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Fabrication of Ce-doped $Gd_3(Al, Ga)_5O_{12}$ Powders Using Co-precipitation Method

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Abstract: Ce-doped $Gd_3(Al,Ga)_5O_{12}$ (GAGG) precursors were co-precipitated from a mixed solution of gadolinium, aluminum and gallium nitrates using ammonium hydroxide as precipitant. and then characterized by TG/DTA analysis. GAGG powders were obtained by calcining the precursors at 800℃, 850℃, 900℃, 1000℃, 1100℃ and 1200℃. Phase evolution of GAGG powders were investigated by XRD analysis which showed that a pure GAGG phase was obtained. SEM observation demonstrated that the obtaimed poovders were mainly amorphous with size mainly about 100-150 nm in diameter. PL spectra of GAGG powders showed strong emission around 560 nm. The highest transparency of as prepared ceramic was obtained when GAGG powders were calcined at 900℃.

Key words: $Gd_3(Al,Ga)_5O_{12}$ ceramic; co-precipitation; calcination; inorganic scintillator

Inorganic scintillators are widely used in radiation detectors for medical imaging, high energy physics, industrial inspection, and dosimetry. In each application, scintillator is the primary radiation sensor that emits light or “scintillates” when struck by high-energy particles[1]. Garnets have been widely studied for scintillator hosts, because of well mastered technology, their optical transparency, and easy doping by rare-earth elements[2]. Ce^{3+} activator ions have fairly simple electron configurations, their ground state and excited state are $4f^1$ and $4f^05d^1$, respectively[3]. Electronic transitions from 5d to 4f of Ce^{3+} ions are of parity- and spin-allowed type. Ce^{3+} ions are characterized by a short lifetime and high luminescence efficiency, so that it is usually applied in scintillator[4]. Kamada reported a new multicomponent garnet, Ce-doped $Gd_3(Al,Ga)_5O_{12}$ (GAGG) single crystal, in 2012. This crystal has excellent scintillation performances compared to other Ce-doped inorganic scintillator, such as high light yield, short lifetime, good energy resolution, and high density[5].

At present, both $Gd_3Al_2Ga_3O_{12}$:Ce (GAGG:Ce) single crystals and ceramics have been studied by several groups. GAGG:Ce single crystals have been mainly grown by the Czochralski(CZ) method[6-8], micro-pulling down(μ-PD) method[9-11], and Floating Zone(FZ) method[12-13]. GAGG crystals grown by micro-pulling-down (μ-PD) process have a light yield of 56,000 photon/MeV when Ga content locates at 2.7 atoms per garnet formula unit and energy resolution of 5.3%[11]. GAGG crystals grown by Czochralski method have light outputs of approximately 58,000±3000 photons/MeV[8]. Compared to GAGG:Ce single crystals, GAGG:Ce ceramics provide a number of unique advantages such as high dopant concentration, uniform dopant distribution, and better cost efficiency[14]. GAGG:Ce ceramics have been mainly prepared *via* the solid-state reaction method[15-17] and co-precipitation method[18-19]. ^{137}Cs γ-ray induces light yields of GAGG:Ce ceramics result 70,000 photons/MeV[20]. However, there is still a need for further research on GAGG:Ce ceramics to meet the practical applications.

In this study, Ce-doped $Gd_3(Al,Ga)_5O_{12}$ (GAGG) precursors were co-precipitated from a mixed solution of gadolinium, aluminum and gallium nitrates using ammonium hydroxide as precipitant, then focused on the calcination temperatures, which have demonstrated to be a crucial parameter in the GAGG phase evolution.

1 Experimental

1.1 Materials

Gallium oxide (Ga_2O_3, 99.99%, 2 μm), gadolinium oxide (Gd_2O_3, 99.99%, 5 μm), cerium carbonate hydrate ($Ce(CO_3)_3\cdot 9H_2O$, 99.99%, 100 nm), nitric acid (HNO_3, analytical grade), and aluminum ammonium sulfate

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($AlNH_4(SO_4)_2·12H_2O$, 99.5%,) were used as starting materials. Ammonium hydroxide ($NH_3·H_2O$, analytical grade) was used as precipitant.

1.2 Preparation of GAGG powders and ceramics

The solution of mother salts was made by dissolving Ga_2O_3, Gd_2O_3, $Ce(CO_3)_3·9H_2O$, and $AlNH_4(SO_4)_2·12H_2O$ in water solution of HNO_3. A Ce: GAGG precursors solution with a molar ratio of n(Gd+Ce):n(Al+Ga)=3:5 in a glass beaker. This solution was added dropwise and then mixed with an aqueous solution of ammonium hydroxide. Then filtration and washing with water were repeated several times, followed by drying. The precursors were calcined in air for 1.5 h at 800℃, 850℃, 900℃, 1000℃, 1100℃, and 1200℃.

As prepared powders were dry-pressed into 25 mm diameter pellets and cold isostatically pressed under a pressure of 250 MPa. The compacts were then sintered at 1650℃ for 2 h in flowing dry oxygen gas.

1.3 Characterization

Thermal gravimetric and differential thermal analysis (TG/DTA) of the original precursors were made on a TG/DTA analyzer (Model Perkin-Elmer Pyris Diamond, USA) in air at a heating rate 10℃/min. Phase identification was performed by the X-ray diffraction analysis (XRD, Model Bruker D8 Advance, Germany) using Cu Kα radiation in the 2θ range of 10°–90°. Infrared (IR) spectra were recorded with a Fourier transform infrared spectrometer (Thermo Nicolet 6700, USA). Particle sizes and morphologies of precursors and calcined powders were examined by field emission scanning electron microscope (FE-SEM, Hitachi S-4800, Japan). Photoluminescence excitation (PLE) spectra and Photoluminescence (PL) spectra of the powders were studied through a fluorescence spectrophotometer (ModelF4600, Hitachi) with a Xe lamp at room temperature.

2 Results and Discussion

2.1 Thermal Analysis of GAGG precursors

Fig. 1 shows TG/DTA curve of the dried precursors at a heating rate of 10 ℃/min from room temperature to 1000℃. The endothermic peak center at 106℃ is assigned to the removal of molecular water. The exothermic peak around 886℃ results from crystallization of GAGG powders.

TG curve indicates a total weight loss of 35wt%. Most of the weight loss, about 23.3wt%, takes place between 50℃ and 300℃. The weight loss in this stage was assigned to the removal of molecular water. The weight loss which takes place between 300℃ and 1000℃ was 11.7wt%. It was assigned to the decomposition of carbonate and sulfate[21].

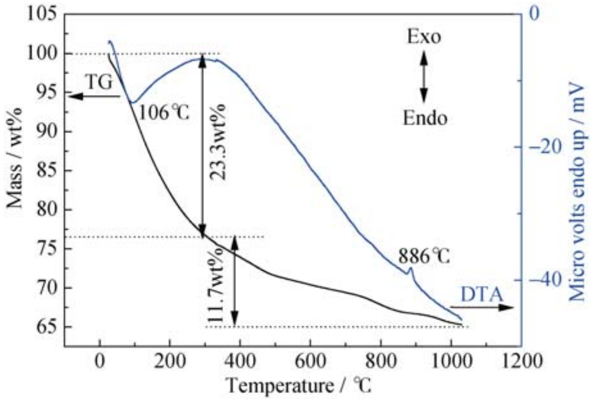

Fig. 1 TG/DTA curve of GAGG:Ce precursors

2.2 X-ray Diffraction of GAGG powders

XRD patterns of the powders calcined at different temperatures are shown in Fig. 2. The powders are mainly amorphous at temperature below 800℃, which have weak peaks of GAGG (PDF#46-0448) and $Gd_2O_2SO_4$ (PDF# 29-0613). For the powders calcined at 850℃, most of the characteristic peaks of GAGG phase appear. At 850℃, characteristic peaks of $Gd_2O_2SO_4$ are also detected. SO_4^{2-} can prevent GAGG powders from agglomeration[22]. $Gd_2O_2SO_4$ is an intermediate phase and does not affect the final phase purity of powders. Above 850℃, continue refinement of peak shapes and intensities were observed, indicating crystallite growth of the GAGG powders as temperatures increase. Characteristic peaks of $Gd_2O_2SO_4$ decrease when the calcination temperatures increase. The characteristic peaks of $Gd_2O_2SO_4$ disappear at 1200℃.

2.3 Infrared Spectra of GAGG powders

IR spectra (400–4000 cm^{-1}) of GAGG:Ce precursors and powders calcined at different temperatures are shown in Fig. 3. The precursors were calcined at 800℃, 850℃, 900℃, 1000℃, 1100℃, and 1200℃. IR spectra of these powders have been recorded by subtracting the absorption of pure KBr measured at ambient conditions.

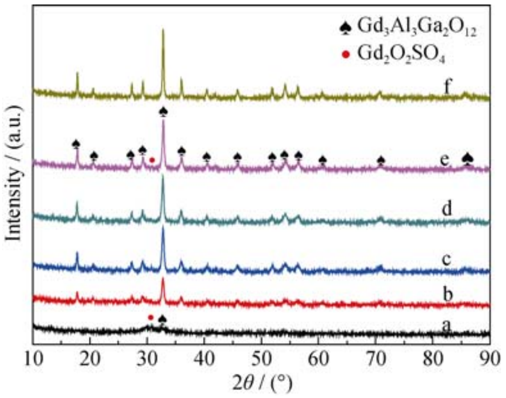

Fig. 2 XRD patterns of GAGG:Ce powders calcined at different temperatures

(a) 800℃; (b) 850℃; (c) 900℃; (d) 1000℃; (e) 1100℃; (f) 1200℃

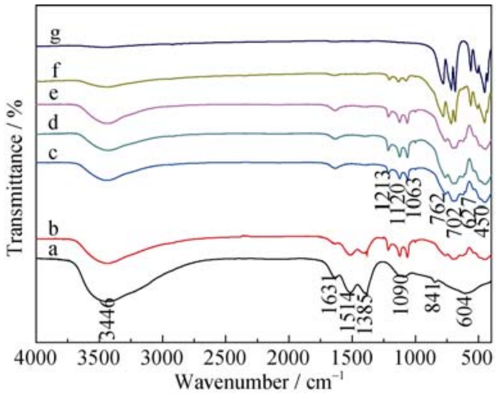

Fig. 3 IR spectra of GAGG:Ce precursors and powders calcined at different temperatures

(a) Precursors; (b) 800℃; (c) 850℃; (d) 900℃; (e) 1000℃; (f) 1100℃; (g) 1200℃

For the precursors, the broad absorption band near 3446 cm^{-1} and the shallow shoulder near 1631 cm^{-1} provide evidence of hydration in the structure or surface absorbed water and are assignable to O–H stretching vibrations and the H–O–H bending mode, respectively. The presence of carbonate ions in the molecular structure was confirmed by the appearance of absorption doublets at ~ 1385 and ~1514 cm^{-1} (CO_3^{2-}). The band at about 1090 cm^{-1} corresponds to the ion of SO_4^{2-} in the precipitated precursor.

For the powders calcined at 800℃, the absorption doublets at ~1385 and ~1514 cm^{-1} (CO_3^{2-}). There is weak absorption at ~1063, ~1120, 1213 cm^{-1}, 702 cm^{-1}, 450 cm^{-1}. Absorption peaks at ~1063, ~1120, 1213 cm^{-1} corresponding to SO_4^{2-} appear. The absorption peaks at 702 cm^{-1}, 450 cm^{-1} corresponding to SO_4^{2-} appear metal methoxides.

The absorption peaks at ~1385 and ~1514 cm^{-1} (CO_3^{2-}) decrease when the calcination temperatures increase. That may be associated with the decomposition of carbonate. After calcination, the absorption triplets at ~1063, ~1120, and 1213 cm^{-1} corresponding to SO_4^{2-} appear. There are three metal ions which reacted with SO_4^{2-}. The characteristic peaks of SO_4^{2-} disappear at 1200℃. The band in the region 400–800 cm^{-1} should be assigned to the bonding of Gd–O, Al–O, and Ga–O[21]. The existence of SO_4^{2-} in the calcined powders by IR is consistent with XRD analysis.

2.4 Morphologies of GAGG powders

Fig. 4 shows SEM morphologies of precursors and GAGG:Ce powders calcined at 800℃, 850℃, 900℃, 1000℃, 1100℃, and 1200℃. For the precursors, which are amorphous, the primary particles size ranges about tens of nanometer. Seen from IR spectra (Fig. 3) and XRD results (Fig. 2), amorphous are composed of carbonate and sulfate. For the powders calcined at 800℃, powders are mainly amorphous, the primary particles of about tens of nanometer. At 900–1100℃, the powders mainly consists of sub- micrometer sized loose aggregates of primary particles with size about 100–150 nm. When calcined at 1000℃, some sintering necks grow. When increasing the calcination temperatures, more sintering necks appear, meanwhile, the particles grow to be more uniform and smooth.

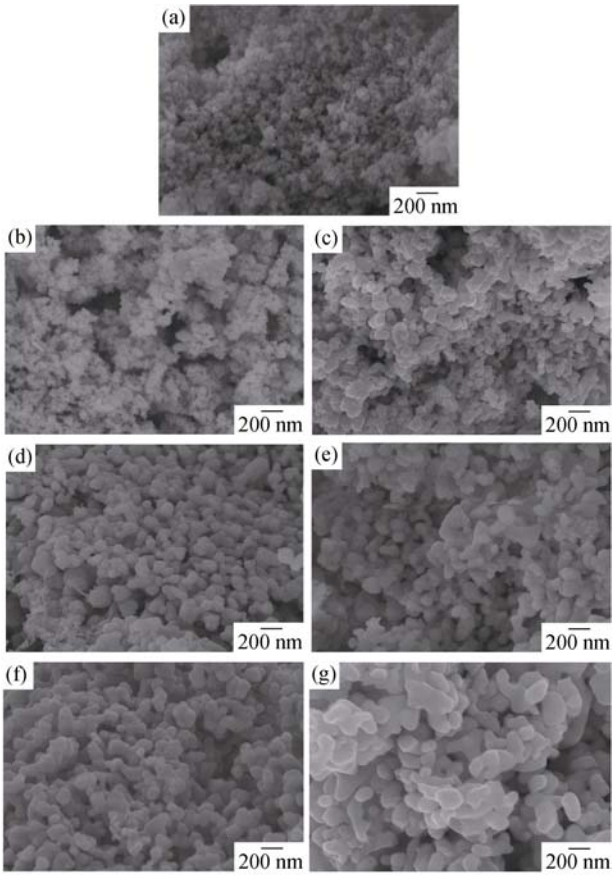

Fig. 4 SEM morphologies of GAGG:Ce precursors and powders calcined at different temperatures

(a) Precursors; (b) 800℃; (c) 850℃; (d) 900℃; (e) 1000℃; (f) 1100℃; (g) 1200℃

For the powders treated at 800℃, powders are mainly amorphous, and the primary particles are about tens of nanometer. When the calcination temperatures are 850–1100℃, a majority of particles size is about 100–150 nm. There also exist some smaller particles of tens of nanometers. The number of smaller particles decreases with the increasing of calcination temperatures. They disappear when the calcined temperature reached 1200℃. It was suggested that the smaller particles are sulfate according to the IR spectra and XRD patterns, as shown in Fig. 2 and Fig. 3. TG/DTA curve of the GAGG:Ce precursors (Fig. 1) indicate that there always exists weight loss up to 1000℃. That confirms that the smaller particles are sulfate.

2.5 Photoluminescence Properties of GAGG powders

Fig. 5 shows PLE spectra of the GAGG:Ce powders calcined at different temperatures. The sample calcined at 800℃ is mainly amorphous, so we don't measure its photoluminescence spectra. Fig. 5 shows PLE spectra of GAGG:Ce powders calcined at 850℃, 900℃, 1000℃, 1100℃, and 1200℃. Emission peaks around 540 nm were focused and examined. All samples have similar excitation behavior with the different excitation intensity. PLE spectra display a number of peaks near 340 nm and 450 nm, which correspond to transition of $4f_{5/2}\rightarrow 5d_2$ and $4f_{5/2}\rightarrow 5d_1$ transition of Ce^{3+}, respectively. Fig. 6 shows PL spectra of the GAGG:Ce powders calcined at different temperatures. The excitation peak is at 450 nm. Similarly, samples calcined at different temperatures perform different emission intensity. The observed broad emission band consists of two Gaussian components, peaking at 540nm and 600 nm. The two emission peaks are attributable to the transitions of $5d_1\rightarrow 4f_{5/2}$ and $5d_1\rightarrow 4f_{7/2}$ transition of Ce^{3+}, respectively[23-24].

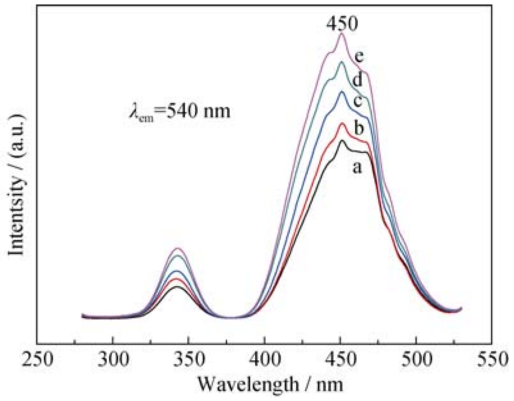

Fig. 5 PLE spectra of GAGG:Ce powders calcined at different temperatures

(a) 850℃; (b) 900℃; (c) 1000℃; (d) 1100℃; (e) 1200℃

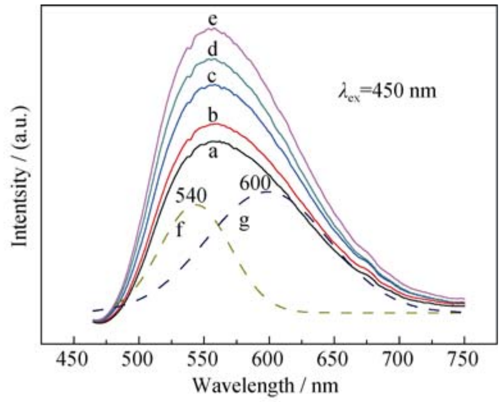

Fig. 6 PL spectra of the GAGG:Ce powders calcined at different temperatures

(a) 850℃; (b) 900℃; (c) 1000℃; (d) 1100℃; (e) 1200℃; (f), (g) Simulated curve

The peaks of PLE spectra and PL spectra increase as the calcination temperatures increase. The crystallization of GAGG:Ce powders is improved with the increase in calcination temperatures. XRD results (Fig. 2.) also indicate crystallite growth of the GAGG powders as temperatures increase.

2.6 GAGG ceramics

Fig. 7 shows the photographs of GAGG:Ce ceramics sintered at 1650℃ for 2 h in oxygen atmosphere from different temperatures calcined powders. When the powders calcined at 800℃, the sintered ceramic was broken. No photograph of GAGG:Ce ceramic of the powders calcined at 800 ℃ was preserved. The transparency of the ceramics has significant change with the calcination temperatures. For the powders calcined at 900℃, the ceramic shows the highest transparency. For the powders calcined at 850℃ and 1000℃, the ceramics were nearly transparent. However, when the powders calcined at 1200℃, the ceramic shows incomplete sintering phenomenon. And when the powders calcined at 850℃, there were second phase in the ceramic. This phenomenon may be caused by powders have much more sulfate impurities. The transparency of the ceramics decreases with the calcination temperatures increase. At the same time, the content of sulfate impurities in the powders decrease with the calcination temperatures increase (Fig. 2, Fig. 3). Certain amount of sulfate impurities in the powders can promote the ceramics sintering ability.

3 Conclusions

GAGG:Ce precursors were co-precipitated from a mixed solution of gadolinium, aluminum, and gallium nitrates using ammonium hydroxide as precipitant. The precursors converted directly to GAGG powders at 850℃. The crystallite growth of the GAGG powders as temperatures increase. Morphology of particles is uniformity and smooth when calcined at 1100℃ for GAGG

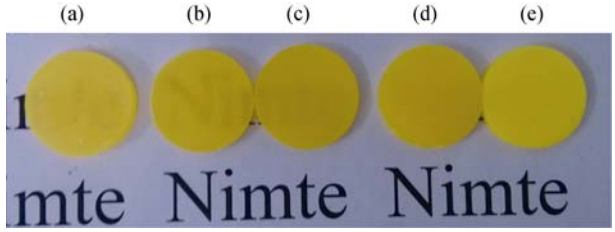

Fig. 7 Photograph of GAGG:Ce ceramics made from powders calcined at different temperatures and sintered at 1650℃ for 2 h in oxygen atmosphere

(a) 850℃; (b) 900℃; (c) 1000℃; (d) 1100℃; (e) 1200℃

powders. The peaks of PLE spectra and PL spectra increase when the calcination temperatures increase. Transparent ceramic was obtained by using the powders calcined at 900℃.

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共沉淀法制备Ce掺杂的$Gd_3(Al, Ga)_5O_{12}$粉体

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摘 要: 通过在含有钆、镓、铝离子的硝酸混合溶液中滴加氨水, 共沉淀生成Ce掺杂的$Gd_3(Al,Ga)_5O_{12}$(GAGG)前驱体, 并采用TG/DTA对GAGG前驱体进行表征。分别在800℃、850℃、900℃、1000℃、1100℃及1200℃对GAGG前驱体进行煅烧处理, 采用XRD对GAGG粉体的物相进行表征, 结果显示制备出纯相的GAGG粉体。采用SEM对GAGG粉体的颗粒大小以及微观形貌进行观察。GAGG粉体的荧光谱图显示在560 nm处有一个很强的发射峰。在900℃煅烧处理的GAGG粉体所烧结的陶瓷具有最高的透明度。

关 键 词: $Gd_3(Al,Ga)_5O_{12}$陶瓷; 共沉淀; 煅烧; 无机闪烁体

中图分类号: TQ174 **文献标识码:** A