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Synthesis of nano-sized $Yb_3Al_5O_{12}$ powders by the urea co-precipitation method

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Abstract

Nano-sized polycrystalline ytterbium aluminum garnet (YbAG, $Yb_3Al_5O_{12}$) powders were successfully synthesized by a simple urea co-precipitation method. The thermal behavior of the YbAG precursor was investigated. The calcined amorphous YbAG precursor was directly converted to 20–30 nm monophase YbAG at as low as temperature 900 °C, without any other intermediate phases. The nano-sized YbAG powders calcined at 900 °C distributed evenly with a slight aggregation, and the specific surface area of the powders reached 29.7 $m^2\ g^{-1}$. The absorption spectrum of the YbAG powders was measured, and there were two strong absorption peaks centered at 931 and 965 nm. The results did not correspond to the absorption peaks of Yb:YAG crystal exactly, as the lattice parameters were different between YbAG and YAG.

Keywords: B. Naonocomposites; C. Thermal properties; C. Optical properties

1. Introduction

Recent advances in high-performance InGaAs laser diode with a wavelength between 0.9 and 1.1 mm have stimulated interest in diode-pumped Yb^{3+} lasers [1]. InGaAs laser diodes allow the elective coupling of pumped light into the gain medium, so as to allow efficient room temperature operation of Yb:YAG. Furthermore, diode pumped Yb^{3+}:YAG laser has several advantages relative to Nd^{3+}:YAG laser, such as low thermal load, long upper state lifetime, large absorption width around the InGaAs laser emission range, relative large emission cross section, high thermal conductivity, and strong energy-storing capacity [2]. As a result, the Yb^{3+}-doped laser crystals are favorable for compact and miniature laser design. YbAG, highly ytterbium-doped YAG concentration up to 100%, is isostructural with YAG, and there is only about a 1.5% difference in unit-cell size [3]. YbAG can be used not only as solid-state laser materials, but also as optical scintillators, thermal barrier coatings, oxidation or erosion resistant materials [4]. In this paper, nano-sized $Yb_3Al_5O_{12}$ powder was synthesized by urea precipitation method, and the thermal and optical properties were studied.

2. Experiment

Aluminum nitrate hydrate ($Al(NO_3)_3{\cdot}9H_2O$, analytical grade, Shanghai Zhenxin Reagent Factory, Shanghai, China), ytterbium oxide (Yb_2O_3, 99.99%, Rare-Chem. Hi.-Tech. Co. Ltd., Guangzhou, China) and nitric acid (HNO_3, excellent grade, Shanghai Lingfeng Chemical Reagent Co. Ltd., Shanghai, China) were used as starting materials in the present work. Urea ($CO(NH_2)_2$, analytical grade, Shanghai Lingfeng Chemical Reagent Co. Ltd.) was used as a precipitant. The stock solution of mother salts was made by dissolving Yb_2O_3 in HNO_3 and then dissolved in deionized water with a stoichiometric amount of aluminum nitrate according to $Yb_3Al_5O_{12}$. The concentration of Al^{3+} was 0.15 M. Then, some amounts of urea and hydroxypropyl cellulose (HPC) were added and well dispersed into the mixed solution. The concentration ratio of urea and the total metal ions was

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15:1. HPC was used as dispersant, and the concentration was 2.0×10^{-3} g cm^{-3}. The temperature of the solution was increased to 95 °C and kept at this temperature for 2 h. Then, the solution was cooled down to room temperature. The precipitated powder was filtered, washed with deionized water, rinsed with alcohol repeatedly, dried at 100 °C for 24 h and calcined at different temperatures for 2 h.

Phase identification was performed via X-ray diffraction analysis (XRD, Model D/MAX-2550V, Rigaku, Tokyo, Japan) and the thermal analysis of the YbAG powder was conducted using thermo-gravimetric/differential thermal analysis (TG/DTA, Model STA449C, Netzsch, Germany). Fourier transform infrared spectroscopy (FTIR, Model NEXVS7000C, Nicolet, U.S.A.) of the precursor and powders calcined at various temperatures were recorded at room temperature using Bio-Rad FTS-185 FTIR Spectrometer. The chemical composition of the powder calcined at 900 °C was analyzed by complexometry and Inductively Coupled Plasma Atomic Emission Spectrometer (ICP-AES, VISTA, Palo Alto, U.S.A.). The morphology of the resultant YbAG powders was examined using transmission electronic microscope (TEM, Model 200CX, JEOL, Tokyo, Japan). The specific surface area measurements were performed by the conventional BET technique with a nitrogen adsorption apparatus (Model ASAP 2010, Micromeritics Instruments, Norcross, U.S.A.).

3. Result and discussion

The purpose of using urea is to control the speed of the releasing OH^- and CO_3^{2-} by controlling the temperature and time. The hydrolysis reaction of urea is related to the temperature. When the temperature is about 90 °C, it obviously begins to hydrolyze in a basic solution and can be described by the following equation [5]:

$$CO(NH_2)_2 + 2H_2O \rightarrow CO_3^{2-} + 2NH_4^+$$

$$NH_3 + H_2O \rightarrow NH_4^+ + OH^-$$

Thus, Al^{3+} and Yb^{3+} can be precipitated totally and homogeneously by the basic carbonate and ammonium anions.

XRD patterns of the powders calcined at various temperatures for 2 h are shown in Fig. 1. Since no obvious diffraction peaks are observed, it can be concluded that the powder remains amorphous below 900 °C. When the temperature is increased to 900 °C, high and sharp peaks are observed. The chemical composition of the powder calcined at 900 °C was analyzed, and the ratio of Yb and Al was about 3:5, the element N was contained 0.061% in weight, and the element C was 0.042% in weight. As the temperature is increased, the peaks become higher and sharper. This is associated with the grain growth of the YbAG crystallite. Only YbAG phase is detected, and no other intermediate phases are observed. Therefore, it can be considered that YbAG crystallizes directly from the amorphous precursor without the formation of any intermediate phases.

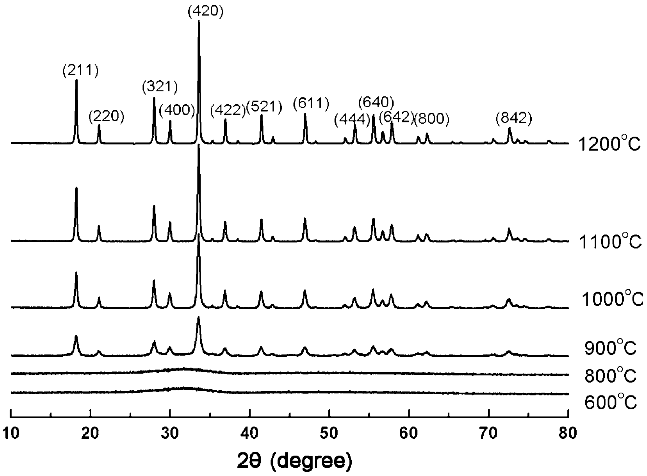

Fig. 1. XRD patterns of the powders.

Fig. 2 shows FTIR spectra of samples calcined at various temperatures. The spectrum of the precursor clearly shows a broad absorption around 3450 cm^{-1}, which is a characteristic stretching vibration of (O–H), and the hydroxyl groups disappear after being calcined at 900 °C, as the hydroxyl compounds are very difficult to decompose. Peaks localized at 1530 and 1420 cm^{-1} are the characteristic asymmetrical split stretching of carbonate. After 900 °C, there are only metal–oxygen vibrations. This is in agreement with the result of XRD mentioned above.

Fig. 3 shows the TG–DTA curves of the precursor. There is a total mass loss of 61.8% when the temperature is increased to 1000 °C. Above 1000 °C, the mass keeps unchanged. The strong endothermic peak at 120 °C is due to the moisture absorbed on the surface of sample, and there is a very sharp weight loss corresponding to the TG curve. The weight loss from 200 to 700 °C in the TG curve is related to the release of H_2O and CO_2 correspondingly, and the endothermic and exothermal peaks are attributed to the decomposition of chemically combined water, carbonate and hydroxyl compounds. This can also be identified by the FTIR spectra. Carbonate is totally changed into carbon dioxide at 700 °C. Hydroxyl compounds are hard to decompose completely until 1000 °C. There is a small exothermic peak appearing at 1008 °C, which can be attributed to the crystal growth of YbAG.

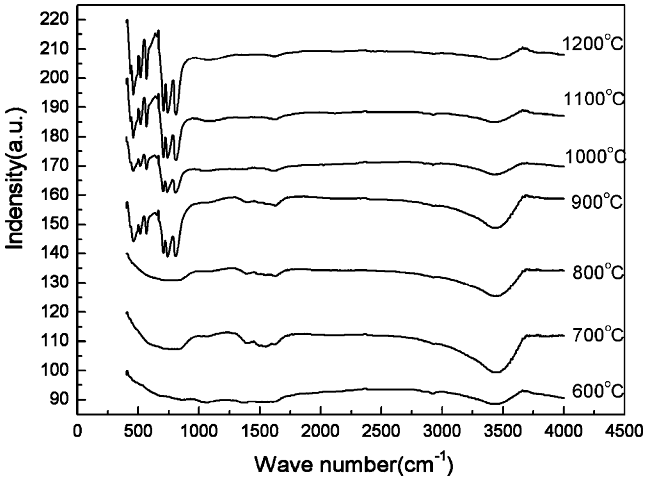

Fig. 2. FTIR spectra of the powders.

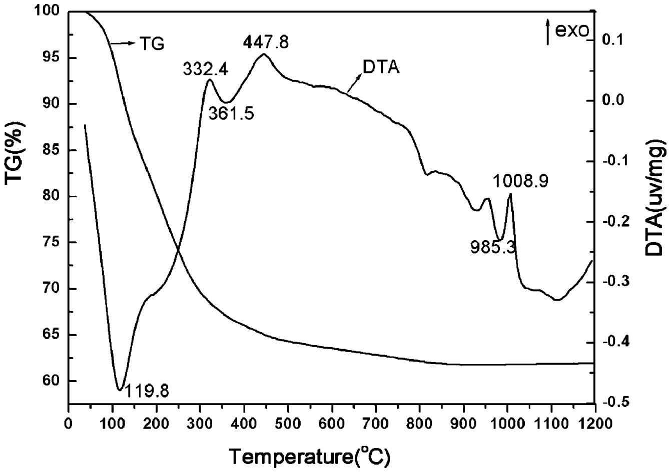

Fig. 3. The TG–DTA traces of the YbAG precursor.

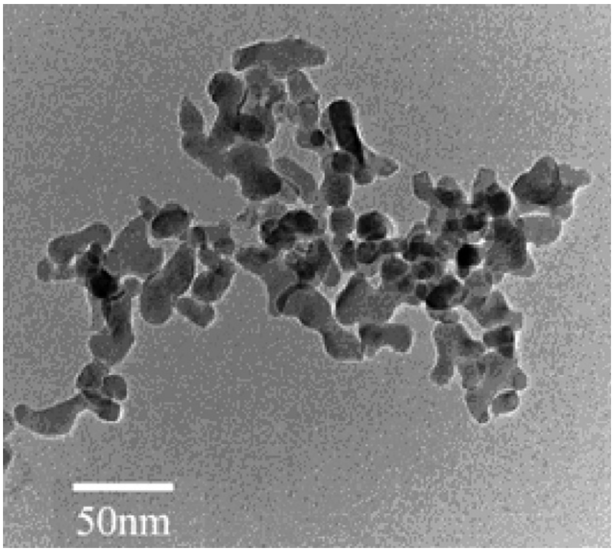

Fig. 4. TEM photograph of the YbAG powders calcined at 900 °C.

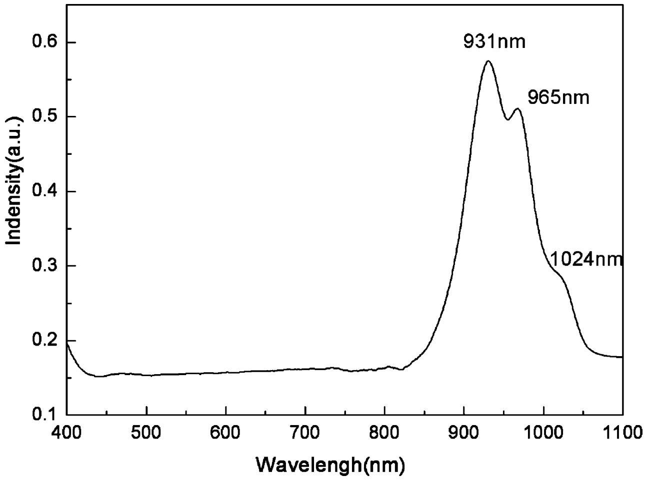

Fig. 5. The absorption spectrum of the YbAG powder calcined at 900 °C.

Fig. 4 shows the morphology of the as-synthesized powders calcined at 900 °C for 2 h. The synthesized YbAG powders are nano-sized with an average particle size of 20–30 nm and have no obvious aggregation. The specific surface area of the powders calcined at 900 °C reaches 29.7 $m^2 g^{-1}$.

Fig. 5 shows the absorption spectrum of the YbAG powder calcined at 900 °C for 2 h. There are two strong absorption peaks at 932 and 962 nm, corresponding to the absorption of Yb^{3+} in the YbAG. An absorption peak centered at 1024 nm is relatively weak. The absorption peaks have a little blue shift compared with those in Yb:YAG, which are centered at 938, 968 and 1030 nm. This may attribute to the difference of cell parameter between YbAG and Yb:YAG. YbAG theoretically has a smaller lattice parameter than that of YAG because the radius of Yb^{3+} (0.86 Å) is smaller than that of Y^{3+} (0.89 Å).

4. Conclusion

Single-phase YbAG powders were synthesized by a simple urea co-precipitation method. The amorphous precursor converted directly to pure YbAG at 900 °C. The synthesized YbAG powders are nano-sized with an average particle size of 20–30 nm. The specific surface area of the powders calcined at 900 °C is 29.7 $m^2 g^{-1}$. There are two strong absorption peaks at 931 and 965 nm. The absorption peaks do not correspond to those in Yb:YAG, which are centered at 938, 968, 1030 nm. This may attribute to the differences of cell parameters between YbAG and Yb:YAG.

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