JOURNAL OF MATERIALS SCIENCE 31 (1996) 3453–3458

Sol–gel processing and sintering of yttrium aluminum garnet (YAG) powders

R. MANALERT, M. N. RAHAMAN
University of Missouri-Rolla, Department of Ceramic Engineering, Rolla, MO 65401, USA

Gels of yttrium aluminum garnet (YAG) with the stoichiometric composition $3Y_2O_3 \cdot 5Al_2O_3$, were prepared by a sol–gel technique and dried by supercritical extraction with CO_2. Powders were produced by lightly grinding the dried gels. Crystallization of the powder occurred at ≈900 °C and within the limits of detection, the X-ray diffraction pattern of the crystallized material was identical to that of the stoichiometric composition. Powder compacts with a green density of ≈0.50 of the theoretical were sintered to nearly full density in O_2 during constant heating rate sintering at 5 °C min^{-1} to 1600 °C. This is better than the density obtained with powders from a similar gel dried conventionally (by evaporation of the liquid) and considerably better than that obtained with powders prepared by solid state reaction. The room temperature flexural strength and fracture toughness of the material fabricated from the supercritically dried gels were 190 MPa and 2.2 MPa.m$^{1/2}$, respectively. These strength and fracture toughness values are higher than those reported in other studies for YAG produced by the sintering route.

1. Introduction

Compounds in the system Y_2O_3–Al_2O_3 are promising materials for optical, electronic and structural applications. Three compositions have received most attention in this system: $3Y_2O_3 \cdot 5Al_2O_3$, $2Y_2O_3 \cdot Al_2O_3$ and $Y_2O_3 \cdot Al_2O_3$. The first two compounds are believed to be stable at ordinary temperatures and pressures. The third one is metastable and decomposes into $3Y_2O_3 \cdot 5Al_2O_3$ and $2Y_2O_3 \cdot Al_2O_3$ after prolonged heating in the temperature range of 1400–1800 °C [1]. The compound $3Y_2O_3 \cdot 5Al_2O_3$, referred to as yttrium aluminum garnet or YAG, adopts the cubic garnet structure. It has been used widely as a laser host material [2]. It has promising properties for applications such as high temperature coatings and high temperature structural components. For structural applications, the bulk material may be used in the monolithic form or as the matrix phase for composites. In either case, an important requirement is that the fabricated material must have nearly full density and a controlled grain size.

A commonly used technique for preparing these binary oxides involves mixing high purity Al_2O_3 and Y_2O_3 powders, followed by calcination at elevated temperatures. This technique generally requires extensive mechanical mixing and calcination temperatures above 1600 °C. Furthermore, at elevated temperatures, it is difficult to control the phase homogeneity and purity. Messier and Gazza [3] reported that prolonged heating of Al_2O_3 and Y_2O_3 mixtures between 1500–1600 °C did not produce pure YAG free from metastable compounds. Several wet-chemical techniques have been used to produce YAG. Sulphates and nitrates have generally been used as the starting materials. The mixtures are commonly doped with either SiO_2 or MgO, presumably as grain growth inhibitors, and decomposed into the corresponding oxides [4] or hydrolyzed to coprecipitate the corresponding hydroxides [5, 6]. Although these studies report lower temperatures for the synthesis of YAG powder, the data on the phase homogeneity, thermal stability and conditions of synthesis are somewhat ambiguous. Keller *et al.* [7] prepared YAG powders by coprecipitation from a mixture of yttrium isopropoxide and aluminum tri-sec-butoxide. The X-ray diffraction pattern of the crystallized material was almost identical to that of YAG. However, the fabrication of dense materials by sintering of the compacted powders required fairly high temperatures (≈1800 °C). Yttrium aluminum garnet has also been prepared by the sol–gel route. Gowda [8] used starting materials consisting of yttrium acetate and aluminum tri-sec-butoxide. The gelled material was dried conventionally. The X-ray diffraction pattern of the crystallized gel was almost identical to that of YAG.

It has been well demonstrated that the sol–gel process offers considerable advantages of good mixing of the starting materials and good chemical homogeneity of the product [9]. The sinterability of the gels is also far better than that of similar compositions prepared by the more conventional route involving sintering of crystalline powders. For mullite gels produced by supercritical drying, Rahaman and Jeng [10] have shown that the sinterability of the mechanically compacted gel is higher than that of a similar gel dried conventionally (by evaporation of the liquid) and far higher than that for a compact of crystalline mullite powders. The use of sol–gel processing coupled with

0022–2461 © 1996 Chapman & Hall

supercritical drying is therefore expected to produce powders with good sinterability.

In the present work, the sinterability and microstructural evolution of YAG powders synthesized by a sol–gel process were investigated. The powders were obtained by lightly grinding the supercritically dried gel. The sinterability of the powders was compared with that for similar powders produced from a conventionally dried gel.

2. Experimental procedure

2.1. Preparation of yttrium aluminum garnet gels

Yttrium aluminum garnet (YAG) with the stoichiometric composition $3Y_2O_3 \cdot 5Al_2O_3$ was prepared by the hydrolysis, condensation and gelation of a mixture of aluminum tri-sec-butoxide, $Al(OC_4H_9)_3$, and yttrium acetate hydrate, $Y(O_2C_2H_3)_3 \cdot x(H_2O)$. The aluminum butoxide (purity 97%) and yttrium acetate (purity 99.9%) were obtained from Aldrich Chemical Company, Milwaukee, Wisconsin, USA. The procedure was similar to that described by Gowda [8]. Briefly, the aluminum butoxide was diluted with dry iso-butanol (molar ratio of iso-butanol:aluminum alkoxide = 5:1) and added dropwise to a solution of yttrium acetate in water (molar ratio of H_2O: aluminum alkoxide = 70:1) at 80–85 °C with vigorous stirring. The solution became clear after 10 min and gelling occurred after another 30 min. Aging of the gel for 24 h in ethanol was repeated three times in order to replace the liquid in the pores with a high concentration of ethanol. This aging step is important for adequate control of the supercritical drying process.

The gelled material was dried either conventionally or supercritically. Conventional drying was carried out by allowing the liquid to evaporate at room temperature. The conventionally dried gel (xerogel) was ground in an agate mortar and pestle to produce a powder. The procedure for supercritical drying by extraction of CO_2 was similar to that described earlier for the drying of mullite gels [10]. Briefly, the alcogel (i.e., gel with alcohol-filled pores) was placed in an autoclave and submerged in ethanol. The ethanol was displaced by flowing liquid CO_2 into the autoclave for 24 h under a pressure of ≈ 6.7 kPa (800 psi). When no trace of ethanol could be detected in the mixture flowing out of the autoclave, the vessel was cooled to ≈ 5 °C for 30 min while maintaining the pressure at 6.7 kPa. The inlet and outlet valves of the autoclave were closed and the system was raised above the critical point for CO_2, i.e., to a temperature of ≈ 40 °C and a pressure of ≈ 10 kPa (1200 psi). After equilibration, which was maintained for 15 min, the fluid was released slowly. The supercritically dried gel (aerogel) had a solids content of $< 10\%$. It was lightly ground in an agate mortar and pestle to produce a powder.

2.2. Compaction and sintering of the gel-derived powder

Prior to compaction, the gel-derived powders were heated for 2 h at 500 °C to burn off any organics remaining in the structure from the chemical reactions occurring during synthesis. In addition, different samples were further heated for 2 h at 700 and 900 °C; these powders were used later to investigate whether a calcination step influenced the subsequent compaction and sintering behaviour.

The powder produced from the conventionally dried gel was compacted by pressing uniaxially in a die at ≈ 20 MPa to form cylindrical pellets (6 mm in diameter by 6 mm). The relative density of the powder compacts was 0.50 ± 0.05. Compaction of the powder produced from the supercritically dried gel was more difficult; in this case the powder was mixed with 5 vol % of cabowax (which served as a binder) and pressed at a higher pressure of ≈ 40 MPa to obtain approximately the same green density. The cylindrical pellets were used for the sintering experiments. For the mechanical testing experiments, beams were formed by pressing the powder in a die with a rectangular cross-section.

The powder compacts were sintered in air in a dilatometer (Model 1600 C, Theta Industries, Port Washington, New York, USA) that allowed continuous monitoring of the shrinkage. The experiments were performed at a constant heating rate of 5 °C min^{-1} to 1500 °C (the maximum temperature available in the dilatometer). The mass and dimensions of the compacts were measured before and after they were sintered. The density, ρ, at any temperature was determined from the initial density, ρ_0, and the measured shrinkage, $\Delta L/L_0$, using the equation:

$$\rho = \frac{\rho_0}{(1 - \Delta L/L_0)^3} \qquad (1)$$

where L_0 is the initial sample length and $\Delta L = L_0 - L$, where L is the instantaneous sample length.

Sintering up to 1500 °C in the dilatometer did not produce adequate densification. In a separate set of experiments, the powder compacts were sintered in air in a controlled atmosphere tube furnace at a constant heating rate of 5 °C min^{-1} to temperatures between 1500–1750 °C. A separate sample was used for each run. The final densities of the sintered samples were checked using Archimedes' principle. The theoretical density of $Y_3Al_5O_{12}$ was assumed to be 4.55 g cm^{-3}.

2.3. Characterization of the gel-derived powders and the sintered materials

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were used to study the changes occurring in the synthesized powders during calcination. The samples were heated at a constant rate of 10 °C min^{-1} to 1500 °C. The microstructure of the sintered samples were observed using scanning electron microscopy (SEM) of fractured surfaces and polished surfaces. The phase composition of the synthesized powder and sintered material was determined by X-ray diffraction (XRD) using CuK_α radiation in the range of 12–70 ° 2θ at a scanning rate of 2 ° 2θ per min.

The flexural strength and fracture toughness of the sintered samples were measured at room temperature using standard ASTM techniques. The flexural strength was determined by three-point bending of beams (2.0 by 4.0 by 25.0 mm) at a cross head speed of 0.05 mm min^{-1}. The test samples were cut from sintered rectangular bars. The sample surfaces were polished with SiC papers (down to 600-grit). The edges were beveled during the polishing process. The fracture toughness was determined by the single edge notched beam (SENB) technique for samples with dimensions of 2.0 by 5.0 by 25.0 mm. The beams were notched at the centre using a diamond blade (thickness 0.5 mm) to produce a notch depth which was 0.2 times the beam width. The beams were fractured in three-point bending (with a 12.5 mm lower span) at a crosshead speed of 0.05 mm min^{-1}. Six specimens were used for each determination of the flexural strength and the fracture toughness.

3. Results and discussion

As outlined earlier, the experiments consisted of the synthesis, sintering and characterization of YAG. The results are discussed in the following sections.

3.1. Powder synthesis and characterization

The synthesized gels were transparent and they remained transparent after drying conventionally by allowing the liquid to evaporate at room temperature. In addition to a large drying shrinkage, extensive cracking occurred. However, for the production of powders, as in this work, the cracking is not a problem; the fragments of the dried gel were ground to produce a powder. The gels prepared by supercritical drying showed almost no shrinkage during drying and were very fragile. The fragile nature of the gels makes them well-suited for the production of powders. They were easily ground in a mortar and pestle. Fig. 1 shows the scanning electron micrograph of the powder produced from the supercritically dried gel. The average particle size is ≈5 μm.

The DTA and TGA results for the powder prepared from the supercritically dried gel are shown in Fig. 2. The DTA curve shows a broad exotherm between ≈200–500 °C which is attributed to the removal of organics and hydroxyl groups from the gel structure. The TGA curve shows a corresponding weight loss of ≈40% after heating to ≈500 °C. Above ≈500 °C, there is almost no weight loss. However, the DTA curve shows a fairly sharp exothermic peak at ≈915 °C. As outlined below for the X-ray diffraction data, this peak is associated with the transformation from the amorphous state to the crystalline garnet. It is interesting to note that the DTA curve shows no evidence for the existence of peaks (or troughs) between ≈500 and ≈915 °C. This indicates that there is no significant crystallization prior to that at ≈915 °C.

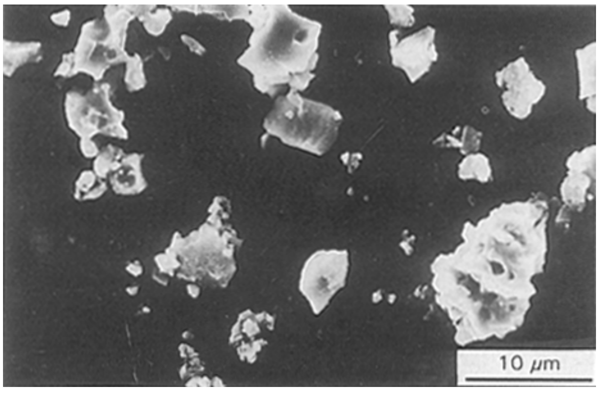

Figure 1 Scanning electron micrograph of the YAG powder prepared from the supercritically dried gel.

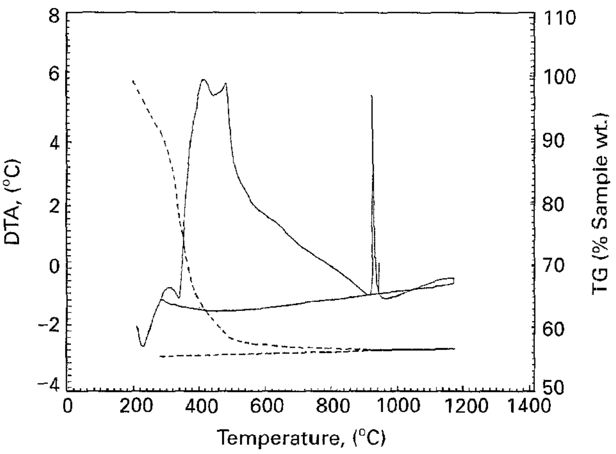

Figure 2 Differential thermal analysis (DTA), shown by the solid line (—) and thermogravimetric analysis (TG) shown by the dashed line (---), curves for the gel-derived powder.

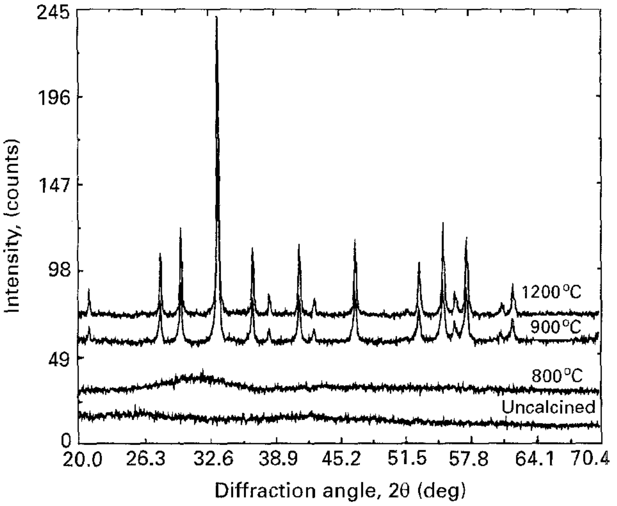

Figure 3 X-ray diffraction patterns of the uncalcined gel-derived powder and the powder heated for 2 h at 800, 900 and 1200 °C.

The X-ray diffraction patterns for the gel-derived powder (referred to as "uncalcined") and the powder calcined for 2 h at 800, 900 and 1200 °C are shown in Fig. 3. The powder is essentially amorphous and remains amorphous to X-rays for calcination temperatures of up to 800 °C. However, the powder calcined at 900 °C shows a high degree of crystallinity. The pattern for the powder calcined at 1200 °C shows well-defined peaks whose positions are almost identical to those of stoichiometric YAG. The results indicate that crystallization of the powder starts to occur at ≈900 °C, which is close to the temperature of the

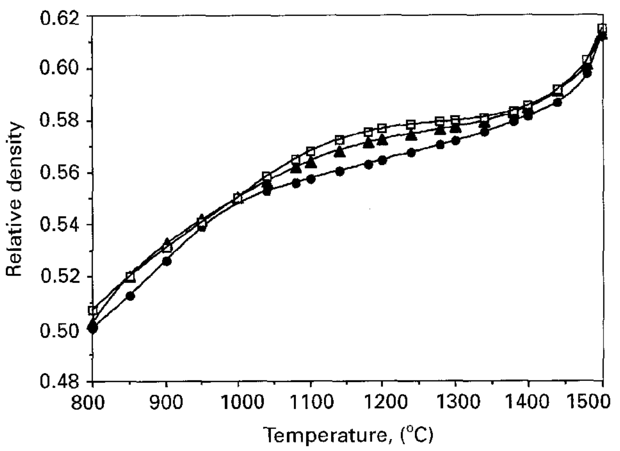

Figure 4 Relative density versus temperature for the compacts formed from the gel-derived powder that was calcined for 2 h at (●) 500, (▲) 700 and (□) 900 °C prior to compaction. the compacts were sintered at 5 °C min^{-1} in air.

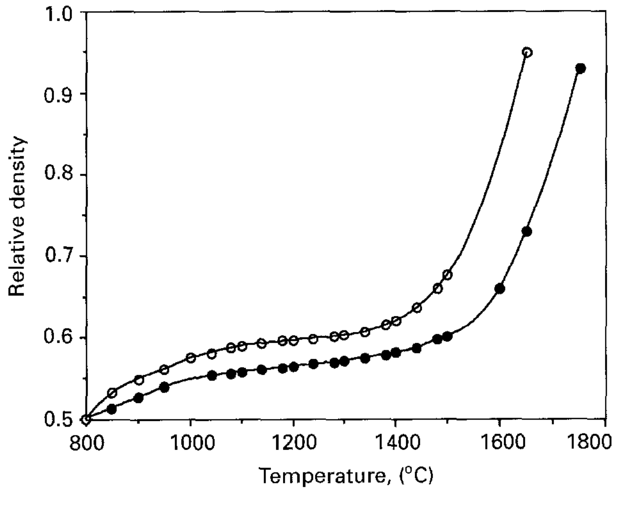

Figure 5 Relative density versus temperature for the powder compacts formed from (○) the supercritically dried gel and (●) the conventionally dried gel during constant heating rate sintering at 5 °C min^{-1} in air.

exothermic peak observed earlier from the DTA analysis. The DTA and X-ray diffraction data are in agreement with the results Gowda [8], who synthesized YAG by a similar sol–gel technique followed by conventional drying.

3.2. Densification and microstructure of the gel-derived powder

As outlined earlier, the effect of a calcination step on the subsequent compaction and sintering of the gel-derived powder was investigated. Samples of the same powder were calcined for 2 h at three different temperatures, 500, 700 and 900 °C, prior to compaction. The calcination treatment had no significant effect on the compaction behaviour. For the same applied pressure, the densities of the powder compacts were almost independent of the calcination temperature. As shown in Fig. 4, for the temperature range available in the dilatometer (up to 1500 °C), the effect of the calcination treatment on the sintering kinetics was also insignificant. When compared to those calcined at lower temperatures, the powder calcined at 900 °C suffered from the smallest weight loss during sintering. Because excessive weight losses are normally detrimental to the achievement of high density during sintering, in all subsequent experiments the powders were calcined for 2 h at 900 °C prior to compaction and sintering.

Fig. 5 shows a comparison of the sintering kinetics for the powder compacts produced from the conventionally dried gels and the supercritically dried gels during constant heating rate sintering in air. As outlined earlier, the data below 1500 °C were obtained continuously by dilatometry while those above this temperature were obtained in intermittent runs up to the desired temperature. The sintering curves have roughly the same shape and, at lower temperatures, do not differ significantly. However, above ≈1400 °C, the compacts formed from the supercritically dried gel show a significant enhancement in sinterability. At 1650 °C, the supercritically dried sample reaches a relative density of ≈0.95, compared to a value of ≈0.75 for the conventionally dried sample. It is not clear why the powder compact formed from the supercritically dried gel has a higher sinterability than that for the conventionally dried sample. At the onset of appreciable densification (above ≈1400 °C), the X-ray diffraction data (Fig. 3) reveal that both samples are fully crystalline. The powder compacts also have the same initial density. Differences in the extent of crystallinity or the initial density cannot therefore be used to explain the higher sintering rate of the powder compact formed from the supercritically dried gel. The origins of the increased sinterability may reside in differences in the microstructure produced by the crystallization process.

The sintering atmosphere was observed to have some effect on the sintering rate at higher temperatures (above ≈1500 °C). Compared to air, the use of O_2 produced an increase in the density of the powder compacts. For the compacts formed from the supercritically dried gel, almost full density was achieved after sintering for 2 h in O_2 at 1600 °C.

Fig. 6 shows scanning electron micrographs of the fractured surfaces of compacts sintered in air at 1650 °C. The compact formed from the conventionally dried gel (Fig. 6a) is highly porous (relative density ≈0.75) with fairly rounded grains (grain size ≈2–4 μm). In Fig. 6b, the compact formed from the supercritically dried gel appears significantly denser (relative density ≈0.95). The pores appear to have two distinct morphologies: the smaller pores have a fairly rounded morphology while the larger pores appear fairly elongated.

For the compacts formed from the supercritically dried gel, Fig. 7 shows scanning electron micrographs of the samples sintered for 2 h at 1600 °C in oxygen. The micrograph of the fractured surface (Fig. 7a) shows a high degree of transgranular fracture in an almost fully dense microstructure. The polished surface (Fig. 7b) shows small precipitates in a dense matrix. Energy dispersive X-ray analysis in the SEM revealed that the precipitates have a composition that is close to that of Al_2O_3. As outlined earlier, the X-ray diffraction data of the gel derived powder (Fig. 3)

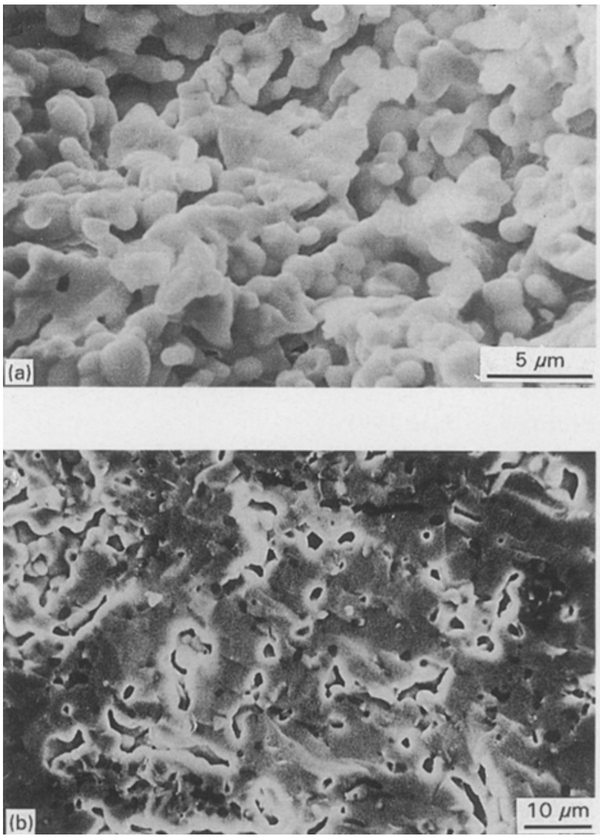

Figure 6 Scanning electron micrographs of the fractured surfaces of the powder compacts formed from (a) the conventionally dried gel (relative density $\approx$ 0.75) and (b) the supercritically dried gel (relative density $\approx$ 0.95), after sintering to 1650 °C in air.

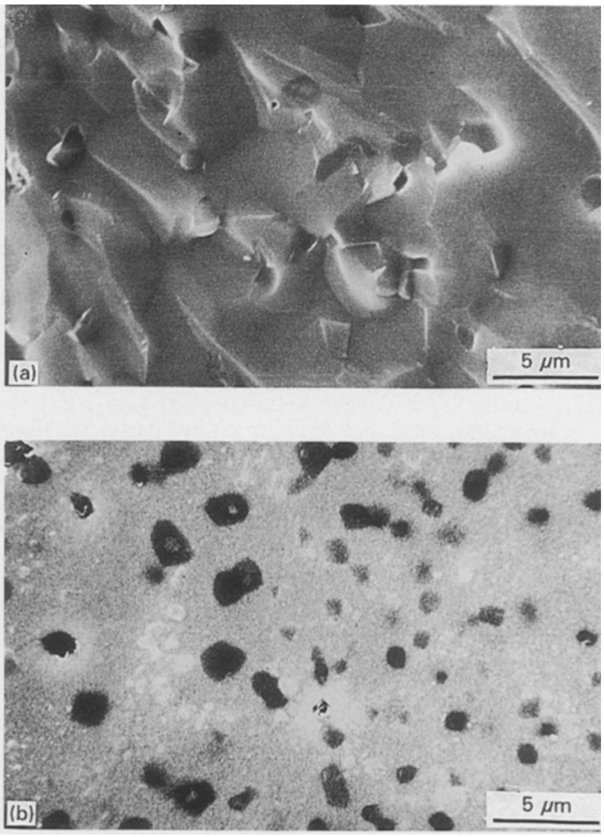

Figure 7 Scanning electron micrographs of (a) the fractured surface and (b) the polished surface of the powder compact formed from the supercritically dried gel, after sintering for 2 h at 1600 °C in oxygen.

heated to 1200 °C was almost identical to that for stoichiometric YAG. The presence of the alumina-rich precipitates may be taken to indicate that some dissociation of the material occurs at the higher temperatures used for sintering.

3.3. Mechanical properties of the sintered materials

The flexural strength and fracture toughness (SENB method) of the sintered samples produced from the supercritically dried gel were measured at room temperature. The powder compacts were sintered for 2 h at 1600 °C in oxygen and, as outlined earlier, reached a density close to the theoretical. Microstructures of the sintered samples are shown in Fig. 7. The values for the flexural strength ($\approx$190 MPa) and fracture toughness ($\approx$2.2 MPa.m$^{1/2}$) obtained in the present work are higher than those (102 MPa and 1.2 MPa.m$^{1/2}$) reported by Keller *et al.* [7] for YAG fabricated by a different route. Keller *et al.* used powders prepared by precipitation from mixed alkoxides; their firing schedule involved higher sintering temperatures (1800 °C) as well as an annealing step (following sintering) of 14 h at 1425 °C in air. As outlined earlier, the samples used in the present work (Fig. 7) consisted of a two-phase microstructure in which fine precipitates are dispersed in the matrix. The presence of these precipitates may be responsible for the higher strength and fracture toughness obtained in this work.

4. Conclusions

Amorphous powders of yttrium aluminum garnet (YAG) were prepared by sol–gel processing followed by supercritical drying with extraction of CO_2. The sinterability of the compacted powders was higher than that for similar powders prepared from a conventionally dried gel. Compared to air, the use of an oxygen atmosphere produced an increase in the sintering rate. Powder compacts formed from the supercritically dried gel were sintered to nearly full density after 2 h at 1600 °C in an atmosphere of O_2. At the equivalent firing temperature, this density is considerably higher than those reported for YAG prepared by other methods.

Crystallization of the gel-derived YAG powder commenced at $\approx$900 °C. Within the limits of detection, the X-ray diffraction pattern of the powder heated for 2 h at 1200 °C was almost identical to that of stoichiometric YAG and no intermediate crystalline phases were detected prior to the onset of crystallization.

The YAG material fabricated by sintering at 1600 °C had a two-phase microstructure consisting of fine alumina-rich precipitates in a dense matrix. Since the X-ray diffraction pattern of the crystallized powder heated for 2 h at 1200 °C was almost identical to that of stoichiometric YAG, the presence of the precipitates indicates that some degree of dissociation of the YAG may be occurring at higher temperatures. For the almost fully dense YAG fabricated by sintering at 1600 °C, the flexural strength and fracture toughness values measured at room temperature were 190 MPa and 2.2 MPa.m$^{1/2}$, respectively.

References

1. O. YAMAGUCHI, K. MATUI and K. SHIMIZU, *Ceramics Internat.* **11** (1985) 107.
2. J. MACHAN, R. KURTZ, M. BESS and M. BIRNBAUM, *Optical Society of America* (*Technical Digest Series*) **20** (1987) 134.
3. D. R. MESSIER and G. E. GAZZA, *Amer. Ceram. Soc. Bull.* **51** (1972) 692.
4. G. DEWITH and H. S. A. VAN DIJK, *Mater. Res. Bull.* **19** (1984) 1669.
5. V. B. GLUSHKOVA, O. N. EGOROVA, V. A. KRZHIZHANORSKAYA, and K. YU. MEREZHINSKII, *Inorg. Mater.* **19** (1983) 1015.
6. L. P. MOROZOVA, E. S. LUKIN, T. V. EFIMOVSKAYA, A. V. SMOLYA and I. F. PANTELEEVA, *Glass Ceramics* **35** (1978) 158.
7. K. KELLER, T.-I. MAH and T. PARTHASARATHY, *Ceram. Eng. Sci. Proc.* **11** (1990) 1122.
8. G. GOWDA, *J. Mater. Sci. Lett.* **5** (1986) 1029.
9. C. J. BRINKER and G. W. SCHERER, "*Sol-Gel Science*", (Academic Press, New York, 1990).
10. M. N. RAHAMAN and D. Y. JENG, *Ceramic Trans.* **7** (1990) 753.

Received 28 June 1995
and accepted 21 December 1995