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Effects of Sintering Aids (Y^{3+}, La^{3+} and Mg^{2+}) on the Optical Transmittance of Translucent Alumina Ceramics

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Abstract: Translucent Al_2O_3 ceramics were prepared by vacuum sintering using Y^{3+}, La^{3+} and Mg^{2+} as sintering aids which were introduced *via* chemical precipitation. Effects of the sintering aids on microstructure, relative density and optical transmittance of the translucent Al_2O_3 ceramics were investigated. The results show that the sintering aids are homogeneously dispersed in translucent Al_2O_3 ceramics. The optimal amount of the sintering aid introduced is Mg^{2+} (0.15wt%), Y^{3+} (0.05wt%) and La^{3+} (0.05wt%), and the corresponding sample shows the highest total forward transmittance (above 80% in the wavelength range of 350–800 nm). Moreover, the addition of Y^{3+} could promote grain growth and decrease porosity, thus the optical transmittance of the translucent Al_2O_3 ceramics is enhanced.

Key words: translucent alumina ceramics; chemical precipitation; sintering aids; optical transmittance

Inspired by Coble's pioneering work on translucent Al_2O_3 ceramics in the 1960s[1], the optical properties of transparent (translucent) alumina ceramics have attracted wide attention due to their potential application in the field of high-pressure sodium lamps, metal-halide lamps, transparent armor, *etc*[2-5]. For example, the mid-infrared transmittance of transparent Al_2O_3 ceramics prepared by spark plasma sintering reaches 85%; The Al_2O_3 ceramics synthesized by Krell, *et al*[2] show a real in-line transmission (RIT) of 55%–65%[3]. However, the optical transmittance of Al_2O_3 ceramics is still far from the requirements of practical application. In order to achieve high transmittance, various methods have been employed to restrain abnormal grain growth and minimize pores formed in translucent Al_2O_3 ceramics during preparation process[6-8].

It is reported that sintering aids have significantly effects on grain size and porosity of transparent (translucent) Al_2O_3 ceramics[9-10]. Generally, MgO and rare earth oxides (Y_2O_3, La_2O_3, ZrO_2, *etc*.) are widely used as sintering aids to optimize grain size, eliminate pores and improve optical transmittance of Al_2O_3 ceramic. In the process of ceramic sintering, MgO plays a role of suppressing grain-boundary migration[11-12]. Rare earth oxides could improve mechanical properties and corrosion resistance of Al_2O_3 ceramics[13]. Moreover, co-doping could increase the solubility of MgO or decrease the evaporation of MgO during sintering process[14-16]. In addition, the dispersibility of these dopants also affects the optical transmittance of the prepared transparent Al_2O_3 ceramics[17-18]. Liu, *et al*[4] found that dopants are more homogeneously dispersed when they were introduced by chemical precipitation compared with conventional ball milling.

Optical transmittance of alumina ceramic is significantly affected by sintering aids and the introduction methods of these sintering aids. Therefore, in this work, translucent Al_2O_3 ceramics were synthesized by vacuum sintering using Y^{3+}, La^{3+} and Mg^{2+} as sintering aids which were introduced *via* chemical precipitation. The effects of the sintering aids on microstructure, densities and optical transmittance of the prepared Al_2O_3 ceramics were investigated.

1 Experimental

Al_2O_3 powder (Aladdin, 30nm, 99.999%) and 2wt% polyethylene glycol 2000 (PEG-2000, Aladdin, 99.99%) were mixed and ultrasonically dispersed for 1 h to destroy the agglomeration of the Al_2O_3 particles. The precursor solution was prepared by dissolving metal nitrates in the obtained suspension. Subsequently, the sintering aids (in the form of nitrate, Aladdin, 99.99%) were in-

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troduced into the Al_2O_3 powder suspension under stirring at room temperature. The samples and their composition are listed in Table 1.

The addition of MgO and La_2O_3 could produce a small amount of liquid phase to improve the density of alumina ceramic, but the amount of La_2O_3 should be limited because excessive liquid phase results in abnormal grain growth and hinders the migration of pores, therefore, a fixed amount of La^{3+} (0.05wt%) were added according to literature [19]. Then ammonia (0.01 mol/L) was slowly added into the suspension with stirring to adjust the pH value in the range of 9.1–9.5[20-21]. The suspension was further stirred for 1 h. Subsequently, the suspension was filtered to obtain solid particles which were dried in an oven at 50℃ for 8 h. The as-prepared powders were sieved using a 200 mesh screen and granulated with a small amount of polyvinyl acetate, and then the mixtures were uniaxially pressed into plates at 10 MPa. After receiving cold isostatic pressing at 200 MPa for 5 min again, the plates were pre-sintered in air at 600℃ for 5 h to remove the organic ingredients. Finally, the samples were obtained by sintering the pre-sintered plates at vacuum (1×10^{-3} Pa), 1750℃. Figure 1 shows the schematic of the adopted chemical precipitation method.

The total forward transmittance of samples (after double-side polishing to the thickness of 1 mm) was measured on a UV-3150-type ultraviolet visible near-infrared (UV/VIS/NIR) spectrophotometer. The phase was investigated by X-ray diffraction (XRD) on an Ultima IV, in

Table 1 Contents of sintering aids in the obtained samples

Samples	Content of sintering aids / wt%		
	Mg^{2+}	Y^{3+}	La^{3+}
MYL-1	0.15	0	0.05
MYL-2	0.15	0.03	0.05
MYL-3	0.15	0.05	0.05
MYL-4	0.20	0.05	0.05
MYL-5	0.25	0.05	0.05

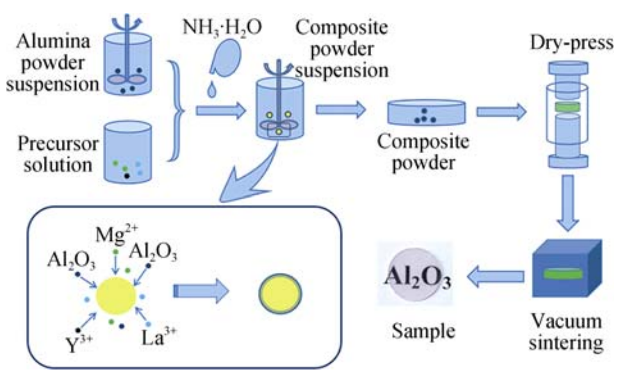

Fig. 1　Schematic and flow chart of the adopted chemical precipitation method

the range of 10°–90° with Cu-Kα radiation, the scanning speed is 8°/min. Microstructure and element distribution were measured by the scanning electron microscope (SEM) equipped with energy dispersive X-ray detector (EDS) with an accelerating voltage of 15 kV. The surface of the samples was polished and then thermally etched for 1 h at 1600℃. The density was measured by Archimedes method. The density (ρ) and relative density (d) of the samples can be calculated by the following formula.

$$\rho = (m_1\times\rho_w)/ (m_3-m_2) \quad (1)$$

$$d=\rho/\rho_0\times100\% \quad (2)$$

Where m_1 is the dry weight; m_2 is the float weight; m_3 is the wet weight; ρ_w is the density of ultra pure water at room temperature; ρ_0 is the theoretical density (3.982 g/cm^3) of alumina ceramics.

All the above measurements were carried out at room temperature.

2　Results and discussion

The relative densities of the prepared samples measured by Archimedes method were MYL-1 (97.89%), MYL-2 (99.13%), MYL-3 (99.62%), MYL-4 (99.46%) and MYL-5 (98.95%). It reveals that relative density of the samples increases with increasing content of Y^{3+}. That is because the co-doping improves the solubility of MgO[14-16], and the dissolved MgO plays a critical role in avoiding pore breakaway and abnormal grain growth so that dense microstructure is obtained[12]. However, When the transparent alumina ceramic is doped with an excess amount of MgO, it will lead to a large amount of discontinuous liquid phase among grain boundaries, resulting in the difficulty of gas escaping out during the sintering process[22]. Therefore, the relative density of the prepared samples decreases with increasing content of Mg^{2+}. With the co-effects of Y^{3+} and Mg^{2+}, MYL-3 (99.62%) has the highest relative density.

Figure 2 shows XRD pattern of the samples. The XRD pattern of all samples shows similar diffraction peaks. These diffraction peaks can be well indexed to the corundum structure, which is the same as the standard card PDF83-2080. The result shows that all samples with different quantities of sintering aids show a single phase and no secondary phase is detected, indicating that the sintering aids have no effect on the main crystalline phase of Al_2O_3.

Figure 3 shows X-ray mapping measurements of Mg, La and Y for sample MYL-5. The existence of the specific doping elements has been well confirmed by their corresponding signals. The sintering aids are uniformly dis

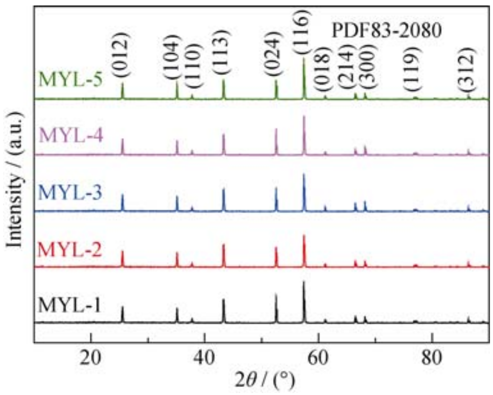

Fig. 2 XRD patterns of the obtained samples

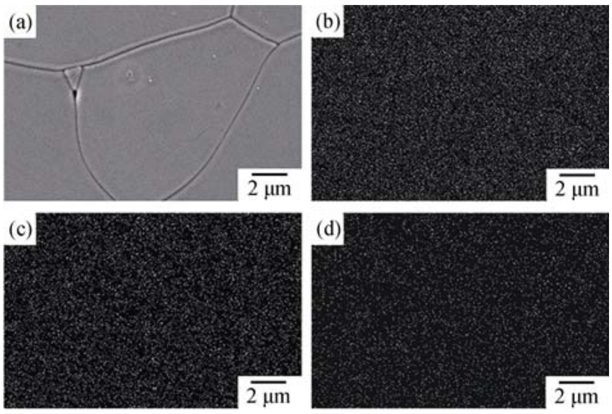

Fig. 3 (a) The surface morphology of sample MYL-5, X-ray mapping of (b) Mg, (c) Y and (d) La for sample MYL-5

persed without agglomeration. Other samples have the similar results. It indicates that the sintering aids can be uniformly dispersed in translucent Al_2O_3 ceramics through chemical precipitation.

Figure 4 presents SEM images of the polished surface of all samples after thermal etching at 1600℃ for 1 h. It can be seen from the figure that the samples with different quantities of sintering aids have different grain sizes. Generally, the grain size increases with increasing content of Y^{3+}. Sample MYL-1 shows grain size of about 8 μm. The grain size of Sample MYL-2 and MYL-3 are about 12 μm and 30 μm, respectively. In addition, with increasing content of Mg^{2+}, the grain size decreases slightly (from sample MYL-3 to sample MYL-5). More information about the grain size and the amount of pores is shown in Fig. 5 which shows SEM photomicrographs of the fracture surface of all samples. Sample MYL-1 (0wt% Y^{3+}) shows a uniform and small grain size (8 μm), with limited pores trapped inside the grains or among grain boundaries. Sample MYL-2 which contains higher content of Y^{3+} varies in grain size (5–30 μm) and traps fewer but bigger pores than sample MYL-1. The grains of sample MYL-3 are uniform in size (25–30 μm) and almost no pores are discovered. Generally, with increasing content of Y^{3+}, the movement of grain boundary and the normal grain growth are promoted, which improves gas escaping rate during sintering process. The grain sizes of Sample MYL-4 and MYL-5 tend to be slightly smaller but still uniform and have more in-grain pores than that of Sample MYL-3. That is because, from Sample MYL-3 to MYL-5, the increasing content of Mg^{2+} leads to excessive liquid phase formed[19], which makes the grains grow too fast and hinders the migration of pores, thus some pores are trapped in grains.

The sintering aids dispersed uniformly in all the obtained samples and no secondary phase is detected. Moreover, the decreased number of boundaries and pores could effectively improve optical transmittance of trans

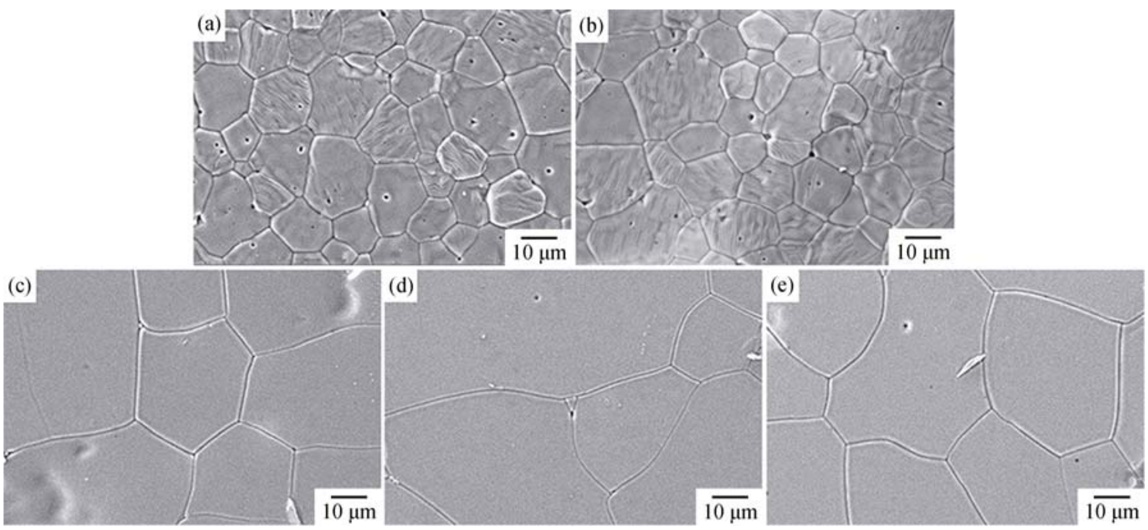

Fig. 4 Surface morphologies of the samples (a) MYL-1, (b) MYL-2, (c) MYL-3, (d) MYL-4, and (e) MYL-5

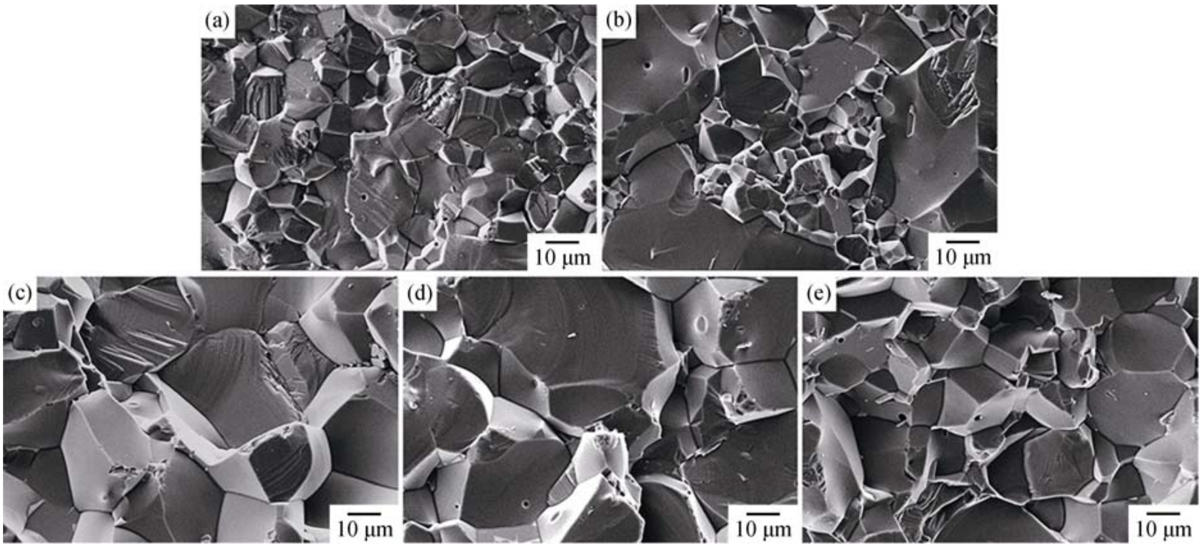

Fig. 5　Fracture surface morphologies of the samples
(a) MYL-1; (b) MYL-2; (c) MYL-3; (d) MYL-4; (e) MYL-5

parent (translucent) ceramics. Therefore, the total forward transmittance (TFT) significantly increases from sample MYL-1 to MYL-3, as shown in Fig. 6 and Fig. 7. However, the TFT decreases from Samples MYL-3 to MYL-5 because more in-grain pores and grain boundaries in sample MYL-4 and MYL-5 are observed (Fig. 6 and Fig. 7). Sample MYL-3 shows the highest TFT which is above 80% in the wavelength range of 350–800 nm. The highest TFT (82.956%) reaches at the wavelength of 482 nm. The results show that the optimal amount of Mg^{2+}, Y^{3+} and La^{3+} in the prepared Al_2O_3 ceramic is 0.15wt%, 0.05wt% and 0.05wt%, respectively.

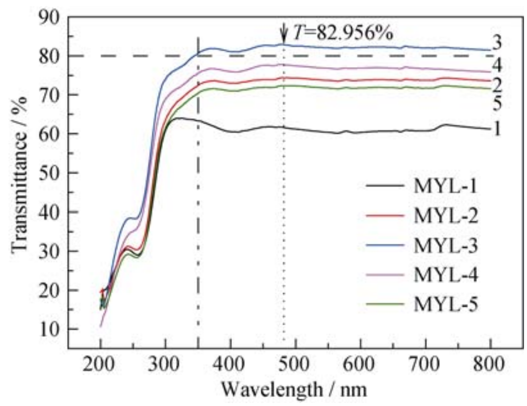

Fig. 6　Total forward transmittance spectra of all samples

Fig. 7　Photograph of all samples
(a) MYL-1; (b) MYL-2; (c) MYL-3; (d) MYL-4; (e) MYL-5

3　Conclusions

Translucent Al_2O_3 ceramics were successfully synthesized by vacuum sintering using Y^{3+}, La^{3+} and Mg^{2+} as sintering aids which were introduced by chemical precipitation. The relative density, phase structures, elements distribution, microstructure and optical properties of the prepared Al_2O_3 ceramics were investigated. The results reveal that the sintering aids are homogeneously dispersed in the translucent alumina ceramics. With increasing content of Y^{3+}, the relative density and grain size increase, the porosity decreases. However, with increasing content of Mg^{2+}, the relative density and grain size decrease slightly and the porosity increases. The optimal amount of the sintering aids introduced is Mg^{2+} (0.15wt%), Y^{3+} (0.05wt%) and La^{3+} (0.05wt%), and the corresponding sample shows the highest TFT (above 80% in the wavelength range of 350–800 nm).

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烧结助剂(Y^{3+}、La^{3+}和 Mg^{2+})对半透明氧化铝陶瓷的透光率的影响

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摘 要: 通过化学沉淀法引入烧结助剂 Y^{3+}、La^{3+}和 Mg^{2+}, 采用真空烧结工艺制备了半透明 Al_2O_3 陶瓷, 并研究了烧结助剂对烧结材料的微观结构、相对密度和透光率的影响。结果表明: 引入的烧结助剂能均匀分散在合成的半透明 Al_2O_3 陶瓷中。烧结助剂的最佳引入量为 Mg^{2+}(0.15wt%)、Y^{3+}(0.05wt%)和 La^{3+}(0.05wt%), 对应的试样在 350~800 nm 的波长范围内显示出的最高的总透光率(TFT)高于 80%。此外, Y^{3+}的掺杂可以促进晶粒生长, 降低孔隙率, 从而提高半透明 Al_2O_3 陶瓷的透光率。

关 键 词: 半透明氧化铝陶瓷; 化学沉淀法; 烧结助剂; 透光率

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