Available online at www.sciencedirect.com
SciVerse ScienceDirect
Ceramics International 38 (2012) 2043–2049
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

The influence of dopants on loss tangent of polycrystalline alumina ceramics

Jozef Chovanec [a,*], Katarína Ghillányová [b], Jozef Ráhel’ [c], Pavol Šajgalík [b], Dušan Galusek [a]

[a] *Vitrum Laugaricio – Joint Glass Centre of the IIC SAS, TnU AD, FChPT STU and RONA, a.s., Študentská 2, SK-911 50 Trenčín, Slovak Republic*
[b] *Institute of Inorganic Chemistry, Slovak Academy of Sciences, Dúbravská cesta 9, SK-845 36 Bratislava, Slovak Republic*
[c] *Department of Physical Electronics, Faculty of Science, Kotlářská 267/2, Veveří, Brno 60200, Czech Republic*

Received 4 August 2011; received in revised form 13 October 2011; accepted 14 October 2011
Available online 20 October 2011

Abstract

Polycrystalline aluminas with various concentrations of oxide dopants CaO, MgO, and TiO_2, ranging from 0.05 wt.% to 5 wt.%, as well as pure alumina references were prepared by slip casting from suspensions with various solid loading (30, 35, and 40 vol.% of Al_2O_3), and sintered at 1350 °C for 1 h as low loss tangent electroceramics. As the key parameter for intended application the loss tangents were measured at room temperature in the frequency range between 1 and 200 kHz. In the case of pure alumina the lowest value of loss tangent was achieved in the materials with minimum residual porosity. The values of loss tangents of doped materials were influenced by the concentration of dopants. The addition of 0.05 and 0.5 wt.% of MgO and CaO decreased the value of loss tangent in the whole frequency range. The effect was related to more homogenous microstructure with lower concentration of defects (pores) resulting from the addition of dopants. The increased values of loss tangent in the materials with higher level of additives (5 wt.%) are related to lower density of the materials, and the presence of residual porosity. Other contributing factors are the formation of secondary phases (calcium, magnesium and titanium aluminates), and the increased concentration of lattice defects due to incorporation of atoms with different valencies to alumina crystal lattice.

Keywords: A. Slip casting; Loss tangent; Aluminal; Dopants

1. Introduction

The commercially available Al_2O_3 ceramics (96% purity) is the essential part of the diffuse coplanar surface barrier discharge (DCSBD) [1–3] electrode system. This has been with success applied for generation of non-isothermal plasma applicable for mass treatment of materials with low added value, specifically textiles, paper, artificial and natural fibres, glass, wood and metal sheets. The Al_2O_3 ceramics is a suitable material for DCSBD due to its high dielectric strength, good thermal conductivity, and resistance to chemical and mechanical erosion. According to the results of applied research in the area of DCSBD, the volume density of electric power (nowadays ~100 W/cm^3) is a key parameter for providing efficient plasmochemic modification. However, the electromechanic limits of contemporary types of electroceramics prevent further increase of the power density. These limits are namely high dielectric losses above the frequency 20 kHz, and the operating voltage, which is close to breakdown voltage of the used Al_2O_3.

Dielectric losses are described by loss angle tan δ, which is the ratio between the imaginary and real part of the permittivity. The dielectric losses can be divided into two groups; intrinsic and extrinsic. Intrinsic losses depend on crystal structure and express the interaction of the crystal lattice with the external electric field. Extrinsic losses relate to materials’ microstructure, e.g. the presence of microstructural defects, porosity, micro cracks and impurities [4]. Each material, which is exposed to external electric field, is polarized. When the elementary particles change their position and orientation we call this process relaxation polarization, which depends on temperature and frequency of the applied electric field. In high-purity sapphire the only dielectric loss over a wide frequency range comes from the interaction of electromagnetic fields with crystal lattice vibrations, resulting in very low loss tangents values [5]. The presence of impurities or deliberately added dopants can influence the polarizability, and loss tangent of alumina in fundamental way. During sintering the dopants react

---

[*] Corresponding author.
E-mail address: jozef.chovanec@stuba.sk (J. Chovanec).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.10.040

with alumina, yielding respective aluminates, or diffuse into the alumina crystal lattice, creating polarizable point defects. The presence of impurities gives rise to relaxation processes in the MHz region and therefore to higher levels of loss tangent which dominate the dielectric loss even at microwave frequencies. By increasing the number of point defects the polarizability of dielectrics increases, with corresponding increase of dielectric losses [6–10]. Important impurities are especially those with a valence different from the host (Al^{3+} in our case). Common examples are H^+, Fe^{2+}, Mg^{2+}, Ca^{2+}, Si^{4+} and Ti^{4+}. The charge imbalance causes the creation of defects in their surroundings for charge compensation, forming an electrical dipole. The natural vibration frequency of defects will result in a peak in dielectric loss-frequency dependence of doped material. A clear effect of Mg on the loss tangent of alumina at 20 GHz has been demonstrated by Mollá et al. [11], who reported the increase of $\tan\delta$ from 10^{-4} to 10^{-3} with increasing the concentration of MgO from 10^{-3}% to 10%.

Reported values of loss tangent for polycrystalline alumina in the frequency range 1–100 kHz are typically in the order of magnitude from 10^{-4} to 10^{-5} [11,21], but the influence of lattice defects introduced by dopants on dielectric losses is not conclusively established. The solubility of dopants in alumina crystal lattice is usually considered to be very low (in the order of 10–100 ppm) [12], but the published data from various authors vary significantly. Greskovich and Brewer [13] established the solubility of MgO in Al_2O_3 to be 75 ppm at 1720 °C, Roy and Coble [12] reported 300 ppm at 1630 °C, Ando and Momoda [14] 55 ppm at 1700 °C, and Miller et al. [15] 132 ppm at 1600 °C. McKee and Aleshin measured the solubility to be 1, 1.8, and 2.5 mol.% at 1400 °C, 1600 °C, and 1700 °C, respectively [16] Winkler et al. established the solubility of TiO_2 to be 500–600 ppm at 1300 °C [17]. The solubility of CaO in Al_2O_3 is estimated to be 30 ppm at 1900 °C in air [18]. The concentrations of dopants exceeding the lattice solubility limits result either in atomic segregation of the additives at alumina–alumina grain boundaries or, at higher concentrations, in the formation of various secondary crystalline phases, such as $MgAl_2O_4$ spinel in case of MgO, various calcium aluminates or Al_2TiO_5 in case of CaO and TiO_2 addition, respectively, with profound influence on final microstructure of the ceramics.

This paper is focused at investigation of the influence of dopants on loss tangent of polycrystalline alumina in the frequency range 20–200 kHz. This frequency area has not been studied deeply since most authors focus on dielectric properties in the frequency range characteristic for microwave radiation [4,19–21]. The influence of the MgO, CaO, and TiO_2 addition and the microstructure parameters, such as residual porosity on loss tangent of alumina ceramics is discussed.

2. Experimental

Polycrystalline alumina samples with various concentrations of oxide dopants CaO, MgO, and TiO_2, ranging from 0.05 wt.% to 5 wt.% as well as pure alumina reference materials were prepared by slip casting from suspensions with various solid loading (30, 35, and 40 vol.%) with the use of a commercial alumina powder (Taimicron TM-DAR, Taimei Chemicals Co., Japan). Nominal average particle size and specific surface area of the powder are 160 nm and 14.5 $m^2\,g^{-1}$, respectively. Alumina suspensions were prepared with Darvan C–N (R.T. Vanderbilt Company, Inc., aqueous solution of ammonium polymethacrylate – 25 wt.% solution) as a commercial dispersant and de-ionised water as a solvent. Doped specimens were in all cases prepared from the aqueous suspension with 35 vol.% of alumina. MgO was added to the suspension in the form of magnesium aluminium spinel $MgAl_2O_4$ (Baikalox S30CR powder, average particle size 190 nm, specific surface area 32 $m^2\,g^{-1}$). TiO_2 was added also in the powder oxide form (extra pure, Riedel de Haen). CaO was added in the form of $Ca(NO_3)_2{\cdot}4H_2O$ (extra pure, Lachema, o.p. Brno, Czech Republic). Doped suspensions were homogenised on rollers in a PE bottle with high purity alumina milling balls for 24 h. The suspensions were poured onto PE plate and allowed to dry under ambient conditions. Dried plates with diameter of 50 mm and 2 mm thick were sintered in an electrical furnace with $MoSi_2$ heating elements (Netzsch GmbH, Selb, Germany) for 1 h at 1350 °C at a heating rate 10 °C min^{-1}.

The density of sintered samples was measured by Archimedes method in water. The loss tangent was measured as follows [22]. The ceramic plates were coated with the ESL 9912-A silver paste to form a three electrode system. The diameter of guarded electrode was 20 mm, the separation between the guard and guarded electrode was 1 mm. The low voltage (1 V) measurement of $\tan\delta$ was performed by the commercial TESLA BM 595 RLCG meter. The maximum available testing frequency was 200 kHz. The measurement at high voltage was carried out at series resonance circuit with three different resonance inductors to set the resonance frequency. As mentioned above, the dissipation factor $\tan\delta$ is defined as the ratio between the real (resistive) and imaginary (capacitive) power delivered to the load. For the dielectric modelled as a resistor and capacitor connected in parallel, the dissipation factor can be expressed as

$$\tan\delta = \frac{I_R}{I_C} \qquad (1)$$

where I_C states for the capacitive current and I_R for the real current. Taking advantage of this expression, we have placed a low loss HV tunable vacuum capacitor (COMET CVBA; 5–250 pF; 15/9 kV) with the capacity of C_v in parallel to the tested specimen with the capacity of C_x. Electrical current in the circuit was monitored by two calibrated Pearson current monitors Model 2877 fed to the digital oscilloscope LeCroy WaveRunner 6100A. The first of the current monitors was set to sense the electrical current of vacuum capacitor. The second current monitor sensed the difference between the electrical current of vacuum capacitor and the tested specimen. This was accomplished by feeding the corresponding wires through the Pearson monitor's central opening in the opposite direction (see [22] for more details). When the capacity of vacuum capacitor is adjusted to $C_v = C_x$, the first current monitor measures the capacitive current I_C and the second current monitor measures the real current I_R. The actual measurement was carried out at 5 kV of applied voltage. In order to suppress a possible discharge (corona) onset on tested materials, the specimens were immersed in the insulating oil during the procedure.

The microstructure of prepared ceramics was examined on polished and thermally etched (temperature 1150 °C, 1 h isothermal dwell in air) polished cross sections by scanning electron microscope Carl Zeiss EVO 40HV. The phase composition was determined by X-ray powder diffraction analysis with the use of a STOE Automatic X-ray Powder Diffractometer Systems, Siemens, in the 2Θ range from 20° to 75°, with the use of Co lampa with the wavelength of 17,902 Å.

3. Results and discussion

The results of density measurement for pure alumina reference materials are summarized in Table 1. The highest relative densities were achieved for the samples prepared from suspensions with solid loading 30 wt.% and 40 wt.% of Al_2O_3, and sintered for 1 h at 1350 °C.

The reference samples prepared from suspensions with 30% and 40% solid loading contain almost no residual porosity (Fig. 1). The graphic dependence of loss tangent on frequency for the reference aluminas is shown in Fig. 2. The highest dielectric losses expressed in terms of the loss tangent were measured in the alumina with highest fraction of residual porosity. In case of pure alumina the value of loss tangent is to large extent determined by its microstructure, i.e. by the volume fraction of pores.

The results of density measurement of doped samples are summarized in Table 2. In all cases the highest density was achieved with the addition of 0.05% of dopants. The addition has positive influence on the development of microstructure, and promotes the elimination of porosity in the ceramics. During sintering process the dopants in part dissolve in the alumina matrix. However, due to low solubility of CaO and MgO in the alumina crystal lattice the amount of dopants exceeding the solubility limits can either segregate at alumina–alumina interfaces or, at higher dopant concentrations, react with alumina, yielding crystalline binary aluminates, as indicated by the results of X-ray diffraction shown in Fig. 3. Grain boundary segregation of dopants and impurities affects the microstructure development in substantial way. The addition of MgO enhances both the grain growth and densification rates during sintering of alumina ceramics, but at the same time efficiently suppresses abnormal grain growth (AGG) [23]. Homogeneous microstructure with equiaxed alumina grains then results from MgO doping (Fig. 4). Some Mg^{2+} ions are dissolved in the alumina crystal lattice forming point defect, but due to low solubility limits the concentration of dipoles is low. CaO is known as one of the additives that trigger AGG, and some works suggest that calcia forms vitreous aluminosilicate phase at grain boundaries, with nominal composition identical, or close to crystalline $CaAl_{12}O_{19}$ phase

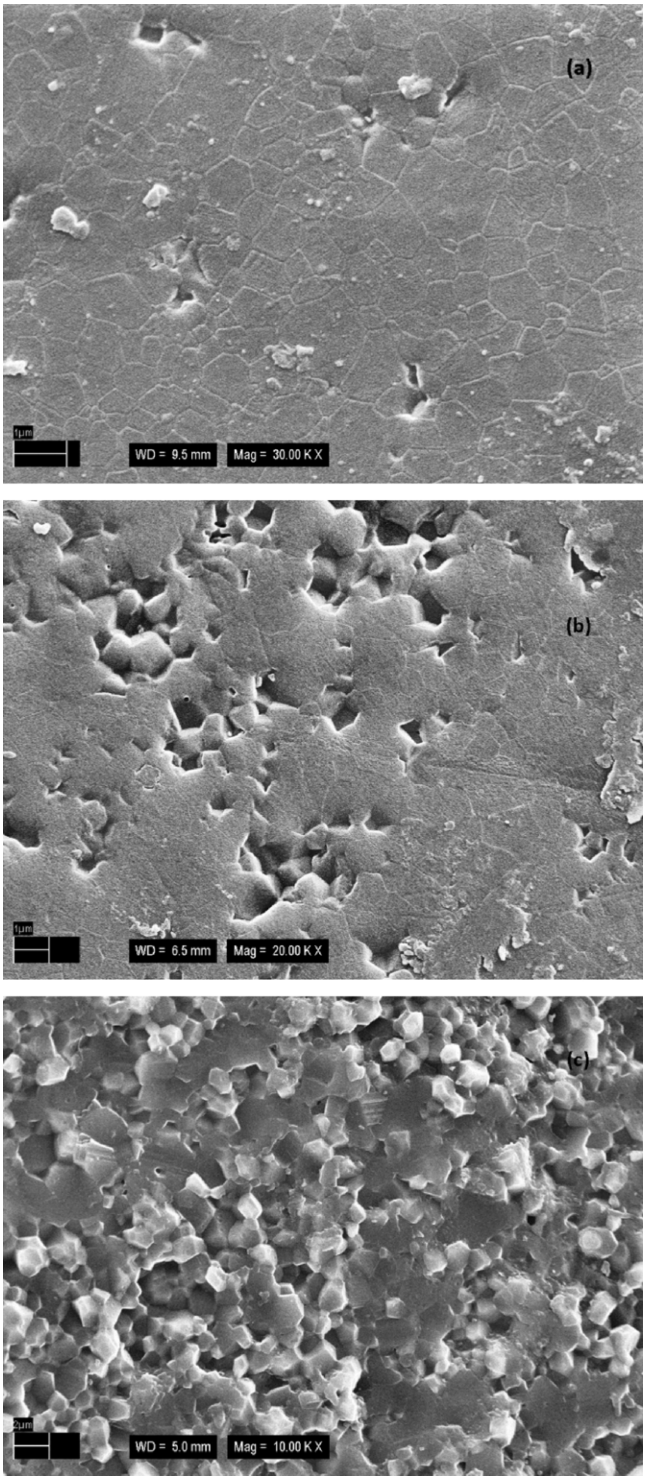

Fig. 1. SEM micrographs of alumina reference materials prepared from suspensions with different solid loading of: 30 (a), 35 (b) and 40 vol.% (c) of alumina.

Table 1
The results of density measurement of pure alumina reference materials.

	Solid loading		
	30 vol.%	35 vol.%	40 vol.%
Density [g/cm^3]	3.973	3.956	3.972
Relative density [%]	99.8	99.4	99.8

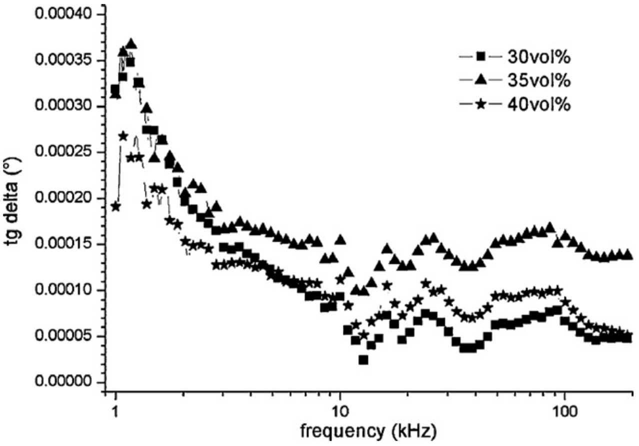

Fig. 2. Frequency dependence of loss tangents of pure alumina references prepared from suspensions with different solid loading.

[24]. Addition of TiO_2 was found to cause precipitation of nano-sized Al_2TiO_5 crystallites along the alumina–alumina grain boundaries from a transient liquid [25]. The precipitation takes place from the addition of 1 wt.% of TiO_2 and the appearance of crystallites was used to define a correlation between the grain size and the doping level in Ti-doped Al_2O_3 [26]. High concentrations of all dopants, which, as demonstrated by the XRD patterns in Fig. 3, formed by reaction with alumina matrix secondary crystalline phases, hinder densification by grain boundary pinning.

Fig. 5(a) summarizes the dependence of loss tangent on frequency for aluminas with different concentrations of MgO. Fig. 5(b) summarizes the dependence of loss tangents on concentrations of MgO at 3 selected frequencies. The addition of 0.05% MgO decreases the value of loss tangent under the level measured for pure aluminas. In turn, the addition of 0.5% MgO slightly increased the loss tangent, but the values measured in the whole frequency range were still lower than those in pure alumina. These results were related to more efficient elimination of residual porosity, resulting in denser and more homogeneous microstructure and uniform grain growth (Fig. 4).

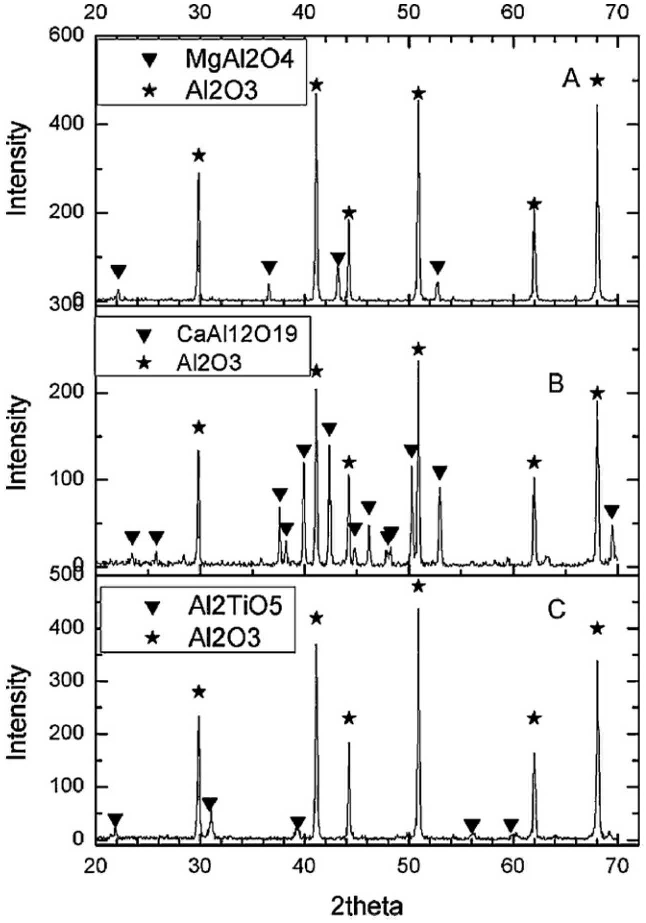

Fig. 3. X-ray diffraction patterns of aluminas doped with 5 wt.% of additives.

The microstructure effects then prevail over the negative influence of point defects introduced into the alumina crystal lattice by dissolution of Mg^{2+} ions. Further increase of MgO addition to 5% significantly increased the loss tangent, which especially in the low frequency range was well above the values measured for pure alumina, or those of MgO-doped specimens with lower level of doping. This effect is attributed to the formation of spinel as a second crystalline phase in the material. Spinel particles segregate at grain boundaries, prevent densification, and increase the residual porosity of resulting material. This effect amplifies the influence of the diffusion of Mg with oxidation number 2+ into the alumina crystals, creating lattice defects with resulting dipole effect [16]. This hypothesis is further supported by the fact that the increase of loss tangent is reduced at high frequencies from 50 to 200 kHz. The alumina with 5% of MgO is thus not suitable as a low loss electromaterial.

Fig. 6(a) shows the frequency dependence of loss tangent for materials doped with CaO. Fig. 6(b) summarizes the dependences of loss tangents on the concentration of CaO at three selected frequencies of the external electric field. Similarly to MgO, CaO at the concentration of 0.05% decreases the loss tangent under the level measured for pure

Table 2
The results of density measurements of doped aluminas.

wt.%	MgO		CaO		TiO_2	
	Density [g/cm^3]	Relative density [%]	Density [g/cm^3]	Relative density [%]	Density [g/cm^3]	Relative density [%]
0	3.956	99.4	3.956	99.4	3.956	99.4
0.05	3.962	99.5	3.956	99.4	3.974	99.8
0.5	3.951	99.3	3.924	98.6	3.970	99.8
5	–	–	3.700	93.8	3.902	97.8

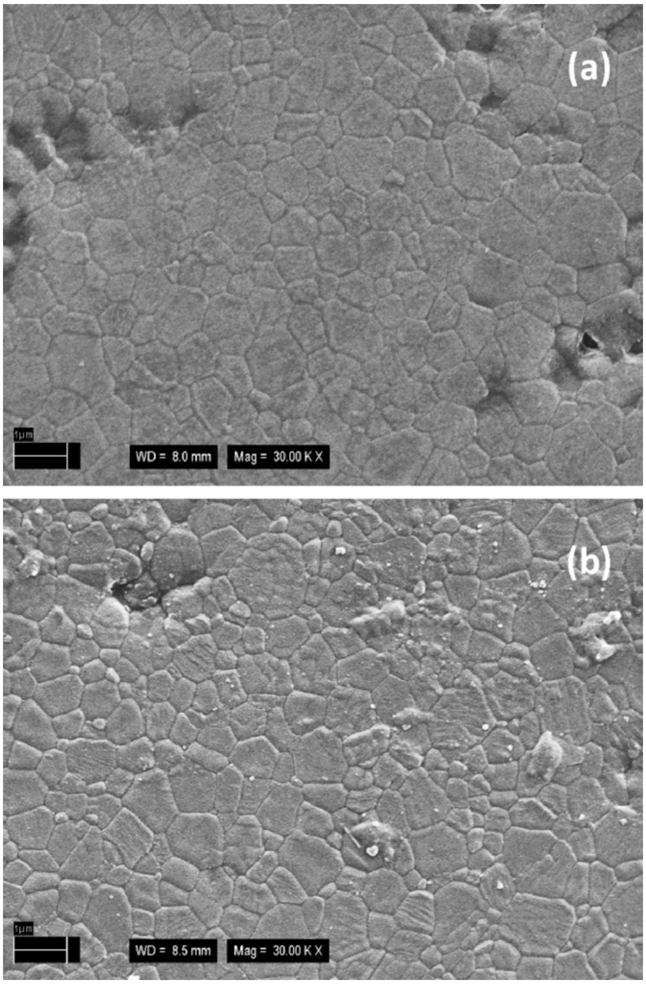

Fig. 4. SEM micrographs of alumina doped with different concentrations of: 0.05 hm.% (a) and 0.5 hm.% (b) of MgO.

alumina. In the low frequency area up to 10 kHz the addition of CaO at the concentration of 0.5% increases the loss tangent high above the level of loss tangent of the material with 0.05% of CaO, and also above the level measured for pure alumina. This observation is related namely to diffusion of Ca with oxidation number 2+ into the lattice, resulting in the formation of electric dipoles. The influence of the dipole effect on loss tangent is more pronounced at lower frequencies of the external electrical field (Fig. 6(a)). Since solubility of CaO in the crystal lattice of Al_2O_3 is relatively small, the elimination of residual porosity and the presence of other phases play the main role in decreasing the loss tangent values. In the high frequency range the loss tangent is under the level measured for pure alumina. In this range the changes in dipole polarity cannot follow the changes of polarity of the external electric field and the influence of lattice defects and dipoles is reduced. Further increase of CaO addition to 5% increases the value of loss tangent by about two orders of magnitude. In this case, significant decrease of relative density (nearly 7% of residual porosity), together with high volume fraction of the $CaAl_{12}O_{19}$ crystalline secondary phase alters the electrical properties significantly.

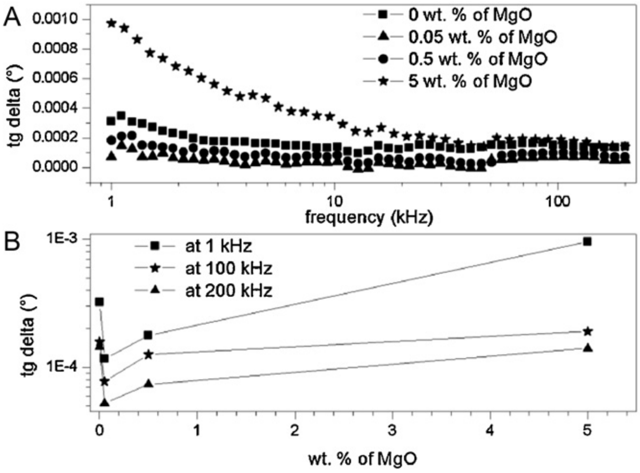

Fig. 5. The frequency dependence of loss tangent of alumina with various MgO concentrations (a), and the influence of MgO addition on loss tangent of alumina ceramics at various frequencies (b).

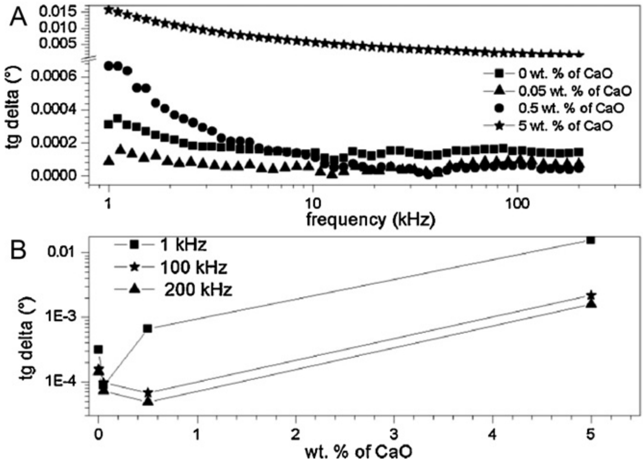

Fig. 6. The frequency dependence of loss tangent of alumina with various CaO concentrations (a), and the influence of CaO addition on loss tangent of alumina ceramics at various frequencies (b).

Fig. 7(a) summarizes the dependences of loss tangents on frequency at different concentrations of TiO_2. Fig. 7(b) summarizes the dependence of loss tangent on the concentration

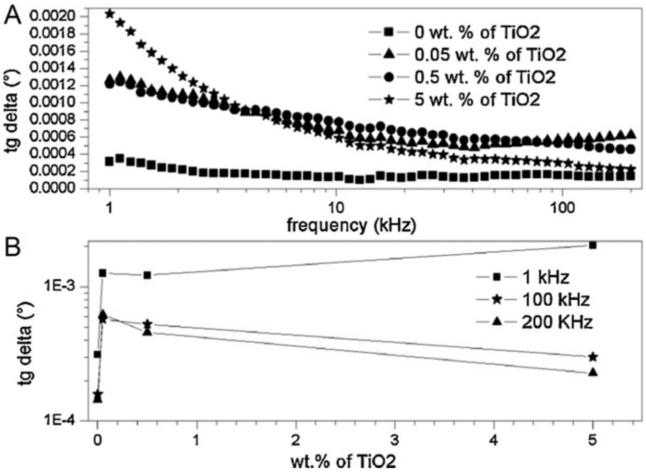

Fig. 7. The frequency dependence of loss tangent of alumina with various TiO_2 concentrations (a), and the influence of TiO_2 addition on loss tangent of alumina ceramics at various frequencies (b).

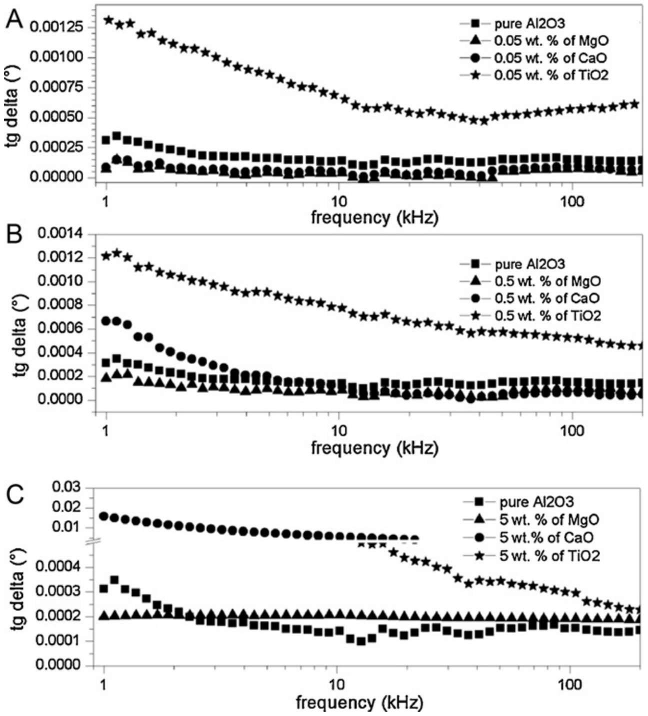

Fig. 8. The comparison of the influence of identical dopants' concentrations on loss tangents of polycrystalline aluminas at 0.05 wt.% (a), 0.5 wt.% (b) and 5 wt.% (c).

of TiO_2 at three selected frequencies of the external electric field. At all concentrations of the dopant, the addition of TiO_2 led to significant increase of the loss tangent in comparison to pure alumina. Along with deterioration of microstructure (increase of relative porosity), and formation of titanium aluminate Al_2TiO_5 in specimens with 5% of TiO_2, the increase of the loss tangent is attributed to the formation of lattice defects. Solubility of Ti with oxidation number 4+ in alumina lattice is substantial [16,17]. Titania ions therefore diffuse into the alumina crystal lattice and create point defects with significant dipole effect. The influence of dipole formation on loss tangent is, similarly to MgO and CaO doped samples, documented by significantly higher tan δ values in the low frequency range, and its decrease at high frequencies.

Fig. 8 summarizes the dependences of loss tangents on frequency at different concentrations of dopants. The addition of 0.05% and 0.5% MgO results in the lowest tan δ values, which are at all frequencies under the level of loss tangents of pure alumina. Very low values of loss tangents were also observed in CaO-doped aluminates at the concentration of 0.05%. According to the values obtained by density measurement, the decrease of loss tangent is related to elimination of residual pores and minimal content of aluminates during sintering. In all cases the addition of 5% of a dopant results in significant increase of loss tangent, and the materials with high level of doping are not suitable as low loss dielectrics.

4. Conclusions

The addition of various dopants, namely MgO, CaO, and TiO_2 on loss tangent of polycrystalline alumina has been studied. The addition of 0.05% and 0.5% of MgO and 0.05% CaO decreases the tan δ values below the level measured for pure alumina. Increased loss tangent values in materials with high level of dopants were related to decrease of relative density, the presence of residual porosity, and the formation of various aluminates as secondary phases. Increased concentration of lattice defects, especially in TiO_2-doped materials with high solubility of Ti^{4+} in alumina crystal lattice impairs the tan δ values in the low frequency range from 1 to 10 kHz due to incorporation of atoms with different valencies to alumina crystal lattice. The addition of dopants shows positive influence only when improving microstructure mainly by minimizing the volume fraction of residual porosity.

Acknowledgments

The financial support of this work by the grant VEGA 2/0076/10, VEGA 2/0178/10, and the APVV grant APVV 0485-06 is gratefully acknowledged. This publication was created in the frame of the project ''Centre of excellence for ceramics, glass, and silicate materials''

References

[1] M. Šimor, J. Rahel, P. Vojtek, A. Brablec, M. Černák:, Atmospheric-pressure diffuse coplanar surface discharge for surface treatments, Appl. Phys. Lett. 81 (2002) 2716–2718.
[2] M. Černák, Int. Patent Appl. PCT/SK02/000008, 2001-May-04.
[3] M. Černák, M. Šimor, J. Ráhel', Electrode element for generating a diffusion co-planar barrier surface electric discharge and production method thereof, SK Patent application SK1362003 A3, 2004 Nov-03.
[4] S.J. Penn, N.M. Alford, A. Templeton, X. Wang, Effect of porosity and grain size on microwave dielectric properties in sintered alumina, J. Am. Ceram. Soc. 80 (7) (1997) 1885–1888.
[5] J. Mollá, R. Heidinger, A. Ibarra, Alumina ceramics for heating systems, J. Nucl. Mater. 212–215 (1994) 1029.
[6] M.P. Harmer, R.J. Brook, The effect of MgO additions on the kinetics of hot pressing in Al_2O_3, J. Mater. Sci. 15 (1980) 3017.
[7] S.J. Bennison, M.P. Harmer, Grain-growth kinetics for alumina in the absence of a liquid phase, J. Am. Ceram. Soc. 68 (1985) C22–C24.
[8] R.L. Coble, H. Song, R.J. Brook, C.A. Handwerker, J.M. Dynys, Sintering and grain growth in alumina and magnesia, structure and properties of MgO and Al_2O_3 ceramics, in: W.D. Kingery (Ed.), Advances in Ceramics, Vol. 10, J. Am. Ceram. Soc., 1984, pp. 839–852.
[9] N.W. Ashcroft, N.D. Mermin, Solid State Physics, Holt-Saunders, Tokyo, 1976 (Chapter 27).
[10] O.F. Schirmer, Smoky coloration of quartz caused by bound small hole polaron optical absorption, Solid State Commun. 18 (1976) 1349.
[11] J. Mollá, R. Moreno, A. Ibarra, Effect of Mg doping on dielectric properties of alumina, J. Appl. Phys. 80 (July (2)) (1996).
[12] S.K. Roy, R. Coble, Solubility of magnesia, titania, and magnesium titanate in aluminium oxide, J. Am. Ceram. Soc. 51 (1) (1968) 1–6.
[13] C. Greskovich, J.A. Brewer, Solubility of magnesia in polycrystalline alumina at high temperatures, J. Am. Ceram. Soc. 84 (2) (2001) 420–425.
[14] K. Ando, M. Momoda, Solubility of MgO in single-crystal Al_2O_3, J. Ceram. Soc. Jpn. 95 (4) (1987) 381–386.
[15] L. Miller, A. Avishai, D.W. Kaplan, Solubility limit of MgO in Al_2O_3 at 1600 °C, J. Am. Ceram. Soc. 89 (1) (2006) 350–353.
[16] W.D. McKee, E. Aleshin, Aluminum oxide-titanium oxide solid solution, J. Am. Ceram. Soc. 46 (1) (1963) 54–58.

[17] E.R. Winkler, J.F. Sarver, I.B. Cutler, Solid solution of titanium dioxide in aluminium oxide, J. Am. Ceram. Soc. 49 (12) (1966) 634–637.

[18] S.I. Bae, S. Baik, Determination of concentrations of silica and/or calcia for abnormal grain growth in alumina, J. Am. Ceram. Soc. 76 (4) (1993) 1065–1067.

[19] N.M. Alford, S.J. Penn, Sintered alumina with low dielectric loss, J. Appl. Phys. 80 (November (10)) (1996).

[20] N.M. Alford, J. Breeze, X. Wang, S.J. Peen, Dielectric loss of oxide crystal and polycrystalline analogues from 10 to 320 K, J. Eur. Ceram. Soc. 21 (2001) 2605–2611.

[21] R. Vila, M. González, J. Mollá, A. Ibarra, Dielectric spectroscopy of alumina ceramics over a wide frequency range, J. Nuc. Mat. 253 (1998) 141–148.

[22] J. Ráhel', D.M. Sherman, The transition from a filamentary dielectric barrier discharge to a diffuse barrier discharge in air at atmospheric pressure, J. Phys. D: Appl. Phys. 38 (2005) 547–554.

[23] S.I. Bae, S. Baik, Critical concentration of MgO for the prevention of abnormal grain growth in alumina, J. Am. Ceram. Soc. 77 (10) (1994) 2499–2504.

[24] J. Jung, S. Baik, Abnormal grain growth of alumina: CaO effect, J. Am. Ceram. Soc. 86 (4) (2003) 644–649.

[25] P. Qian, H. Gu, M. Chi, The emergence of intergranular precipitates in TiO_2-doped α-Al_2O_3 ceramics, J. Am. Ceram. Soc. 93 (2) (2010) 326–329.

[26] S. Lartigue-Korinek, C. Legros, C. Carry, F. Herbst, Titanium effect on phase transformation and sintering behavior of transition alumina, J. Eur. Ceram. Soc. 26 (12) (2006) 2219–2230.