

Microwave assisted synthesis of nanocrystalline YAG

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Received: 9 March 2005 / Accepted: 19 October 2005 / Published online: 8 July 2006
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Abstract Using nitrate precursors, a novel microwave assisted citrate gel process for the preparation of nanocrystalline yttrium aluminium garnet (YAG) phase has been developed. Synthesis of single phase polycrystalline YAG was achieved at temperatures as low as 600 °C using the microwave methodology whilst conventional approaches currently available require ≥ 1000 °C. The microwave prepared YAG powder was characterised using X-ray diffraction, FTIR spectroscopy, TEM and EDAX. The microwave method was found to yield YAG particles of ~ 40 nm diameter, whilst the conventional route yielded 150 nm particles. Also substantial morphological differences were observed between the YAG particles and their agglomerates produced by the different processing methods.

Introduction

Yttrium aluminium garnet (YAG) with the chemical composition $Y_3Al_5O_{12}$ is an important advanced optical material [1]. Owing to the relatively stable lattice structure and large thermal conductivity, it is used as a host for lasers and as a coating on electronic devices. It is also a promising high temperature engineering material for insulating or refractory coatings because of its low creep rate, high oxidation resistance and low electrical conductivity. YAG

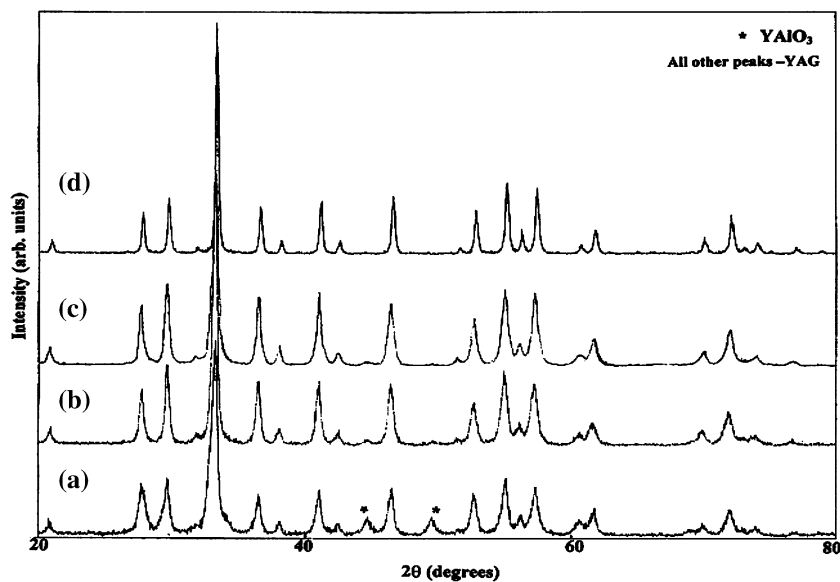
doped with Eu or Tb are useful phosphors to prepare high resolution display devices, which require thin fluorescent screens with fine grain phosphors. To achieve the desired phase purity and particle size, the process of conventional solid state reaction usually needs lengthy high temperature treatment (>1600 °C) and extensive ball milling, which generally introduces additional impurities and defects. Therefore wet chemical processes such as hydroxide coprecipitation, alkoxide- and glycothermal based routes, as well as combustion synthesis, have been used [2, 3] for producing YAG as a fine powder. All these processes require a relatively long duration calcination step involving temperatures in excess of 900 °C. The alkoxide approach is restricted due to the rather difficult synthesis and the limited commercial availability of various metal alkoxides. Due to the explosive character of the combustion process, the particle size cannot be controlled easily. Control over phase-pure YAG is not always achieved because the yttria-alumina system exhibits several other phases, including Al_2O_3 , Y_2O_3 , monoclinic $Y_4Al_2O_9$ (YAM), metastable hexagonal $YAlO_3$ and orthorhombic $YAlO_3$ [4]. In the present work, a novel microwave assisted approach to the synthesis of single phase YAG using a citrate gel process involving nitrates of Al and Y is described.

Experimental

Stoichiometric mixtures of nitrates of aluminium ($Al(NO_3)_3 \cdot 9H_2O$) and yttrium ($Y(NO_3)_3 \cdot 6H_2O$) were dissolved in an aqueous solution of citric acid (99.9% purity, Aldrich Chemicals Ltd., UK). The prepared solution was 2 M in citric acid, 0.2 molar in aluminium nitrate and 0.12 molar in yttrium nitrate. This solution was heated at 80 °C under continuous stirring to obtain a gel. The latter

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Fig. 1 XRD patterns of the microwave prepared YAG samples. (a) 600 °C, (b) 700 °C, (c) 800 °C and (d) 900 °C with a soaking time of 30 min



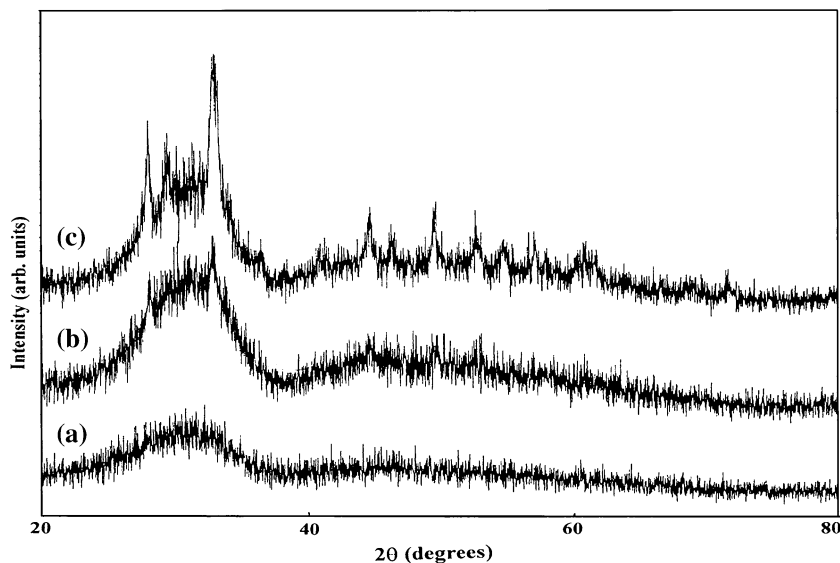
was dried at 110 °C for 24 h and the resultant powder was microwave heated between 500–1000 °C in a silica crucible using a 2.45 GHz multimode microwave cavity. A maximum of 1 kW output power was used and the sample temperature was measured using a shielded, Pt sheathed R type thermocouple and an infrared pyrometer (LAND Instruments, UK) as described elsewhere [5–7]. Fiberfrax insulation was used for heat containment and cooling was achieved by switching off the magnetron. Comparative conventional heating experiments were carried out using an electric furnace. The microwave and conventionally prepared powders were characterised using XRD and EDAX for phase-composition analysis. Mean crystallite size was calculated using X-ray peak broadening and the Scherrer equation. The particle size and morphology were

investigated using STEM coupled with selected area diffraction measurements. IR spectroscopic measurements were performed using the KBr pellet method [7].

Results and discussion

Figure 1 provides the XRD patterns of the microwave prepared YAG samples as a function of processing temperature. It may be observed that even at 600 °C YAG was found to be the major phase and only a very small amount of $YAlO_3$ phase was present. This completely disappeared via transformation to YAG [8] at ≥ 700 °C. It is also interesting to note that the soaking time at the processing temperatures was only 30 min during the microwave

Fig. 2 X-ray diffractograms of the conventionally heated samples at (a) 700 °C, (b) 800 °C and (c) 900 °C for 60 min



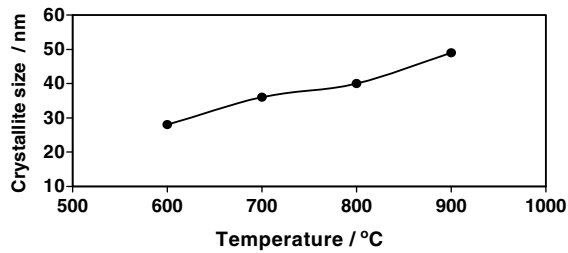
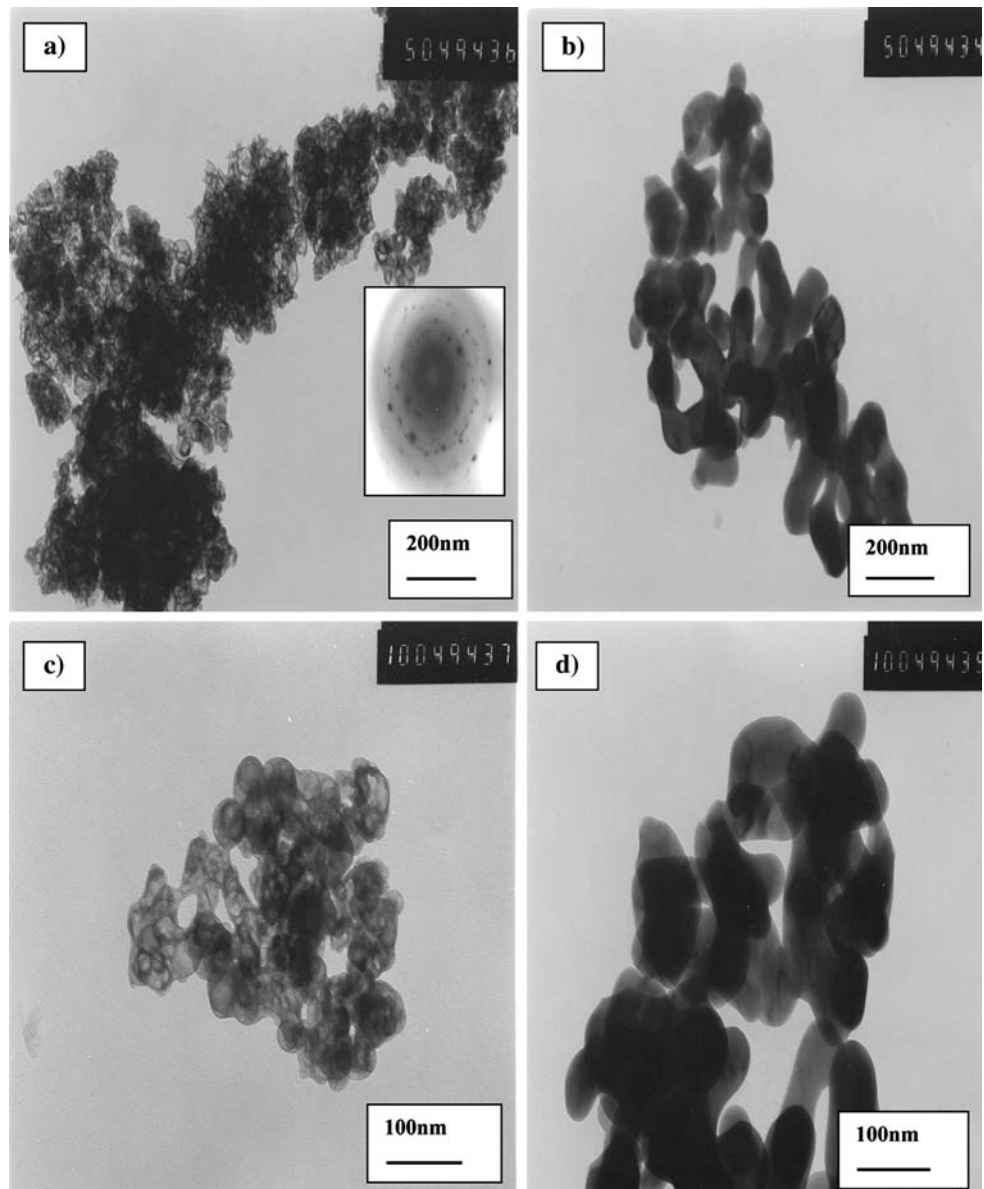


Fig. 3 XRD mean crystallite size of the microwave prepared YAG as a function of processing temperature

experiments. Indeed at 800 °C even a 5 min soak time resulted in the formation of single phase YAG. The rapidity of YAG formation is indicative of bulk nucleation occurring and the homogeneous availability of the cations at the

stoichiometric ratio in the precursor. The lattice parameter of the microwave prepared cubic YAG was found to be $a = 12.001 \text{ \AA}$, matching very well with the literature reports ($a = 12.008 \text{ \AA}$; JCPDS card no: 33–40). Compositional analysis performed on the samples indicated a cation ratio of Al:Y of 1.659, which matches well with the expected value of 1.66 for the stoichiometric composition of $\text{Y}_3\text{Al}_5\text{O}_{12}$ [9]. Spot elemental analysis performed at different regions of the sample provided similar results indicating the chemical homogeneity of the product. Figure 2 provides the X-ray diffractograms of the conventionally processed samples. It is clear that the sample remained amorphous up to 800 °C for the soaking time of 60 min. At 900 °C/60 min evidence of YAlO_3 formation may be observed. It took 120 min soaking at 1000 °C to

Fig. 4 TEM images of microwave (left-900 °C/30 min) and conventionally (right-1000 °C/120 min) prepared YAG samples at different magnifications indicating the nanocrystalline nature of the sample and the different levels of agglomeration. The inset in 4(a) shows the selected area diffraction pattern indicating the well crystallized nature of the YAG particles



obtain a well crystallised phase pure YAG, which is at least 300 °C higher and 10 times as long as that required by the microwave process.

The mean crystallite size of the microwave prepared YAG particles, estimated from the X-ray line broadening of the (420) peak, is depicted in Fig. 3, the values increasing from 25–50 nm over the temperature range investigated. Figure 4 provides low and high magnification TEM images of the microwave and conventionally prepared YAG. Whilst the primary particle size of the microwave synthesised YAG was ~40 nm and the particles were approximately spherical, the conventionally prepared sample resulted in irregular elongated shapes approximately 150 nm long. Both powders were heavily agglomerated. Selected area diffraction patterns obtained on the microwave prepared YAG particle, see inset in Fig. 4a, clearly indicate the well crystallised nature of the particles and the TEM primary particle size of 40 nm matches well with the XRD crystallite size, indicating that each particle is a single YAG crystal. The FTIR spectrum of the microwave prepared YAG sample exhibited well defined peaks at 790, 725 and 693 cm^{-1} due to stretching vibrations of the AlO_4 tetrahedra and absorption peaks at 570, 513, 470 and 430 cm^{-1} associated with the stretching of AlO_6 octahedra, all of which matched with reported data for a well crystallised YAG [10]. The rapidity of the microwave-assisted YAG formation suggested enhanced reaction kinetics, uniform and bulk nucleation. This could be due to the better microwave absorption characteristics of the precursors and the effective utilisation of the reaction enthalpy to increase the reaction rate. It is also found that the product was a good microwave absorber, thus helping to sustain the heating process.

Conclusions

Single phase, nanocrystalline YAG powder of ~40 nm particle size has been synthesised using a microwave-assisted citrate gel process at temperatures as low as 600 °C. The rapidity of the microwave technique, the lower processing temperatures employed and the fine grained nature of the product obtained makes this an attractive alternative procedure compared to conventional YAG preparation methods.

Acknowledgements The authors thank the EPSRC in the UK for financial support.

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