A low viscosity slurry system for fabricating chromium doped yttrium aluminum garnet (Cr:YAG) transparent ceramics

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\textbf{Abstract}

We study the dependence of the rheological properties of slurries, as well as hydration reaction of the oxide powders during fabricating the transparent Cr:YAG ceramics out of Al\textsubscript{2}O\textsubscript{3}/Y\textsubscript{2}O\textsubscript{3}/Cr\textsubscript{2}O\textsubscript{3} powders via slip casting shaping and vacuum sintering. We demonstrated that the dispersant can absorbed the Y(III) and Al(III) species that have dissolved in the slurry, absorbed them on the surface of the undissolved oxide powders, and changes the pH and rheological property of the slurry and therefore further affect the process of the slip casting and the sintering of the ceramic. By adopting appropriate dispersants, we obtained Cr:YAG ceramic with average grain size of ∼6.2 μm and in-line transmittance > 84% at 1450 nm after sintering the green samples at 1800 °C under vacuum for 40 h.

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1. Introduction

Polycrystalline YAG ceramic has been generally considered as a multi-functional material superior to the single crystal, as they can be fabricated in a simple but low-cost way, yielding products (single phase or composite) with large size, complex appearance and high doping concentration of ions as activators\cite{1}. In 1995, Ikuesu et al.\cite{2,3} first manufactured the polycrystalline Nd:YAG ceramics via solid-state reaction (SSR) with optical properties and laser performances equal to or even better than Nd:YAG single crystals, shortly after that, Konoshima Corp. manufactured the large-sized (115 × 115 × 22 mm) Nd:YAG ceramics using a different method which includes co-precipitation of high performance YAG nanopowders, slip-casting, and densification by vacuum sintering\cite{4}. Among these techniques, the detail of slip casting were nonetheless barely reported in the literatures by Konoshima Corp. In the slurry, the organic additives, such as dispersants, plasticizers, and binders, as well as the ratios between them, are essential for the slip casting, for the fact that the characteristics of the slurry determine the qualities of both the green bodies and the sintered ceramics\cite{5}. In general, high-quality green bodies for highly transparent ceramics with less pores or defects can only be obtained out of the slurries which simultaneously have low viscosity, high solids loading ratio (SLR), and good dispersibility\cite{6,7}. These requirements can be fulfilled practically by organic additives to prevent agglomeration or coagulation of the ceramic powders due to the attractive van der Waals forces among particles. Some researchers\cite{8,9} used poly (acrylic acid) and NH\textsubscript{4}PAA as dispersants for the commercial Al\textsubscript{2}O\textsubscript{3} and Y\textsubscript{2}O\textsubscript{3} powders, and fabricated transparent YAG and Nd:YAG ceramics by slip-casting, respectively. Jia et al.\cite{10} has also obtained high SLR suspensions consisting of the Al\textsubscript{2}O\textsubscript{3} /Y\textsubscript{2}O\textsubscript{3} /Nd\textsubscript{2}O\textsubscript{3} powders with Dispex A as dispersant of which main ingredient was polycarboxylic acid ammonium. However, these studies failed to take into account the hydration reaction of the oxide powders in the slurry. Some previous works\cite{11,12} revealed that yttria powders became hydrate as water molecules are physically absorbed onto their surface, and they dissolve to produce trivalent yttrium cations and hydroxo complexes. Moreover, the yttria slurry keeps aging when blended, as the rapid increase in its viscosity, which has been well demonstrated in binary suspensions of yttria–slica and of yttria–alumina\cite{13,14}. Mehrdad et al.\cite{14} reported the effect of hydroxylated benzoic acid monomers on the stability of binary yttria–alumina aqueous colloidal suspension, the results showed that the dispersibility of hydroxylated benzoic
is larger than that of poly(methacrylic acid) salt. The reason is that it is hard for benzoic acid to absorb the ions in the slurry, therefore one should take into account the effect of hydrolytic oxide when choosing the dispersants. Whereas, we found that the dewatering process is very slow during the forming of green-body from the dispersive yttria–alumina slurry, although adopting hydroxylated benzoic acid as dispersant can effectively disperse the binary aqueous colloidal suspension. The slow absorption process can easily separate the \(\text{Al}_2\text{O}_3\) and \(\text{Y}_2\text{O}_3\) particles from the binary slurry system during casting slurry, leading to ingredients mismatch in the green body.

In this work, we investigated the effect of both various dispersants and the hydration reaction of oxides on the rheological properties of the slurries and, consequently, on the quality of both the resulted green bodies and sintered ceramics. It is found that the adoption of Dolapix CE64 together with glycine as additives with appropriate dosage can result in slurry with low viscosity, short-time casting, and green body of high density, all of which are beneficial to the realization of impurity-free transparent ceramics with fine microstructure.

2. Experimental procedure

Submicron (0.1–0.3 \(\mu\text{m}\)) \(\alpha\)-\(\text{Al}_2\text{O}_3\) powder (Sumitomo Corporation, purity > 99.99%), micron (2–6 \(\mu\text{m}\)) \(\text{Y}_2\text{O}_3\) powder (Jiangyin Jiahua Material Resources Co., Ltd., China, purity > 99.99%) and micron (average size 5 \(\mu\text{m}\)) \(\text{Cr}_2\text{O}_3\) powder (Alfa Aesar, purity > 99.995%) were used as starting materials. 0.2 wt.% CaO (Alfa Aesar, purity > 99.999%) was used as a sintering aid. Dolapix CE64 (Zschimmer & Schwarz Chemical Co., Ltd.), 2,3-dihydroxybenzoic acid (Acros Organics) and citric acid (Aladdin Industrial Inc., China) were used as dispersants. Glycerine (Aladdin Industrial Inc., China) was plasticizer. The oxide powders were mixed with respect to the expected chemical composition and ball-milled in de-ioned water with different dispersants. The starting \(\text{pH}\) of the aqueous solutions was adjusted to 8.5 by instilling ammonia water. The as-obtained dispersive slurries were slip cast and then dried in a gypsisiferous mold to obtain the desired shape, followed by extra drying in air at 50 °C and subsequent heating at 800 °C for 5 h to burn out the organic compound. The as-obtained green bodies were then vacuum sintered for different hours under various temperatures. After being annealed and mechanically polished, the high quality transparent 0.5 at.% Cr:YAG ceramics were obtained.

During ball-milling, samples of slurry, of which each volume is 3 ml, were taken out at given time points, each with specific time interval, and then centrifuged, the concentrations of residual metal ions and dispersant in the supernate were detected by the Ultima2 ICP optical emission spectrometer and IR spectra. The \(\text{pH}\) values and the viscosities of the slurries were measured by using a digital \(\text{pH}\) meter (PHS-3E, Precise scientific instrument Corp, Shanghai) and a rotary viscometer (LVDV-II+ PRO, Brookfield, USA), respectively, while the Zeta electrical potential was measured by ZS90 (Malvern, UK). Morphology observation was performed on a JSM-6700F field emission scanning electron microscope (FE-SEM, JEOL, Japan). High-resolution TEM (HRTEM) images were taken by using a JEOL JEM-2010 transmission electron microscope. XRD patterns were recorded by using a Rigaku Dmax2500 X-ray diffractometer. The density was measured by the Archimedes method, using ethyl alcohol as the immersion medium. The in-line transmittance was obtained by using a UV/Vis/NIR spectrophotometers (Lambda-900, PerkinElmer, USA).

3. Results and discussion

During the process of slip-casting, except for the choosing of dispersions, we should also take into account the reaction between water and the raw materials, because such reactions may affect the properties of slurry during the ball-milling. In this work, Dolapix CE64 was chosen as a representative dispersant, and the ratio of Dolapix CE64 to the oxide powders was 0.8:100. The slurry was ball-milled and investigated. Fig. 1 shows the change in viscosity and \(\text{pH}\) of the solution subjected to ball-milling at different time point. For \(\text{Al}_2\text{O}_3\) slurry, at the shear rate of 14.68 s\(^{-1}\), with increasing ball-milling time, the viscosity increases slightly from 8.55 mPa s to 11.21 mPa s, and the \(\text{pH}\) almost keeps constant around 9.2; whereas for the \(\text{Al}_2\text{O}_3–\text{Y}_2\text{O}_3\) binary system, both the viscosity and the \(\text{pH}\) keep raising during ball-milling: the viscosity increases nearly linearly from 350 mPa s to 850 mPa s while the \(\text{pH}\) raises from 8.5 to 10.5. Note that the increase in \(\text{pH}\) gradually slows down and becomes stable when \(t > 20\) h, indicating that by the time the system has come to the equilibrium. It is known that the adsorption of \(\text{H}_2\text{O}\) molecule on the surface of \(\text{Y}_2\text{O}_3\) could lead to the formation of \(\text{Y}_2\text{O}_3\text{(H}_2\text{O)}\) or \(\text{YOH}\)-like species, and then generate \(\text{Y(OH)}_3\). So the predominant dissolving ions are mainly \(\text{Y}^{3+}, \text{YO}^-, \text{and OH}^-\). Therefore, the slow but progressive hydration of \(\text{Y}_2\text{O}_3\) would raise the \(\text{pH}\) of the system. However, \(\text{Al}_2\text{O}_3\) is an amphoteric oxide, which means its reaction with water would not significantly affect the \(\text{pH}\) of the system. On the other hand, the dispersant, Dolapix CE64, is mainly polycarboxylic acid that totally dissociated above \(\text{pH}\) 9, which carboxylic sites could easily combine with the positive charges of yttria dissolving in solution (e.g., \(\text{Y}^{3+}, \text{YO}^+, \text{and Al}^{3+}\)). At the same time, Dolapix CE64 could be gradually adsorbed on the surface of oxides particles during the ball-milling process. Therefore, the particle surfaces are coated with multivalent cations, resulting in the formation of a relatively thin electrical double layer and further decreases the repel force of granule interaction, which alters the suspension stability and increases the viscosity of the slurry solution for \(\text{Al}_2\text{O}_3–\text{Y}_2\text{O}_3\) binary system, as shown in Fig. 1(b). This proposed presumption can be confirmed by the
variation of the zeta potential of the binary yttria–alumina aqueous slurries with ball-milling time. As shown in Fig. 1(c), the surfaces of the powder particles were negatively charged, and the absolute value of the Zeta potential decreases with the ball-milling time, which can be ascribed to the combination of dissolved cations with organic molecules that adsorbed on the surface of the oxides particles. On the other hand, for \( \text{Al}_2\text{O}_3 \) slurry, the amphoteric nature of \( \text{Al}_2\text{O}_3 \) depresses the formation of thin electrical double layer, while Dolapix CE64 can effectively disperse the alumina powder in aqueous solution. As a result, the viscosity was limited and high fluidity was presented, as shown in Fig. 1(a).

Fig. 2 shows the dependence of dissolved Y(III) (as mentioned previously, in the form of \( \text{Y}^{3+} \) or \( \text{YO}^+ \)) and Al(III) (e.g., \( \text{Al}^{3+} \) or \( \text{AlO}_2^- \)) species in the slurry on ball-milling duration. At short ball-milling time, the concentration of Y(III) and Al(III) is high, which indicates that the oxides such as \( \text{Al}_2\text{O}_3 \) and \( \text{Y}_2\text{O}_3 \) do react with water. Whereas, the concentrations of Al and Y elements in the solution both decline dramatically to \( \sim 1 \) ppm right after the 8-hour ball-milling, which may be ascribed to the absorption by the dispersant, as mentioned above.

In Fig. 3, the IR spectra indicates the variation in concentration of Dolapix CE64 dispersant in the supernates, which we obtained by centrifuging the slurries taking at different ball-milling duration. The ceramics’ phases YAP, YAG, YAM, YAP, YAG, YAM, YAP, YAG, YAG, and their initial pH values were invariably adjusted to 8.50 by adding ammonium hydroxide, and then the slurries were ball-milled for 20 h. As shown in Table 1, in terms of pH and viscosity, 2,3-dihydroxybenzoic acid and citric acid, used in sample 1–3 as dispersants, are functioning well both in dispersing particles in water and in limiting the fluctuation in pH of the slurry (for these there sample, the viscosities were as low as about 4 mPa·s at the shear rater of 14.68 s\(^{-1}\), while the pH values were increased slightly from 8.50 to 9.12–9.35), whereas when 0.5 wt.% Dolapix CE64 and 0.2 wt.% glycerine were respectively employed as dispersants with different dosages into the mixture of oxides of 0.5 at.% Cr:YAG, as listed in Table 1.

In order to investigate the effect of dispersant on the rheological property of the precursor of 0.5 at.% Cr:YAG, several dispersers with different dosages were employed into the blended oxides slurries respectively, and the experimental results were listed in Table 1 and Fig. 4. For a clear comparison, the solid content for all the five group of slurries (see Table 1) was set to be 50 wt.\% invariably, and their initial pH values were invariably adjusted to be 8.50 by adding ammonium hydroxide, and then the slurries were ball-milled for 20 h. As shown in Table 1, in terms of pH and viscosity, 2,3-dihydroxybenzoic acid and citric acid, used in sample 1–3 as dispersants, are functioning well both in dispersing particles in water and in limiting the fluctuation in pH of the slurry (for these there sample, the viscosities were as low as about 4 mPa·s at the shear rater of 14.68 s\(^{-1}\), while the pH values were increased slightly from 8.50 to 9.12–9.35), whereas when 0.5 wt.% Dolapix CE64 and 0.2 wt.% glycerine were respectively employed as dispersants with different dosages into the mixture of oxides of 0.5 at.% Cr:YAG, as listed in Table 1.

<table>
<thead>
<tr>
<th>Samples’ serial number</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dispersants</td>
<td>A</td>
<td>B</td>
<td>B + C</td>
<td>C + D</td>
<td>C + D</td>
</tr>
<tr>
<td>Content of dispersants (wt.%)</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5 + 0.5</td>
<td>0.5 + 0.2</td>
<td>1 + 0.2</td>
</tr>
<tr>
<td>Viscosity (mPa·s)/shear rater: 14.68 s(^{-1})</td>
<td>3.65</td>
<td>4.30</td>
<td>4.00</td>
<td>839.8</td>
<td>3.60</td>
</tr>
<tr>
<td>pH value</td>
<td>9.12</td>
<td>9.26</td>
<td>9.35</td>
<td>10.50</td>
<td>10.53</td>
</tr>
<tr>
<td>Time of casting process (h)</td>
<td>1.2</td>
<td>1.5</td>
<td>1.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>Green density (%)</td>
<td>39.87</td>
<td>38.05</td>
<td>38.35</td>
<td>33.25</td>
<td>41.68</td>
</tr>
<tr>
<td>The ceramics’ phases</td>
<td>YAP,YAG</td>
<td>YAG,YAM YAP</td>
<td>YAG,YAM YAP</td>
<td>YAG</td>
<td>YAG</td>
</tr>
</tbody>
</table>

* A 2,3-dihydroxybenzoic acid, B citric acid, C Dolapix CE64, D glycerine; the chemical composition for any of the five samples was 0.5 at.% Cr:YAG.
Fig. 4. Dependence of viscosity on shear rate for samples 1–5.

Fig. 5. XRD patterns of the samples sintered under 1800 °C without holding time.

For samples 1–3, it took about 1.2–1.5 h to yield green ceramics with the size of Ø30 mm × 5 mm via slip-casting, whereas, for the samples 4–5, it takes only ~0.5 h. It is also found that the densities of green bodies fabricated out of low-viscosity slurry, i.e., the samples 1–3 and 5, are obviously larger than that of the sample 4 (shaped from high viscosity's slurry). In other words, the
Table 2
Quantitative EDS analysis of the polished surface of the samples sintered at 1800 °C without holding time.

<table>
<thead>
<tr>
<th>Atom (%)</th>
<th>Y</th>
<th>Al</th>
<th>Y:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>22.15</td>
<td>18.32</td>
<td>3:2.5</td>
</tr>
<tr>
<td>Spectrum 2</td>
<td>23.32</td>
<td>20.54</td>
<td>3:2.6</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>17.18</td>
<td>24.47</td>
<td>3:4.3</td>
</tr>
<tr>
<td>Spectrum 4</td>
<td>16.28</td>
<td>20.82</td>
<td>3:3.8</td>
</tr>
<tr>
<td>Spectrum 5</td>
<td>13.79</td>
<td>17.47</td>
<td>3:3.8</td>
</tr>
<tr>
<td>Spectrum 6</td>
<td>16.80</td>
<td>24.85</td>
<td>3:4.4</td>
</tr>
</tbody>
</table>

species and amounts of the dispersants have a great influence on both the casting time and density of the green ceramics. Generally, time-consuming casting process is unfavorable. As we known, different raw materials in the slurry, such as Al₂O₃ and Y₂O₃ in this work, have different densities, particle sizes and shape. Therefore, nonuniform sediment occurs inevitably during the slip-casting process. The local mismatch in the Y:Al ratio will lead to the generation of impure phases, which was demonstrated by XRD observation.

Fig. 5 shows the XRD patterns of the five samples sintered at 1800 °C without holding time. Obviously, impurity phases such as YAP and YAM were observed apart from YAG phase for samples 1–3, while bare YAG phase was detected for samples 4 and 5. It is further found that the impurity phases in samples 1–3 could not be eliminated entirely even these samples were sintered under 1800 °C for 40 h (XRD results were not shown here).

Fig. 6 shows the surface morphologies of the samples sintered at 1800 °C without holding time. For samples 4 and 5, the average grain size was about 2 μm, and all the grains were growing regularly and uniformly, whereas in Sample 1–3, abnormal grain growth was observed. For example, irregular grains with size far larger than that of the other grains were observed in sample 1, and point-like projections and recesses were common found in sample 2 and 3. The abnormal grain growth for these three samples may be resulted from the local composition mismatch, as mentioned above. In order to identify the chemical compositions of these irregular grains, EDS analysis was performed. The detected areas were labeled in Fig. 6(a, b) and the results were listed in Table 2. For the micro-areas labeled 1–3 in sample 1 (i.e., spectra 1–3 in Fig. 6(a)), the ratios of Y to Al were 3:2.5, 3:2.6, and 3:4.3, respectively. Obviously, the former two were closer to that of YAlO₃ (YAP) while the later one was closer to that of Y₃Al₅O₁₂ (YAG), indicating the chemical composition of the irregular and regular grains might be YAP and YAG, respectively. Similarly, the chemical composition of the abnormal grain can be attributed to the minor amount of YAP phase, rather than the major phase of YAG. In other words, the EDS analysis confirmed that the abnormal grain growth was caused by the local composition mismatch, which was consistent with the XRD results.

These samples were further studied by the 40-hour-vacuum-sintering the green ceramics at 1800 °C. For samples 1–3, the minor phase of YAP cannot be fully eliminated, and their density was lower than 99.2%, whereas, the density was about ~100% for both samples 4 and 5. Only sample 5 was further studied, due to the analogue under high-temperature sintering for samples 4 and 5. However, for the sample 4, excessive slurry viscosity is harmful for forming green bodies. Fig. 7(a) shows the FESEM image of the sample 5 that sintered at 1800 °C for 40 h. No pores, defects or impurity phase can be detected. The grains were clean and the grain boundaries were clear. The distribution of particle size was narrow and the average grain size was about 6.2 μm. The typical HRTEM image, as shown in fig. 7(b), indicates fine crystallinity without defects such as dislocation or deformation twin. A set of lattice fringe with spacing of 0.316 nm were observed, which matches the (321) facet of YAG phase well. Besides, (024), (332) facets were also observed, as shown in the FFT image. The uniform microstructure without pores, impurity phases and defects can significantly reduce the scattering losses in the ceramic and thereby ensures high transmittance of the sample.

Figs. 8 and 9 shows the photograph and transmittance spectra of the sample 5 (0.5 at.% Cr:YAG ceramic with a thickness of 3 mm) sintered under vacuum at 1800 °C for 40 h, respectively. After the long-time sintering, highly transparent ceramic was obtained. The color was green, and the optical transmittance attained to 84.64% at the wavelength of 1400 nm. By annealing in oxygen atmosphere at
1400 °C for 10 h, the optical transmittance kept nearly unchanged at 1400 nm, but declined significantly as the wavelength was less than 700 nm and an additional broad absorption peak located at 1030 nm was observed. The changes in color and transmittance spectra are mainly caused by the valence variation of Cr cation from 3+ to 4+ during annealing. The absorption band in the 800–1200 nm spectral region is more likely to caused by the $^3B_1(^3A_2)→^3A_2, (^3T_1)$ transition than by the $^3B_1(^3A_2)→^3E(^2T_2)$ transition [15].

4. Conclusion

Pore-free and fully dense Cr:YAG transparent ceramics were successfully fabricated from the slurry comprising commercial $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3/\text{Cr}_2\text{O}_3$ powders via the slip-casting and, the sintering at 1800 °C for 10 h, the optical transmittance kept nearly unchanged at 1400 nm, but declined significantly as the wavelength was less than 700 nm and an additional broad absorption peak located at 1030 nm was observed. The changes in color and transmittance spectra are mainly caused by the valence variation of Cr cation from 3+ to 4+ during annealing. The absorption band in the 800–1200 nm spectral region is more likely to caused by the $^3B_1(^3A_2)→^3A_2, (^3T_1)$ transition than by the $^3B_1(^3A_2)→^3E(^2T_2)$ transition [15].

to less local mismatches and impurity phases, thereby obtaining high transmittance transparent ceramic after sintered at appropriate temperature. The average grain size is 6.2 μm after 40-hour sintering at 1800 °C, without defects spotted and the in-line transmittance exceeds 84% at 1400 nm.

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