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YAG powder synthesis by the modified citrate process

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Abstract

Nd:YAG powder was synthesized by the citrate process. Isopropyl alcohol promotes crystallization of the final phase. Heating the samples using the DTA equipment to pre-selected temperatures allowed us to follow the formation of phases in the system. It was found that the primary phase consists of non-stoichiometric YAG and YAP ($YAlO_3$). The amorphous phase present in the system reacts with the crystalline phases and finally the stoichiometric YAG appears. Compacts of the agglomerated final powder achieve higher density during sintering performed at slow rate of temperature increase compared to fast firing.

Keywords: Precursor-organic; Calcinations; Sintering; YAG

1. Introduction

In the Y_2O_3–Al_2O_3 system, apart from the end-member phases three compounds stable at ambient pressure are known: $Y_3Al_5O_{12}$ (YAG), $YAlO_3$ (YAP) and $Y_2Al_4O_9$ (YAM) of cubic garnet, orthorombic or hexagonal perovskite and monoclinic symmetry structure, respectively.

Yttrium–aluminium garnet has received much attention because of its interesting optical and mechanical properties. Rare-earth doped YAG single crystals have been used as a laser host material. Attempts to synthesize polycrystalline translucent YAG ceramics for laser application have been reported in.[1–3] Another application of rare-earth doped YAG in the powder form as phosphor for displays, due to its good stability to high intensity electron irradiation, should be mentioned.[4] High temperature creep resistance is an attractive YAG property. A study by Parthasarathy et al.[5] revealed that creep rate of polycrystalline YAG at 1400 °C is three times slower than that of alumina.

Synthesis of YAG by the solid state reaction within the Y_2O_3–Al_2O_3 mixture requires extensive heat treatment at temperatures >1600 °C in order to eliminate intermediate phases YAM and YAP.[6,7] It leads to hard agglomerates and causes extensive grain growth.

Various wet chemical methods have been developed in recent years for low-temperature production of phase-pure YAG. An aqueous solution of $Al(NO_3)_3$ and $Y(NO_3)_3$ sprayed on a hot plate gave a homogeneous mixture of these salts.[8] Its calcination at 1000 °C resulted in single-phase YAG. At lower temperatures an amorphous phase and residual Y_2O_3 were observed.

Co-precipitation from water solution of relative nitrates with ammonia[9,10] and ammonium hydrogen carbonate[11] revealed that due to amphoteric properties of Al, pH of the process has to be kept close to 8. The precipitated amorphous gels transformed to YAG structure at moderate temperatures. Run of the process depended on the concentration of the salts of Y–Al solution and on the temperature of the system during precipitation. Ammonium hydrogen carbonate applied as the precipitating agent lead to the powder composed of softer agglomerates.

The preparation of YAG homogeneous powders was studied using citric acid as chelating agent.[12–19] The starting Al and Y nitrate solution with the citric acid additive forms amorphous gel after dewatering. Its pyrolysis at moderate temperatures results in the phase pure YAG. However, isothermal calcination at temperatures lower than necessary to receive 100% YAG material, usually shows presence of intermediate $YAlO_3$ (YAP) phase.

Using the DTA equipment YAG crystallization from the citrate precursor was studied in the present work under dynamic heating conditions. Apart from citric acid, 2-propanol was used as an additional factor effecting YAG crystallization. Sintering of the ground powder was observed.

2. Experimental

The selected composition corresponds to the formula $Y_{2.94}Nd_{0.06}Al_5O_{12}$. Proper amounts of yttria and neodymia (4N)

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were dissolved in hot nitric acid (1:1). Then the solution was dried to remove excess acid. The resulting nitrides were dissolved in distilled water and added to the aluminium nitrate solution of analytical grade. Concentration of the cations solution corresponded to 1.7375 mole (Y + Nd + Al)/L. In the next step citric acid was added to this solution in the amount of 2.5 moles for every 1 mol of $Y_{2.94}Nd_{0.06}Al_5O_{12}$. Different amounts of 2-propanol were introduced. It will be shown later on that it influences YAG synthesis. Drying and heating up to 300 °C for 0.5 h resulted in a stiff body.

Differential thermal and thermo-gravimetric analysis in air atmosphere (DTA and TG, respectively) were conducted using 10 °C/min rate of temperature increase up to 1000 °C in order to follow changes taking place in the material at elevated temperatures. The same equipment (Derivatograph, model C, MOM, Budapest) allowed us to prepare samples for the X-ray diffraction phase analysis by heating the samples up to the pre-selected temperatures and quick cooling down. The X-ray diffraction (Cu $K\alpha_1$ radiation, X'Pert Pro, Phillips PANalytical) was used to determine phase composition of the samples and the YAG lattice parameter. Rietveld refinement technique was applied in the both cases. Gases secreted during the heating of the sample in air atmosphere were analysed using quadrupol mass spectrometer (Mass Spectrometer QMD 300 Thermostar, Balzers). Specific surface area of the powders was measured by nitrogen adsorption at liquid nitrogen temperature with use of the BET isotherm (Sorpty 1700, Carlo Erba).

The powder prepared for sintering was attrition ground for 3 h in 2-propanol with 2 mm zirconia balls. Cylindrical samples of 22.5 mm diameter and 2 mm thickness were prepared by uniaxial powder pressing under 50 MPa, followed by isostatic repressing under 300 MPa. No lubricants were added. Sintering was performed in vacuum in a furnace equipped with tungsten heating elements.

3. Results and discussion

Samples derived from the systems of different 2-propanol concentration were calcined at 900 °C for 30 min with the rate of temperature increase of 5 °C/min. Fig. 1 shows the results of the X-ray phase analysis. It can be noticed that the YAG concentration essentially depends on the 2-propanol/(Y + Nd + Al) molar ratio. Balance to 100% was $YAlO_3$ (YAP). The 2-propanol additive promotes YAG crystallization. The optimum molar ratio of 2-propanol/(Y + Nd + Al) corresponds to 2.69.

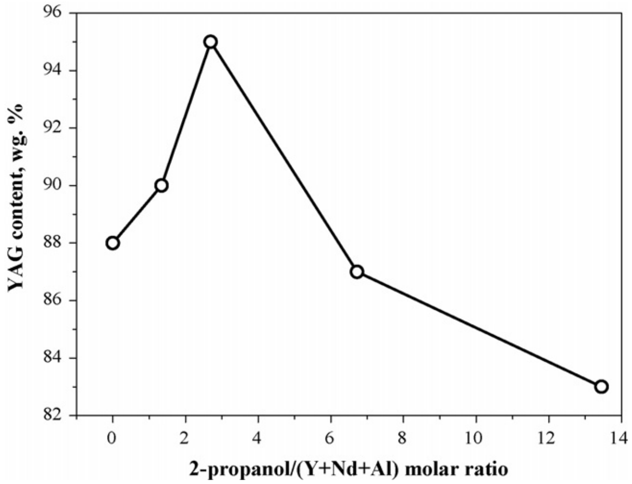

Fig. 1. YAG concentration vs. 2-propanol/(Y + Nd + Al) molar ratio.

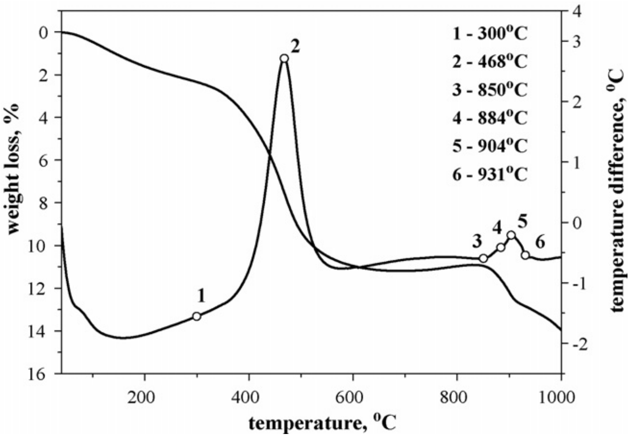

Fig. 2. DTA/TG curves. Heating rate 10 °C/min, air atmosphere. Starting sample calcined at 300 °C.

A batch of about 100 g was prepared using this value. The starting solution after drying was calcined at 300 °C for 1 h, which resulted in the dark brown body. Fig. 2 demonstrates the DTA/TG curves of this material and Fig. 3 the analysis of gases emitted from the sample. Broad exotherm with the maximum at 475 °C corresponds plausibly to decomposition and oxidation of the organic part of the system. This conclusion is corroborated by the weight loss (TG curve in Fig. 2) as well as CO_2 and H_2O presence in the gases secreted from the sample (Fig. 3). At about 900 °C another exothermic peak occurs, accompanied by the weight loss. Simultaneously, CO_2 appears in the sample atmosphere again. It appears also at still higher temperature. In this temperature range no signal from water is present. It indicates that all hydrogen was removed from the sample. So, most probably the exothermic effect should be ascribed to the oxidation of carbon remaining after decomposition and dehydration

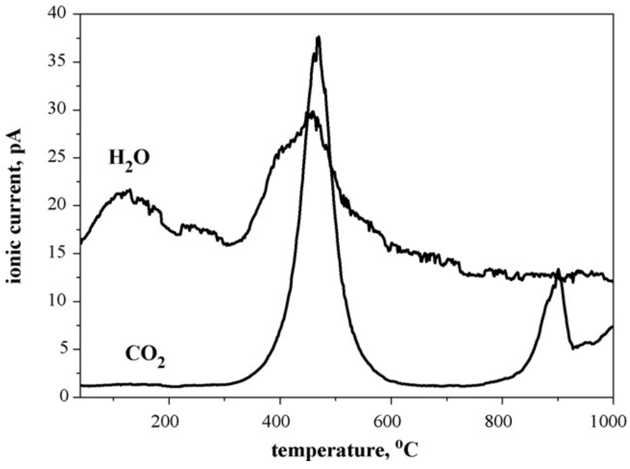

Fig. 3. Analysis of gases emitted from the starting sample. Heating rate 10 °C/min.

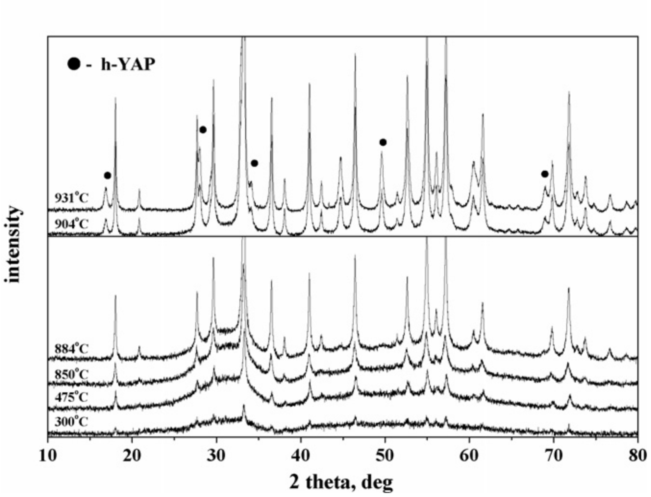

Fig. 4. X-ray diffraction patterns of the materials heated up in the DTA apparatus to the preselected temperatures. The 10 °C/min rate of temperature increase was applied. Starting material was calcined at 300 °C. (●) Corresponds to the h-YAP phase. Other peaks represent the YAG phase.

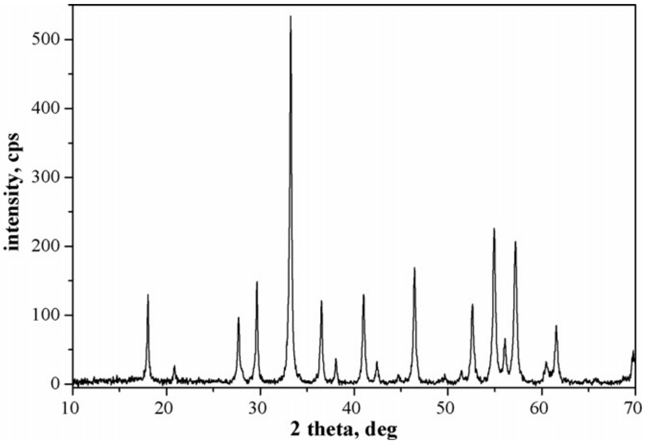

Fig. 5. X-ray diffraction pattern of the material heat treated at 900 °C for 3 h, rate of temperature in crease 5 °C/min.

of the system. It cannot be excluded that part of this effect is related to the heat of the system evolution. It was studied by the X-ray diffraction using samples heated up in the DTA equipment (see temperatures indicated in Fig. 2). Before discussing this problem let us notice that no signal coming from nitrogen oxides was observed in the mass spectrograph tests. It indicates that during preliminary heat treatment of the material at 300 °C total denitrification of the system occurs.

In Fig. 4 X-ray diffraction patterns of the materials heat-treated at indicated temperatures are shown. In Table 1 the development of the phase composition with temperature is summarised.

It is interesting to notice that even in the starting sample, i.e. the one which was initially calcined at 300 °C, reflections characteristic of YAG phase are visible. Increased background intensity indicates the presence of the amorphous part in the system. Its fraction decreases with temperature in relation to the crystalline phases. However, it seems to be still present in the sample heated up to 904 °C. At this temperature $YAlO_3$ of hexagonal symmetry (h-YAP) appears. The same material calcined isothermally at 900 °C for 3 h transforms totally to the YAG phase (Fig. 5). Combining all these facts we postulate that the X-ray amorphous, alumina-rich phase exists in the system. Reaction of this phase with $YAlO_3$ results in the YAG synthesis (Table 1).

Table 1
Phase composition of the material heat-treated with the DTA equipment

Temperature (°C)	Phase composition
300 (starting)	YAG + amorphous phase
475	YAG + amorphous phase
850	YAG + amorphous phase
884	YAG + amorphous phase
904	YAG + h-YAP + amorphous phase
931	YAG + h-YAP + Al_2O_3(?)
900[a]	YAG + h-YAP + Al_2O_3(?)
900[b]	YAG

The rate of temperature increase 10 °C/min. No soaking time.

[a] Sample calcined at 900 °C for 1.5 h, rate of temperature increase 5 °C/min.

[b] Sample calcined at 900 °C for 3 h, rate of temperature increase 5 °C/min.

h-YAP–$YAlO_3$ of hexagonal symmetry.

Fig. 6 shows the value of the YAG lattice parameter versus heat treatment temperature. Its increase between 475 and 850 °C can plausibly be explained by changes in the oxygen sub-lattice. Since crystallization of the YAG phase takes place in the presence of the carbon-rich environment, oxygen deficit seems possible. Re-oxidation of the system is most probably the reason of small, but visible in the TG curve, gain of the sample weight in the temperature range of about 700–850 °C (Fig. 2). The number of lattice sites occupied by big oxygen ions, which increase with temperature should lead, indeed, to the lattice parameter increase.

Proper stoichiometry of the system is confirmed by the single-phase product of the isothermal calcination at 900 °C for 3 h (see Table 1 and Fig. 5). So, the appearance of $YAlO_3$ in the samples calcined dynamically suggests that the primary YAG is lacking of Al. If so, its reaction with the postulated alumina-rich amorphous phase should result in the lattice parameter decrease, which is the case (Fig. 6). This is so because aluminium ionic

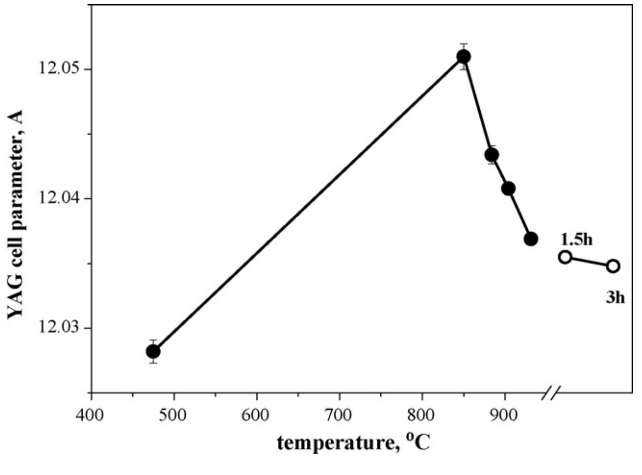

Fig. 6. YAG lattice parameter vs. temperature of heat treatment.

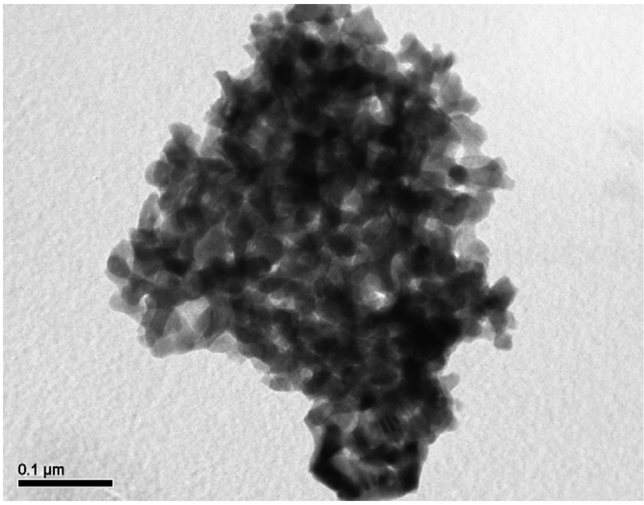

Fig. 7. TEM of the YAG powder.

Table 2
Relative densities of green samples and the ones sintered for 4 h at 1650 °C in vacuum

Sample	Relative density (%)
Green sample	51.3
1650 °C, 10 °C/min	91.9
1650 °C, 1 °C/min	98.5

Rate of temperature increase indicated. YAG physical density 4.56 g/cm^3.

radius is much smaller than that of yttrium and neodymium. Further decrease of the YAG lattice parameter occurs in samples calcined for 1.5 and 3 h. Open circles in Fig. 6 show this effect.

Fig. 7 shows transmission electron micrograph of the powder calcined at 900 °C for 3 h and attrition ground. The powder is composed of agglomerates, which were not destroyed during milling. Compacts were sintered at 1650 °C for 4 h in vacuum. Two different rates of temperature increase were applied (10 and 1 °C/min). It can be noticed that the rate of temperature increase has a profound effect on densification of the system. Slow increase of temperature promotes higher density of the final material (Table 2). A plausible explanation of this fact is that in case of high rate of temperature increase, fast densification of agglomerates takes place, which is followed by the opening of pores between them. Slow rate of temperature increase allows building up contacts among crystallites within agglomerates during early stages of sintering. It slows down densification of agglomerates at higher temperatures. In this case the difference of the rate of closing of inter- and intra-agglomerate pores becomes smaller compared to that observed in fast sintered samples. The analogous phenomenon occurs in so called pre-coarsening described in.[20]

4. Conclusions

(i) Optimum amount of isopropyl alcohol added to citric acid promotes crystallization of Nd:YAG from dewatered and denitrified mixture of Nd, Y, Al nitrates.

(ii) Calcination in air atmosphere of this mixture leads to oxidation of the organic part of the system and the non-stoichiometric YAG phase appears, followed by YAP ($YAlO_3$) crystallization.

(iii) Most probably the amorphous phase rich in alumina reacts with non-stoichiometric YAG and YAP. It results in the synthesis of stoichiometric $Y_{2.94}Nd_{0.06}Al_5O_{12}$.

(iv) Slow rate of temperature increase promotes better densification of the agglomerated YAG powder compared to fast sintering.

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