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Thermal behavior of the YAG precursor prepared by sol–gel combustion process

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Abstract

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) powders were synthesized by a sol–gel combustion process from a mixed solution containing aluminum and yttrium nitrates. The thermal behavior of the precursor was determined by DSC–TG–MS techniques. FTIR and XRD techniques were used to characterize the processed precursor. It was found that excess citric acid and carboxylate mixture decomposed at about 400 °C to form carbonates. The YAG phase was supposed to nucleate directly from the amorphous precursor at about 800 °C. Mono-phase YAG crystallites could be formed without the formation of any intermediate phase at 900 °C.

Keywords: A. Sol–gel process; YAG; Thermal behavior

1. Introduction

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) is an important ceramic material with promising chemical stability, optical and mechanical properties [1–4]. It can be used as refractory coating for electronic devices and as the host for rare-earth-doped phosphors and for promising solid-state laser [4–7].

There are three stable phases in the system Y_2O_3–Al_2O_3 with the compositions of $Y_4Al_2O_9$ (YAM), $YAlO_3$ (YAP) and $Y_3Al_5O_{12}$ (YAG) [1]. Traditional solid-state reaction techniques for the preparation of YAG require repeated mechanical mixing and extensive heat treatment (>1600 °C) to achieve the desired phase purity. To reduce the formation temperature of YAG and improve the properties of final product, several wet chemical methods have been developed and successfully used for powders preparation [8–12]. However, mono-phase YAG is not readily achieved because of the existence of several detrimental intermediate phases.

It is important to keep composition homogeneous for obtaining pure and fine powders of materials [13]. Citrate–nitrate sol–gel combustion process is a main powder preparation method of the combination of a sol–gel process and combustion process, where a particular ratio of citrate and nitrate is maintained to initiate the self-propagating process between the reducing citrate and oxidizing nitrate group. The process exploits the advantages of inexpensive precursors, a simple preparation method, and results in ultrafine, homogeneous, highly reactive powder [14].

In the present work, the yttrium aluminum precursor for mono-phase YAG was synthesized by a sol–gel combustion method at a relatively lower temperature. The thermal behavior of the precursor was investigated.

2. Experimental

A sol–gel combustion process was carried out to prepare the precursors. Aluminum nitrate and yttrium nitrate solution were prepared and mixed into each other according to the stoichiometric ratio of $Y_3Al_5O_{12}$. Then, the citric acid ($C_6H_8O_7 \cdot H_2O$) solution was added to the mixed solution.

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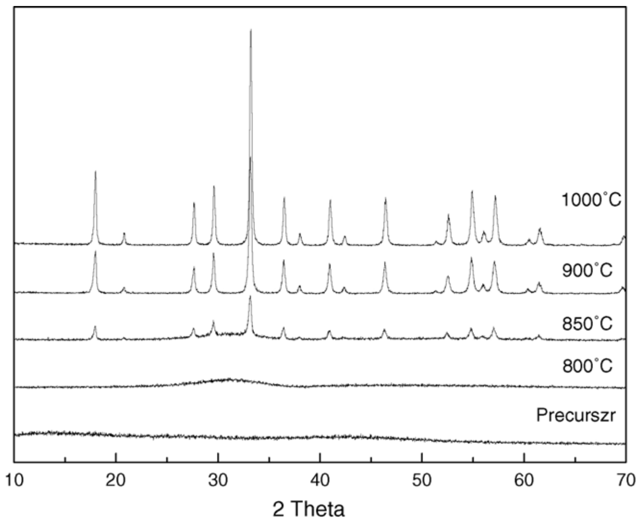

Fig. 1. The XRD patterns of the precursor and the powders calcined at various temperatures.

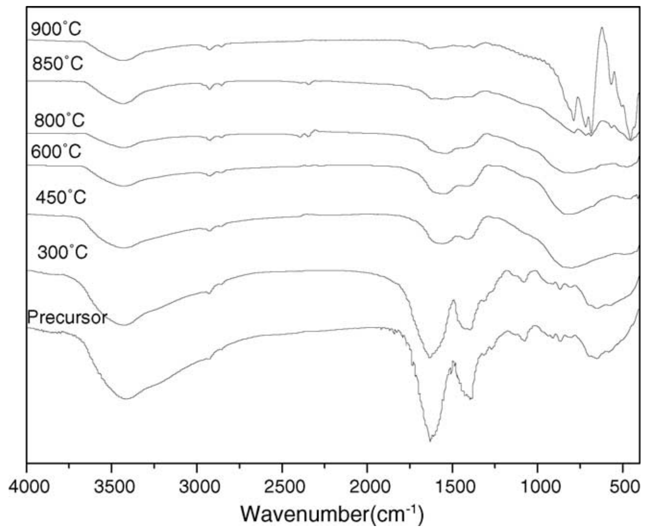

Fig. 2. FTIR spectra of YAG precursors calcined at different temperatures.

The molar ratio of nitrate to citrate was 1:1. The solution was heated at 60 °C and strongly stirred using a magnetic agitator for several hours. It performed as yellowish sol and converted to transparent sticky gel when heated at 80 °C. The gel was rapidly heated to 180 °C and an auto combustion process took place accompanied with the release of brown fumes. Finally, a yellowish product, fluffy precursor was achieved. The precursor was then calcined at temperatures from 300 to 900 °C (the interval of 100 °C) in a muffle furnace in air.

The phases in the samples were identified by XRD (Model D/MAX-2550V) using nickel filtered Cu Kα radiation in the range of $2\theta = 10–70^\circ$. Thermal analysis of the precursor was carried out from ambient temperature to 1000 °C with the differential scanning calorimetry (DSC), thermogravimetry (TG), and mass spectrum (MS) (DSC–TG–MS; Model STA 449C, Netzsch, Germany). The heating rate was 10 °C/min. FTIR spectra were performed on Nicolet 7000-C with 4 cm^{-1} resolutions. Powder samples were dispersed in KBr pellets for IR analysis.

3. Results and discussion

XRD patterns of the precursor and samples calcined at various temperatures are shown in Fig. 1. Since no obvious diffraction peaks are observed, it can be concluded that the precursor remains amorphous below 800 °C. At 800 °C, the characteristic peaks of YAG phase appear with rather weak peaks, which is indicative of microcrystalline YAG material. When the temperature is elevated to 900 °C, high and sharp peak is observed. This might be associated to the grain growth of the YAG crystallite. Although YAM and YAP are often present as intermediate phases in the course of synthesis of YAG powder by other wet chemistry methods [8,9,11], in the present situation, only YAG ($Y_3Al_5O_{12}$) phase (with the resolution limit of XRD) is detected and no intermediate phase is observed. Therefore, it could be considered that YAG crystallizes directly from the amorphous precursor without the formation of any intermediate phase. Such assumption can be further supported by following FTIR and DSC–TG–MS results.

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 hydroxyl groups (O–H). Peaks localized at 1640 and 1400 cm^{-1} are assigned to asymmetrical and symmetrical stretching vibration of carboxylate (O–C=O), respectively [9]. For samples calcined at 450 °C, the spectrum reveals that the carboxylate of the precursor transforms into the carbonate with the characteristic asymmetrical split stretching localized at 1530 and 1420 cm^{-1} [15]. At 850 °C, mono-phase YAG is formed together with a trace of carbonate vibrations as an impurity, as indicated in the FTIR patterns. This is in agreement with the result of XRD mentioned above. However, in spectrum

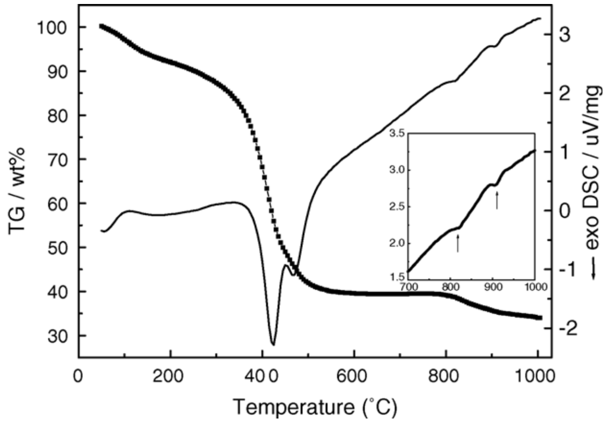

Fig. 3. TG/DSC curves of YAG precursor at a heating rate of 10 °C/min.

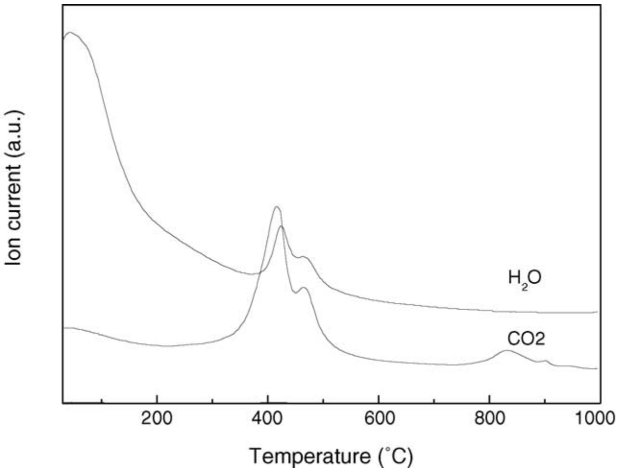

Fig. 4. MS curves of the YAG precursor at a heating rate of 10 °C/min.

of 900 °C the absorption of carbonate entirely disappears and is replaced by metal–oxygen vibrations at 655, 605, and 566 cm^{-1} due to lattice vibration of YAG unit cell [15,16].

Figs. 3 and 4 show TG–DSC and MS spectra of the precursors, respectively. A total mass loss of 68% up to 900 °C indicates that the auto combustion reaction of the precursor at 180 °C is not complete (in Fig. 3). The sharp weight loss appears at temperature range of 350–500 °C and tends to stop at around 900 °C. The substantial weight loss results from the release of CO_2 and H_2O gases due to the decomposition of excess citric acid and carboxylate precursor, as detected by the MS (Fig. 4). The corresponding DSC curve displays sharp exothermal peaks in the same temperature region (Fig. 3). The weight loss from 500 to 900 °C in the TG curve is related to the release of CO_2. No H_2O is detected according to the MS pattern. Considering the FTIR profiles in Fig. 2, it could be supposed that excess citric acid and precursor of carboxylate decomposed at below 500 °C to form carbonate. Close observation shows that two distinct exothermal peaks appear at 825 and 905 °C, respectively. These two peaks have never been detected in the as-reported literatures. We consider that the former might result from the crystallization of amorphous YAG due to the decomposition of the carbonate. The latter at 905 °C might be attributed to the crystal growth of YAG [15]. This assumption could be supported by the results of XRD, in which no intermediate phase is detected (with the XRD resolution limit). The diffraction intensity significantly increases with increasing temperature at 900 °C compared to that of 850 °C (Fig. 1), therefore it could be concluded that the peaks at 905 °C is attributed to the crystal growth.

4. Conclusions

Mono-phase YAG can be prepared by citrate–nitrate sol–gel combustion process. Two distinct exothermal peaks are detected at 825 and 905 °C, which probably correspond to the crystallization of amorphous YAG and grain growth of YAG crystallites, respectively. Excess citric acid and carboxylate mixture decompose at about 400 °C to form carbonates, which decompose at above 450 °C. The YAG is supposed to nucleates directly from the amorphous precursor without the formation of any intermediate phase at about 800 °C. Mono-phase YAG crystallites can be formed at 900 °C.

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