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Effect of La doping on microwave dielectric properties of translucent polycrystalline alumina ceramic

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Abstract

In this paper, the microstructure and microwave dielectric properties of translucent polycrystalline alumina (PCA) with different amounts of La_2O_3 (co-doped with 500 ppm MgO) were investigated. Compared with those doped only with 500 ppm MgO, the translucent PCA co-doped with 500 ppm La_2O_3 exhibited a higher $Q \times f$ value, which might be caused by the significantly larger ionic radius of La^{3+}. As the La_2O_3 content was further increased, the presence of an increasing amount of impurities ($LaAl_{11}O_{18}$) would deteriorate the $Q \times f$ value significantly.

Keywords: B. Grain size; B. Impurities; C. Dielectric properties; D. Al_2O_3

1. Introduction

Translucent (transparent) polycrystalline alumina (PCA) is an important alumina ceramic first discovered by Coble in the 1960s [1]. Since then it has been widely used in high-pressure sodium lamps and metal-halide lamps because of its high thermal resistance and high chemical durability. Meanwhile, many investigations have been carried out with the aim to improve the transparency of PCA, such as adjusting of the sintering additives [2,3] and applying of new sintering technology (e.g. HIP [4,5] and SPS [6,7]). Translucent PCA has also been used as a substrate and RF windows in the fields of vacuum electronics and microwave circuits due to its high purity, high surface smoothness and high thermal conductivity. Unfortunately, few studies have been conducted involving the dielectric properties of translucent PCA. Recently, we investigated the effect of Mg, Zr doping on the microwave dielectric properties of translucent polycrystalline alumina (PCA). The $Q \times f$ value of the translucent PCA with 500 ppm MgO addition could be improved significantly in comparison with undoped PCA [8]. Moreover, double ZrO_2 and MgO doping in equal proportions of 500 ppm could further decrease the dielectric loss [9]. As an important rare-earth element, La is often used as a dopant in many ceramic systems to improve their properties. Introducing La into alumina ceramic has been the subject of investigations. Stuer et al. [10] found that co-doping La–Mg into alumina could increase the real inline transmittance by reducing the grain size. Cho et al.'s investigations [11–13] show that lanthanum doped as oversized, isovalent cation into alumina could improve the creep resistance qualitatively. Rani et al. [14] claimed that the high toughness of La-doped alumina can be attributed to the microstructural modification and the effect of crack-bridging. However, whether the La addition can improve the microwave dielectric properties of alumina or not, from the best of our knowledge, has never been reported.

In this work, we attempted to co-dope La into the PCA together with Mg and investigated the influence of La on the microstructure and microwave dielectric properties of translucent PCA.

2. Experimental procedure

Commercially available α-Al_2O_3 powder (99.99% pure) with a BET specific surface area of 7.24 m^2/g was used as

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the starting materials. MgO, La_2O_3 dopants (in the form of nitrate) were introduced into the alumina powder suspension. The MgO dosage was fixed at 500 ppm for all samples, which was confirmed to make the specimens more translucent [10,15]. For quantitative investigation of the effect of La_2O_3 on the transparency and microwave dielectric properties, a series of "A–F" samples was prepared: 500 ppm MgO (A), 500 ppm MgO + 500 ppm La_2O_3 (B), 500 ppm MgO + 1000 ppm La_2O_3 (C), 500 ppm MgO + 2000 ppm La_2O_3 (D), 500 ppm MgO + 3000 ppm La_2O_3 (E) and 500 ppm MgO + 4000 ppm La_2O_3 (F). The pH value of the suspension was controlled at 9.0 by $NH_3 \cdot H_2O$. The prepared suspensions were then dried at 80 °C for 24 h. After milling the dried powders, the samples were filtered by a 500 μm mesh nylon sieve before being pressed into pellets. The pellets were pre-fired at 1100 °C in air for 4 h to remove the binders and the final sintering was carried out at 1800 °C for 4 h in a H_2 atmosphere.

The density of the ceramic was measured by the Archimedes method. The crystal phases of the sintered samples were determined by X-ray diffraction (XRD) analysis, using a Bruker D8 Advance X-ray diffractometer (Karlsruhe, Germany) (Cu*Ka* radiation generated at 40 kV and 40 mA). The microstructures of the samples were evaluated under a backscattered electron microscope (Hitachi TM3000, Japan) and the average grain sizes were calculated from the SEM micrographs using the lineal intercept method with at least 300 intercepts counted [16]. The dielectric constant (ε_r) and the quality values Q at microwave frequency were measured using Hakki and Coleman's dielectric resonator method, as modified and improved by Courtney. A vector network analyzer (E8362, Agilent Technologies, Loveland, CO) was used for the measurement.

3. Results and discussion

Fig. 1 denotes the photograph of the prepared translucent PCA samples. Apparently, sample (B) exhibited a slightly higher translucency in comparison with (A), probably due to the co-doping strategy [10]. The translucency of the samples decreased with increasing content of La_2O_3 addition.

The densities of the translucent PCA as a function of La_2O_3 addition changing from 0 ppm to 4000 ppm were demonstrated in Fig. 2. As shown in the figure, the density of each sample was close to the theoretical value (3.987 g/cm^3), and no significant changes could be found. This result is consistent

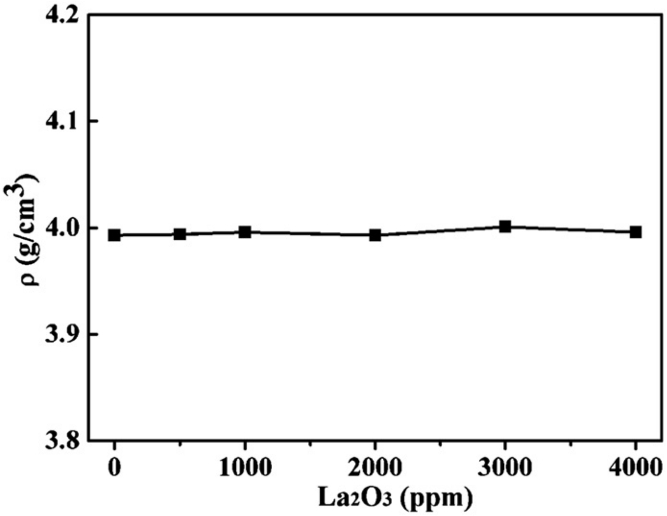

Fig. 2. Densities of the translucent PCA with different amounts of La_2O_3 addition.

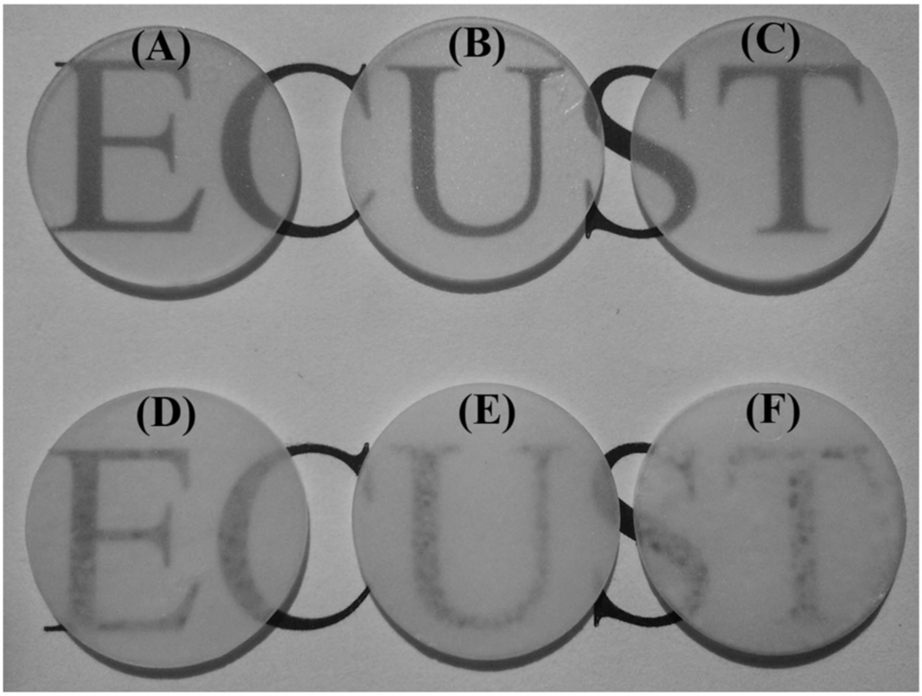

Fig. 1. Photograph of the translucent PCA samples doped with La_2O_3, samples are 0.8 mm thick and polished on both sides. The text was not retro illuminated.

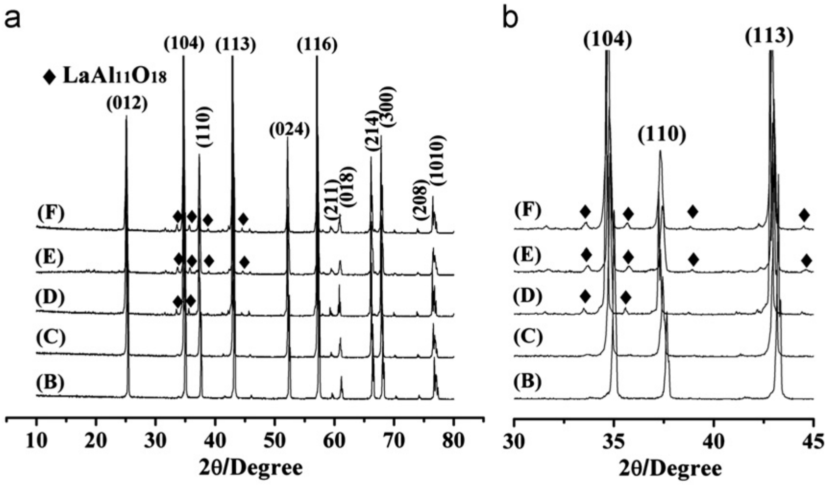

Fig. 3. X-ray diffraction patterns of (a) the translucent PCA with different amounts of La_2O_3 addition and (b) the enlarged image in the 2θ range from 30° to 45°.

with many other reports which confirmed that although doping La^{3+} might decrease the sintering rate of alumina due to the larger rare-earth cations segregating strongly to the grain boundaries [11,14,17], the densification process would not be inhibited when the sintering temperature is high enough (≥ 1400 °C) [14].

The X-ray diffraction patterns of the specimens with different amounts of La_2O_3 addition are shown in Fig. 3. For 500/1000 ppm La_2O_3 doped (La-(B)/(C)) samples, only the single phase of corundum could be found. The peaks of the secondary phase ($LaAl_{11}O_{18}$ [11]) began to appear when the PCA was doped with 2000 ppm La_2O_3, while as the La_2O_3 content increased, the intensity of these peaks became higher and higher (see Fig. 3(b)). Enlarged patterns (Fig. 3(b)) also show that the diffraction peaks of (104), (110) and (113) shifted toward the lower 2θ value as the content of La_2O_3 increased to 2000 ppm, indicating that larger La^{3+} (1.032 Å, CN=6) cations have substituted Al^{3+} (0.535 Å, CN=6) and the cell size kept increasing. With more La_2O_3 added, some variation of the shifting trend could be observed, which may be attributed to the lattice distortion [18].

Fig. 4(A–F) illustrates the backscattered electron image of the surface of the translucent PAC with La_2O_3 addition. As can be seen, all samples showed the classic equiaxed morphology, no pores or abnormal growth could be observed. As 1000 ppm La_2O_3 was added, a second phase (white zones) could be observed, indicating the presence of impurities, although below the detectability limit by XRD. As La_2O_3 addition increased, the secondary phase grew up and distributed uniformly at the grain boundaries of the alumina phase. This behavior was also confirmed by the above XRD results. Some investigators found that La^{3+} has a strong potential to modify the morphology of alumina [11,12,14]. With only 500 ppm La_2O_3 added, the grain will anisotropic elongate. But in Fig. 4, it could be seen that all the Al_2O_3 grains were exquiaxed. This interesting phenomenon might be the result of a La^{3+} and Mg^{2+} co-doping effect. Previous investigations by Du et al. [18] and Song et al. [19] have shown that co-doping with Mg^{2+} can reduce the anisotropy of Al_2O_3 and inhibit the formation of plate-like grain caused by the existing of Ca^{2+}, La^{3+}, Si^{4+} and other ions. In contrast to their reports, our investigation results show that even when the content of La_2O_3 is very much higher (4000 ppm) than that of MgO (500 ppm), the Al_2O_3 grains could still keep equiaxed, which is exceeding our expectations. Work is in progress to identify the relationship between the concentration ratio (Mg/La) and the microstructure of alumina.

Fig. 5 shows the dependence of the average grain size on the amount of La_2O_3 addition. Roughly, this curve can be divided into two parts as the La_2O_3 content kept increasing: for La_2O_3 content ≤ 1000 ppm, the grain size decreased rapidly from ~ 33 μm to 24 μm; while for La_2O_3 content ≥ 1000 ppm, the grain size decreased significantly slower and finally reached a size of ~ 20 μm. These different grain growth behaviors could be explained by different mechanisms acting in the different concentration intervals. For the low content La_2O_3 (≤ 1000 ppm) doped sample, the grain boundary mobility might be reduced by La-solute drag [17]; when more La_2O_3 was doped and the second phase kept increasing as shown in Figs. 3 and 4, particle pinning would control the grain growth speed. Further work about the mechanism of the grain growth is currently being performed.

Fig. 6 shows the microwave dielectric properties of the translucent PAC as a function of different amounts of La_2O_3, from 0 ppm to 4000 ppm. As can be seen, addition of La_2O_3 did not show any significant effect on the microwave dielectric constant, which was similar to when doped with other cations such as Mg^{2+}, Zr^{4+}, Y^{3+} [8,9,19] were doped. However, the variation in $Q \times f$ value exhibited a complicated trend. Initially, the $Q \times f$ value of translucent PCA increased from 190,000 GHz to 215,275 GHz when La_2O_3 content increased from 0 ppm to 500 ppm. However, when more La_2O_3 was added, the $Q \times f$ value began to decrease. The higher the La_2O_3 content, the lower the $Q \times f$ value. Similar to the grain growth behavior, this phenomenon can be attributed to two different effects of La doping. Firstly, the ionic radius of La^{3+} (1.032 Å) is much larger than that of Al^{3+} (0.535 Å) and Mg^{2+} (0.72 Å [20]). Investigations [21–23] show that Mg^{2+} dissolved in alumina crystal lattice may create polarizable point defects, these defects would form dipoles with high mobility under an external electric field which would lead to an increased dielectric loss. When La^{3+} was co-doped, its large ionic radius would result in a lattice distortion and form additional stress surrounding the dipoles. Therefore, the mobility of these dipoles would be restrained, and the dielectric loss would decrease correspondingly. Secondly, the second phase of $LaAl_{11}O_{18}$ would form, which has very low $Q \times f$ value ($\sim$15,000 GHz [24]). As shown in Figs. 3 and 4, $LaAl_{11}O_{18}$ phase could be found when La_2O_3 content exceeded 1000 ppm. Although the mobility of the dipoles continued to be restrained in the crystal lattice as the La_2O_3 content increased, the $Q \times f$ value of the translucent PCA would

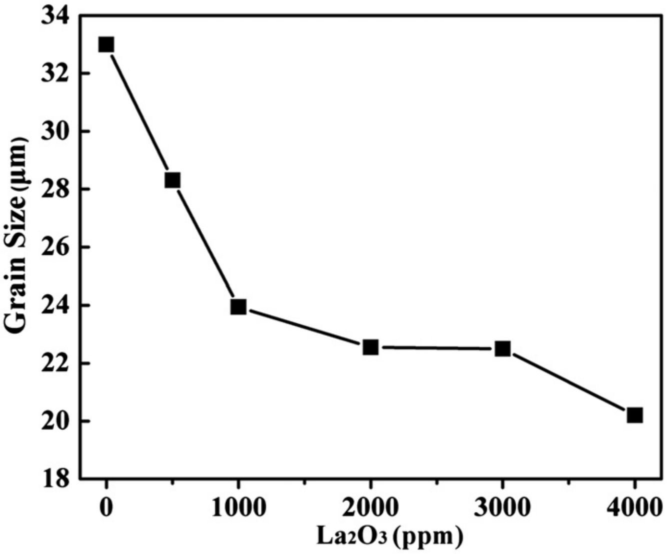

Fig. 5. The average grain size as a function of PCA samples with different amounts of La_2O_3 addition.

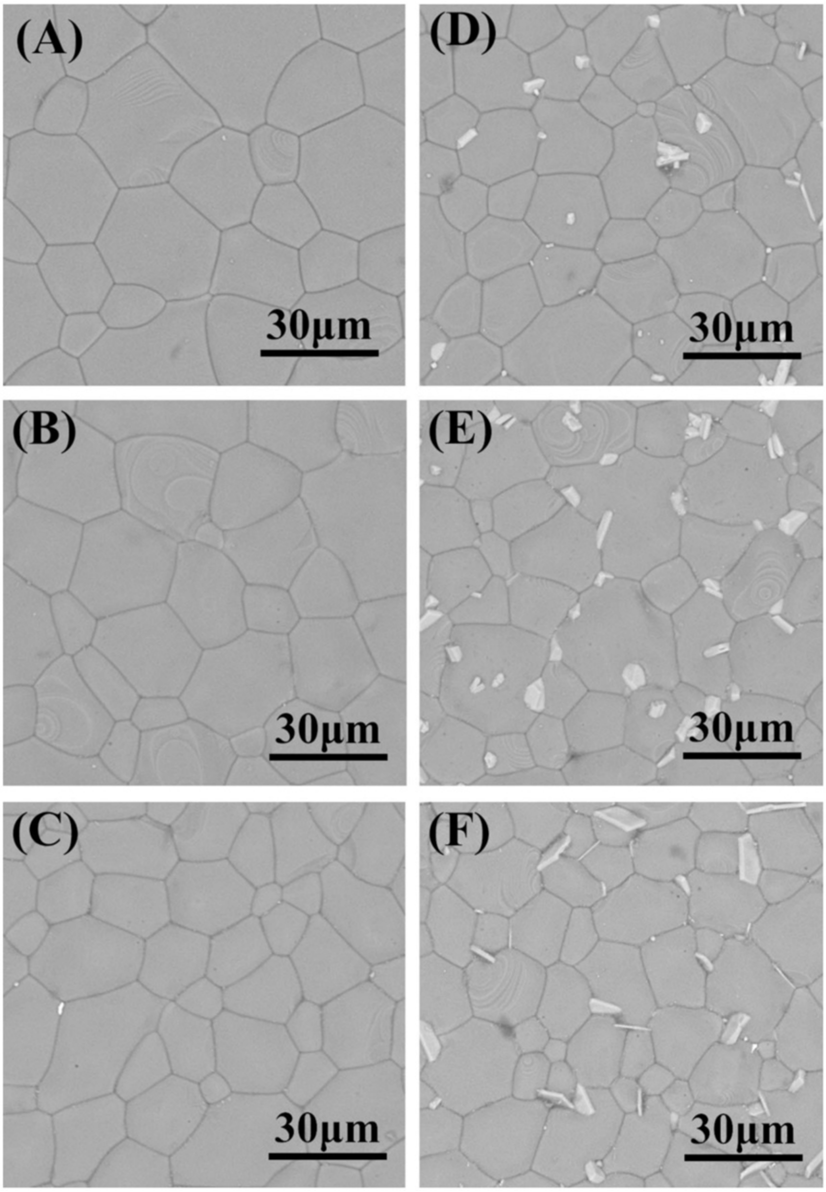

Fig. 4. The backscattered electron image of the surface of PAC samples doped with different contents of La_2O_3.

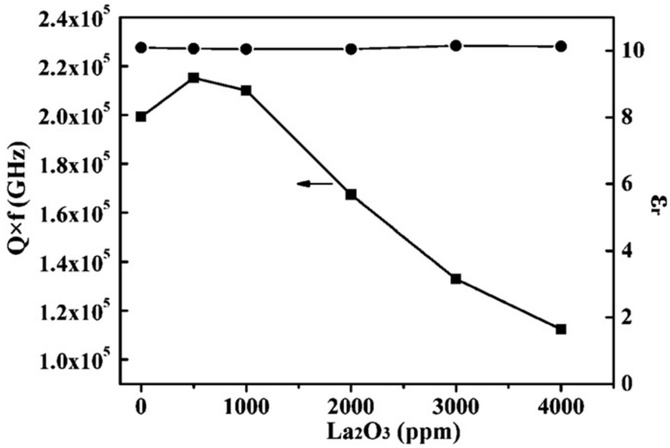

Fig. 6. Dielectric constants and $Q \times f$ value of the translucent PCA with different amounts of La_2O_3 addition.

unavoidably keep decreasing since more and more $LaAl_{11}O_{18}$ phase was formed.

4. Conclusion

(1) Translucent PCA could be obtained by adding 500–1000 ppm La_2O_3 (co-doped with 500 ppm MgO).

(2) As the content of La_2O_3 increased, alumina grains could still keep in a fine-equiaxed shape because of the co-doping with Mg^{2+}, while the grain size of translucent PCA decreased, the La-solute dragging and precipitates pinning effect might control the changing speed.

(3) La_2O_3 and MgO co-doping in equal proportions of 500 ppm yielded a higher $Q \times f$ value of 215,275 GHz in comparison with doping singly with 500 ppm MgO, as a result from the restrained polarizable point defects obtained by adding La^{3+} with a much higher ionic radius.

(4) Higher content of La_2O_3 addition would lead to a lowering of the $Q \times f$ value due to the presence of an increasing amount of impurities ($LaAl_{11}O_{18}$) at the grain boundaries.

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