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Short communication

Synthesis of lutetium aluminum garnet powders by nitrate–citrate sol–gel combustion process

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Abstract

Polycrystalline lutetium aluminum garnet ($Lu_3Al_5O_{12}$) powders were prepared by a simple sol–gel combustion method using aluminum nitrate, lutetium oxide and citric acid as the starting materials. The XRD results showed that the amorphous precursor converted directly to pure LuAG at 900 °C. The TEM investigations revealed that the synthesized LuAG powders are nano-sized with an average particle size 20–30 nm.

Keywords: A. Sol–gel processes; Powders; $Lu_3Al_5O_{12}$

1. Introduction

Crystalline lutetium aluminum garnet ($Lu_3Al_5O_{12}$, hereinafter referred to as LuAG) exists in cubic form and has a garnet structure. Recently, because of its high density (6.73 g/cm^3, 94% of bismuth germanate (BGO), which is a kind of traditional scintillation crystal used in positron emission tomography (PET)) and other physical properties such as shock resistivity and chemical radiation stability, LuAG has been known to be a promising host structure for scintillating materials. This host lattice containing rare earth ions as luminescent activators, in special cerium (Ce^{3+}), yields fast decay and is an efficient high response scintillator [1]. On the other hand, Tm^{3+}-doped [2], Ho^{3+}-doped [3] or Yb^{3+}-doped [4] lutetium aluminates are very promising for microchip laser or neutrino physics. Rare earth-doped oxide powders were usually prepared by sol–gel processing [5], hydroxide co-precipitation [6], homogeneous precipitation [7], glycothermal treatment [8] and combustion synthesis [9]. Recently, preparation of nano-sized LuAG powders by these methods is in progress in our group.

In this report, LuAG powders were synthesized by a simple nitrate–citrate sol–gel combustion process, which is a novel way with a unique combination of sol–gel process and auto-combustion process. This method has great potential in the preparation of ceramic materials because of its success in producing fine particle size, multicomponent, crystalline, homogeneous powders at considerably lower temperatures and with reduced processing time and inexpensive precursors. Different oxide ceramic powders have been synthesized by this method in our group [10]. However, there has not been reported for LuAG host.

2. Experimental

Aluminum nitrate ($Al(NO_3)_3{\cdot}9H_2O$, AR grade), lutetium oxide (Lu_2O_3, 99.99%), nitric acid (HNO_3, GR grade) and hydrated citric acid ($C_6H_8O_7{\cdot}7H_2O$, AR grade) were used as starting materials in the present work. Stoichiometric Lu_2O_3 and $Al(NO_3)_3{\cdot}9H_2O$ (Lu/Al = 3/5 in mole ratio) were used to form LuAG powder. The molar ratio of citric acid to metal cations is 1:1.

Lu_2O_3 was firstly dissolved in nitric acid to form lutetium nitrate solution. Stoichiometric aluminum nitrate was then added and together dissolved in deionized water with appropriate dosage of citric acid. After the mixed solution was heated to 60 °C and continuously stirred using a magnetic agitator for several hours, the solution turned to yellowish sol. Then, heated to 80 °C and stirred continuously, the sol transformed into transparent sticky gel. The gel was then heated to 180 °C. At any moment, an auto combustion

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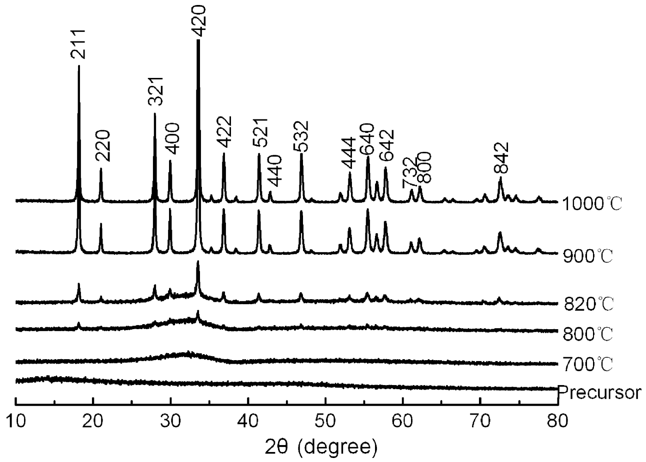

Fig. 1. XRD patterns of the precursor and powders calcined at various temperatures for 2 h.

process took place companying with the evolution of brown fume. Finally, a yellow-greenish, fluffy precursor was yielded. The precursor was calcined at various temperatures for 2 h in a muffle furnace in air to analyze the phase development.

Phase identification was performed via X-ray diffraction analysis (XRD, Model D/MAX-2550V) using nickel-filtered Cu Kα radiation in the range of 2θ 10–80°. Fourier transform infrared spectroscopy (FTIR) of the precursor and powders calcined at various temperatures were recorded at room temperature using Bio-Rad FTS-185 FTIR Spectrometer. The particle size and morphology of the resultant LuAG powders were examined using transmission electronic microscope (TEM, Model 200CX, JEOL, Tokyo, Japan).

3. Results and discussion

Fig. 1 shows XRD patterns of the precursor and powders heat treated at different temperatures for 2 h. The precursor was found to be amorphous until about 800 °C. At 820 °C, however, the precursor began to crystallize and the obvious diffraction peaks appeared. The observed d-lines match the reported values for the cubic LuAG phase (JCPDS no. 73-1368). At 900 °C and above, continued refinement of peak shapes and intensities were observed, indicating crystallite growth of the LuAG powder with the calcined temperature increasing.

Fig. 2 shows the FTIR spectra of the precursor and powders calcined at various temperatures. The spectrum of the precursor shows that the precursor was composed of metal carboxylate and a little of nitrate. This can be deduced from the appearance of the antisymmetrical stretching vibration of carboxylate ligand at 1631 cm^{-1}, the symmetrical stretching vibration of carboxylate at 1427 cm^{-1}, and a small stretching vibration of nitrate at 1076 cm^{-1}. By 700 and 800 °C, due to the appearance of the wide bending peak at 833 cm^{-1} and a split antisymmetrical stretching of carbonate at 1585 and 1427 cm^{-1} [11], it can be concluded that carboxylate and nitrate were decomposed and transformed into carbonate between room temperature and 700 °C. When the calcined temperature was further increased to 900 and 1000 °C, the characteristic peaks of carbonate disappeared and were replaced by the fingerprint vibrations of the isolated [AlO_4] tetrahedral and [AlO_6] octahedral at 802, 736, 701, 570, 512 and 455 cm^{-1} [12], which indicated that pure LuAG phase was formed. This result well coincides with the XRD patterns in Fig. 1. Additionally, there is a hydroxyl band at 3428 cm^{-1} on each FTIR spectra, which was caused by H_2O absorbed in air. The reactive process was also indicated by the changes in color of the calcined powders. The precursor is yellow; it changes to black at 700 °C and then to white at 900 °C.

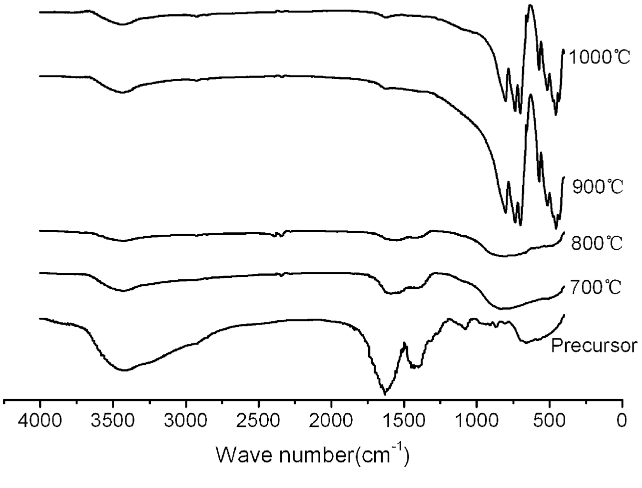

Fig. 2. FTIR spectra of the precursor and powders calcined at different temperatures for 2 h.

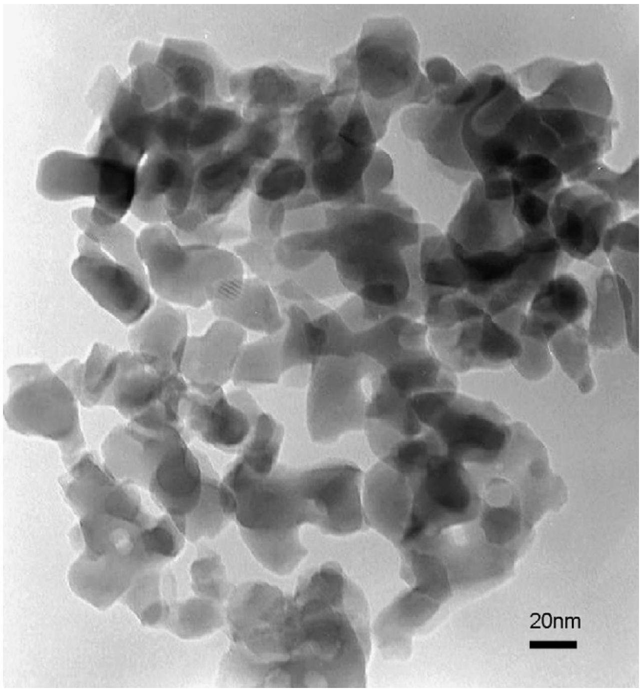

Fig. 3. TEM photograph of the LuAG powders calcined at 900 °C for 2 h.

Fig. 3 shows the morphology of the as-synthesized powders calcined at 900 °C for 2 h. The synthesized LuAG powders are nano-sized with an average particle size 20–30 nm.

4. Conclusions

Single-phase LuAG powders were synthesized by a simple nitrate–citrate sol–gel combustion process. The amorphous precursor converted directly to pure LuAG at 900 °C. The synthesized LuAG powders are nano-sized with an average particle size 20–30 nm.

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