

Synthesis of YAP phase by a polymeric method and phase progression mechanisms

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Abstract The phase formation kinetics of YAP (YAlO_3) synthesized through the polymeric precursor method was investigated by thermal analysis, X-ray diffraction and FT-IR spectroscopy. We demonstrated that the YAP synthesis is highly dependent on the heat and mass transport during all stages of the synthesis route. In the first stages, during the preparation of amorphous precursor, “hot spots” need to be suppressed to avoid the occurrence of chemical inhomogeneities. Very high heating rates combined with small amorphous particles are advantageous in the last stage during the formation of crystalline phase. We were able to synthesize nanosized particles of YAP single phase at temperatures around 1100 °C for future preparation of phosphors or ceramics for optics.

Keywords Chemical synthesis · YAlO_3 · YAP · Nanopowder · Polymeric precursor method

Introduction

YAlO_3 (YAP) is a very attractive material to be used for example as host laser [1], phosphors [2], scintillation and

thermoluminescent material [3, 4]. It is formed in the Al_2O_3 - Y_2O_3 system that presents three stable crystalline phases: the own YAP, with an orthorhombic perovskite structure, a cubic garnet structure with the Al-rich composition $\text{Y}_3\text{Al}_5\text{O}_{12}$ (YAG) and a monoclinic compound presenting the $\text{Y}_4\text{Al}_2\text{O}_9$ (YAM) Y-richer composition [5]. In addition, a metastable hexagonal phase can be formed during the synthesis of YAG and YAP by soft chemistry routes [6]. This hexagonal phase presents the same stoichiometry of YAP, i.e. YAlO_3 , and it is labeled YAH.

YAP exhibits a high melting point, 1917 °C, and its synthesis by conventional solid state reaction requires high temperatures, around 1800 °C, as reported by Medraj et al. [5], thus soft chemistry processes have been preferred [7–11]. These methods are advantageous because they involve better chemical homogeneity, smaller particles sizes, and low synthesis temperatures, reducing the cost production. On the other hand, kinetics of these processes are complex and generally the details of the chemical reactions involved are not well known.

The YAP synthesis has been reported by several authors using different soft chemistry routes. For example, Lo and Tseng [7] have synthesized YAP from sol–gel method with 1500 °C thermal annealing, concluding that the initial formation of YAM and YAG makes the YAP phase synthesis complex. Tanner et al. [8] reported the YAP preparation at 1200 °C by a derived sol–gel method; they claimed that accurate amounts of reactants were essential to get pure YAP phase at this rather low temperature. Mathur et al. [9] reported a complex method for the synthesis of YAP at 1000 °C that requires a preliminary synthesis of a heterometallic alkoxide of Y and Al. They claimed that the synthesis of this expensive intermediate precursor was required to ensure the 1:1 ratio of Y to Al. Harada et al. prepared the pure YAP phase using a less

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expensive polymeric precursor method with annealing at 1150 °C [10] and 1100 °C [11]. They used citric acid and ethylene glycol with the metal precursors aluminum isopropoxide and yttrium acetate [10] or aluminum nitrate and yttrium nitrate [11] to prepare the starting resin; its drying at about 300 °C produced a black solid mass. After crushing the solid mass to fine powder, they obtained the YAP phase by fast heating directly at high temperatures, 1150 °C [10] and 1100 °C [11]. Heating such organic-rich powder under air is always associated with an intense combustion reaction, highly exothermic, making thus difficult to determine the actual synthesis temperature.

Thus, several points concerning the synthesis of YAP nanopowder for the preparation of phosphors or ceramics by wet chemical routes are still challenging especially for some points still unclear: (1) how to preserve the correct stoichiometry at the molecular level during all the process even when using simple methods; (2) why is the reason for intermediate phases to appear and how to avoid it, (3) how to optimize the synthesis temperature and avoid “hot spots” problems. In this context, the aim of this work was to study in details the phase formation during the synthesis of fine YAP powders using the polymeric precursor method. Thermal analyses, X-ray diffraction (XRD), Fourier transform infra red spectroscopy (FT-IR), and scanning electron microscopy (SEM) have been used.

Experimental

YAlO₃ fine powders were produced by a modified polymeric precursor method. Yttrium nitrate (Y(NO₃)₃ · 6H₂O, 99.9%, Strem Chemicals) and aluminum nitrate (Al(NO₃)₃ · 9H₂O, ≥98.5%, Riedel-de Haen) were used as metal precursors. Because these nitrates are highly hygroscopic, special care was taken during their weighting in a dry glove box to ensure the correct stoichiometry. Yttrium and aluminum nitrates in 1:1 molar ratio were dissolved into deionized water at 80 °C followed by the addition of citric acid (99%, Sigma-Aldrich) with the metal (Y, Al) to citric acid molar ratio set at 1:3. After complete dissolution of these starting compounds, D-Sorbitol (98%, Sigma-Aldrich) was added to promote the polyesterification reactions between Y and Al citrates. The molar ratio of citric acid to sorbitol was 3:2. A clear solution was obtained after few minutes at pH = 1.6 and an overnight heating at the same temperature of 80 °C leads to a homogeneous viscous resin, with slight yellow coloration; this solution was stable during several months. All the process was assisted by a vigorous magnetic stirring. Figure 1 shows the different stages of the synthesis process.

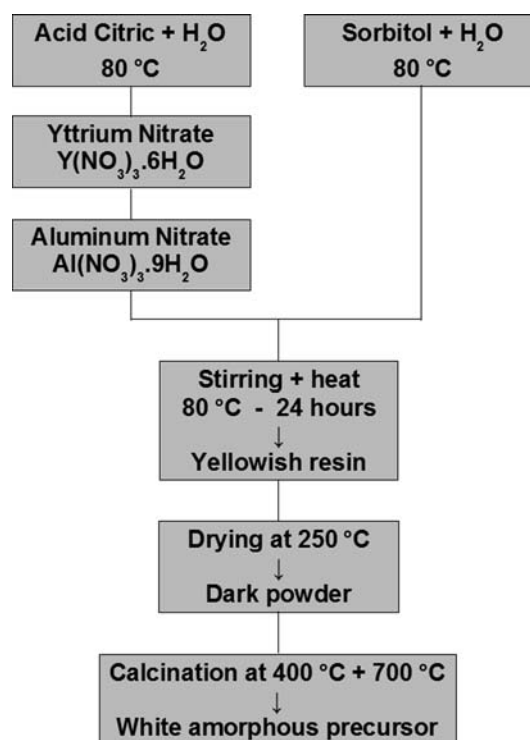


Fig. 1 Fluxogram of the synthesis of the amorphous precursor of YAP

Drying the resin was a critical step to preserve the chemical homogeneity of the samples. Indeed, the fast heating of the resin to temperatures around 300 °C under air atmosphere led to the formation of hot spots, i.e., localized combustion associated to non-uniform solvent evaporation, producing chemically inhomogeneous powder. This is in agreement with the report of G. Xia et al. [12] according to which the heating of a gel of citric acid and metal nitrates at temperatures of about 200–280 °C induce the reaction and ignition of the components producing a self-sustaining combustion process. In present work, to avoid this uncontrolled combustion, the resin was slowly dried using a heating rate of 0.5 °C/min until 250 °C under N₂ flux during 30 min. This procedure resulted in a soft dark brown solid that was easily crushed in agate mortar to produce a fine and homogeneous amorphous powder, here named as *dark powder*.

The phase formation was investigated using a coupled differential thermal and thermogravimetry analyses (DTA-TG) carried out in a Setaram (TAG 1600) equipment using alumina crucibles and air synthetic flux. The XRD powder patterns were measured by a Siemens D5000 diffractometer with CoK_α radiation while FT-IR spectra were recorded using a Bio-Rad FTS-60A spectrophotometer. SEM micrographs for grain size and morphology evaluation were obtained with a Jeol 940A electron microscope.

Results and discussion

DTA-TG data are shown in Fig. 2, they were obtained from the dark powder previously heated at 400 °C during 24 h to remove the main part of the organic compounds. The broad exothermic band (DTA) observed between 100 °C and about 850 °C corresponds to the burning of organic residues previously in excess followed by the formation of a carbonate - metal ions amorphous network (see IR results below). This process is accompanied by a mass loss of about 13%. Four well defined exothermic peaks appearing at 875, 920, 1000 and 1080 °C were attributed to YAM, YAH, YAG and YAP phases, respectively, as verified by XRD (see Fig. 5 below). This is accompanied by a weak mass loss, observed by TG in Fig. 2, which is due to the decomposition of carbonates during the transition from amorphous to crystalline phases.

The FT-IR spectra recorded at different stages of the YAP synthesis are shown in Fig. 3. The curve in Fig. 3a was measured for the amorphous *dark powder* dried at 250 °C, it is characterized by a very broad band from 2000 to 3700 cm^{-1} related to organics and water, and two other bands, not well defined, around 1700 and 1300 cm^{-1} . These bands become well defined and centered at 1540 and 1410 cm^{-1} after calcinations at 400 °C, Fig. 3b, and 700 °C, Fig. 3c, and they are due to COO^- antisymmetric and symmetric stretching modes, respectively [8]. They are associated to the amorphous network and disappear after the crystallization of YAP, Fig. 3d. The bands in the region below 1000 cm^{-1} are due to metal-oxygen vibrations [9].

Based on DTA and FT-IR results, we investigated a new route for the calcination of the amorphous *dark powder* consisting of two steps: a first annealing step at 400 °C during 24 h to remove the major fractions of organics and

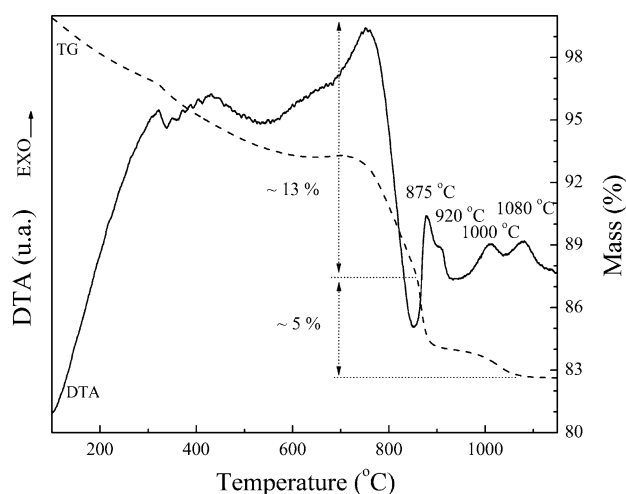


Fig. 2 DTA-TG obtained at a heating rate of 5 °C/min for the dark powder previously annealed at 400 °C during 24 h in O_2 flux

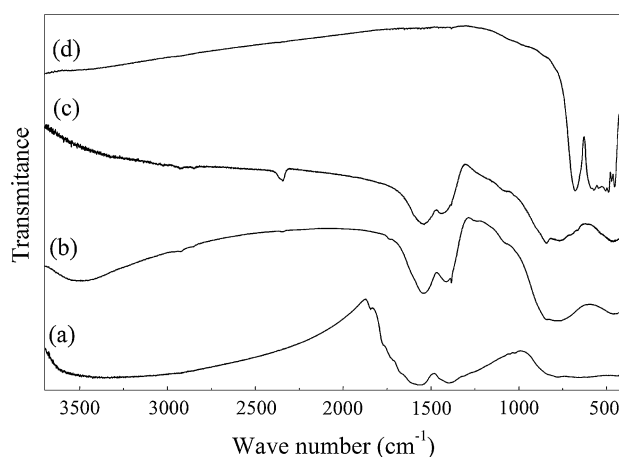


Fig. 3 FT-IR of powders obtained at different stages of the synthesis of YAP. (a) Dark amorphous powder dried at 250 °C, (b) dark amorphous powder calcinated at 400 °C during 24 h, (c) calcinated amorphous powder after an additional calcination at 700 °C during 24 h, (d) crystallized YAP obtained at 1300 °C

to avoid their entrapment as pyrolytic carbon in the final crystallized product, a second step at 700 °C during 24 h to complete the total removal of organics and consolidate the amorphous network of metal ions with oxygen. In both cases heating rates of 5 °C/min were used. At the end of this last stage, a completely white amorphous powder was obtained and labeled here as the *calcinated amorphous precursor*, which was used as the precursor in the following YAP syntheses.

In a first approach, the crystallization of YAP was done starting from the *calcinated amorphous precursor* and using low or moderate heating rates (1 °C/min to 20 °C/min). The precursors crystallized above 800 °C and resulted in a multi-phase powder containing YAM, YAH, YAG and YAP phases whose relative fractions depended on the temperature of the final annealing. Figure 4a shows the DTA curve of the *calcinated amorphous precursor* recorded by using a heating rate of 5 °C/min where four consecutive exothermic peaks between about 850 and 1100 °C correspond to the crystallization of YAM, YAH, YAG and YAP phases, respectively measured at 885, 909, 1010 and 1075 °C. The crystallization of these phases is associated with a mass loss of about 5% (TG curve Fig. 4a). The formation of these consecutive four phases was verified by XRD measurements shown in Fig. 5. At 700 °C during 24 h the powder was completely amorphous, Fig. 5a; it was then transformed to a mixture of YAM and YAH after heating at 850 °C during 3 h, Fig. 5b. At 950 °C the same two phases appear, but YAH became the major one while traces of YAG can also be observed, Fig. 5c. Between 1050 and 1100 °C, YAH metastable phase was completely transformed in YAP, which is thus the main phase while the weak fractions of YAM and YAG

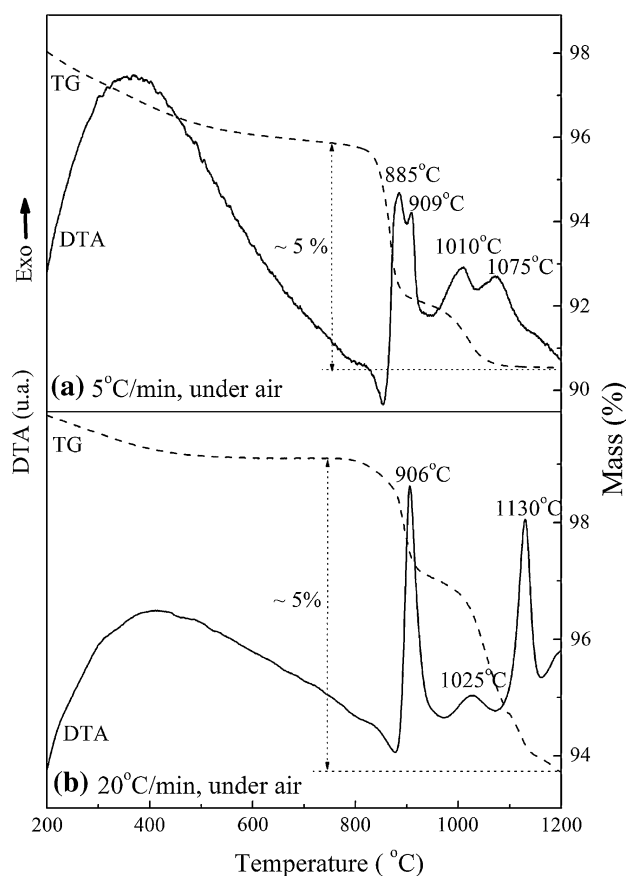


Fig. 4 DTA and TG curves of calcinated amorphous precursor powder under air at heating rates of (a) 5 °C/min and (b) 20 °C/min

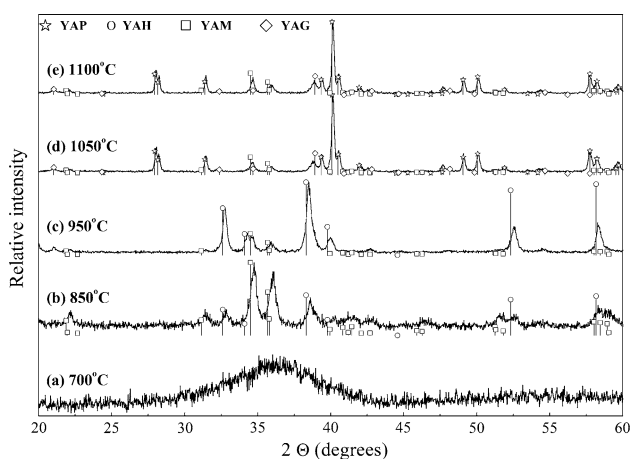
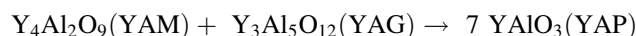


Fig. 5 X-ray diffraction showing the sequence of phase formation for different temperatures

remain almost unchanged, Fig. 5d, e. So, the crystallization and structural transitions end at about 1100 °C. As YAH is metastable it is easily converted to YAP, however this is not so easy for YAM and YAG because at the end of the process a mixture of YAP and weak amounts of YAM and

YAG is observed. Single phase YAP powder can be obtained from these mixtures by the transformation of YAM and YAG according to the following reaction:



However, this reaction requires high energy to overcome diffusional and energetic barriers, like in the conventional solid state reaction synthesis, and so, high temperature values are necessary to complete the formation of pure YAP powder, over to 1500 °C [5].

MacKenzie and Kemmitt [13] studying the formation of crystalline aluminates from gel-derived precursors noted that Al has a mobility significantly higher than that of Y due to a smaller ionic radius. In addition, Al ions can occupy three different sites (tetrahedral, octahedral and penta-coordinated sites), which exhibit gradual changes in the amorphous network during annealing. These significant differences in chemical bonding and mobilities of Al and Y ions favor the initial formation of YAM and YAG resulting in inhomogeneities at the molecular level issued from low heating rates. Figure 4(b) shows the DTA of the same *calcinated amorphous precursor* but measured at a higher heating rate of 20 °C/min. This higher rate reduced drastically the formation of the undesired intermediate stable phases YAM and YAG. Indeed, the DTA curve shows two intense peaks centered at 906 and 1130 °C related to the formation of YAH and YAP, respectively, while the intermediate residual peak at 1020–1050 °C is related to the formation of a weak amount of YAG. Like in the previous process, Fig. 4a, the mass loss during these crystallizations was around 5% due to the carbonates decomposition (Fig. 3).

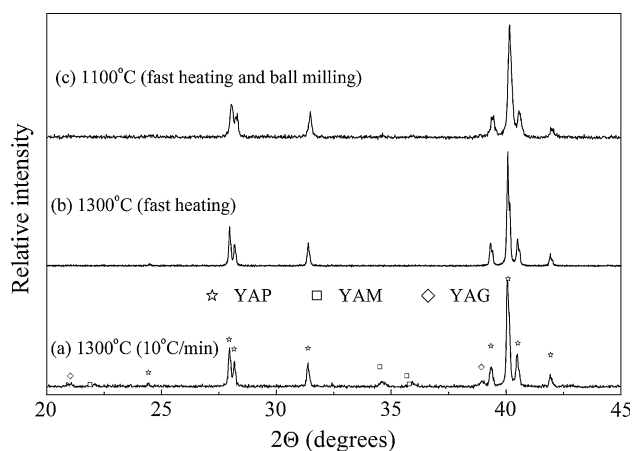
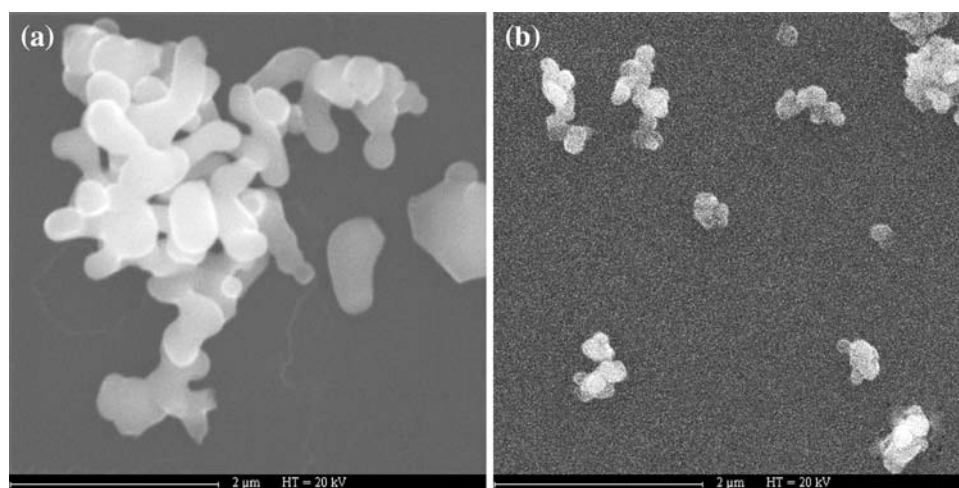


Fig. 6 X-ray diffraction of synthesized powder starting from the *calcinated amorphous powder*. (a) synthesized at 1300 °C during 3 h, using a heating rate of 10 °C/min, (b) synthesized at 1300 °C during 3 h, using fast heating, (c) synthesized at 1100 °C during 3 h, using fast heating after ball milling

Fig. 7 Scanning electron microscopy images of YAP particles synthesized at (a) 1300 °C and (b) 1100 °C



Due to this promising result, we adopted a new heating procedure to synthesize the YAP powder: we used the so-called *fast heating* that consists in introducing the samples into the furnace previously heated at the final synthesis temperature. The improvement of this new treatment is illustrated on Fig. 6 where XRD of *calcinated amorphous precursor* treated with various heating rates but with the same 3 h soaking time are shown. Curve (a) and (b) compares the effect of increasing the heating rate at 1300 °C. It is obvious that the pure YAP phase was obtained by fast heating at 1300 °C while YAM and YAG remain after the heating at a rate of 10 °C/min. The temperature of 1300 °C can be significantly lowered by decreasing the grain size (to 100–300 nm) of the *calcinated amorphous powders* through a ball milling and decantation procedure. Ball milling was accomplished using yttria-stabilized zirconia spheres (5 mm diameter) in a plastic bottle. The ball milled powder was ultrasonically processed using acetone as liquid medium and the deflocculated suspension was left in rest during 5 minutes for decantation of the larger particles at the beaker bottom. The remaining suspension was then separated and dried at 80 °C. The ball milling effect is well shown on curve c) of Fig. 6 where fast heating on ball milled particles lowers the synthesis temperature to 1100 °C.

These important changes in the synthesis behaviors confirm the hypothesis that the time dependent diffusional processes are dominant in the onset of molecular level inhomogeneities when low heating rates are used. Moreover, the temperature reduction of pure YAP synthesis with decreasing particle size is also in agreement with a lowering of the mass diffusion lengths. In all cases, it is crucial to start with a homogeneous resin because any chemical inhomogeneities caused by hot spots or diffusional differences between Al and Y induces the intermediate formation of YAM and YAG compounds.

The morphologies of grains synthesized at 1300 °C and at 1100 °C are revealed by SEM images shown in Fig. 7. The bigger grains evidencing significant grain growth and coalescence were obtained at 1300 °C, Fig. 7(a), while smallest grains were obtained for particles synthesized at 1100 °C (100–250 nm, Fig. 7b). These results are promising for the preparation of YAP ceramics that is under development.

Conclusion

The formation of single YAP phase at low temperature requires an homogeneous distribution of Y and Al cations at the molecular level in the amorphous precursor. We demonstrate that this can be achieved by a simple polymeric precursor method if the formation of “hot spots” during the preparation of amorphous precursor is avoided. On the other hand, the differences in Y- and Al-mobilities inside the amorphous network make the final stage of crystalline phase formation highly dependent on both heat and mass transport. Improvement in the heat and mass transport efficiency is crucial to avoid the formation of intermediate stable phases. The best route involves fast heating that favours the formation of YAP through the metastable YAH phase. Indeed, when intermediate stable phases are formed the end of the YAP synthesis process is dominated by the conventional solid state reaction synthesis that requires temperatures higher than 1500 °C to be completed. The combination of small particles of the amorphous precursor with high heating rates can improve the synthesis process making possible to obtain YAP single phase at temperatures around 1100 °C.

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