Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 2109–2113

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effect of MgO/La_2O_3 co-doping on the microstructure, transmittance and microwave dielectric properties of translucent polycrystalline alumina

Lu Yuan[a], Huijun Wang[a], Huixing Lin[b], Wei Li[a,*], Xiaowei Li[a], Jianlin Shi[a,b]

[a]*School of Materials Science and Engineering, East China University of Science and Technology, 130 Mei long Road Shanghai 200237, China*
[b]*Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Ding Xi Road, Shanghai 200050, China*

Received 3 July 2013; received in revised form 24 July 2013; accepted 25 July 2013
Available online 2 August 2013

Abstract

In this paper, a systematic experimental design is used to study the influence of different content ratios of MgO/La_2O_3 co-doping on the microstructure, real inline transmittance (RIT) and microwave dielectric properties of translucent polycrystalline alumina (PCA). Compared with those doped only with MgO, translucent PCA co-doped with different ratios of MgO/La_2O_3 demonstrates a higher and more stable $Q \times f$ value. The increased solubility of La in alumina and the elimination of the second phase are possible reasons for the decrease in dielectric loss. An optimized $Q \times f$ value of ~300,000 GHz could be attained for samples co-doped with 1500 ppm MgO/300 ppm La_2O_3. Besides, a high RIT of ~30% at a wavelength of 600 nm could be achieved when 500 ppm MgO/500 ppm La_2O_3 was co-doped, the reasons for these phenomena are also discussed in the paper.

Keywords: B. Grain size; C. Dielectric properties; D. Al_2O_3; Co-doping

1. Introduction

It is well-documented that traces of co-dopants can change the properties of alumina radically by affecting various aspects such as grain size, shape and grain-boundary structure [1–3]. Over the past decades, many efforts in developing new co-doping strategies have been made to further improve the optical performance of translucent (transparent) PCA since it was first discovered by Coble in the early 1960s [4]. Wei et al. [5] found that PCA co-doped with Y_2O_3/ZrO_2 demonstrates a better sodium resistance than when doped with only MgO, which is beneficial for arc tubes in HPS discharge lamps. In a study by Granger et al. [6], CaO/TiO_2 co-doping yielded a finer grain size for a fixed relative density, and exhibited superior optical properties in comparison to pure alumina due to the low intragranular residual porosity. Recently, La_2O_3 has aroused interest as a potential co-dopant to be co-doped with MgO in hope of achieving improved light transmittance. For conventional H_2 sintering, early reports on MgO/La_2O_3 co-doping via ball milling declared that translucent PCA co-doped with MgO and La_2O_3 could achieve a higher real in-line transmittance (RIT) (~15%), at the 600 nm wavelength than if only doped with MgO [7]. The latest work by Xie [8] claimed that incorporating $MgO/La_2O_3/Y_2O_3$ additives using infiltration and gelling technique could increase the RIT of translucent PCA to as high as ~33% at 600 nm. For novel spark plasma sintering (SPS), compared with the single doping (Mg or La), double doping of MgO/La_2O_3 significantly increases the RIT of transparent PCA and reduces the sensitivity on the doping level and pressure [9]. Unfortunately, MgO/La_2O_3 co-doped translucent PCA reported to date either showed a RIT lower than 20%, or the preparation process is currently not suitable for mass production. Also, systematic researches concerning the relationship between the co-doping content ratio of MgO/La_2O_3 and the RIT remain limited.

---

[*] Corresponding author. Tel./fax: +86 216 425 2599.
E-mail address: liweiwei@ecust.edu.cn (W. Li).

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.07.125

With many advantages such as high surface smoothness, high thermal conductivity and chemical stability, translucent PCA have great potential for being used as substrates and in RF windows for vacuum electronics and microwave circuits. Recently, we found that translucent PCA with a 500 ppm MgO addition exhibited a significantly lower microwave dielectric loss. In addition, by adding a proper amount of MgO in comparison to undoped PCA, the $Q\times f$ value increased dramatically – from 115,000 GHz to 199,231 GHz [10]. Further investigation showed that higher $Q\times f$ values could be achieved by MgO/La_2O_3 (215,275 GHz) or MgO/ZrO_2 (220,084 GHz) co-doping, which demonstrated that the incorporation of ions with different sizes and valencies may be beneficial to the microwave dielectric properties of translucent PCA [11,12]. However, those high $Q\times f$ values were very sensible to the amount of added MgO, with a rapid decrease as the MgO content increased. In the case of both MgO/La_2O_3 and MgO/ZrO_2 co-doping, the optimal performance of translucent PCA is highly susceptible to the content of dopants.

Based on prior research work, the aim of our current work was to fabricate translucent PCA with high RIT and more stable $Q\times f$ values by co-doping with Mg^{2+}/La^{3+} ions. The influences of co-doping (MgO/La_2O_3) with different cationic ratios on the structure, RIT and microwave dielectric properties of translucent PCA were also investigated.

2. Experimental procedure

Ultrapure α-Al_2O_3 powders (99.99% pure) with a specific surface area of 7.24 m^2/g were used as the starting materials. Doping was carried out by dispersing 25 g of the powder in 200 ml deionized water and adding the required dopant solutions $Mg(NO_3)_2\cdot 6H_2O$ and $La(NO_3)_3\cdot 6H_2O$, to achieve the desired cationic dopant ratio. After dopant addition, $NH_3\cdot H_2O$ was added to control the pH value of the suspension at 9.0. The suspension was stirred for 2 h and dried at 80 °C for 24 h. Then, the prepared powders were sieved through a 200 mesh and pressed into pellets. The pellets were pre-fired at 1100 °C in air for 4 h to remove binders and the final sintering was carried out at 1800 °C for 4 h under a H_2 atmosphere.

The microstructural observations and analysis of the sintered surface were performed using a backscattered electron microscope (Hitachi TM3000, Japan) and the average grain size was calculated from SEM micrographs, using a line-intercept method which takes at least 300 grains into account [13]. All samples were carbon coated before SEM examination. The apparent densities of the sintered pellets were measured by the Archimedes method. The transmission spectrum of polished samples with a thickness of 0.8 mm was measured between the wavelengths 300–800 nm using a UV spectrophotometer (UV-5220, Shimadzu, Japan).The dielectric constant (ε_r) and the quality values Q at microwave frequencies were measured using Hakki and Coleman's dielectric resonator method [14,15], as modified and improved by Courtney. A vector network analyzer (E8362, Agilent Technologies, Loveland, CO) was used for the measurement.

3. Results and discussion

Similar to our previous results, densities of translucent PCA with different ratios of MgO/La_2O_3 were close to the theoretical value [10,12], and varied in a very narrow range of $3.98\sim 3.99$ g/cm^3. It is supposed that the effects of the MgO/La_2O_3 co-doping on the densification of the samples could be negligible because of a high sintering temperature. SEM images show that all the samples have equiaxial morphology without abnormal grain growth or trapped pores. However, there is a difference in morphology between the samples with various MgO/La_2O_3 compositions as detected by the back-scattered electron image. For samples doped with MgO, as well as for MgO/La_2O_3 co-doped samples with a content ratio of $MgO/La_2O_3 < 1$, some white zones could be detected located at the grain boundaries. In contrast, for samples with $MgO/La_2O_3 >$, the above mentioned white zones were, surprisingly, almost eliminated and no trace of the second phase could be identified. This microstructure difference is shown in Fig. 1, which confirms the disappearance of the second phases at the grain boundaries as $MgO/La_2O_3 > 1$, although the total contents of dopants have been as high as 4000 ppm. In addition to the surface characterization, the fracture surface for sample (c) and (d) also shows similar observations, with no evidence of a second phase.

Notably for the early work [16–18], co-doping into alumina could present an enhancement in mutual solubility of dopants. Thus, a possible explanation for the disappeared white zones may partly be due to the increased solid solubility of dopants in the alumina matrix. However, considering the relatively large amounts of dopants presents ($MgO+La_2O_3 > 500$ ppm), it is not likely to be the dominant mechanism. A more plausible explanation is that the dopant loss was controlled by evaporation [5]. That is, the evaporating amount of the second phase may change along with the varied ratio of MgO/La_2O_3. Hence it is suggested that as the content ratio of MgO/La_2O_3 was > 1, a large portion of dopant evaporation would perhaps explain the absence of second phases.

Fig. 2 shows the dependence of the average grain size given different concentration ratios (MgO/La_2O_3) for translucent PCA. When only MgO is used as a dopant, the grain size decreases rapidly as the MgO content increases from 500 ppm to 3000 ppm. The grain size of the MgO/La_2O_3 co-doped samples was smaller than that of the only MgO doped one as the MgO amount was 500 ppm. This is due to the segregations of MgO or La_2O_3 along the grain size dragging the grain growth. But this decreasing trend is seemingly restrained as more MgO was co-doped. Especially, when 1000 ppm La_2O_3 and 3000 ppm MgO was added, the grain size grew rapidly to $\sim$28 μm. Based on the above SEM analysis, it suggests that the decrease or even disappearance of second-phase particles would be the reason for the restrained decrease of grain size, where effect of particle pinning, which is known to retard the grain growth in alumina would be alleviated.

The $Q\times f$ value of translucent PCA as a function of different MgO/La_2O_3 composition are presented in Fig. 3. Here, again, the influence of dopants (Mg, Zr, La, etc.) on the ε_r of

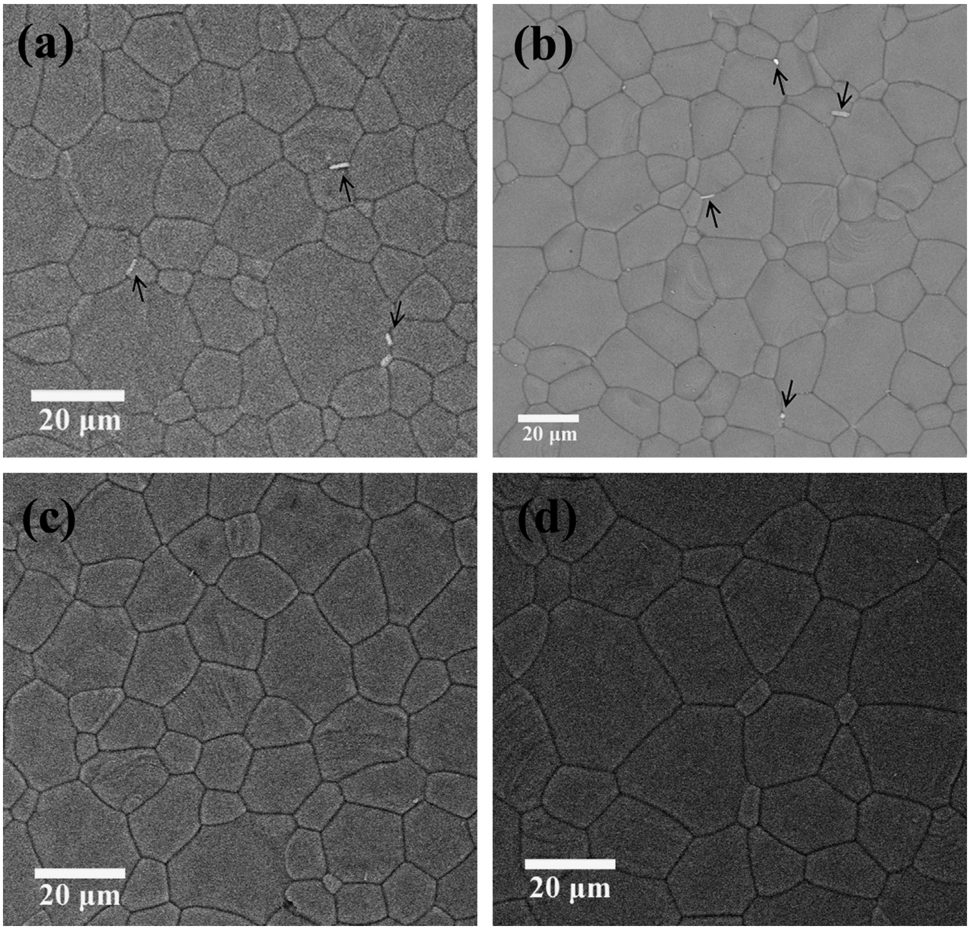

Fig. 1. The backscattered electron images of (a) 500 ppm MgO/800 ppm La_2O_3, (b) 500 ppm MgO/1000 ppm La_2O_3, (c) 1500 ppm MgO/1000 ppm La_2O_3 and (d) 3000 ppm MgO/1000 ppm La_2O_3 co-doped samples.

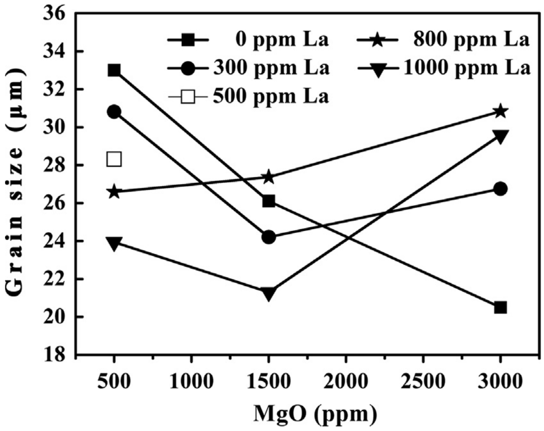

Fig. 2. The grain sizes of samples with different MgO/La_2O_3 compositions.

translucent PCA is almost negligible [10–12]. However, MgO/La_2O_3 addition shows significant effects on the $Q \times f$ value. For samples with only MgO added, the $Q \times f$ value decreases as the MgO content increases, which may be caused by MgO aggregation or $MgAl_2O_4$ precipitation at the grain boundaries [17]. However, with MgO/La_2O_3 co-doped, the variation of the $Q \times f$ value is completely different. (1). Compared to doping only with MgO, samples with MgO/La_2O_3 co-doped all show higher $Q \times f$ values. Typically, with 1500 ppm MgO+300 ppm La_2O_3 doped, a maximal value of ~300,000 GHz could be obtained (as compared to $Q \times f \sim 130{,}000$ GHz when only 1500 ppm MgO was added). (2).The $Q \times f$ value does not decrease synchronously with the increasing content of dopants. One reason that can be postulated for this interesting phenomenon is the increased solubility of La in alumina. To the author's knowledge, Mg^{2+} dissolved in alumina crystal lattice creates polarizable point defects with significant dipole effect, resulting in an increase of dielectric loss [19,20]. When La^{3+} was added as a co-dopant, a lattice distortion and an additional stress surrounding the dipoles would form due to its much larger ionic radius [12]. As a result, the dielectric loss would decrease correspondingly. When MgO content increased, more La^{3+} would be incorporated into the lattice and the effect hence reinforced. Another reason is the disappearance of the second phase. In most cases, the forming of the second phase increases the dielectric loss. Following the above SEM analysis, the second phase was almost eliminated when MgO/La_2O_3 > 1, which is beneficial to the decrease of dielectric loss.

The real in-line transmission (RIT) of MgO/La_2O_3 co-doped samples and their corresponding appearances are shown in

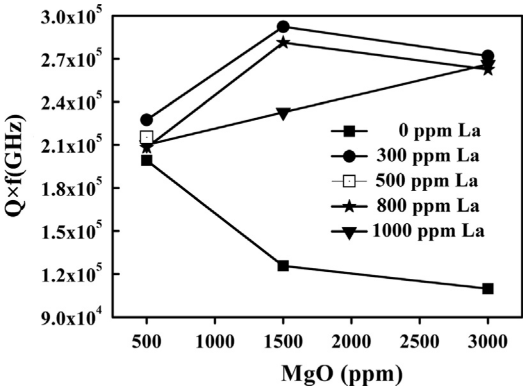

Fig. 3. The Q × *f* value of translucent PCA with different MgO/La_2O_3 compositions.

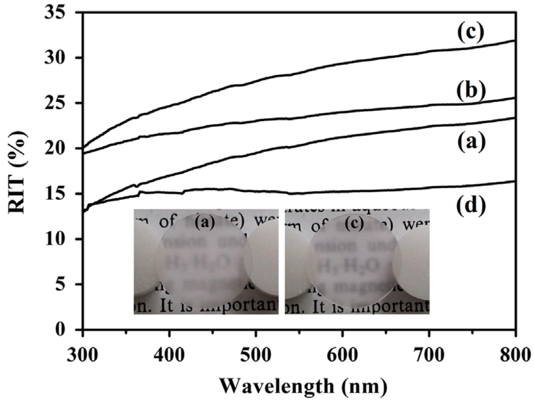

Fig. 4. The real in-line transmission of samples with (a) 500 ppm Mg, (b) 500 ppm MgO/300 ppm La_2O_3, (c) 500 ppm MgO/500 ppm La_2O_3 and (d) 500 ppm MgO/800 ppm La_2O_3, the appearances of(a) and (c) at a distance of 7 mm over a printed paper.

Fig. 4. Notably, the RIT changed rapidly with an increasing La_2O_3 content. Initially, with increasing La_2O_3 co-doping, there was a rapid increase of the RIT, the highest achieved RIT of ~ 30% at a wavelength of 600 nm was reached when 500 ppm La_2O_3 was co-doped. This positive effect is probably generated by the increased accommodation of La_2O_3 in the oxygen vacancy and atomic size distortion caused by MgO doping [12]. Then, as the La_2O_3 content became higher, the RIT decreased, which might be caused by the forming of a second phase at the grain boundaries.

4. Conclusion

(1) When the content ratio of MgO/La_2O_3 was ≥ 1, the second phase locating at the grain boundaries for translucent PCA would be eliminated, due to the enhanced mutual solubility and the evaporation of the dopants.

(2) The decreasing trend of grain size caused by the MgO addition is suppressed gradually when La_2O_3 was co-doped, which is probably attributed to the evaporation and alleviated effect of grain boundary phase.

(3) Samples with MgO/La_2O_3 co-doping showed higher and more "stable" Q × *f* values than those only doped with MgO, which may be caused by the restrained dipole mobility and the disappearance of second phases.

(4) Translucent PCA with proper amounts of MgO/La_2O_3 co-doped gave higher RIT than those only doped with MgO, a peak RIT performance of ~ 30% was attained when 500 ppm MgO/500 ppm La_2O_3 was co-doped.

References

[1] A. Tewari, S. Galmarini, M. Stuer, P. Bowen, Atomistic modeling of the effect of codoping on the atomistic structure of interfaces in α-alumina, Journal of the European Ceramic Society 32 (11) (2012) 2935–2948.

[2] C. Elsässer, T. Elsässer, Codoping and grain-boundary cosegregation of substitutional cations in α-Al_2O_3: a density-functional-theory study, Journal of the American Ceramic Society 88 (1) (2005) 1–14.

[3] Y.-M. Kim, S.-H. Hong, D.-Y. Kim, Anisotropic abnormal grain growth in TiO_2/SiO_2-doped alumina, Journal of the American Ceramic Society 83 (11) (2000) 2809–2812.

[4] R.L. Coble, Transparent alumina and method of preparation, in: US Patent, 1962.

[5] G.C. Wei, A. Hecker, D.A. Goodman, Translucent polycrystalline alumina with improved resistance to sodium attack, Journal of the American Ceramic Society 84 (12) (2001) 2853–2862.

[6] G. Bernard-Granger, C. Guizard, A. Addad, Influence of co-doping on the sintering path and on the optical properties of a submicronic alumina material, Journal of the American Ceramic Society 91 (5) (2008) 1703–1706.

[7] Q. Yang, Z. Zeng, J. Xu, H. Zhang, J. Ding, Effect of La_2O_3 on microstructure and transmittance of transparent alumina ceramics, Journal of Rare Earths 24 (1) (2006) 72–75.

[8] G. Liu, Z. Xie, W. Liu, L. Cheng, Y. Wu, Fabrication of translucent alumina ceramics from pre-sintered bodies infiltrated with sintering additive precursor solutions, Journal of the European Ceramic Society 32 (4) (2012) 711–715.

[9] M. Stuer, Z. Zhao, U. Aschauer, P. Bowen, Transparent polycrystalline alumina using spark plasma sintering: effect of Mg, Y and La doping, Journal of the European Ceramic Society 30 (6) (2010) 1335–1343.

[10] H. Wang, W. Li, C. Ternström, H. Lin, J. Shi, Effect of Mg doping on microwave dielectric properties of translucent polycrystalline alumina ceramic, Ceramics International 39 (2) (2013) 1583–1586.

[11] H.J. Wang, W. Li, H.X. Lin, J.L. Shi, Effect of Zr doping on structure and microwave dielectric properties of translucent polycrystalline alumina ceramic, International Journal of Applied Ceramic Technology (2013) (accepted for publication).

[12] H. Wang, H. Lin, W. Li, J. Shi, Effect of La doping on microwave dielectric properties of translucent polycrystalline alumina ceramic, Ceramics International 39 (5) (2013) 4907–4911.

[13] M.I. Mendelson, Average grain size in polycrystalline ceramics, Journal of the American Ceramic Society 52 (8) (1969) 443–446.

[14] B. Hakki, P.D. Coleman, A dielectric resonator method of measuring inductive capacities in the millimeter range, IEEE Transactions on Microwave Theory and Techniques 8 (4) (1960) 402–410.

[15] W.E. Courtney, Analysis and evaluation of a method of measuring the complex permittivity and permeability microwave insulators, IEEE Transactions on Microwave Theory and Techniques 18 (8) (1970) 476–485.

[16] Y.-Z. Li, C. Wang, H.M. Chan, J.M. Rickman, M.P. Harmer, J. M. Chabala, K.L. Gavrilov, R. Levi-Setti, Codoping of alumina to enhance creep resistance, Journal of the American Ceramic Society 82 (6) (1999) 1497–1504.

[17] K. Gavrilov, S. Bennison, K. Mikeska, R. Levi-Setti, Role of magnesia and silica in alumina microstructure evolution, Journal of Materials Science 38 (19) (2003) 3965–3972.

[18] H.N. Yoshimura, H. Goldenstein, Light scattering in polycrystalline alumina with bi-dimensionally large surface grains, Journal of the European Ceramic Society 29 (2) (2009) 293–303.

[19] J. Chovanec, D. Galusek, J. Ráheu, P. Šajgalík, Low loss alumina dielectrics by aqueous tape casting: the influence of composition on the loss tangent, Ceramics International 38 (5) (2012) 3747–3755.

[20] J. Chovanec, K. Ghillányová, J. Ráhel', P. Šajgalík, D. Galusek, The influence of dopants on loss tangent of polycrystalline alumina ceramics, Ceramics International 38 (3) (2012) 2043–2049.