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Aqueous slip casting of transparent yttrium aluminum garnet (YAG) ceramics

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Abstract

Transparent YAG ceramics were prepared by slip casting an aqueous dispersed mixture of commercial Al_2O_3 and Y_2O_3 powders. The powders were co-dispersed with poly(acrylic acid) and citric acid. Polyethylene glycol of 0.5 wt.% (PEG 4000) and 0.5 wt.% tetraethyl orthosilicate were added as binder and a sintering aid, respectively. Dried samples were vacuum sintered at 1800 °C for 16 h. In general, YAG ceramics cast from Newtonian suspensions were optically transparent and had optical transmittances >80% from 340 to 840 nm. Slightly flocculated dispersions, as evidenced by higher viscosity and non-Newtonian rheology, resulted in translucent samples with large pores and lower optical transmittances.

Keywords: A. Slip casting; Yttrium aluminum garnet; Transparent ceramics; Dispersion; Vacuum sintering

1. Introduction

Nd:YAG lasers, because of their thermal stability and good thermal shock resistance, have gained recognition and acceptance within the military, scientific, industrial and medical communities [1–3] for numerous applications. Single crystal Nd:YAG is mostly used for laser applications. Recent progress in the processing of polycrystalline transparent ceramics, however, indicates that the ceramic approach results in materials with equivalent, if not better, properties than Czochralski grown crystals. The ceramic approach offers manufacturing advantages such as size and shaping capability not possible for crystal growth processes. These advantages may also lead to more cost effective manufacturing of transparent ceramics; especially for use in laser applications [4–9] and transparent armor.

Transparent ceramics represent a unique challenge to the manufacturing community since they require exceptionally low pore concentrations (<150 vol. ppm) [10], clean grain boundaries and no second phases [3,4]. These stringent requirements place unusual demands on the purity of the initial powders as well as on the processing and forming techniques.

Even though there is extensive literature on transparent ceramics, there are only a few papers about the forming processes to achieve such high quality ceramics. Most papers report use of dry pressing to fabricate ceramics but there are no papers about the slip casting of aqueous yttria and alumina mixtures to produce transparent YAG. Slip casting, and other colloidal forming techniques, are attractive processes for manufacturing transparent YAG ceramics since defects such as aggregates and agglomerates can be more readily managed by separation and dispersion techniques, respectively [11,12]. Pores, inclusions, and second phases significantly degrade optical transparency of YAG ceramics and thus, slip casting must be carried out with slurries that are well dispersed.

In this paper we correlate the optical characteristics of vacuum sintered YAG ceramics with the dispersion properties of alumina and yttria mixtures. In this way we demonstrate a means to co-disperse a mixture of the powders for the production of transparent YAG ceramics by slip casting.

2. Sample preparation and characterization

Submicron (0.1–0.3 μm) α-Al_2O_3 powder (>99.99%, Sumitomo Chemical Co., Japan) and 2–4 μm Y_2O_3 powder

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(>99.99%, Nippon Yttria Co., Japan) were used. 0.5 wt.% of tetraethyl orthosilicate (TEOS, 99.99%, Alfa, Ward Hill, MA, USA) was used as a sintering aid. Poly(acrylic acid) (PAA, molecular weight ~450,000, Sigma–Aldrich Inc., USA) with concentrations varying from 0.1 to 0.35 wt.% (PA10 to PA35) was added as a dispersant. A small amount (0.5 wt.%) of polyethylene glycol (PEG 4000, J.T. Baker Chemical Co., Phillipsburg, NJ, USA) was added as a binder. The concentration of citric acid (anhydrous, >99.5%, Aldrich Chemical Company), which was used as a pH modifier, was kept constant at 0.6 wt.%. At this concentration the pH was maintained between 7 and 8. Slurries with a solids loading of 20 vol.% were used for slip casting in plaster of Paris molds. After slip casting the casts were dried in air and the organic additives were removed by heating the samples for 2 h in air at 600 °C. Samples were vacuum sintered at 5×10^{-6} Torr at 1800 °C for 16 h.

Rheological properties of the slurries were determined up to a shear rate of 500 s^{-1} with a rotational stress controlled rheometer (Carimed CSL 100, New Castle, DE, USA). The measurements were performed at a constant temperature (25 °C) using a cone and plate configuration. Zeta potential was measured by the electro/acoustic spectroscopy technique at 3–99 MHz.

Bulk densities of the cast samples were measured according to ASTM specification C373 [17]. Microstructural evolution of sintered bodies was observed using scanning electron microscopy of samples polished and thermally etched at 1550 °C for 30 min. The in-line transmittance was measured on polished samples with a UV–vis spectrophotometer (Cary 3, Varian, Walnut Creek, CA, USA). The measurements were carried out on samples with a standard, dual light beam arrangement.

3. Results and discussion

Fig. 1 shows SEM micrographs of the starting alumina and yttria powders, and Fig. 1c is a micrograph of the Al_2O_3 and Y_2O_3 powder mixture after milling for 16 h with 5 mm diameter high purity alumina media. After 16 h of milling the Y_2O_3 particles were reduced in size from about 4 μm to less than 2.5 μm.

The rheological properties of the YAG slurries are strongly dependent on the amount of dispersant added (Fig. 2). At low dispersant concentrations the slurries were Newtonian. The lowest viscosity was obtained with only 0.1 wt.% PAA. Increasing the dispersant concentration increases the viscosity and results in a weak yield point.

Adding dispersant beyond what gives maximum coverage of the particles' surface can lead to an excess of dispersant in solution, which would exert detrimental effects on rheology by two possible mechanisms: (i) acting as a free electrolyte, increasing the ionic strength and thus screening the electrostatic forces among particles and (ii) forming a complete monolayer or even a second adsorbed layer at the surface of particles with an opposite orientation, thus completely reversing the surface charge. The former may lead to depletion flocculation as a result of the osmotic force or pressure created by the exclusion of the unadsorbed polymer chains between two approaching particles coated by the dispersant. The latter, on the other hand, may lead to repulsive electrosteric particle interactions at higher dispersant concentrations.

Fig. 3 shows the zeta potential measurements as a function of pH at various dispersant concentrations. Given that pure alumina and yttrium oxide particles display isoelectric points in the pH range of ~8.5–9.5 and ~10.5–11.0, respectively

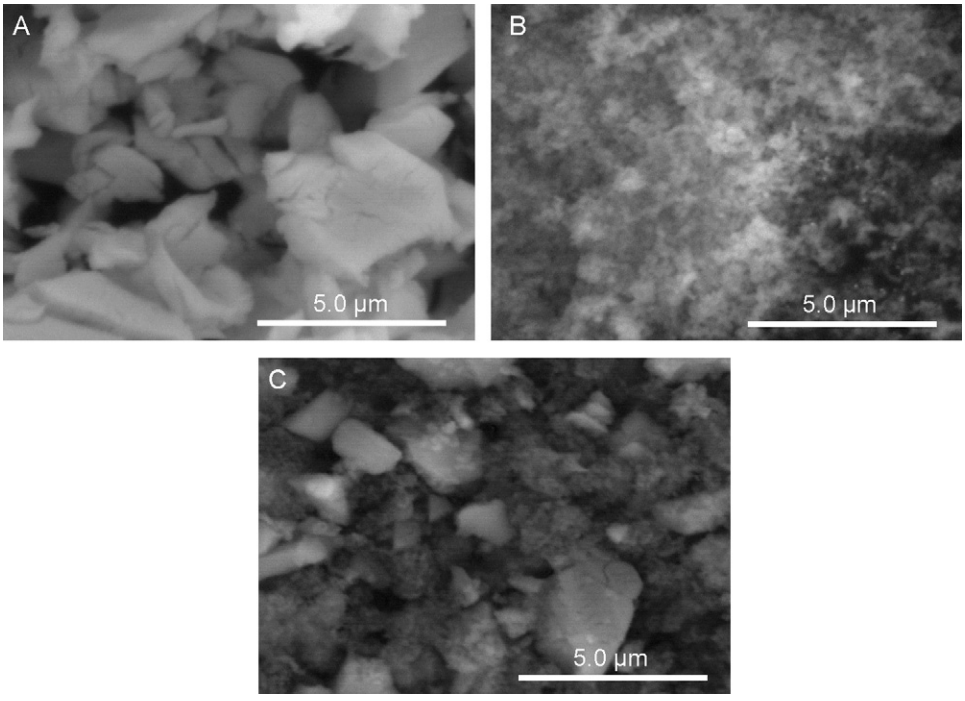

Fig. 1. Microstructures of powders after milling for 16 h: (A) Y_2O_3, (B) Al_2O_3 and (C) YAG batch.

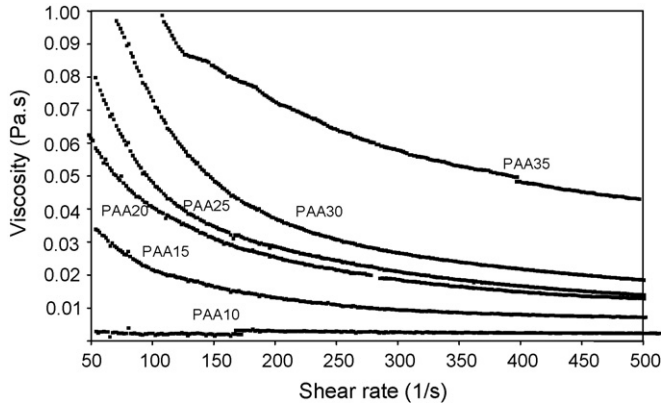

Fig. 2. Viscosity as a function of shear rate of alumina and yttria co-dispersions as a function of dispersant concentration (pH 7–8).

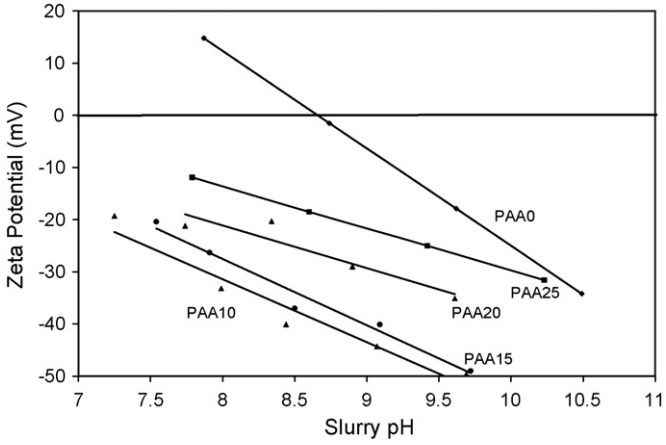

Fig. 3. Zeta potential of alumina and yttria co-dispersions as a function of slurry pH and PAA concentration.

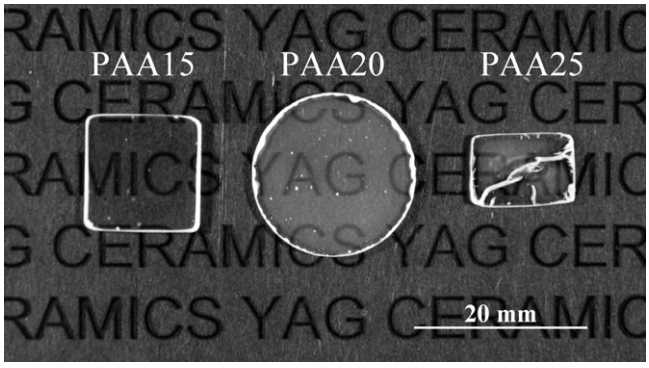

Fig. 5. Variation of transparency of 1 mm thick PAA15, PAA20 and PAA25 YAG samples.

[13–16], and the expectation that both oxide surfaces will contribute to the overall average charge of the oxide composite, an apparent zeta potential behavior can be followed. In the absence of PAA, the higher apparent yield stress indicates that the two oxide powders agglomerate. Consequently, an apparent isoelectric point for the co-dispersed oxide powders occurs at pH 8.75 [13,14,16].

The pK_a of PAA (dispersant) is ∼4.3 [18] and the pH of the freshly prepared slurry was between 7 and 8. Within this pH range, the PAA carboxyl (–COOH) pendant groups will be hydrolyzed or at least partially dissociated into carboxylate (COO^-) ions. Addition of 0.1 wt.% PAA (PAA10) showed the maximum absolute zeta potential. The fact that the zeta potential shifted into the negative region indicates that the anion from the dissociated PAA was specifically adsorbed on the surface of the particles. Further increase in the dispersant concentration led to a decrease in the zeta potential. These observations suggest that at a PAA concentration of 0.1 wt.%, the adsorbed polymer layer is close to monolayer coverage of the dispersed alumina and yttria particles at 20 vol.% solid loading.

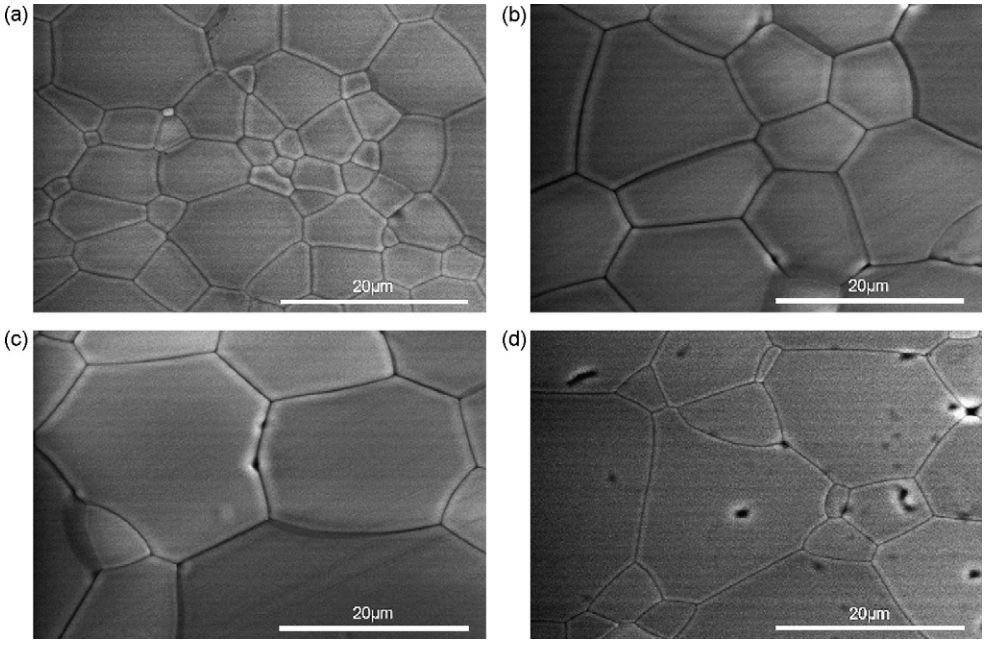

Fig. 4. Micrographs of sintered YAG prepared by slip casting samples containing: (a) 0.1 wt.% PAA, (b) 0.15 wt.% PAA, (c) 0.20 wt.% PAA and (d) 0.25 wt.% PAA.

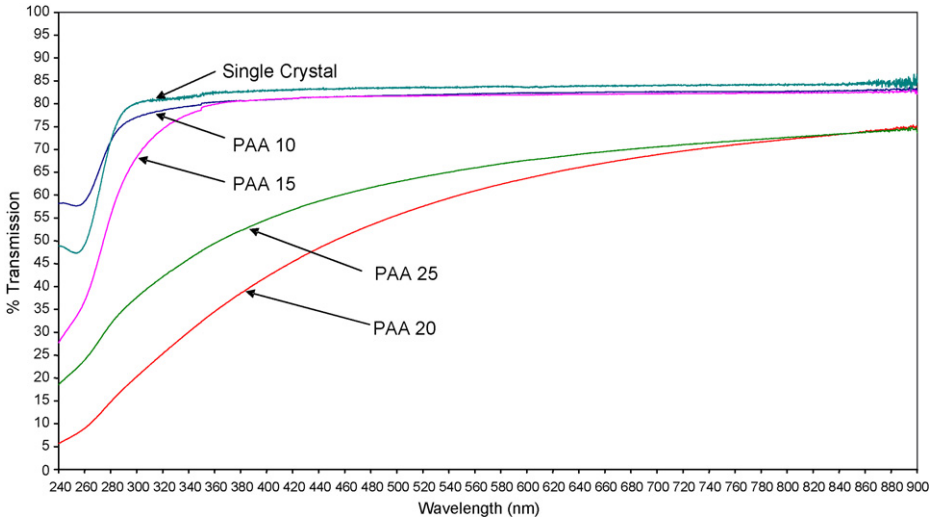

Fig. 6. In-line transmission of 1 mm thick YAG samples slip cast PAA samples and single crystal YAG.

At any specific pH the zeta potential decreases as the dispersant concentration increases. Dispersant concentration of 0.1 wt.% PAA gave the most stable and Newtonian slurries. The bulk density decreased from 58.5% for PAA10 to 51.2, 48 and 45.8% for PAA15, PAA20 and PAA25, respectively. These data correlate to the decrease in the absolute zeta potential of the dispersion zeta potentials (Fig. 3).

Fig. 4 shows the microstructures of the YAG specimens sintered at 1800 °C for 16 h. After sintering the samples were gray due to oxygen defects caused by sintering in vacuum [19]. The specimens were heat treated at 1400 °C in air to remove the gray color and to obtain transparent and translucent samples shown in Fig. 5. Fig. 4a is a specimen obtained from well-dispersed slurry prepared with a dispersant concentration of 0.1 wt.% (PAA10). Generally, it was observed that well-dispersed Newtonian slurries gave very homogeneous green bodies like the transparent sample shown in Fig. 5. The best dispersed sample (PAA10) was ∼100% dense. The PAA15 and PAA samples are 99.3–98.3% dense, respectively. Specimens made from non-Newtonian slurries were only translucent as a result of residual pores after sintering which act as scattering centers as shown in Fig. 5. To better visualize the scattering sites the images in Fig. 5 were obtained by shining white light on the samples placed on a black background. Scatter sites (i.e., pores in this case) cause the foggy appearance. The blackness of the PAA15 clearly shows the much lower concentration of pores relative to PAA20 and PAA25.

The in-line transmission of the sintered samples is shown in Fig. 6. Samples cast from Newtonian YAG suspensions had >80% transmission and were comparable to YAG single crystal grown by the Czochralski method. The YAG transmission, in agreement with the appearance of the samples in Fig. 5, decreases significantly as the slurries become non-Newtonian.

4. Conclusion

Transparent YAG ceramics were fabricated by aqueous slip casting of PAA dispersed slurries composed of a mixture of high purity oxide powders. The lowest dispersant concentration (PAA10) gave stable Newtonian suspensions. As the dispersant concentration increased the suspensions became less stable and become weakly flocculated and non-Newtonian. The transparency of the final product depended on the degree of slurry dispersion. Well-dispersed Newtonian suspensions gave YAG with good visual transparency whereas slightly flocculated, non-Newtonian suspensions gave products that were visually translucent. The in-line transmittance of the YAG products obtained from well dispersed, Newtonian slurries were >80% and comparable to YAG single crystals grown by the Czochralski technique.

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