Synthesis and characterization of yttrium aluminium garnet (YAG) powders

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Abstract

In this paper synthesis and characterization of YAG powders, prepared by a process based on complexing properties of citric acid, was reported. Influence of citric acid estrification induced by 2-propanol or ethylene glycol on the system homogeneity was investigated. These reagents were introduced to aqueous solution of yttrium and aluminium nitrates. A variety of powders from Al_2O_3-Y_2O_3 system with different phase composition were obtained by altering the citrate to nitrate ratio. Evolution of the powders phase composition vs. temperature was investigated using DTA/TG, XRD, and FT-IR methods. The most interesting results were observed in case of the citric acid – propanol – relative nitrates system. The mole ratio of these reagents equal to 1: 2.5: 2.5 (nitrates (Al,Y): citric acid: 2-propanol) allowed to synthesize pure YAG phase powders at temperature as low as 950°C.

Keywords: YAG, citric acid, citrate gel method

I. 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), having 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. Thus, rare-earth doped YAG single crystals have been used in laser technology. Attempts to synthesize polycrystalline translucent YAG ceramics for laser application have been also reported [1–3]. Another application of rare-earth doped YAG in the powder form as phosphor for displays, due to its good resistance to high intensity electron irradiation, should be also 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.

Owing to such application potential of Nd: YAG ceramics, different methods for the synthesis of pure and homogeneous YAG or Nd: YAG powder have been adopted. YAG powders have been prepared traditionally by a solid state reaction [6] from the corresponding oxides, which requires prolonged mechanical mixing and extensive heat treatment at high temperature to eliminate intermediate phases. Various wet-chemical routes have been proposed to lower the synthesis temperature and eliminate the intermediate phases. These methods include sol-gel [7–8], precipitation [9–12], hydrothermal treatment [15–16], spray pyrolysis [17] and combustion synthesis [18–19]. In order to prepare homogeneous YAG powders many researchers have used a citric acid as a chelating agent [20–27]. In this paper the influence of citric acid estrification induced by propanol or ethylene glycol on homogeneity of the obtained powders has been investigated.

II. Experimental

The YAG powders, having composition corresponds to the formula $Y_3Al_5O_{12}$, were synthesized from yttrium and aluminium nitrates. Proper amounts of yttria were dissolved in hot nitric acid (1 : 1) and the obtained solution was dried to remove excess acid. The resulting yttrium nitrate was dissolved in distilled water and add-

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ed to the aluminium nitrate solution of analytical grade. Concentration of the cations ($Y^{3+} + Al^{3+}$) in the solution corresponded to 1.8286 mol/l. In the next step citric acid was added to this solution in the amount of 2.5 moles for every 1 mol of $Y_3Al_5O_{12}$ and then ethylene glycol or 2-propanol (in the same amount as that of citric acid). Thus, three different systems were prepared: one containing only citric acid (NC), another one with citric acid and 2-propanol additive (NPC) and the last one with citric acid and ethylene glycol additive (NEC). 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 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 different temperatures and quickly cooling them down. The X-ray diffraction (CuKα_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 both cases. Gases emitted during the heating of the sample in air atmosphere were analysed using a quadrupol mass spectrometer (Mass Spectrometer QMD 300 Thermostar, Balzers). Before measurements the precursor was dried at 110°C to the constant weight. Samples were also analysed using vibrational spectroscopy in the IR range. IR spectra were measured in the transmission mode in the range of 4000–400 cm^{-1} (BioRad fourier diffractometer FT600V).

III. Results and Discussion

(Y+Al) nitrates – propanol – citric acid (NPC) system

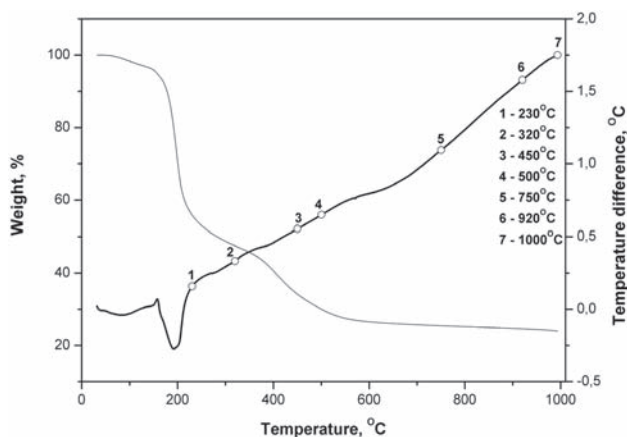Fig. 1 demonstrates the DTA/TG curves of the material obtained form a mixture of Y and Al nitrates with citric acid and 2-propanol. Mass spectrometric analysis of gases emitted from the NPC sample is shown in Fig. 2. The endothermic peak at about 200°C corresponds, most probably to the dehydroxilation of the system. This statement was corroborated by the mass spectroscopic measurements (Fig. 2), which shows emission of water vapour at this temperature. Simultaneously decarbonisation of the sample occurs as is indicated by the CO_2 emission. Most probably both effects are responsible for the loss of weight at temperatures up to 200°C. Emission of CO_2 occurs also at higher temperatures from about 300°C to 550°C.
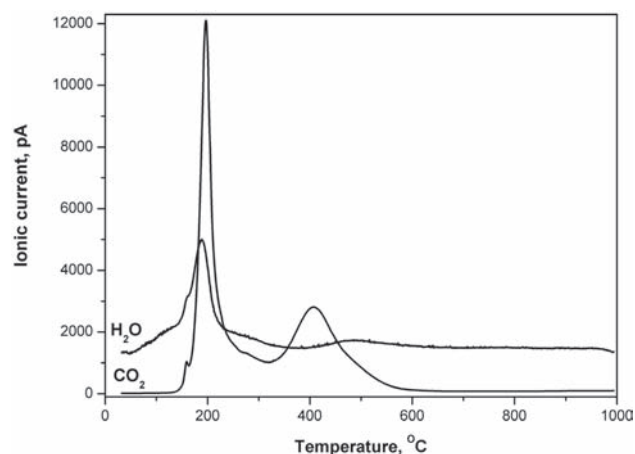

Figure 2. Mass spectrometric analysis of gasses emitted with temperature from the NPC sample

Additional information on the decomposition process was delivered by the infrared measurements. Samples for such investigations were prepared by the dynamic heating at a rate of temperature increase of 10°C/min up to the pre-selected temperatures (given in Fig. 1) and quickly cooled down. Fig. 3 shows the resulting IR spectra. The broad absorption bands in the range 3200–3550 cm^{-1} are due to the stretching vibrations in (O–H) groups, which are present both in cit-

Figure 1. DTA/TG curves of the NPC system. Calcination temperatures of the samples for further characteristics are indicated
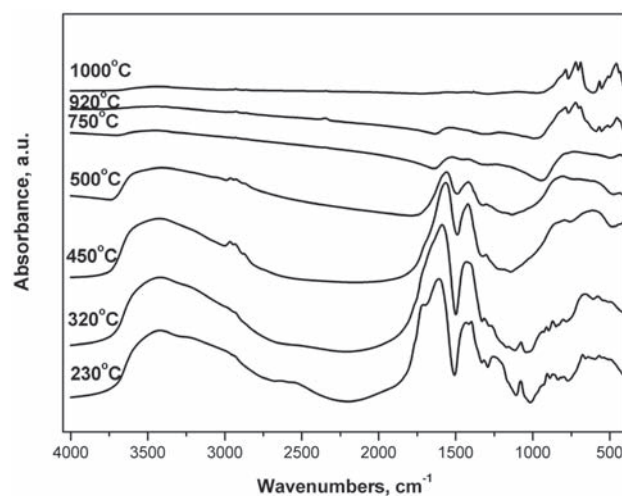

Figure 3. Transmission IR spectra of the NPC material calcined at indicated temperatures

ric acid and 2-propanol. These absorption bands are present in the samples calcined at temperatures up to 500°C. In the samples heat-treated from 230°C up to 500°C bands at 1400–1390 cm⁻¹ and 1320–1240 cm⁻¹ appear. These bands are assigned to the vibrations within carbonate groups. They are present up to 500°C. The peaks at 780–430 cm⁻¹ in the samples calcined at 920°C and 1000°C are characteristic of the metal–oxygen (Y–O and Al–O) vibrations. In Fig. 4 X-ray diffraction patterns of the same materials as those applied in infrared investigations are presented. Dynamic calcination at 920°C and 1000°C results in the crystalline materi-
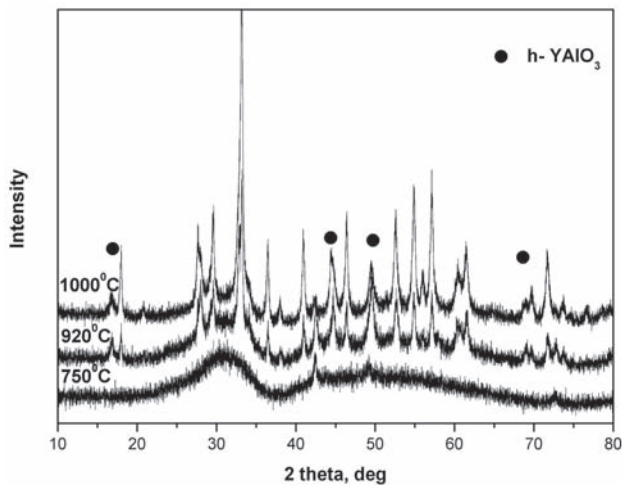
Figure 4. X-ray diffraction patterns of the material heated up in the DTA apparatus to the preselected 10°C/ min rate of temperature increase was applied. NPC system

al. However it cannot be excluded that in the sample heat treated at 920°C and probably at 1000°C a certain fraction of amorphous matter is still present. It is substantiated by the increased X-ray background. Except YAG reflections, peaks indicating presence of the hexagonal $YAlO_3$ (h-YAP) phase are visible. Most probably crystallization of this phase results from a certain
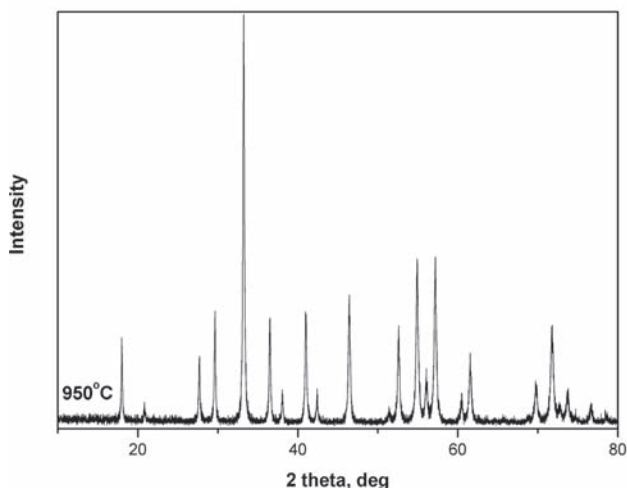
local heterogeneity of the sample. These peaks disappear when isothermal heating at 950°C for 1 h is applied (Fig. 5). In this case heating rate was lower than previously (5°C/min), thus, it can be assumed that prolonged heat treatment under such conditions allows the system to be homogenised.
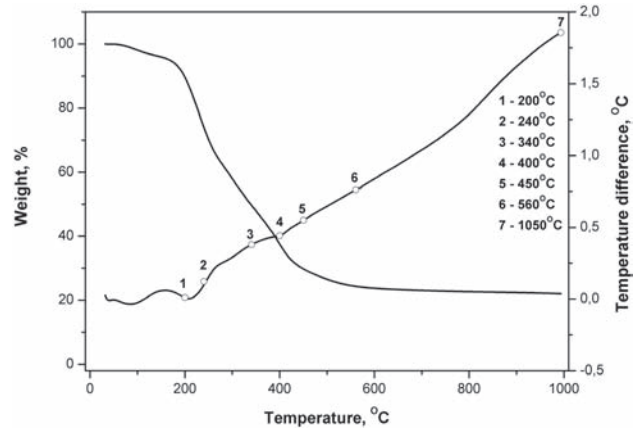
Figure 6. DTA/TG curves of the NEC system. Calcination temperatures of the samples for further characteristics are indicated
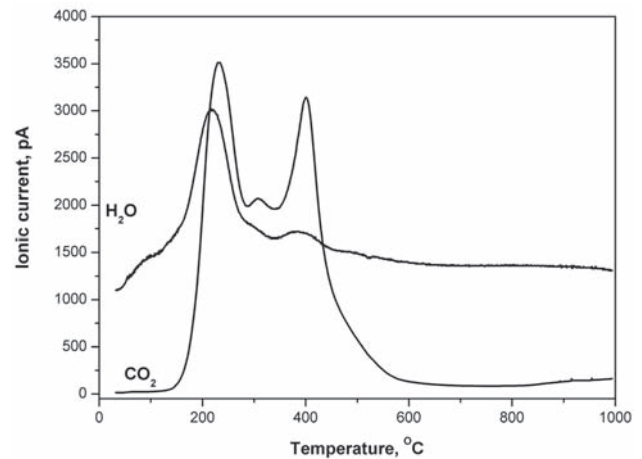
Figure 7. Mass spectrometric analysis of gases emitted with temperature from the NEC sample

Figure 5. X-ray diffraction patterns of the material heated up 950°C. Rate of temperature was 5°C/ min. NPC system
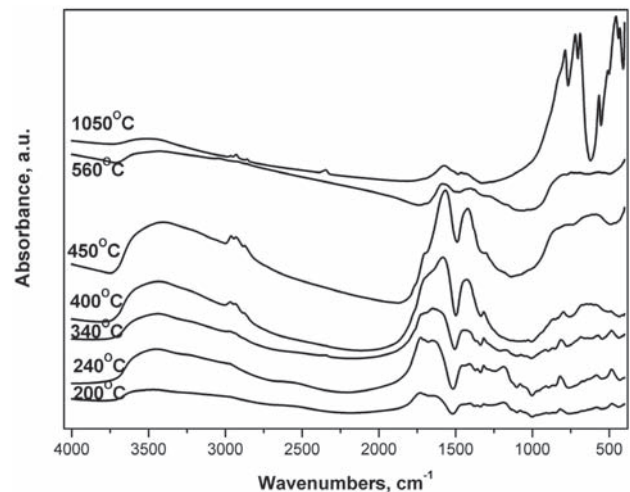
Figure 8. Transmission IR spectra of the NEC material calcined at indicated temperatures

(Y+Al) nitrates – ethylene glycol – citric acid (NEC) system

The DTA/TG results (Fig. 6) and analysis of gases (Fig. 7) show indicate on the similar behaviour of the NEC powder with the NPC one. However, infrared spectra (Fig. 8) and X-ray diffraction patterns (Fig. 9) show essential differences between the samples NEC and NPC. The IR spectra of the sample calcined at temperature up to 400°C have a large number of absorption bands, which makes their interpretation difficult. However, bands in the 1430–1499 cm^{-1} range most probably indicate the C-N bonds. In the NPC sample, described above, no such bands were present. Another important feature of the studied system comes from the X-ray diffraction (Fig. 9). The powder calcined at 950°C for 1 h (with heating rate of 5°C/min) shows reflections characteristic not only for YAG but also for the Y$_2$O$_3$ phase. Of course under dynamic heating up to 950°C (with heating rate of 10°C/min) the Y$_2$O$_3$ phase is present too. These facts suggest that the NEC sample with ethylene glycol is not as homogenous as in the NPC sample with 2-propanol as an estrification additive.
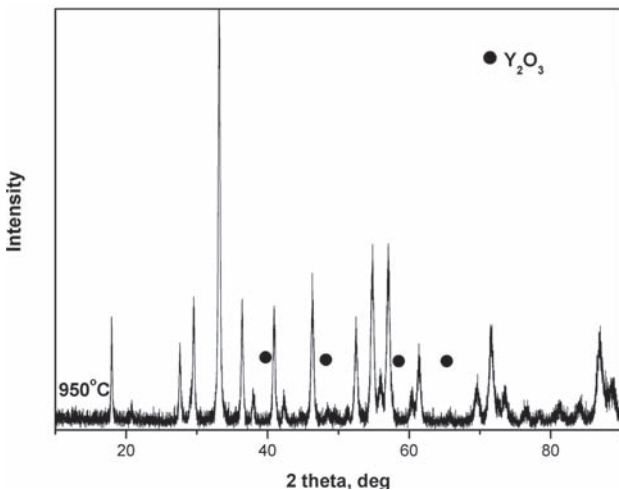

Figure 9. X-ray diffraction patterns of the material heated up in the DTA apparatus to the preselected temperature. 10°C/min rate of temperature increase was applied. NEC system

(Y+Al) nitrates – citric acid (NC) system

The DTA/TG curves of this system are shown in Fig. 10. One can conclude from the infrared measurements (Fig. 11) that absorption bands caused by the stretching vibrations in (OH) groups exist in the material calcined up to 580°C. Undoubtedly, these groups belong to citric acid. At somewhat higher temperatures these absorption bands disappear because of the citric acid decomposition. The TG curve (Fig. 10) confirms this process. Absorption bands 1500–1420 cm^{-1} due to the C-O vibrations also disappear at 580°C. Their intensity decreases with temperature.
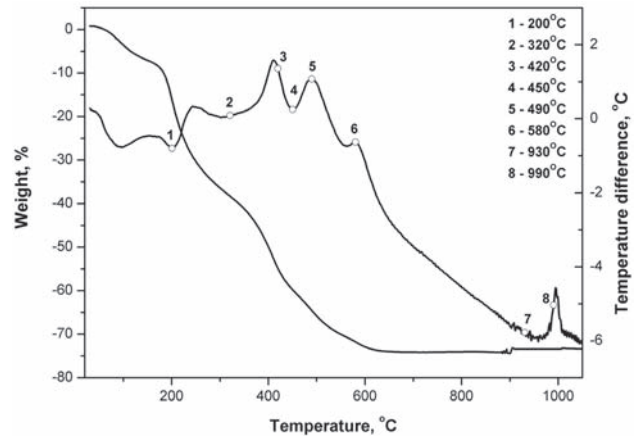

Figure 10. DTA/TG curves of the NC system. Calcination temperatures of the samples for further characteristics are indicated
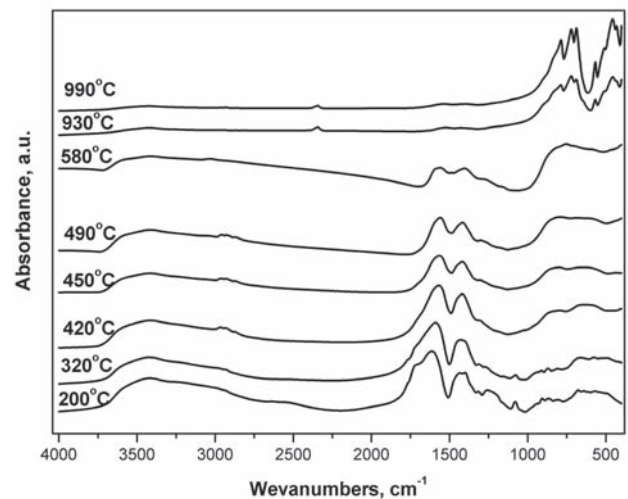

Figure 11. Transmission IR spectra of the NC material calcined at indicated temperatures
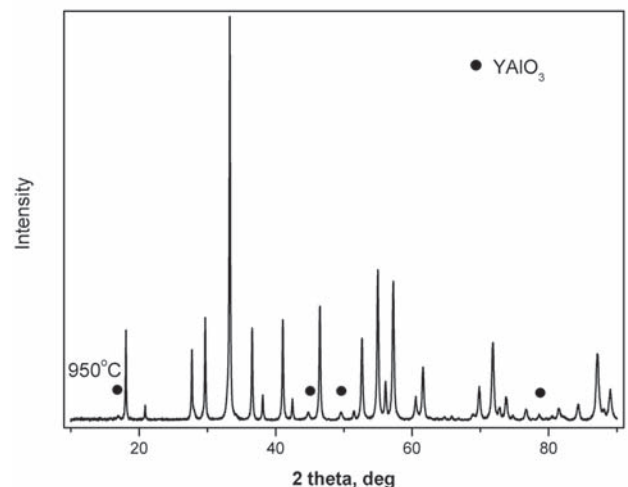

Figure 12. X-ray diffraction patterns of the material heated up in the DTA apparatus to the preselected temperature. 10°C/min rate of temperature increase was applied. NC system

These facts also confirm decomposition of citric acid. At somewhat higher temperatures absorption spectra reveal bands in the range 780–430 cm^{-1}. As it was found previously they are due to the Y-O and Al-O bonds. X-ray diffraction at 950°C (Fig. 12) for 1 h resulted in bi-phasic material composed of YAG as the major phase and YAP (h-YAlO$_3$).

IV. Conclusions

Table 1 summarises our results. The data clearly indicate the influence of the kind of estrification factor. 2-propanol promotes crystallization of pure YAG. Worse results were observed in case of ethylene glycol and citric acid as the only additive. These conclusions confirm our previous investigation [27] and indicate that ethylene glycol, contrary to the literature statements [20–26], homogenises the YAG system to the lesser extent than 2-propanol. That is why in case of 2-propanol as an estrification factor, reaction becomes completed at temperature as low as 950°C.

Table 1. Composition of prepared samples

Sample	Temperature [°C]	Time [h]	Phase
NPC	950	1	YAG
NEC	950	1	Y$_2$O$_3$, YAG
NC	950	1	YAP, YAG

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