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YAG ceramic processed by slip casting via aqueous slurries

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Abstract

Stable YAG ($Y_3Al_5O_{12}$) aqueous slurry with ammonium polyacrylate (NH_4PAA) polyelectrolytes as dispersant was prepared by ball mill method. The effects of polyelectrolyte concentration and pH value on the stability of the suspension is described here, and the stability maps are constructed at different pH value and polymer concentration. The rheological behavior of YAG slips of different solid loading (60–70%) has been studied by measuring their viscosity and shear stress as a function of shear rate and pH of the slurry. An optimal amount of dispersant and pH value for the suspension was found. YAG suspension displays a maximum in zeta potential values and a minimum viscosity in pH range of 9–11. Slips behaved as near Newtonian at the pH value up to a solid loading of 60 wt% and as non-Newtonian with thixotropic behaviors above this solid loading value. The density and the green as well as sintered microstructure of the cast products bear a direct relationship to the state of this slips induced by the alternation in the pH and the concentration of the dispersant as well as solid loading.

Keywords: Slip casting; Sintering; Microstructure; YAG; Polyelectrolytes; Aqueous dispersion; Viscosity; Zeta potential

1. Introduction

Yttrium aluminum garnet ($Y_3Al_5O_{12}$, YAG) is an important ceramic material with promising chemical stability, optical and mechanical properties [1–3]. It can be used as refractory coating for electronic devices and as the host for rare earth doped phosphors and for promising solid state laser. Recently, as an alternative of single crystal YAG, polycrystalline YAG ceramic was given much attention. Since high density and transparency are made possible by synthesizing the YAG powders and using ceramic processing techniques. Polycrystalline YAG also has a potential use as an advanced structural ceramic material because of its good creep resistance. However, previous reports about YAG ceramic forming methods are usually dry-pressing [4], iso-static pressing [5], few work was investigated by using slip casting method.

Slip casting has been proved to be a reliable and simple technology to produce homogeneous and dense green bodies [6,7], especially for multi-component systems or composites. The homogenization and the rheological behavior of the suspensions have been shown to play an important role on the slip casting processing, and in turn, on the microstructure and properties of the final products [8]. A well dispersed slurry can be obtained by choosing a suitable dispersant, a critical concentration of this dispersant and a proper pH value [9]. The dispersant is usually absorbed on the surface of the ceramic particles up to a critical concentration. Beyond this concentration, dispersant remains in solution and the interfaces with the stabilization of the suspensions. The effects of the electrolyte dispersant concentration on the surface charge depended not only on the pH value but also on the concentration and nature of the specifically adsorbing and indifferent ions. A screening effect of dispersant concentration was also observed due to repulsion between charges that were already absorbed, and newly arriving ions [10].

Solid loading also affects the properties of the suspension. In some particle systems, green densities could initially show an increase to a maximum, followed by a decreasing trend with increasing solid loading [11]. A linear increase in packing density with solid loading was also observed in some other suspensions. However no relationship between solids loading and green density was found in other systems.

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Though a number of studies on dry pressing of YAG ceramic are available, little work has been reported on achieving effective stabilization of YAG in an aqueous medium by polyelectrolyte and pH control. In the present study various slip/slurry characterization techniques zeta potential, rheology and viscosity measurement have been used for optimizing the aqueous YAG slips. As a comparison, the microstructure of green and sintered bodied obtained at different conditions is also studied.

2. Experimental procedure

Since the YAG powders are not commercially available, the powder preparation was performed in our laboratory. The YAG powders were prepared by a co-precipitation method, detailed reports see Ref. [12]. The calcined YAG powders were milled in a polythene jar using alumina balls as planetary milling media to improve the particle size distribution for 12 h. The average particle size and the specific surface area were measured to be of 40 nm and 16.5 m^2/g, respectively. In this study, a water soluble polyelectrolyte (ammonium polyacrylate, NH_4PAA) was chosen as a dispersant to prepare YAG slurries.

The phase component and microphotograph of the obtained YAG powder was characterized by XRD and TEM technology. The powders were dispersed in deionised water with continuous magnetic stirring and the pH of the slurry was adjusted to various values ranging from 3 to 12 using HCl for the acidic and sodium hydroxide (NaOH) or ammonia (NH_4OH) solution for the alkaline range, respectively. Zeta potential of 20 wt% solid loaded YAG suspensions (with and without dispersant, i.e., ammonium polyacrylate, NH_4PAA) were measured as a function of pH (in the range of 3–12) via measurement of their electrophoretic mobilities (Zeta potential analyzer, model 1202, M/S Micromeritics, USA). The zeta potential values of the YAG suspensions as a function of NH_4PAA concentration at different pH values were measured. The rheological behavior of YAG slips of different solid loading (50–70%) has been studied by measuring their viscosity and shear stress as a function of shear rate and pH of the slurry (Rotational viscometer, Sear type, Viscotester VT-500, M/s Haake, Germany). Microstructure and phase analysis of the green bodies were carried out by using scanning electron microscopy (FEI QUANTA200). The density of the slip cast tape and sintered bodies measured by helium pycnometry.

3. Result and discussion

Fig. 1 shows the particle size of the as-synthesized YAG powder is about 40 nm.Fig. 2a also shows a minimum in the zeta potential values at pH 10 indicating that the slip is well dispersed at this pH value. At the high pH value of 10, a substantially high ionic strength increases the charge in the liquid phase and reduces the potential difference between the powder surface and liquid medium, resulting in a decrease of the absolute value of zeta potential. As a manifestation of this effect the YAG slips at pH 10 shows a small degree of the flocculation with a slight non-Newtonian behavior.

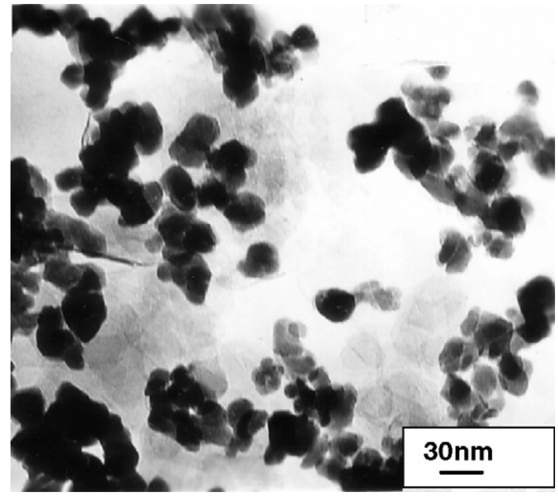

Fig. 1. TEM photograph of the as-synthesized YAG powder by co-precipitation method.

The study of the electro-kinetic behavior through measurement of zeta potential becomes important for understanding the dispersability of ceramic particles in a liquid medium. The zeta potential measured for the prepared YAG powders presented in Fig. 2a.YAG powder has its iso-electric points (IEP) (i.e. the pH at which the net charge on the particle surface is zero) at pH value of 7. Near the iso-electric points (IEP), due to the absence of repulsive forces, the slip gets highly flocculated by Vander Waals forces of attraction between the particles [13]. It also can be seen that a dramatic shift of IEP occurs when the suspension is doped with polyelectrolytes, as is shown Fig. 2b when NH_4PAA (M_w = 10,000) is added (0.5 wt%), the zeta potential becomes more negative and the IEP is displaced towards acidic values, reaching a pH value of 3.0. The apparent difference of curve appearances between pure YAG and those dispersant doped occur in the range of pH 3–7, in which zeta potential becomes more sensitive to pH changes. Obviously, polyelectrolyte NH_4PAA dispersant interacts with ceramic particles in the aqueous suspensions.

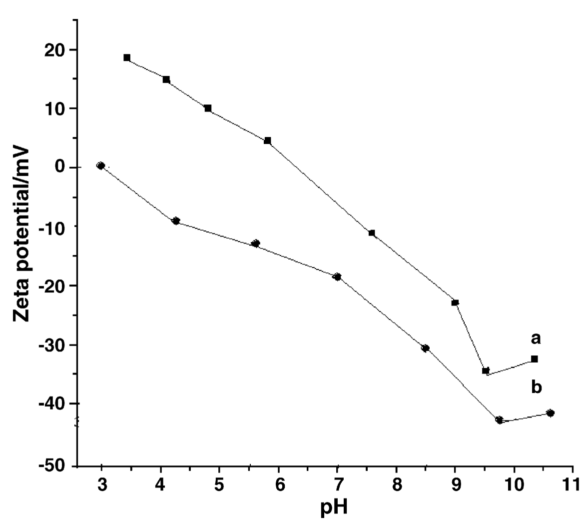

Fig. 2. Zeta potential for the YAG slurry as a function of pH.

Fig. 3 show that the zeta potential of YAG particles in the aqueous suspension as a function of concentration of polyer NH_4PAA at different pH values. At all the pH values, the surface charges become more negative as concentration of NH_4PAA increases, then get a minimum values. For example, at fixed pH 10 the zeta potential of the slurry is about −47 mV when the concentration of NH_4PAA is 1.5 wt%. Yu and Somasundaran [14] reported that at pH 10, NH_4PAA is fully ionized and adsorption is dominated by electrostatic interactions between the ionized sites on the polymer and the surface charged sites on the solid. The zeta potential remains −45 mV or so, though the NH_4PAA concentration increases further in more alkaline region. According to the theory extended by Ohshima [15], the electrophoretic mobility of adsorbed YAG particles is dominated by the charges of the polyelectrolyte layer, which greatly depends on the polyelectrolyte concentration.

Apart from the adsorption and the degree of ionization of the dispersant, the conformation of the ad layer can affect the dispersability. At high pH, the adsorbed dispersant is highly charged with a more stretched conformation, resulting in an increase in the steric length and a strong repulsion of YAG powders. At low pH value, the dispersant chains relax into a highly coiled conformation with a low electrostatic repulsion. This point is in good agreement with our results, i.e., the higher is the pH value, the lager value of the zeta potential. Thus suspensions can be considered stable only in the alkaline pH area up to a concentration of 1.5 wt% of NH_4PAA, is able to decrease the yield stress through an electric effect of the absorbed polymers.

The rheological behavior of YAG–NH_4PAA slips was further studied by measuring the viscosity and shear stress at varying shear rates maintained at different pH values as shown in Figs. 4 and 5. At a pH of 10, the slip (60 wt% solid loading) is nearly Newtonian (linear shear stress versus Shear rate curve passing through the origin) and its viscosity is constant at all shear rates indicating a well dispersed, homogeneous slip. The flow curves at pH 5 show the characteristics of a highly flocculated suspension with a yield stress of about 7 Pa and display a shear thinning behavior. This is because liquid is immobilized in the inter-particulate pore spaces of the flocs and floc network of the suspension, resulting in an increased effective solid loading relative to a well dispersed suspension. On application of a shear stress, shear thinning flow results due to the breakdown of the flocculated structure and the release of entrapped liquid [16]. At a higher pH value of 12, a slight shear thickening behavior (dilatant flow) characteristic of heavy solid loaded suspensions or suspension in which very large inter-particle electrostatic repulsive forces exist, is observed [17].

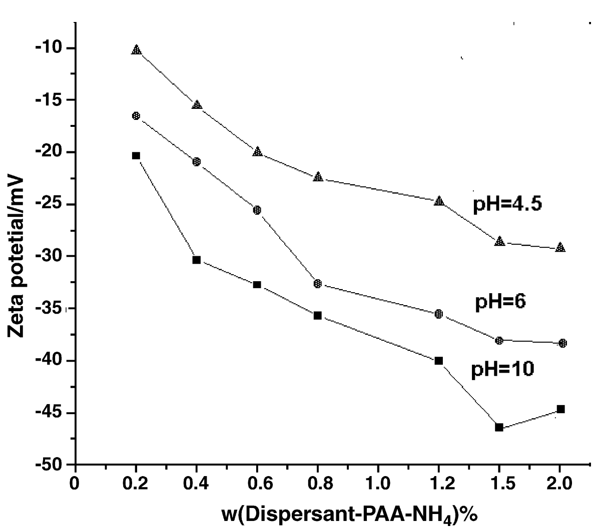

Fig. 3. pH effect on the zeta potentials for the YAG slurry at different NH_4PAA concentrations.

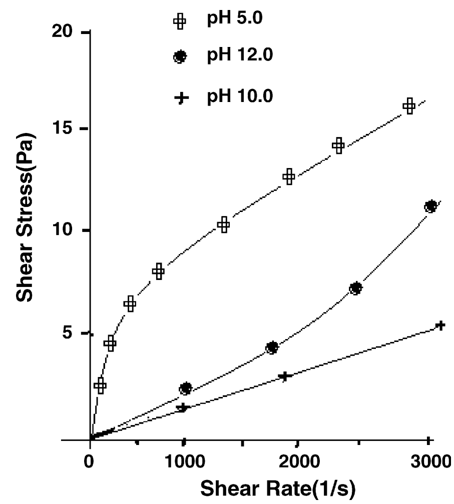

Fig. 4. Shear rate vs. shear stress flow curve for YAG slurry as a function of pH.

Fig. 6 shows that the rheology of suspensions depends on the solid loading (60 wt%) at pH 10. For instance, almost near Newtonian behavior was exhibited at lower solid loading of 60 wt%; whereas shear thickening behavior with thixotropy was observed at solid loading of 65 and 70 wt%. The dilatancy of highly solid loaded suspensions could be attributed to either shear induced flocculation or to a transition from ordered to disordered flow. This effect is more pronounced and occurs at lower shear rates at higher solid loading since the structural changes require less shear energy due to smaller inter-particulate separation on an average [16].

Fig. 7 shows the microstructure of fracture surfaces of green bodies (60 wt%) with different dispersant concentration.

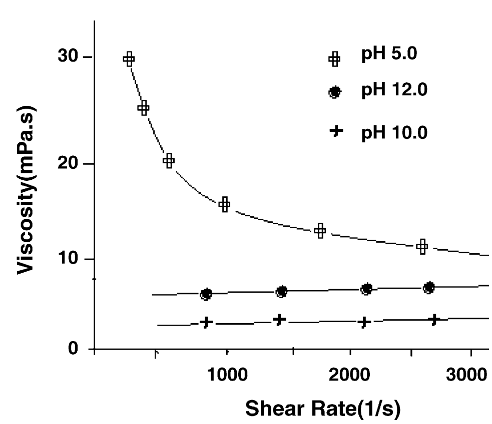

Fig. 5. Viscosity vs. shear rate flow curves for YAG slurry as a function of pH.

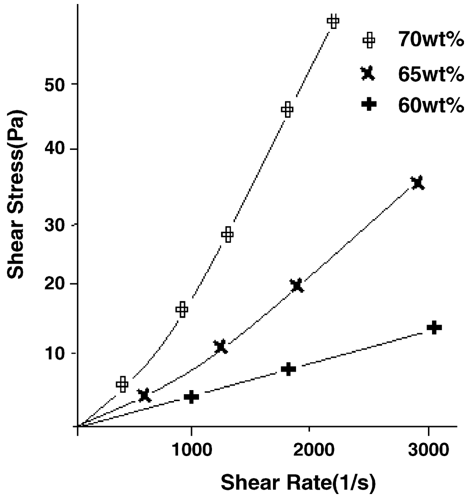

Fig. 6. Shear rate vs. shear stress curves for YAG slurry at pH 10 as a function of solid loading.

Obvious difference in the homogeneity could be observed among these samples. At the intermediate dispersant concentration (1.5 wt%), a well-defined and more uniform microstructure can be observed as is shown in Fig. 7a. Some flocculation among the particles can be observed again when the dispersant concentration increases further. Serious agglomerates and more pores exist in green body sample b, indicating that a amount of the NH_4PAA (0.5 wt%) is not sufficient to disperse correctly the YAG powders.

Slips of YAG powders prepared by dispersing them to different high solid loadings (60 wt%) in deionised water at the optimized pH value of 10 were cast into plaster mould of different shapes to obtain green bodies. The green compacts were vacuum sintering 1600–1750 °C for several hours. The various casting parameters employed, the green density of compacts and the results of vacuum sintering are different. The higher green density of 70% of theoretical value (3.2760 g cm^{-3}) at higher (60 wt%) solid loading at optimum dispersion conditions. The study results also shows that YAG ceramic density reaches the maximum value (4.5488 g cm^{-3}) when the solid loading 60 wt% and the concentration of dispersant is 1.5 wt%. This indicates that the addition of 1.5 wt% of the dispersant into the suspensions with 60 wt% could lead to a green body with smallest pore diameter and more uniform pore size distribution. These results are in good agreement with those of other discussion results above mentioned.

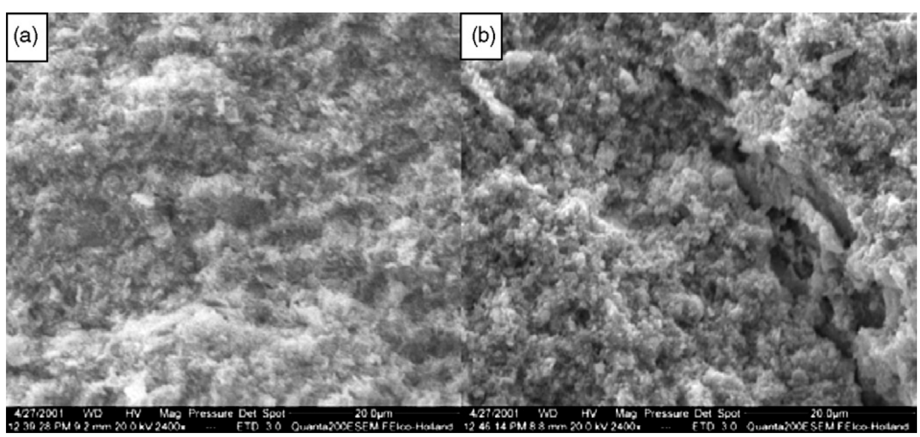

Fig. 7. SEM microphotographs of fracture surfaces of slip cast YAG green bodies of different dispersant concentration: (a) 1.5 wt% and (b) 0.5 wt%.

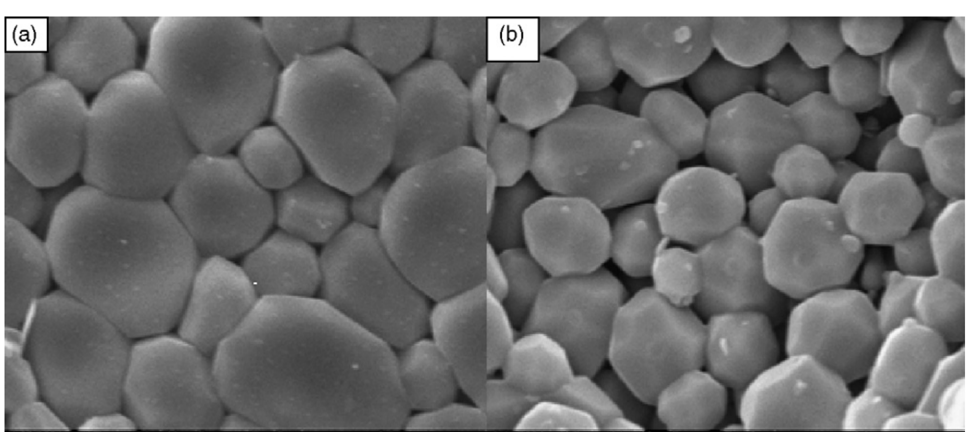

Fig. 8. The microstructures of YAG sintered bodies of different solid loadings at the same dispersant concentration 1.5 wt% and pH 10 (1700 °C for 5 h): (a) 60 wt% and (b) 50 wt%.

Fig. 8 compares the microstructure of slip casting products at different solid loadings heated at 1700 °C for 5 h. The pore size of the sintered sample a prepared is smaller than that sample b. A more uniform pore size distribution can be observed sample a. Therefore, slip casting proves to be a more suitable technique to prepared YAG ceramic with homogeneous microstructure.

4. Conclusion

It is revealed in the present studies that high density and homogeneous microstructure YAG ceramic can be prepared by using slip casting forming method and vacuum sintering technique. The dispersion of YAG powders in deionised water was studied in the pH range of 3–12. The results show that slip is fairly good dispersion in the pH range 9–11. The highest dispersion/deflocculation was observed at pH value of 10, as revealed by a minimum in viscosity and in zeta potential for the slip. PAA-NH_4-suspensions at pH 10 show near-Newtonian behavior up to intermediate solid loadings of 60%, whereas at higher solid loadings they become shear thickening. At the optimum pH value of 10, a 60 wt% solid loaded YAG slip could be slip cast to produce dense and homogeneous microstructure ceramic.

Acknowledgement

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References

[1] K.M. Kinsman, J. Mckittrick, Phase development and luminescence in chromium-doped yttrium aluminum garnet (YAG:Gr) phosphor, J. Am. Ceram. Soc. 77 (11) (1994) 2866–2872.

[2] J.E. Geusic, H.M. Marcos, L.G. Van Uitert, Laser oscillation in Nd-doped yttrium aluminum, yttrium galluim, and gadolinium garnet, Appl. Phys. Lett. 4 (10) (1964) 182–184.

[3] A.H. Chokshi, J.R. Porter, Analysis of concurrent grain growth during creep of polycrystalline alumina, J. Am. Ceram. Soc. 69 (2) (1986) C37–C39.

[4] G.S. Corman, High-temperature creep of some crystal oxides, Ceram. Eng. Sci. Proc. 12 (9–10) (1991) 1745–1766.

[5] A. Ikesue, T. Kinooshita, K. Kamata, et al., Fabrication and optical properties of high-performance polycrystalline Nd:YAG ceramics for solid-state lasers, J. Am. Ceram. Soc. 78 (1995) 1033–1040.

[6] M. Naito, Y. Fukuda, N. Yoshikawa, H. Kamiya, J. Tsubaki, Optimization of suspension characteristics for shaping processes, J. Eur. Ceram. Soc. 17 (1997) 251–257.

[7] Y. Hirata, Theoretical aspects of colloidal processing, Ceram. Int. 23 (1997) 93–98.

[8] F.F. Lange, Powder processing science and technology for increase reliability, J. Am. Ceram. Soc. 72 (1989) 3–15.

[9] R.R. Rao, H.N. Roopa, T.S. Kannan, Effect of pH on the dispersability of silicon carbide powders in aqueous media, Ceram. Int. 25 (1999) 223–230.

[10] B. Dobia, X.P. Qui, W.V. Rybinski, Solid-liquid Dispersions, Marcel Dekker Inc., New York, 1999, pp. 161–163.

[11] L.M.F. Ferreira, M.M.D. Henrique, Effect of solid loading on slip casting performance of silicon carbide slurries, J. Am. Ceram. Soc. 82 (8) (1999) 1993–2000.

[12] X. Li, H. Liu, J.Y. Wang, H.M. Cui, F. Han, Preparation and properties of YAG nano-sized powder from different precipitating agents, Opt. Mater. 25 (2004) 407–412.

[13] M. Persson, A. Forsgren, E. Carlstrom, L.K. Kronberg, Steric stabilization of silicon carbide slips, in: P. Vincenzini (Ed.), High Tech. Ceramics, Elsevier Science Publisher, Amsterdam, 1987, pp. 623–632.

[14] X. Yu, P. Somasundaran, Processing of aqueous $SiO_2$and Al_2O_3 suspension with polyelectrolytes, J. Colloid Interf. Sci. 177 (1996) 283.

[15] K.S. Chou, L.J. Lee, Effect of dispersants on the rheological properties and slip casting of concentrated alumina slurry, J. Am. Ceram. Soc. 72 (1989) 1662–1667.

[16] M.D. Sacks, Properties of silicon suspensions and cast bodies, Am. Ceram. Soc. Bull. 63 (1984) 1510–1515.

[17] F.F. Lange, Powder processing science and technology for increase reliability, J. Am. Ceram. Soc. 72 (1989) 3–15.