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Synthesis of polycrystalline yttrium iron garnet and yttrium aluminium garnet from organic precursors

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Polycrystalline $Y_3Fe_5O_{12}$ (YIG) and $Y_3Al_5O_{12}$ (YAG) garnets have been prepared by the organic solution technique using a novel organic precursor. The thermal decomposition of the precursor and subsequent formation of the garnet phases was studied by thermal analysis, X-ray diffraction and Fourier transform infra red spectroscopy (FTIR) including diffuse reflectance FTIR (DRIFT). The precursor of YIG decomposes to give the garnet phase as the main component at 800 °C. $YFeO_3$ and Fe_2O_3 are also present, and react to give YIG at higher temperatures. Single-phase YAG can be obtained from its precursor at 1100 °C. The reaction proceeds via a hexagonal $YAlO_3$ intermediate which is formed at 850 °C.

1. Introduction

Polycrystalline $Y_3Fe_5O_{12}$ and $Y_3Al_5O_{12}$ ceramics have been widely used in solid-state devices because of their respective magnetic and refractory properties. Yttrium iron garnet (YIG) is a ferrimagnetic material which is used as a filter in microwave circuitry and also as an electronic resonator [1]. Yttrium aluminium garnet (YAG) is a hard material which can be used as a refractory coating for electronic devices and as the host for a series of robust rare-earth-doped phosphors [2]. These two mixed metal oxide phases, which have a body centred cubic crystal structure, belong to the garnet series of ceramic compounds which have the same crystal structure as the mineral grossalurite, $Ca_3Al_2\ [SiO_4]_3$. They are prepared conventionally by the ceramic method of reacting the individual reactant metal oxides. This process involves extensive heat treatments at high temperatures and repeated mechanical mixing to achieve the desired phase purity. Stoichiometric mixtures of Y_2O_3 and Al_2O_3 react to give YAG after heating extensively at 1600 °C [3], whereas mixtures of Y_2O_3 and Fe_2O_3 react to give single-phase YIG when heated above 1200 °C [4].

Other techniques used to synthesize garnets range from chemical wet methods using nitrate precursors [5] to hydroxide coprecipitation [6, 7]. The rate of the reaction will be increased if the reactant cations are intimately mixed on the atomic scale and if an amorphous mixed metal oxide phase is retained until polycrystalline garnet is formed. The above chemical methods achieve an increase in reaction rate over the ceramic technique, leading to lower synthesis temperatures as the cations are intimately mixed although intermediate phases produced are not amorphous. YIG has been synthesized by the sol–gel method using an amorphous citrate gel [8] and also by the hydrolysis of metal alkoxides [9]. YAG has also been synthesized using the sol–gel process by polymerizing metal alkoxides and acetates [10]. In each case, an amorphous intermediate phase is produced which leads to homogeneous garnet formation at low temperatures, 800 °C for YIG and 810 °C for YAG.

This report describes the experimental work carried out in synthesizing both YIG and YAG by the organic solution technique, using a novel organometallic precursor. The thermal decomposition of the precursor was studied by FTIR and thermal analysis, and any crystalline phases formed during the course of the subsequent reaction were identified using X-ray powder diffraction (XRD).

2. Experimental procedure

The organometallic precursor used in this work consisted of a mixture of the metal nitrates dissolved in a polyester matrix of glycerol and malonic acid. Stoichiometric mixtures of $Y(NO_3)_3{\cdot}6H_2O$ and $Fe\ (NO_3)_3{\cdot}9H_2O$ were dissolved in glycerol to give a Y:Fe ratio of 3:5. The resultant solution was then reacted with malonic acid to give a metal malonate containing polyester resin. The organic solution produced can be diluted with methanol and be used to form thin films of YIG on alumina substrates.

The precursor of YAG was formed in a similar way by dissolving $Y(NO_3)_3{\cdot}6H_2O$ and $Al\ (NO_3)_3{\cdot}9H_2O$ in glycerol and reacting the solution formed with malonic acid to give a viscous yellow solution.

A Nicolet 5DXC FTIR spectrometer was used to record all IR spectra and the spectra of all solid samples were obtained by diffuse reflectance. Thermal analysis was carried out using a Stanton Redcroft TG770 thermal balance and a Stanton Redcroft DSC1500. A Philips X-ray diffractometer was used

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with a Co source for YIG samples and a Cu source for YAG samples.

3. Thermal decomposition of the GLMA precursor and formation of polycrystalline YIG

The thermal decomposition of the glycerol–malonic acid (GLMA) precursor of YIG was studied by FTIR in conjunction with thermal analysis. The thermogram of a sample which had previously been heated to 180 °C, in order to remove all excess glycerol, shows that the organic matrix has decomposed by 425 °C although the sample is not mass stable until 760 °C (Fig. 1a).

The FTIR spectra of the GLMA precursor of YIG (Fig. 2) show the changes in chemical environment of the sample as the temperature is increased. The spectra of the initial undiluted solution shows that a polyester has formed along with a metal carboxylate compound. This can be seen from the carbonyl stretching vibrational peak at 1735 cm^{-1} and the antisymmetrical carboxylate stretching vibration at 1645 cm^{-1}. As the temperature is increased, unreacted glycerol is evaporated off and the intensity of the carboxylate band relative to the polyester band increases, indicating further metal carboxylate formation. By 330 °C, most of the polyester has decomposed and the symmetrical stretching vibration of the carboxylate ligand at 1435 cm^{-1} is now visible. The intensity of both carboxylate vibrations has increased even further and there is still a conspicuous O–H stretching band, suggesting that the organic matrix contains basic metal malonate salts. The frequency of the antisymmetrical carboxylate peak has moved to a lower frequency, indicating a change in coordination from unidentate to bidentate [11].

By 400 °C, the carboxylate peaks have disappeared and have been replaced by carbonate bands. This can be seen in the spectrum of a sample heated to 600 °C (Fig. 2) which shows the out-of-plane bending peak at 845 cm^{-1} and a split antisymmetrical carbonate stretching band at 1530 and 1420 cm^{-1}. The splitting of this band indicates that the carbonate has C_{2V} symmetry and is acting as a bidentate ligand [12]. The large split in frequency of the band indicates bidentate complexation with C_{2V} symmetry and distinguishes it from a unidentate carbonate which would show only a small frequency difference between the two split peaks [11]. The spectrum of the 750 °C sample shows very weak carbonate vibrations. At 800 °C the carbonate and hydroxyl bands have disappeared and been replaced by metal–oxygen vibrations at 655, 605 and 566 cm^{-1} which are due to the lattice vibrational modes of the YIG unit cell [13]. Examination of the spectra obtained above this temperature show weak vibrations below 566 cm^{-1}, which are not due to YIG, that decrease in intensity at higher temperatures. Therefore the FTIR spectra indicate that YIG is formed at 800 °C as the main oxide phase.

Combining the information obtained from both these techniques, it can be assumed that the organic polyester matrix decomposes via a metal carboxylate mixture to a basic carbonate at 425 °C. As basic ferric carbonate decomposes by 400 °C [14] and a GLMA precursor of Fe_2O_3 was found to be mass stable before 400 °C (Fig. 1b), it is possible that Fe_2O_3 and the basic carbonate of yttrium (Y (OH) CO_3) exist after the decomposition of the organic matrix. With increasing

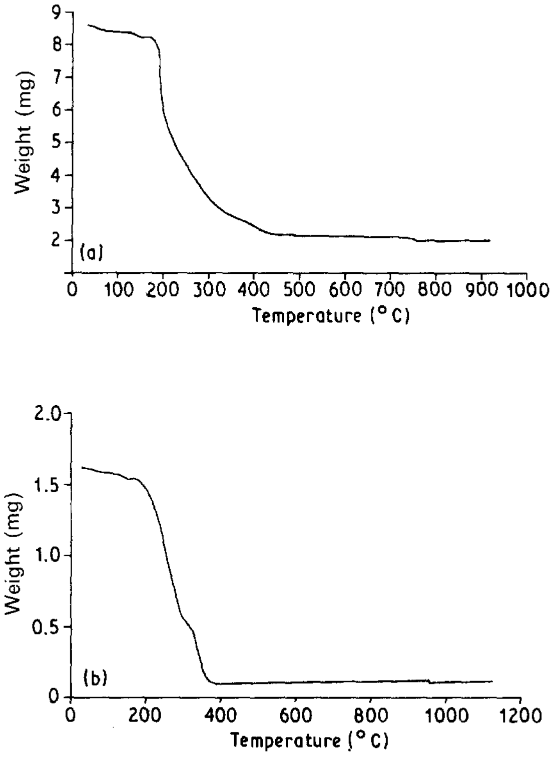

Figure 1(a) GLMA precursor of YIG, heating rate 20°C min^{-1}; (b) GLMA precursor of Fe_2O_3, heating rate 20°C min^{-1}.

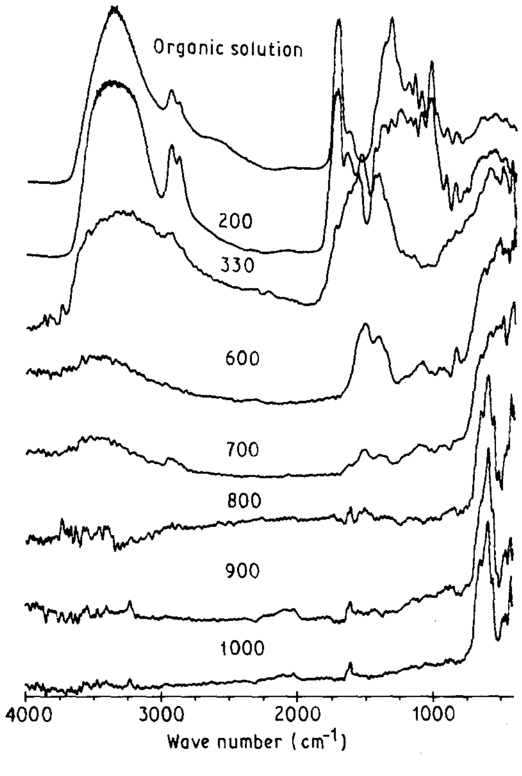

Figure 2 FTIR spectra of GLMA precursors of YIG heated to different temperatures.

temperature, the intensity of the hydroxyl and carbonate vibrations in the IR spectra decrease, indicating basic carbonate decomposition.

The loss of weight from 425 °C to 760 °C in the TG of YIG is very small (Fig. 1a) indicating that possibly only basic carbonate on the surface of Y_2O_3 is decomposing. This is very likely as diffuse reflectance tends to give information mainly about the surface of the particles interacting with the IR radiation beam [15] where the depth of penetration depends on the density of the material and also its particle size [16].

The DSC thermogram (Fig. 3) of a sample of the GLMA precursor of YIG, which had been heated to 450 °C in order to remove any organic material present, shows a single exotherm with an onset temperature of 757 °C. Yanovskaya *et al.* [9] obtained a similar exotherm when preparing YIG from the hydrolysis of alkoxides and also the coprecipitation of hydroxides, and attributed it to the crystallization of the $YFeO_3$ orthoferrite and YIG garnet phases. The XRD patterns of the GLMA precursor of YIG (Fig. 4) show crystalline phases appearing above 750 °C. Below this temperature no reflections were obtained, showing that only amorphous phases exist. The crystalline phases appearing at 750 °C correspond to YIG, which gives the most intense reflection and is the main phase, with either $YFeO_3$ or Fe_2O_3 or both as minor phases.

Making a distinction between crystalline $YFeO_3$, which has its most intense reflection at 0.2692 nm (JCPDS 19–1417), and Fe_2O_3, which has its most intense reflection at 0.2690 nm (JCPDS 13–534), is very difficult.

As the temperature increases the intensity of the 0.269 nm reflection decreases, indicating that the amount of $YFeO_3/Fe_2O_3$ is reduced. Also as the temperature is increased the colour of the sample changes. At 400 °C it is red; by 800 °C it has changed to a tan colour. Increasing the temperature further changes the colour to yellow then yellow/olive. Both $YFeO_3$ and Fe_2O_3 are red, whereas YIG is yellow/olive in colour. This change in colour with increasing temperature gives an indication of the extent of the reaction.

4. Discussion

The diffuse reflectance spectrum of a sample of Y_2O_3

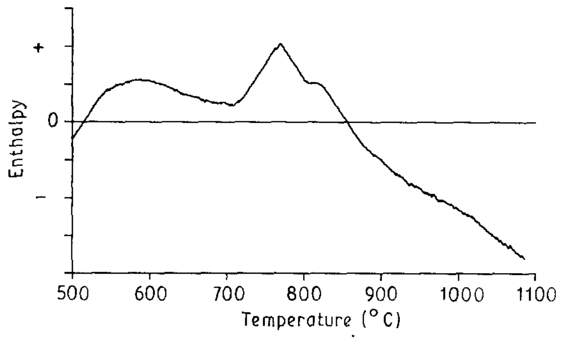

Figure 3 DSC curve of a GLMA precursor of YIG, heating rate 20 °C min^{-1}.

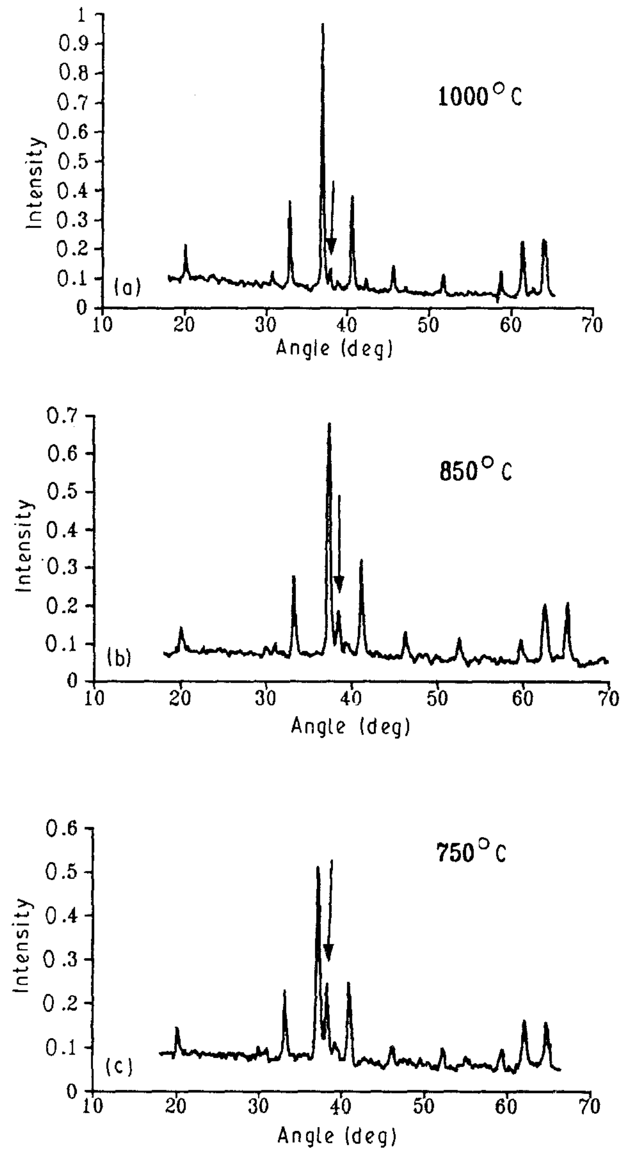

Figure 4 XRD patterns of GLMA precursors of YIG heat treated at 750, 850 and 1000°C for 60 min. $Fe_2O_3/YFeO_3$ reflections marked with arrow.

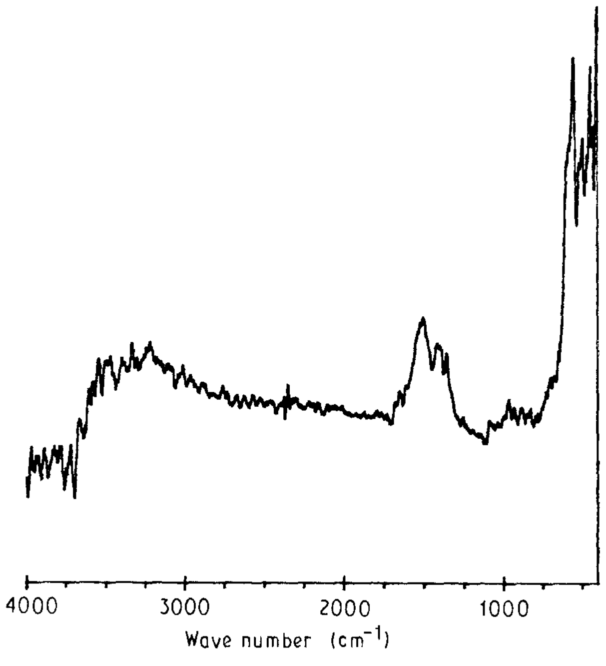

Figure 5 DRIFT spectra of Y_2O_3.

(Fig. 5) calcined at 900 °C shows hydroxyl and carbonate bands. It is known that water and carbon dioxide adsorb onto the surface of yttrium oxide to form a surface layer of carbonate and hydroxide [17]. Therefore any Y_2O_3 present in the precursor would be detected as Y_2O_3 along with hydroxyl and carbonate bands due to the reacted surface layer. As diffuse reflectance is a highly surface-sensitive technique, the absence of hydroxyl and carbonate bands in the FTIR spectra of GLMA samples of YIG above 750 °C suggests that Y_2O_3 is not present.

The results suggest that the decomposition of the GLMA precursor produces crystalline YIG at 760 °–800 °C as the major phase along with $YFeO_3$ and Fe_2O_3. Ferric oxide is obtained at 400 °C from the decomposition of the organic matrix and co-exists with the basic carbonate of yttrium in an amorphous phase until 760 °C. The results also suggest that a solid-state reaction occurs above 760 °C between crystalline $YFeO_3$ and crystalline Fe_2O_3. The following reaction would explain the observed results

$$\begin{array}{ccccc} Fe_2O_3 & + & 3YFeO_3 & \rightarrow & Y_3Fe_5O_{12} \\ \text{(red)} & & \text{(red)} & & \text{(yellow/olive)} \end{array}$$

The change in colour at higher temperatures and the decrease in intensity of the 0.269 nm reflection in the XRD patterns both indicate further YIG formation. The single-phase YIG is not formed at around 800 °C because of the slow solid-state reaction between the orthoferrite and ferric oxide phases which also crystallize at 760 °C.

5. Thermal decomposition of the GLMA precursor and formation of polycrystalline YAG

Thermogravimetric analysis (TGA) of the initial yellow powder obtained by evaporating off the glycerol in the initial solution at 180 °C shows that the organic matrix has decomposed by 435 °C, although the precursor is not mass stable until 850–900 °C (Fig. 6). A slight increase in mass occurs from this temperature to 700 °C. Chemical testing of the intermediate phase above 435 °C was positive for a carbonate. This is confirmed by FTIR (Fig. 7) which shows that a basic carbonate is formed after decomposition of the organic matrix. The sample analysed by DSC had previously been heated to 700 °C and was a black coloured powder which is shown from its FTIR spectrum to be a carbonate. A possible formula for this sample could be YAlO $(CO_3)_2$. XRD of this sample showed it to be amorphous as no reflections were obtained on scanning from 15 to 60°2θ. The thermogram obtained from the DSC (Fig. 8) shows three distinct exotherms. The first, which starts at 839 °C, is suspected to be due to the crystallization of amorphous $YAlO_3$. $YAlO_3$, which is white, is obtained by the decomposition of the carbonate. The following reaction could be attributed to the process occurring at this temperature

$$\begin{array}{ccccc} YAlO\,(CO_3)_2 & \xrightarrow{-2CO_2} & YAlO_3 & \longrightarrow & YAlO_3 \\ \text{(black)} & & \text{(white)} & & \text{(white)} \\ \text{amorphous} & & \text{amorphous} & & \text{crystalline} \end{array}$$

Decomposition and crystallization occur consecutively at this temperature. The onset temperature of this exotherm corresponds to the decomposition of

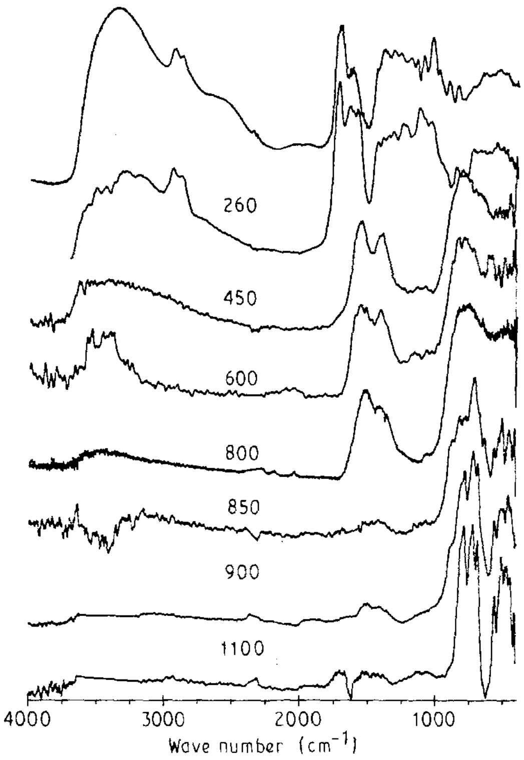

Figure 7 FTIR spectra of GLMA precursors of YAG heated to different temperatures.

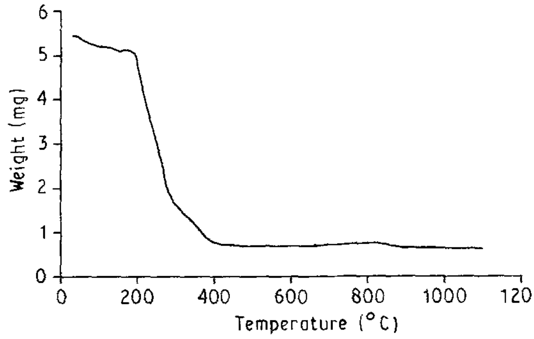

Figure 6 TG curve of a GLMA precursor of YAG, heating rate 5° C min^{-1}.

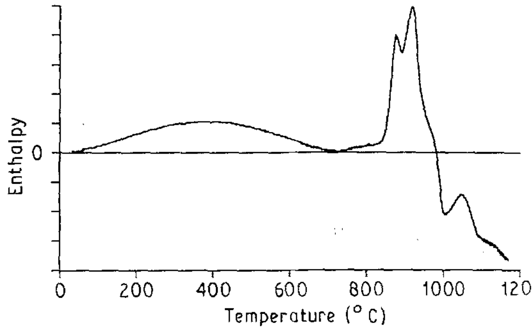

Figure 8 DSC curve of a GLMA precursor of YAG, heating rate 20°C min^{-1}.

the carbonate with the mixed oxide crystallizing from an amorphous phase. XRD data of YAG precursor (Fig. 9) shows that only an amorphous phase exists at 800 °C and at lower temperatures, but that crystalline $YAlO_3$ exists at 850 °C.

The DSC of a GLMA precursor of $YAlO_3$ (Fig. 10) shows the same exotherm, and there are no further exotherms after this temperature. It appears likely that this exotherm is due to the crystallization of $YAlO_3$. Therefore, the first exotherm in the DSC of the GLMA precursor of YAG (Fig. 7) is caused by the crystallization of a $YAlO_3$ intermediate from an amorphous mixed metal-oxide phase. The second exotherm could therefore be due to the solid-state reaction between crystalline $YAlO_3$ and amorphous Al_2O_3 to give $Y_3Al_5O_{12}$, i.e. YAG

$$\underset{\text{(crystalline)}}{3\,[YAlO_3]} + \underset{\text{(amorphous)}}{Al_2O_3} \longrightarrow \underset{\text{(crystalline)}}{Y_3Al_5O_{12}}$$

This is supported by the appearance of YAG reflections in the XRD pattern of the 900 °C sample, which also shows a concomitant reduction in the intensities of the reflections due to $YAlO_3$. No crystalline Al_2O_3 is seen so it can be assumed that it is amorphous and has not yet crystallized. The FTIR spectrum of 900 °C sample (Fig. 7) shows that YAG has formed, as can be seen from the fingerprint vibrations due to the isolated AlO_4 tetrahedra and isolated AlO_6 octahedra of YAG's unit cell [18]. A third exotherm starting at 1000 °C could be due to YAG crystal growth. DSC of a sample heated to 450 °C, which should contain no organic matrix from TG data, gives an exotherm beginning at 470 °C. As the TG shows a slight increase in weight in this region this may be due to CO_2 absorption and carbonate formation.

On studying the thermal decomposition of a GLMA precursor of Al by TG and FTIR, it was noticed that the aluminium malonate intermediate decomposes to aluminium hydroxide, which suggests that the black colour is due to carbon which burns off at higher temperatures.

The IR spectra in Fig. 6 show that the organic matrix decomposes to a basic carbonate which is converted to the carbonate at higher temperatures. At 850 °C, the carbonate is decomposed leaving a sample which gives metal–oxygen vibrations below 900 cm^{-1}.

The characteristic spectrum of YAG appears at 900 °C and this remains at higher temperatures. No crystalline phases are produced until the precursor reaches 850 °C, i.e. after decomposition of the amorphous carbonate intermediate. This 800 °C sample is black and amorphous whereas the 850 °C sample was white and crystalline. The reflection observed for the 850 °C sample corresponded to the hexagonal $YAlO_3$ compound (JCPDS 16–219). This was later confirmed by studying the decomposition of a GLMA precursor of $YAlO_3$ which showed the same reflections.

By 900 °C YAG begins to appear in the heating of the 3Y:5Al material, and the intensity of the reflections in the XRD pattern due to YAG increases with increasing temperature, possibly caused by crystal growth. At 1000 °C, $YAlO_3$ is barely discernible and by 1100 °C, YAG is the only phase present. Intense peaks are given for this last sample, indicating crystal growth.

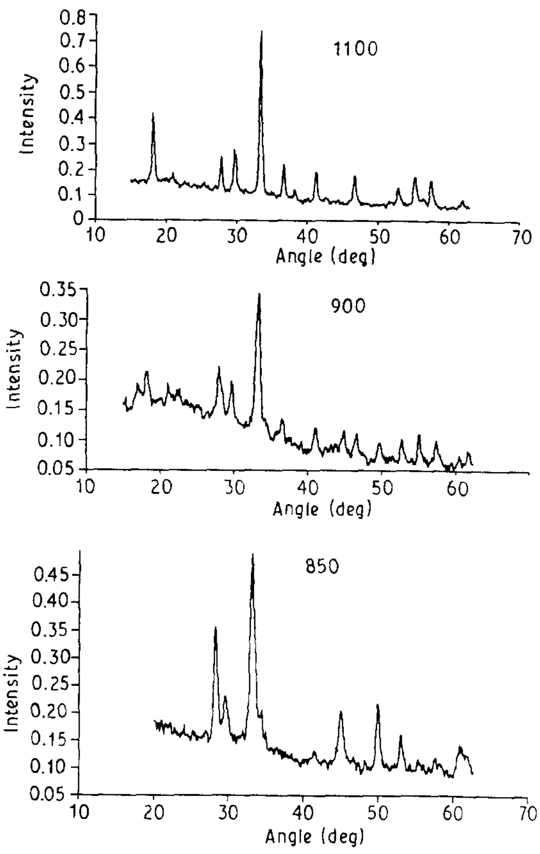

Figure 9 XRD patterns of GLMA precursors of YAG heat treated to 850, 900 and 1100 °C.

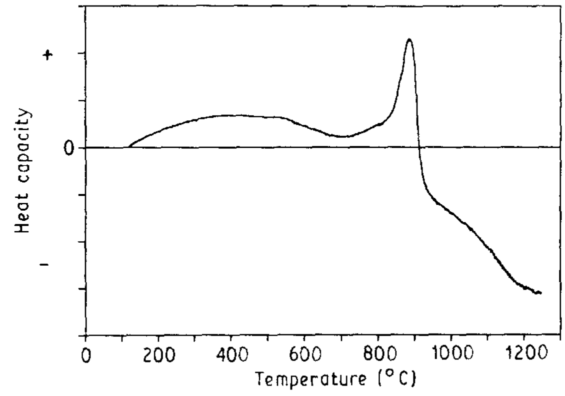

Figure 10 DSC curve of a GLMA precursor of $YAlO_3$.

6. Conclusions

Single-phase YAG can be obtained by the organic solution technique using a glycerol/malonic acid matrix. The formation of YAG is via a $YAlO_3$ intermediate. YAG starts to form at 900 °C and the reaction is complete by 1100 °C. The reaction is assumed to be between crystalline $YAlO_3$ and amorphous Al_2O_3, hence the short reaction time.

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References

1. J. HELSZA Jr. (ed.), "Yttrium Iron Garnet Resonators and Filters", (Wiley, New York, 1985).
2. M. S. SCHOLL and R. S. TRIMMER, *J. Electrochem. Soc.* **133** (1986) 643.
3. D. R. MESSIER and G. E. GAZZA, *Amer. Ceram. Soc. Bull.* **51** (1972) 692.
4. W. R. HOLMQUIST, C. F. KOOI and R. W. MOSS, *J. Amer. Ceram. Soc.* **44** (1961) 194.
5. G. DEWITH and J. A. VAN DIJK, *Mater. Res. Bull.* **19** (1984) 1669.
6. V. B. GLUSHKOVA, *Inorg. Mater.* **19** (1983) 1015.
7. V. P. CHALIY and DANILCHENKO, *Izv. An. SSSR Neorg. Mater.* **9** (1973) 1208.
8. V. K. S. NARAYANAN, N. S. GAJBHIYE and D. BAHADUR, *J. Mater. Sci. Lett.* **6** (1987) 281.
9. M. I. YANOVSKAYA, T. U. ROGOVA, S. A. IVANOV, N. V. KOLGANOVA and N. TUROVA, *ibid.* **6** (1987) 274.
10. G. GOWDA, *ibid* **5**·(1986) 1029.
11. K. NAKAMOTO, "IR and Raman Spectra of Inorganic and Coordination Compounds, 4th edn (Wiley, New York, 1986) pp. 232 and 253.
12. S. D. ROSS, "Inorganic Infrared and Raman Spectra" 1st Edn (McGraw-Hill, London, 1972) p. 150.
13. N. T. MCDEVITT, *J. Opt. Soc. Amer.* **59** (1968) 1240.
14. L. MARKOV, V. BLASKOV, D. KLISSURSKI and S. NIKOLOV, *J. Mater. Sci.* **25** (1990) 3096.
15. M. P. FULLER and P. R. GRIFFITHS, *Anal. Chem.* **50** (1978) 1906.
16. R. K. VINCENT and G. R. HUNT, *Appl. Optics* **7** (1968) 53.
17. F. A. COTTON and G. WILKINSON, "Advanced Inorganic Chemistry" 5th edn (Wiley, London, 1988) p. 965.
18. P. TARTE, *Spectrochim Acta B* **18** (1962) 467.

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