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Nd:YAG nano-crystalline powders derived by combining co-precipitation method with citric acid treatment

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Abstract

Nd-doped YAG nanocrystalline powders were prepared by combining a co-precipitation method with a citric acid treatment. Structural evolution features of the as-prepared nanocrystalline powders were studied by Fourier transform infrared spectroscopy, differential scanning calorimetry, thermogravimetry analysis, X-ray diffraction analysis, and transmission electron microscopy. Results indicate that the mass loss of the precursor occurs with the citric acid being introduced into the cationic solution, however, the composition of the raw materials can be invariably kept unvarying, which is confirmed by an existence of only the pure YAG crystalline phase. It is also found that the shape of the obtained particles can be changed and the dispersion of the particles can be obviously improved with the addition of the citric acid. Furthermore, effect of the citric acid on the formation of the particles during the co-precipitation has been theoretically explained.

Keywords: Nd:YAG; Nanocrystalline; Co-precipitation; Citric acid

1. Introduction

Yttrium–aluminum garnet (YAG) single crystal has been widely used as optical materials owing to its cubic form, garnet structure and no birefringence effect at the grain boundaries, which lead to an excellent optical property [1]. However, it is difficult for such a single crystal to make a big size, high doping concentration and low production cost. One promising substitute is a sintered polycrystalline YAG transparent ceramic that has a low production cost, excellent optical and good high temperature mechanical properties as compared to YAG single crystal [2–4].

YAG powders are usually prepared by solid-state reaction process [5], but a lot of studies show that the YAG powders prepared by wet-chemical methods are preferable for sintering transparent ceramics, because the solution-based techniques can achieve better chemical homogeneity [6]. Consequently, several wet-chemical synthesis methods have been developed, such as sol–gel [7–10], co-precipitation [11–13], homogeneous precipitation [14], spray pyrolysis [15,16], hydrothermal treatment [17], and combustion method [18–20], etc. As compared with the other methods, the co-precipitation method is one of the most promising techniques because of the inexpensive starting materials, ease of mass production, a simple synthesis process and commonly available apparatus. However, the shape of the YAG powders prepared by those reported co-precipitation methods is spherical and thus the agglomeration problem, which takes place during the drying process, is practically hard to avoid in those reported co-precipitation methods.

In this paper, Nd:YAG nanocrystalline powders with a new shape were prepared by combining the co-precipitation method with the citric acid treatment. Here, the citric acid was introduced into the cationic solution as an additional factor to adjust the YAG crystallization. In addition, effect of the citric acid on the resultant powders was also investigated. Results indicate that the shape of the as-prepared Nd:YAG particles can be adjusted and the dispersion of the particles can be improved with the addition of the citric acid.

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2. Experimental

2.1. Experiment 1

The composition of the raw materials employed in experimental study corresponds to the formula of $Nd_{0.06}Y_{2.94}Al_5O_{12}$, which Nd was chosen as a doping element due to its special excitation wavelength at 1064 nm. Suitable amounts of the Nd_2O_3 and Y_2O_3 were firstly dissolved in the concentrated HNO_3 and the solution was then dried and evaporated to remove the surplus HNO_3, followed that the obtained nitrate solution was dissolved in de-ionized water and mixed with the aluminum nitrate solution. Then, different amounts of the citric acid were introduced into the cationic solution, The molar ratio of the citric acid to M^{3+} ($M^{3+} = Y^{3+} + Nd^{3+} + Al^{3+}$) was selected, which includes 0 (sample 1#), 0.0625 (sample 2#), 0.125 (sample 3#), 0.1875 (sample 4#) and 0.25 (sample 5#), these five samples will provide plenty of experimental data to study the effect of the citric acid on the formation of the particles during the co-precipitation process. Finally, the nitrate solution was dripped into the solution, which consists of the ammonium hydrogen carbonate aqueous and ethanol, under a mild agitation by a magnetic stirrer [21]. In order to ensure the cations (Nd^{3+}, Y^{3+} and Al^{3+}) can be completely precipitated, the pH value of the solution should be always kept in the range of 7.2–7.8. The reaction process was carried out at room temperature under a vigorous stirring. After the titration process was finished, the precipitate was collected by using a centrifuge and then washed with de-ionized water and ethanol several times to remove the impurities such as NO_3^-. Thus, five kinds of precursors with different amounts of the citric acid as an additive were obtained by drying them at a temperature of 60 °C.

2.2. Experiment 2

The nitrate solution was prepared as the same as Section 2.1, and different amounts of the citric acid were introduced into the cationic solution. The molar ratio of the citric acid to M^{3+} ($M^{3+} = Y^{3+} + Nd^{3+} + Al^{3+}$) is 0 and 0.125. Followed the nitrate solution was dripped into the solution, which consists of the ammonium hydrogen carbonate aqueous and ethanol, under a mild agitation by a magnetic stirrer. It should be noted that the pH value of the solution should be always kept higher than 7.8, so that the Al^{3+} is not be fully precipitated. Also, the reaction process was carried out at room temperature under a vigorous stirring. After the titration process was finished, the precipitate was collected by using a centrifuge and then washed with de-ionized water and ethanol several times to remove the impurities such as NO_3^-. The precursors were prepared by drying them at a temperature of 60 °C and the products were thus obtained by calcining the precursors at 900 °C for 2 h.

Thermal decomposition behavior of the yttrium carbonate precipitate precursor was analyzed by differential scanning calorimetry and thermogravimetry (DSC/TG) analysis using a thermal analyzer (NETZSCH STA 449C, Germany) in air with a heating rate of 20 °C min^{-1}. Fourier transform infrared (FTIR) spectra of the precursors in KBr discs were measured in the range of 4000 cm^{-1}–400 cm^{-1} from a Bruker Vetex 70. X-ray diffraction (XRD) analysis was employed to investigate the phase structure of the as-prepared YAG powders, using a D/max 2400 X Series X-ray diffractometer. The X-ray radiation source used was Cu *Kα*, obtained at 40 kV, 100 mA and the scanning speed was 15° min^{-1} at a step of 0.02°. Transmission electron microscopy (TEM, JEM-200CX, JEOL Inc., Japan) was employed to observe the morphological properties of the as-prepared YAG powders.

3. Results and discussion

Fig. 1(a) shows a relationship between the mass loss of the precursor and the molar ratio of the citric acid to the M^{3+}. It can be seen from Fig. 1 that different mass loss percentages of the precursor can be clearly seen with the addition of the citric acid introduced into the cationic solution. The mass loss percentage of the precursor for sample 1# is zero, since the citric acid is not introduced into the cationic solution. But for other samples, the cationic (M^{3+}) is obviously lost, which can be confirmed by the

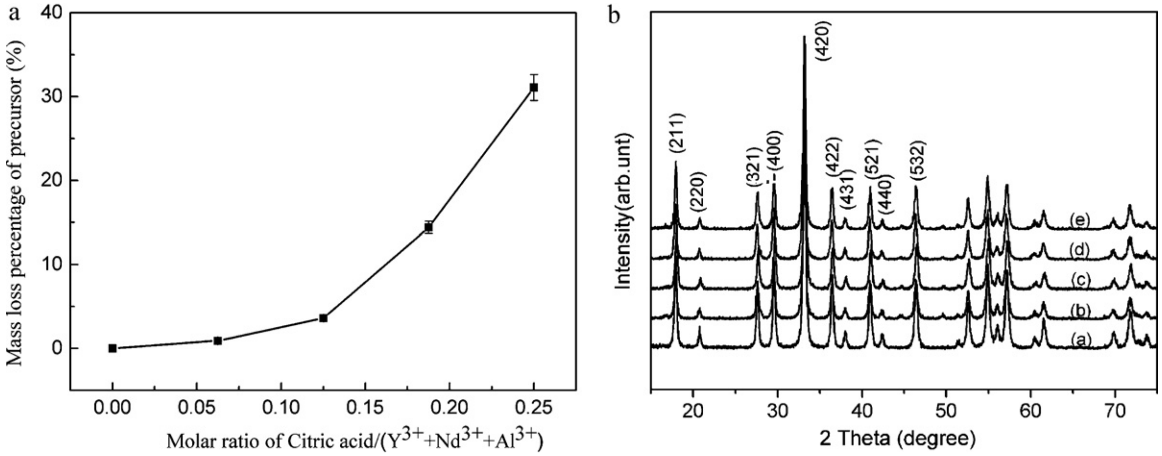

Fig. 1. (a) Relationship between the mass loss of the precursor and the molar ratio of the citric acid to the M^{3+}. (b) XRD patterns of the products calcined at 900 °C for 2 h. (a) sample 1#, (b) sample 2#, (c) sample 3#, (d) sample 4# and (e) sample 5#.

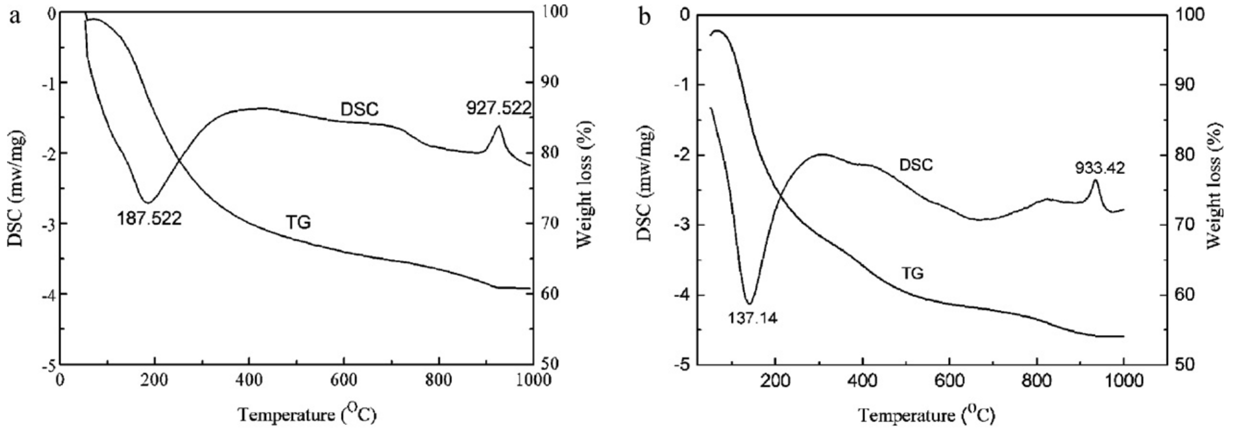

Fig. 2. DSC–TG curves of the precursor samples: (a) sample 1# and (b) sample 3#.

mass loss of the precursor. Normally, the lost of the cationic (M^{3+}) always means that there is a change of the composition of the raw materials. However, it can be interestingly found from the XRD patterns as shown in Fig. 1(b) that all measured samples show only a pure YAG crystalline phase and no any intermediate phases are detected, that is to say, the addition of the citric acid does not impact the phase structure of the YAG powders and the molar ratio of the (Nd^{3+} + Y^{3+}):Al^{3+} can keep unvarying (3:5) under present experiment conditions.

The DSC/TG curves of the synthesized precursors are presented in Fig. 2. The broad endothermic peak at about 187 °C accompanied by a weight loss is due to the evaporation of water [22]. The exothermic peak at about 930 °C is attributed to the crystallization of the precursor as seen in Fig. 4, and it is also noted that no weight loss can be detected above 930 °C. The TG curve indicates that the precursor is completely decomposed into oxides below 930 °C. The weight loss of the sample increases with increasing temperature from room temperature to 800 °C continuously. It can be seen that the weight loss is about 39 wt% for the sample 1# as shown in Fig. 2(a) and 45 wt% for the sample 3# in Fig. 2(b), it is mainly due to the removal of the absorbed and molecular water and the gradual decomposition of the precursor.

Fig. 3 shows the FTIR spectra of the precipitate precursor samples. The wide band at about 3430 cm^{-1} can be assigned to the stretching vibration of the O–H bands [23], which include water and aluminum/yttrium hydroxyl groups. The band at about 2349 cm^{-1} corresponds to the CO_2 in the air, two major peaks at 1385 cm^{-1} and 1518 cm^{-1} may result from the diagnostic of the $CO_3{}^{2-}$ [24]. For the FTIR spectra of the samples 2# and 3#, according to the sadlter IR database, the absorption band appeared at about 2965 cm^{-1} should correspond to the stretching vibration of the C–H, the bands at 1260 cm^{-1} and 1030 cm^{-1} can be assigned to the C–O–C. These results from the FTIR spectra indicate that the citric acid is embedded in the precursor.

Fig. 4 shows the TEM images of the YAG powders including samples 1# and 3#, which were obtained by calcination at 900 °C for 2 h. As can be observed in Fig. 4 (a), the size of the elliptical particles is about 70 nm in average, and the agglomeration of the particles is very serious. However, with the addition of the citric acid into the cationic solution, it can be seen from Fig. 4(b) that the shape of the particles is not elliptical and the particles show a better dispersion as compared with that as seen in Fig. 4(a). These results indicate that the citric acid, which is introduced into the cationic solution, can lead to the change of the shape of the particles. That is to say, the agglomeration of the particles becomes weaker and the particles have a better dispersion due to the addition of the citric acid. As reported in Ref. [25], the cationic can be completely chelated by the citric acid in sol–gel process when the molar ratio of the citric acid to the M^{3+} ($M^{3+} = Y^{3+} + Nd^{3+} + Al^{3+}$) is 0.1. Thus, the pure YAG crystalline phase of the sample 3# indicates that the complexation reaction in sol–gel process is reversible ($C + M^{3+} \leftrightarrow R_0$, where C is the citric acid and R_0 is one kinds of the complex compound), and the precipitation process of the cationic can be prevented by this reaction. According to the probability statistics, the molar ration of the (Nd^{3+} + Y^{3+}):Al^{3+} can be invariably kept at 3:5 both in the R_0

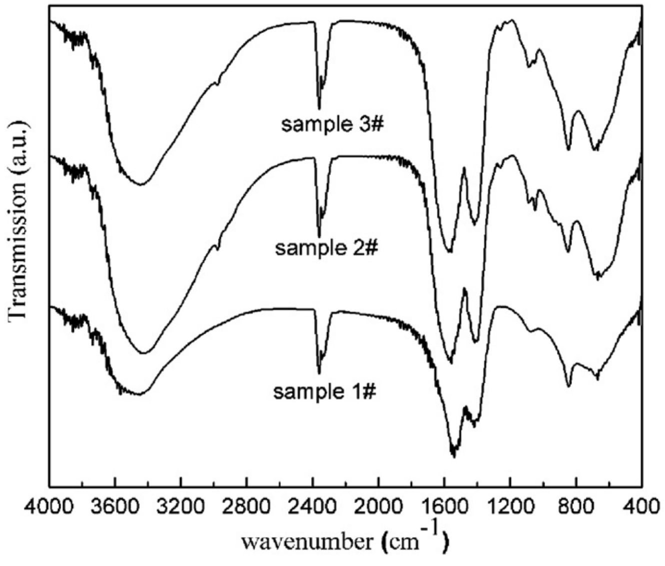

Fig. 3. FTIR spectra of the precipitate precursor samples.

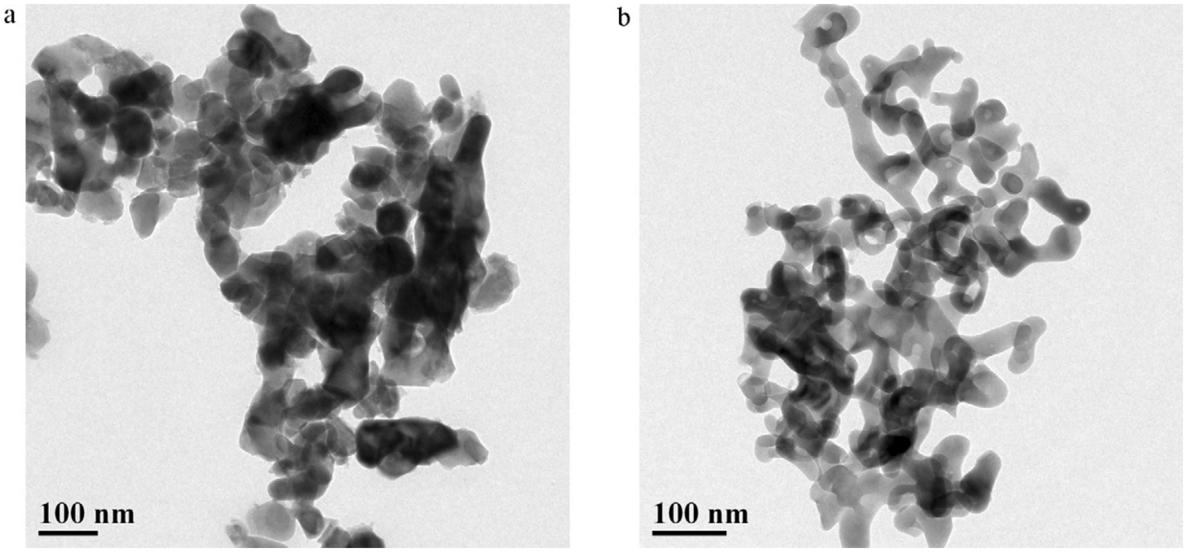

Fig. 4. TEM images of the YAG powders calcined at 900 °C for 2 h: (a) sample 1# and (b) sample 3#.

and in the precursor, if the cationic (Y^{3+}, Nd^{3+} and Al^{3+}) can be completely mixed in nitrate solution. Considering the amorphous precursors (P) have potential by absorbing charged ions in the solution, thus, they can be considered as metal ions and can be also chelated by the citric acid in the solution. Therefore, the reaction both $C + M^{3+} \leftrightarrow R_0$ and $C + P^{x+} \leftrightarrow R_1$ should exist in this co-precipitation process, which can be indicated by the experimental data of Section 2.2 as follows.

Fig. 5 shows the XRD patterns of the products prepared in Section 2.2 and calcined at 900 °C for 2 h, it can be seen that the curve (b) shows main YAG crystalline phase and only very weak YAP crystalline phase as compared to the curve (a) which shows almost only YAP crystalline phase, indicating the addition of the citric acid is a strong effect on restraint change of the composition of the raw materials during the co-precipitation process, while the pH value was always kept higher than the 7.8. This phenomenon can be attributed to the reaction $C + P^{x+} \leftrightarrow R_1$ (where C is the citric acid, P^{x+} is the precursors (P) with potential and R_2 is one kinds of the complex compound in the co-precipitation,). When the pH value of the solution is not in the range of 7.2–7.8 during the co-precipitation process, the citric acid can chelate the P^{x+} and M^{3+} together, which weakens the change of the composition of the raw materials, while the cationic in the solution can precipitate as a complex.

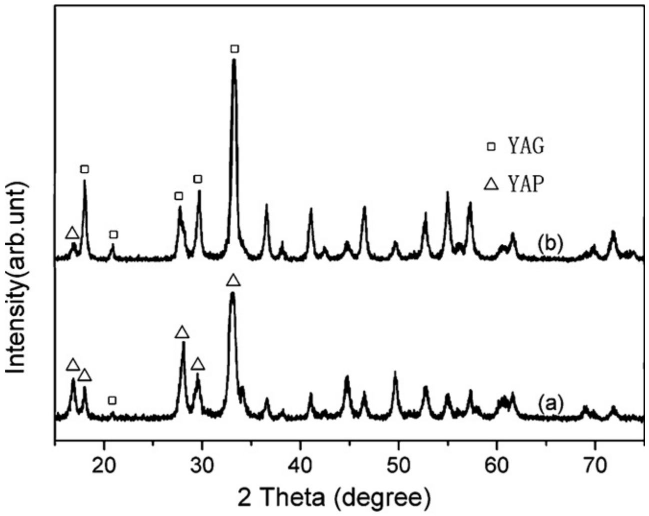

Fig. 5. XRD patterns of the products calcined at 900 °C for 2 h. (a) Product prepared without the citric acid and (b) product prepared with the citric acid.

As compared with the other modified co-precipitation methods, the YAG powders obtained by combining the co-precipitation process with the citric acid treatment can get a better dispersion and different shapes as shown in Fig. 4. As we know, the hard reunion of the YAG powders can be mainly attributed to the evaporation of the water molecules during the drying process. For the those co-precipitation methods as reported in [26,27], dispersing agent is usually used to increase the electronegative property of the precursors, which is used to improve the agglomeration problem of the precursors by enhancing the repulsive force between the precursor particles. But only a limited improvement is obtained by employing these different dispersing agents, since the water molecules to

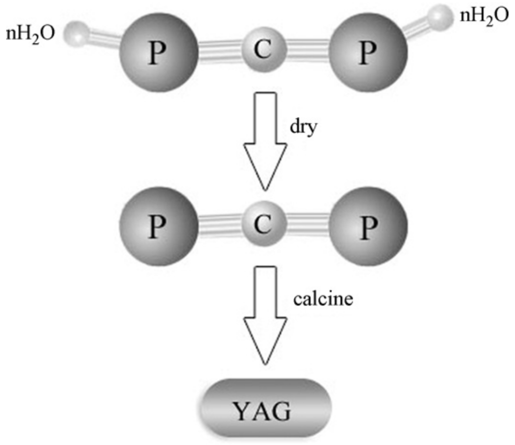

Fig. 6. Schematic diagram of the forming process of the YAG particles.

combine the precursors are still not be dispelled. However, a very different result can be obtained while the YAG powders synthesized by combining the co-precipitation method with the citric acid treatment due to the chelate feature of the citric acid. A possible interpretation is that the elongated YAG particles can be obtained by the reaction of the $C + P^{x+} \leftrightarrow R_1$, which is the main reaction during the co-precipitation process. Fig. 6 shows the schematic diagram of this reaction ($C + P^{x+} \leftrightarrow R_1$). It can be seen that the amorphous precursors (P^{x+}) are combined with the citric acid molecules (C) rather than with the water molecules. Consequently, the hard reunion can be completely avoided, since it is impossible for the citric acid to appear a thermal decomposition during a low drying process (the drying temperature is only at 60 °C). But while the precursors are calcined at 900 °C with the heating rate of 5 °C $\min^{-1}$, the elongated YAG particles can be formed due to the fusion between this precursors (P^{x+}) and the citric acid at 900 °C for 2 h.

4. Conclusions

YAG precursors have been successfully synthesized by the co-precipitation method with the citric acid treatment. When the citric acid is introduced into the cationic solution as an additive, it is found that the molar ratio of the ($Nd^{3+} + Y^{3+}$) to Al^{3+} invariably keeps at 3:5 both in the co-precipitation process and in the polymer. Thus, the amorphous precursors are combined with the citric acid molecules instead of the water molecules, which lead to the formation of the dispersive and elongated Nd:YAG particles.

Acknowledgments

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