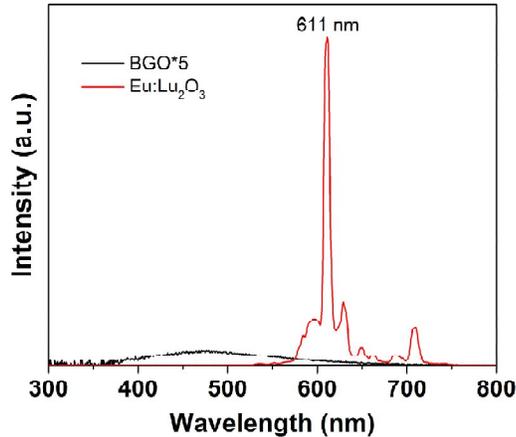


Fig.7 X-ray excitation emission spectra of 5at%Eu:Lu₂O₃ ceramics and commercial BGO single crystals.

In this experiment, a standard commercial BGO single crystal with a uniform size of about 8500 ph/MeV was used for comparison. The X-ray excitation emission spectrum of the commercial BGO single crystal showed a broad emission band. The X-ray excitation of ceramics The emission is a narrow emission peak, and the main emission peak is located at 611 nm, which is the same as the peak position of the photoexcitation emission spectrum in Figure 6(b) above. Researchers^[14] integrated the emission spectrum of ceramics at 550-750 nm to compare the integrated area of the emission spectrum of commercial BGO single crystals at 350-650 nm. The integrated area of the emission spectrum of 5at% Eu:Lu₂O₃ ceramics at 550-750 nm is The commercial BGO single crystal has twice the integrated area of the emission spectrum in the 350-650 nm range, and the light output of the ceramic sample can be about 85000 ph/MeV. This is a great advantage for scintillation materials. Combined with the extremely high density and effective atomic number of Eu:Lu₂O₃ material itself, it implies that Eu:Lu₂O₃ ceramics have certain application potential.

3. Conclusion

- (1) In this paper, by using wet chemical method to synthesize the precursor, calcining the precursor at 1100°C for 4 h, nano-sized, well-dispersed and nearly spherical nano-ceramic powder is prepared. The Eu:Lu₂O₃ ceramic powder is close to single crystal, and The particle size is 68.5nm.
- (2) The Eu:Lu₂O₃ ceramic powder was vacuum sintered at 1650°C to prepare high transmittance Eu:Lu₂O₃ ceramics. Through testing, the linear transmittance of the ceramic at 611 nm can reach 66.7%, because there are still a few pores inside the ceramic Or impurities, this is the main reason for the difference between the transmittance of ceramics and the theoretical transmittance.

- (3) By comparing the X-ray excitation emission spectra of the prepared ceramics and commercial BGO single crystals, it can be concluded that the absolute light yield of the Eu:Lu₂O₃ ceramic prepared in this experiment is 85000 ph/MeV. This implies that Eu:Lu₂O₃ ceramics have huge potential applications in X-ray imaging and other fields.

Funding: The work was financially supported by National Natural Science Foundation of China (51002002) and open fund of Key Laboratory of optical functional inorganic materials of Chinese Academy of Sciences (No KLTOIM201609).

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