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SHORT COMMUNICATION

Sol-gel Synthesis and Characterisation of Nanocrystalline Yttrium Aluminum Garnet Nanopowder

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ABSTRACT

The synthesis of yttrium aluminum garnet (YAG) ($Y_3Al_5O_{12}$) nanopowder was carried out by sol-gel method. $Y(NO_3)_3.6H_2O$, $Al(NO_3)_3.9H_2O$ in the presence of citric acid as complexing agent were used as starting materials. YAG nanopowder was characterised by FTIR, TGA, and XRD. To get phase-pure nanocrystalline YAG powder at relatively lower temperature, calcination at various temperatures was studied and calcination temperature was optimised. Particle size, estimated by XRD using Scherrer's equation, was found to be 28–35 nm which was further confirmed by transmission electron microscopy. The particle morphology was studied by SEM.

Keywords: Yttrium aluminum garnet, sol-gel synthesis, YAG nanopowder, synthesis, crystal characterisation

1. INTRODUCTION

Yttrium aluminum garnet (YAG, $Y_3Al_5O_{12}$) has excellent optical and mechanical properties. Single crystal YAG has been extensively used in solid-state lasers; however, transparent polycrystalline YAG is fast emerging as an alternative to single crystal YAG, and glass-based laser host materials[1-3]. The preparation of transparent polycrystalline YAG involves compaction and sintering of nanocrystalline YAG powder to near-theoretical density. Synthesis of nanocrystalline YAG by conventional, solid-state reaction[4] requires prolonged heating at high temperatures (~1600 °C) followed by intensive grinding. In this process, it is difficult to control the homogeneity and purity of YAG powders. Thus, preparation of YAG was undertaken by a wet chemical method namely sol-gel process, to synthesise a high purity material at lower temperature. Sol-gel process has gained the attention[1,2,5] due to lower synthesis temperatures and the finer and more homogeneous particles produced. In this process, gelation is obtained from a solution of inorganic metal salts and a complexing agent.

To achieve the compositional homogeneity of the final oxide powder, the preparation of a homogeneous gel wrt the distribution of cations is very important. The citrate-gel method has advantage of better control over the stoichiometry, as the complexing agent (citric acid) complexes well with all the metal ions in the solution. In this method, a citrate solution containing the metal ions is converted into a gel, which is dried and subsequently calcined to form the oxide powder (YAG). A uniform distribution of metal ions in the precursor can be maintained throughout the process. In the present study, synthesis of YAG by citrate-gel method using nitrates of the metals and citric acid has been carried out. Nanocrystalline YAG has been synthesised achieving YAG formation at 800 °C.

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2. EXPERIMENTAL PROCEDURE

Yttrium nitrate hexahydrate (99.9 %, REO, Alfa Aesar), aluminum nitrate nonahydrate (99.9 %, Alfa Aesar) and citric acid (99.5 %, Alfa Aesar) were used as obtained. Water purified by Elix-10 (millipore) with resistivity > 10 MΩ.cm was used in the synthesis.

YAG formation was identified by FT-IR analysis of the powders. Thermogravimetric analysis (TA Instruments) of the precursor was conducted in air at a heating rate of 10 °C/min from room temperature to 1000 °C. The calcined powders were examined by x-ray diffraction (Philips X'pert XRD instrument) analysis using *CuKa* radiation. The microscopic examination of the powders was performed by TEM and morphology was observed by SEM.

Yttrium nitrate hexahydrate and aluminum nitrate nonahydrate were taken in the stoichiometric quantities and dissolved in an aqueous solution of citric acid to give a molar ratio of 3 : 5 : 16, respectively. The solution was ultrasonically stirred at 80 °C/7 h. The gelling was done at 80 °C for 15 h. This gel was aged and dried at 110 °C/60 h. This precursor or the dry gel obtained was ground and calcined at 800 °C for 16 h and at 1000 °C for 5 h.

3. RESULTS AND DISCUSSION

The weight losses observed in the TGA of the YAG precursor (dry gel) (Fig. 1) indicated dehydration, decomposition of the citrate, and decarbonisation

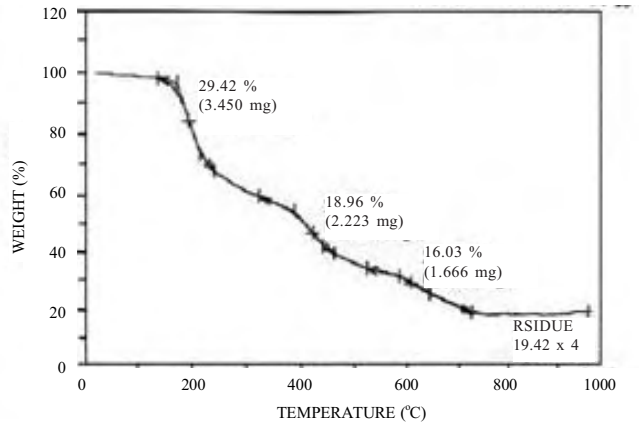

Figure 1. TGA of YAG precursor.

(oxidation) of the decomposition products, respectively. The weight loss ~ 150 °C can be attributed to dehydration. Citrates appear to decompose rapidly above 380 °C leading to weight losses at ~ 400 °C. Weight loss at ~600 °C is attributed to the decarbonisation of the decomposed products, a process which continues beyond 700 °C, though slowly. The weight loss was negligible after 720 °C. Thus, the TGA analysis concluded that the decomposition of the gel was nearly completed by 720 °C with a weight loss[6] of ~ 80 per cent.

The *Y-O* and *Al-O* bonds are known[5,7] to show characteristic peaks in the region 400–800 cm^{-1}. In the FTIR spectra of gels treated at 110 °C and 140 °C (Fig. 2), no peaks in this metal-oxide region were seen. The bands at ~1700 cm^{-1}, 1400 cm^{-1} and 1200 cm^{-1} were assigned to the carboxylic group's

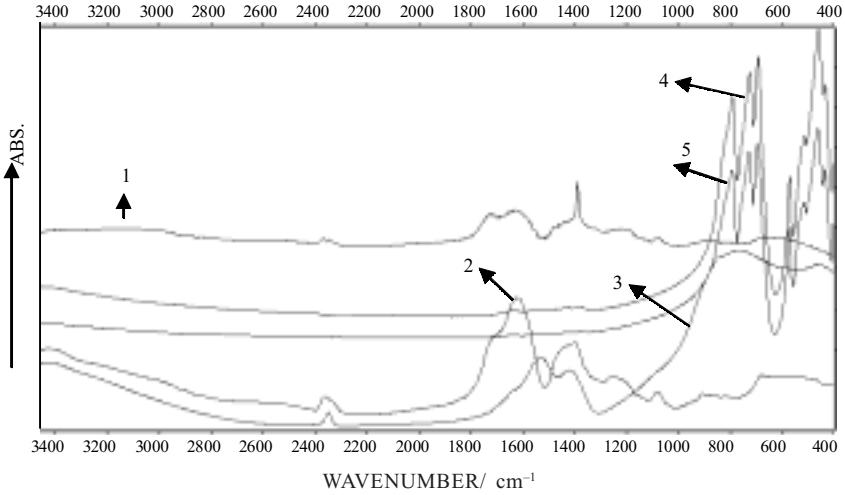

Figure 2. FT-IR of YAG precursor calcined at various temperatures 1--110 °C, 2--140 °C, 3--650 °C, 4--800 °C, 5--1000 °C.

vibration. However, when heated up to 650 °C, the bands at 1700 cm^{-1} and 1200 cm^{-1} disappeared and a new band at ~ 1500 cm^{-1} appeared. This new band, and the one at 1400 cm^{-1} were assigned to ionised carboxylates and carbonates resulting from the rupture of citrate molecules. A broad band in the metal-oxide region indicated the onset of the formation of metal-oxide bonds. The characteristic bands of YAG were observed for the samples calcined at 800 °C and 1000 °C. The FT-IR analysis concluded the citrate structure breakdown with some residual carbonates up to 700 °C. These results were consistent with that obtained by TGA[8].

The XRD was done to calculate particle size using Scherrer's equation[9], and to confirm the time and temperature of calcination for complete crystallisation of YAG.. The XRD of YAG calcined at 800 °C for 4 h (Fig. 3) showed the peaks as given in standard[7] JCPDS 33– 40 but the background intensity was very high indicating incomplete conversion to YAG. After 6 h of calcination this background absorption reduced, and the best result was obtained after a calcination period of 16 h. However, similar results could be achieved at 1000 °C in a much reduced time, i.e., 5 h (Fig. 3).

The primary particle size for powders calcined at 800 °C/16 h was found to be 25 nm. The particle size of the samples calcined at 1000 °C for 5 h and 8 h was found to be 28 nm and 35 nm, respectively. The particle size was also confirmed

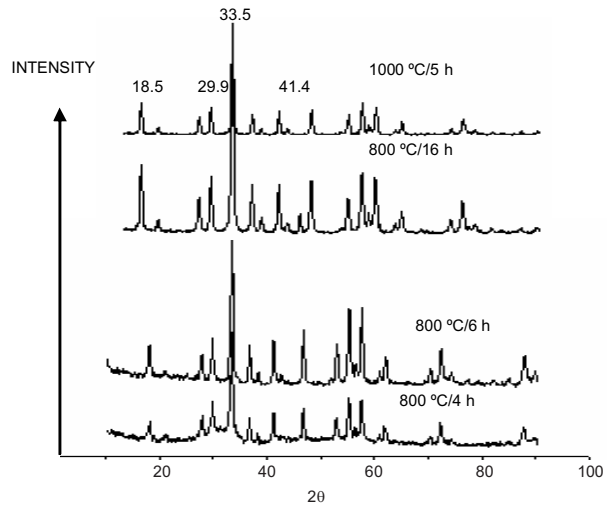

Figure 3. XRD of YAG precursor calcined at different temperatures.

by TEM (Fig. 4), which indicated the presence of particles ~ 20–50 nm.

Studies using SEM showed nearly spherical particles. Nanoparticles tend to agglomerate due to

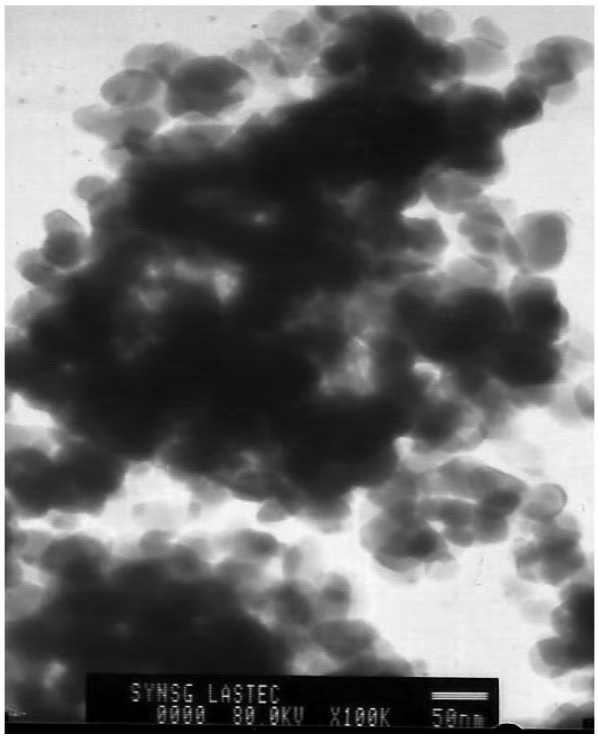

Figure 4. TEM of YAG.

high surface charges. In the present study, the primary particles appeared to form agglomerates ranging from sub-micron size to few microns. This problem of agglomeration of nanoparticles need to be investigated, as this aggregation of particles is detrimental in further processing of YAG nanopowder, *en route* making of transparent ceramics. Aggregation was observed with agglomerates ranging from sub-micron size to few microns (Fig. 5).

4. CONCLUSIONS

Citrate gel method was used to synthesise YAG nanopowder. The TGA showed maximum weight loss up to 700 °C with 80 per cent weight loss of the gel. The FTIR spectra of calcined precursor at various temperatures led to the conclusion that YAG formation was complete at 800 °C/16 h and 1000 °C/5 h. The XRD further supported the results. Primary particle size by XRD was 28–35 nm. TEM

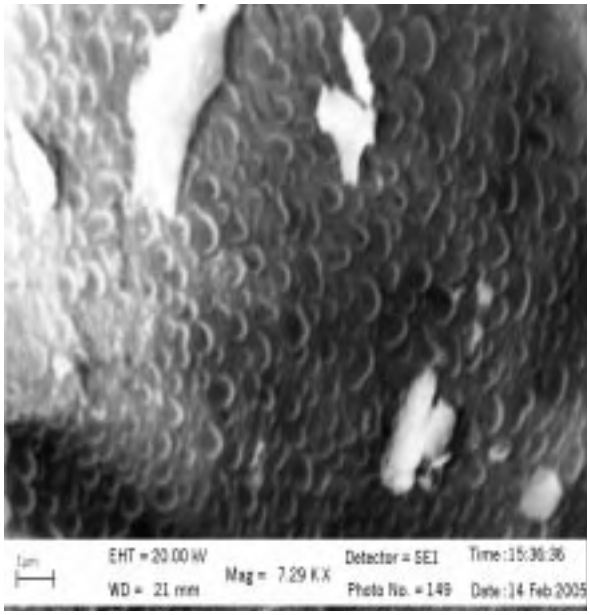

Figure 5. SEM of YAG nanopowder.

studies confirmed that the primary particle size was < 50 nm. Thus, the sol-gel method can be used for the synthesis of nanopowders of YAG at significantly lower temperatures with improved characteristics as compared to conventional solid-state synthesis.

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REFERENCES

1. Hreniak, D.; Strek, W. & Mazur, P. Preparation, spectroscopy and morphology of Nd:YAG nanostructures. *Materials Science*, 2002, **20**(2), 39-45.

2. Barnakov, Yu A.; Veal, I.; kabato, Z.; Zhu, G.; Bahoura, M. & Noginov, M.A. Simple route to Nd:YAg transparent ceramics. *In* Centre for Materials Research, Norfolk State University, 700 Park Avenue, Norfolk.

3. Lu, J.; Yagi, H.; Takaichi, K.; Uematsu, T.; Bisson, J.-F.; Feng,Y.; Shirakawa, A.; Ueda, K.-I.; Yanagitani, T. & Kaminskii, A.A. 110W ceramic Nd^{3+}:$Y_3Al_5O_{12}$ laser. *Applied Physics B,* 2004, **79**, 25-28.

4. Li, Xia.; Liu, Hong.; Wang, Jiang.; Zhang, Xudong & Cui, Hongmei. Preparation and properties of YAG nano-sized powder from different precipitating agents. *Optical Materials*, 2004, **25**, 407-12.

5. Boyer, Damien; Gnevieve, Bertrand-Chadeyron & Rachid, Mahiou. Structural and optical characterizations of YAG: Eu^{3+} elaborated by the sol-gel process. *Optical Materials*, 2004, **26**, 101-05.

6. Byung-Joo, Chung; Joon-Young, Park & Soo-Man, Sim. Synthesis of Yttium Aluminum Garnet by a citrate-gel method. *J. Ceramic Proc. Res.*, 2003, **4**(3), 145-50.

7. Wang, H.M.; Simmonds, M.C.; Huang, Y.Z. & Rodenburg, J.M. Synthesis of nanosized powders and thin films of *Yb*-doped YAG by sol-gel method. *Chemistry of Materials*, 2003, **15**, 3474-480.

8. Vaqueiro, P. & Lopez-Quintela, M.A. Influence of complexing agent & pH on Yttrium-irn Garnet synthesized by the sol-gel method. *Chemistry of Materials*, 1997, **9**, 2836-841.

9. Rodrigues-Rojas, R.A.; Rosa-Cruz, E. De La; Diaz-Torres, L.A.; Salas, P.; Melendrez, R.; Barboza-Flores, M.; Meneses-Nava, M.A. & Barbosa-Garcia, O. Preparation, photo- and thermo-luminescence characterization of Tb^{+3} and Ce^{3+} doped nanocrystalline $Y_3Al_5O_{12}$ exposed to UV-irradiation. *Optical Materials*, 2004 **25**, 285-93.

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