Section 4. Physical properties of unirradiated and irradiated ceramics

Dielectric spectroscopy of alumina ceramics over a wide frequency range

R. Vila *, M González, J. Mollá, A. Ibarra

CIEMAT, Av. Complutense, 22, E-28040 Madrid, Spain

Abstract

Aluminum oxide (either in single or polycrystalline form) is one of the insulator materials with broad application in high radiation environments. Despite this demanding use, very different values for the dielectric properties have been found in the literature before and after irradiation. In order to obtain a reliable database, the dielectric properties of several unirradiated commercial alumina grades have been measured over a wide frequency (1 kHz to 15 GHz) and temperature range (100 to 300 K). Loss tangent differences over three orders of magnitude have been observed. The possible explanations and the role of some impurities (mainly Mg and Fe) are analyzed. © 1998 Elsevier Science B.V.

1. Introduction

Many material problems have to be solved before the construction of future fusion machines such as the international thermonuclear experimental reactor (ITER). More specifically, the choice of material for radio frequency (RF) windows and different antenna supports and insulators for the heating systems is an unresolved issue. These windows, acting as a vacuum and tritium barrier, should be able to transmit high power ($\sim$ 1 MW) of radio frequency in three different frequency ranges: approximately 40–80 MHz for Ion Cyclotron Heating, 1–5 GHz for Lower Hybrid Heating, and 100–200 GHz for Electron Cyclotron Heating. The absorption of a small fraction of the transmitted power will produce high temperature gradients with the risk of breaking the material due to mechanical stress. Some diagnostics will also need insulators working at lower frequencies. Although mechanical and thermal properties are also important, the main parameter to be considered in this framework is the dielectric loss (DL).

It has been demonstrated that, in high purity sapphire, the only DL over a wide frequency range comes from the interaction of electromagnetic fields with crystal lattice vibrations, producing a very low loss tangent at microwave frequencies [1,2]. However it is known that the presence of defects give rise to relaxation processes in the kHz to MHz region and therefore to higher levels of loss tangent that dominate the DL over a wide range of frequencies [3].

It is not easy to correlate the type of defects with the different peaks that appear in the loss tangent versus frequency curves. Previous work found in the literature were done in different samples and at different frequencies, so it was even more difficult to obtain a clear picture of the frequency and defect dependence of the loss tangent. The present article belongs to a long-term program that has been carried out in order to study this problem, mainly by doping in a controlled way with several common impurities. The database so obtained is also of interest for many other applications where alumina is an important candidate or for microwave sintering in which the rate of heating of the material is a function of its loss tangent [4].

2. Experimental

The work here presented has been done on several commercial alumina grades. They have been chosen from very high (99.99%) down to quite low purity (92%) although the majority are of high purity. The manufacturer

---

* Corresponding author. Tel.: +34-1 346 6580; fax: +34-1 346 6005; e-mail: vila@ciemat.es.

Table 1
Main characteristics of the samples studied

	Producer	Nominal purity (%)	Density (g/cm^3)	Grain size (μm)
W995	Wesgo (USA)	99.5	3.84	30
W300	Wesgo (USA)	97.3	3.80	
MM999.	Morgan Matroc (UK)	99.9	3.97	1.4
MM995	Morgan Matroc (UK)	99.5	3.82	
MM975	Morgan Matroc (UK)	97.5	3.73	
BIO	Friedrichsfeld (Germany)	99.9	3.93	0.9
C997	Ceratén (Spain)	99.7	3.84	1
C9999	Ceratén (Spain)	99.99	3.90	2.5
RB92	Feldmühle (Germany)	99.9	3.99	10
KA473	Kyocera (Japan)	92	3.53	

and some characteristics of each one are shown in Table 1. The majority of them are fine grained with the exception of RB92 and Wesgo samples. The density has been measured using the Archimedes method. Data about the impurity content shown in Table 2 have been taken from several sources in literature [5–7].

The dielectric properties of sintered samples have been measured at room temperature from 1 kHz to 15 GHz. In the frequency range from 1 kHz to 100 MHz the half-power-gap variation method has been used. It is a resonant technique in which the response of a resonant circuit is measured when the sample is between the parallel plates of a condenser and compared with the same measurement without the sample [8]. The measurements are made using a commercial system from Japan-E&M (model DPMS-1000). This system allows one to measure loss tangent values higher than 3×10^{-6} with a precision better than $\pm(3 \times 10^{-6} + 0.5\%)$ and permittivity better than 5%. The precision in absolute permittivity is limited by the precision in the sample thickness. Better resolution is achieved in the measurement of permittivity with frequency where changes as low as 0.3% can be measured.

The measurements of dielectric properties at 1.2 and 15 GHz are also based on resonant methods, using closed cylindrical resonant cavities (for 15 GHz) and a closed coaxial cavity (at 1.2 GHz). The dielectric properties are obtained from the comparison of the characteristics of the resonance with and without the sample inside the resonator. This system allows the determination, under optimum conditions, of the permittivity with an error less than 0.1% and the loss tangent with an error less than 10% down to values of about 10^{-5} at 15 GHz [9] and about 3×10^{-4} at 1.2 GHz.

3. Results and discussion

It is very interesting to observe the obtained loss tangent values at room temperature for the whole set of alumina samples in a wide frequency range as represented in Fig. 1. Due to the high number of samples, the curves have been separated in two groups. Higher purity samples have been represented in Fig. 1a together with the loss tangent of single crystal sapphire for comparison. Lower

Table 2
Alumina impurity content (μg/g)

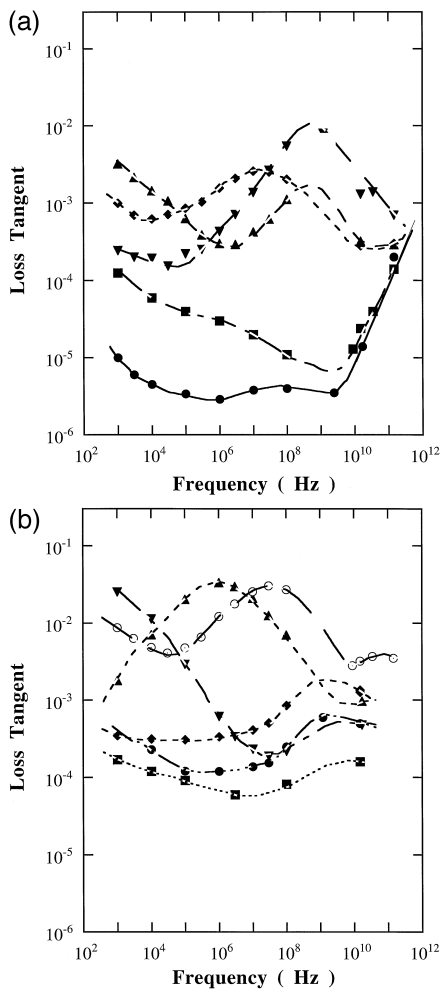|	W995	W995 [7]	W300	MM975	MM995	MM999	BIO	C997	C9999	KA473	RB92
% →	99.3	99.5	97.328	97.5	99.5	99.9	99.9	99.7	99.99	92	99.9
Si	2200	1370	14000	8150	650	690					
Fe	760	340	810	165	160			28			
Ca	950	424	11000	2600	210	10	< 30	< 50	4		
Mg	3100	2490	330	5250	1500	300	260	> 400	2		
Zr	80	70	90	15	9	2					
Ba	< 50	< 20		9.6	5						
Na	270	210	390	375	24	50		< 28	14		
Ti	50	100	30	29	28	5					
Cr		< 100		5.5	5.9	10					
Ni		< 20		< 10	< 10	< 10					
Cu				< 2	< 2						

Fig. 1. Frequency dependence of loss tangent at room temperature for several alumina types: (a) high purity grades – RB92 (◆), BIO (▲), C9999 (■), MM999 (▼) and UC sapphire (●), (b) low purity grades – KA473 (◆), MM995 (▲), W995 (■), MM975 (▼), C997 (○) and W300 (●). Lines are only guides to the eye.

purity samples are plotted in Fig. 1b. All the data are also given in Table 3 to provide exact data readily.

The obtained permittivity values at 15 GHz are given in Table 4. The error is composed of the measurement error plus the statistical deviation of the several samples from the same batch. Sample W300 is not shown because it is a unique sample and has a larger error due to its small thickness (1 mm).

As a first comment, it is clear that single crystal aluminum oxide has the lowest loss tangent value over the entire frequency range. This very low value, near 10^{-6}, extends from 1 kHz up to 10 GHz. The sharp increase at higher frequencies has been previously related to the intrinsic lattice absorption at optical frequencies (in the

infrared region) [10]. As an ionic material the photon–phonon interaction is quite strong [11]. Therefore this loss will appear even in the most pure and perfect Al_2O_3 crystal.

A second important comment is about the C9999 sample. It was developed with the manufacturer in order to achieve the highest purity available (99.99%). As it can be seen in Fig. 1a, it has the lowest dielectric loss among all the ceramic samples studied. Only at high frequencies the intrinsic DL increases the $\tan \delta$ value in the same amount that in the single crystal case. This sample shows that polycrystalline (sintered) aluminum oxide may have losses as nearly low as single-crystal material at some frequencies. Similar results have been obtained by other groups [12,13] for high purity sintered alumina.

For all the other samples, a remarkable result is the large differences in the dielectric behavior of very similar samples. Loss tangent values change from 10^{-5} to more than 10^{-2} and DL peaks appear at very different frequencies.

The loss tangent of Wesgo samples can be found in several published reports ([6] and references herein cited) and therefore a comparison can be made with the values here obtained In the range $10^8-2 \times 10^9$ Hz, where a frequency overlap of measurements occurs. We see that, for both samples, relatively good agreement is obtained for high frequencies. For example our values near 15 Ghz fit very well in the curve published in Ref. [6]. For lower frequencies our measurements are higher. At 100 MHz previous values [6] are 5×10^{-5} and 14.2×10^{-5} for Wesgo 995 and W300 respectively. These must be compared to $8. \times 10^{-5}$ and 25×10^{-5} in our case. Finally, at 10 MHz our values are almost 3 times higher than those quoted by manufacturer. But for this frequency no other measurements are available.

Looking carefully at Fig. 1a, b one observes that purity is not a simple parameter to classify alumina losses. Although only the samples of very high purity (99.99%) present a very low loss tangent over the whole frequency range. When samples of about 99.9% purity are compared with lower purity (97–98%), clearly most of the 99.9 materials have higher losses at radio frequencies. Therefore the total amount of impurities by itself is not the controlling factor.

It is well known that dielectric properties of insulating ceramics can be influenced by several factors which will be discussed in relation with our results.

(a) Grain size: With the obtained results we did not observe any effect of this parameter on dielectric loss. This confirms results from a previous work in which high purity powder was sintered under different conditions to increase the grain size and no significant differences were observed [3]. Anyway this result is not completely proved. Other authors claim that there is a grain size effect. In a recent work [14] an increase of loss tangent is obtained by increasing the grain size, in contrast to the results obtained in other ceramic materials, where a higher grain size

Table 3
Loss tangent values ($\times 10^{-5}$) of the different aluminas at several frequency points

Sample	Frequency (Hz)							
	10^3	10^4	10^5	10^6	10^7	10^8	$1 \pm 0.1 \times 10^9$	$15 \pm 1 \times 10^9$
UC.Sapph	1.0	0.45	0.34	0.29	0.38	0.4	0.45	1.4
W995	17	12	9.2	9	8.5	8.2		16
C9999	12.5	6.0	4.0	3	2	1.1	1.3	3
C997	873	484	478	1220	2560	2710	280	340
RB92	100	62.5	86	156	258	203		28
BIO	321	144	63	30	42	112		30
W300	–	23	12	12	14	25	60	50
KA473	35	32	31	34	41.5	86		130
MM999	6.1	7.3	10.5	20	55.6	275	400	81
MM995	180	705	2040	3350	2100	700		97
MM975	2530	1130	292	62	23.3	22		48

implies a reduction of grain boundaries and therefore a loss reduction.

(b) Microstructure: Here we can include other factors like aspect ratio of the grains, orientation, density, ..., etc. An extensive study has not been achieved until now but it must be stressed that, from a theoretical point of view, these mechanisms would modify an existing DL process already present in the material but would not, by themselves, give rise to DL in a perfect insulator. That is, if the bulk alumina has some dipolar-defect, the measured DL would change if the aspect ratio or the density is changed. This has been explained by many dielectric laws for composite materials (see for example [15,16]). But in a perfect material, a density or grain orientation change by itself does not alter the intrinsic defect structure. It would be relevant only if the experimental procedure applied to modify these parameters (for example different sintering temperatures and/or times) produces some other changes (impurities, grain boundary composition...).

The only clear effect of the microstructure has been observed in permittivity. At high enough frequencies, where there is no influence of lower frequency DL peaks, permittivity is governed by the density as shown in Fig. 2. In this figure the permittivity of several alumina samples is plotted versus the porosity of each one, calculated from its density, showing a linear relationship. This effect can be very well explained taking into account that a lower density corresponds to higher porosity. So more air exists inside the sample. Considering then the ceramic as a composite of alumina and air ($\varepsilon = 1$) and applying some classic models we obtain the observed decrease of permittivity with porosity with small differences between theory and experiments. Fig. 2 shows the predictions obtained using different models (Looyenga [17], Bruggeman [18], Maxwell–Garnett [19] and refractive index [20]). From our results, the porosity does not show any influence on the loss tangent, but it should be pointed out that this is probably due to the limited range of densities studied in this work. In a recent work [12,13] it has been shown that the presence of a large quantity of pores can induce an increase of loss tangent.

(c) Impurities: From early studies in doped alkali halides and fluorites ([21] and references herein cited), it is well
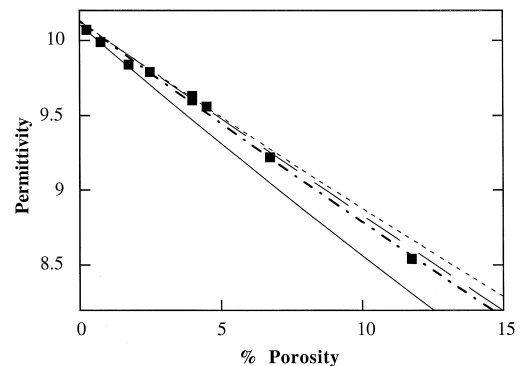
Table 4
Measured permittivity values of the different aluminas at 15 GHz

Sample	Permittivity	Error
W995	9.63	0.08
C9999	9.79	0.02
C997	9.60	0.01
RB92	10.07	0.02
BIO	9.84	0.02
KA473	8.54	0.15
MM999	9.99	0.01
MM995	9.56	0.02
MM975	9.22	0.02

Fig. 2. Permittivity of the different samples used in this work (■) as a function of the porosity, compared to the value predicted by the Looyenga (————), Maxwell–Garnett (- - -), Bruggeman (— — — —) and refractive index (– · –) models for a composite of alumina and air.

known that impurities can play an essential role in the DL of ionic crystals. In the works mentioned, an impurity-vacancy dipole is formed in certain conditions giving rise to clear DL peaks. The discussion about impurity effects can be subdivided into several points:

(i) Important impurities are those with a valence different from the host (Al^{3+}). So, in our case, common examples are H^+, Fe^{2+}, Mg^{2+}, Ca^{2+}, Si^{4+} and Ti^{4+}. This charge imbalance will cause the creation of some other defects in the surroundings for charge compensation, forming an electrical dipole. The natural vibration frequency of this defect will give the DL peak position.

(ii) The thermal treatments (in different atmospheres) can have strong influence on the impurity charge state. For example, it has been observed that redox treatments can change the Fe^{2+} to Fe^{3+} and vice versa [22]. So the dipole can be created or destroyed by such treatments. This is a first clue to show that the type and amount of impurities are not the only critical parameters. We also need to know the thermochemical history of the sample to be able to correlate DL with impurities. An example of this strong influence of thermal treatments will be given later in this article.

(iii) The effect of an impurity can be also quite different when another one is added to the crystals. This is usual in semiconductors where double doping with a donor and an acceptor is made. In the case of insulating crystals, the isolated impurity will have some electric compensation realized by some intrinsic defect (for example oxygen vacancy or aluminum interstitial). Adding another impurity with different valence may produce a cross-compensation. The defect structure could then change completely. So, a dielectrically active dipole could be destroyed or created, depending on which one is active. Both types of compensation can induce dielectric loss, but at very different frequencies. The amount of each impurity is then important. For example, an effect of the ratio Si/Mg on the loss tangent in alumina has been observed by Ando et al. [23].

This last feature, together with the large number of impurities already present in each commercial sample makes it very difficult to obtain a clear correlation of DL peaks with impurity content. A clear picture can be obtained only by selective doping with a single element at a time. Due to this, two studies will be presented now, one set of samples doped with Mg and the other with Fe.

3.1. Mg-doped samples

The effect of Mg in alumina was presented in a previous work [24]. When a small quantity of MgO (near 0.05 wt%) is added to the starting high purity alumina powder, a peak in the loss tangent appears near 100 MHz, as observed in Fig. 3. But, surprisingly, further increasing of the magnesia concentration gives rise to a decrease in the peak height. In fact, at magnesia content of 1%, the loss tangent peak is not more present (see Fig. 3). It is interest-
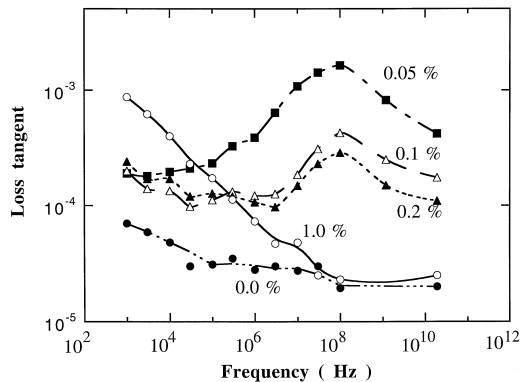

Fig. 3. Frequency dependence of loss tangent at room temperature for alumina with different magnesia content: 0.0% (●), 0.05% (■), 0.1% (△), 0.2% (▲) and 1.0% (○).

ing to note that, at low frequency, one observes a monotonic increase in loss tangent with increasing magnesia content. It must be noted that the position of the peak and the total loss is comparable to that found in two other commercial aluminas which also contain Mg in a similar content (see samples BIO and MM999).

For this high frequency relaxation process, the fact that the maximum of loss tangent appears at a concentration value of about 0.05% of magnesia was explained as follows: This value is the approximate solubility limit of Mg in Al_2O_3 at the sintering temperature employed [25,26] and therefore at higher concentrations the excess magnesium does not produce point defects but small aggregates and, for higher magnesia concentrations, spinel precipitates. These defects would then behave as sinks during sintering and the total point defect concentration would decrease. This is in agreement with the general trend observed in the commercial aluminas, where higher total impurity contents reduce high frequency losses.

As it was mentioned previously a study of the dielectric loss under several thermal treatments is important. We performed four experiments in the sample with 0.05% Mg-doped: An annealing in air at 1480 K, a quenching from this temperature and an annealing in argon at 1780 K. Furthermore, an 1.8 MeV electron irradiation at room temperature up to 270 MGy was performed. None of these treatments could change the peak, indicating a high degree of stability of the defect responsible.

Although a model involving the $[Mg]^0$ was previously proposed, the EPR signal and thermal stability obtained do not correspond with the observed ones for the $[Mg]^0$ in single crystals [27,28]. In that case the $[Mg]^0$ centers can only be produced by quenching in air from temperatures above 1200 K and are destroyed by annealing in air or inert atmosphere. So, it seems that, although the peak is correlated with Mg, the defect responsible is still unclear and could involve another structure like $[Mg'-F^+]$ which are known to exist in Mg-doped samples [29].
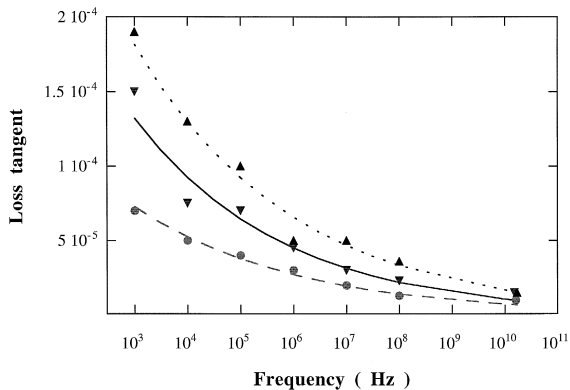
Fig. 4. Frequency dependence of loss tangent at room temperature for alumina with different iron content: 20 ppm (▼), around 600 ppm (●), more than 600 ppm (▲).

From these studies we conclude that the observed peak in the 0.1 to 1 GHz range for the MM999 and RB92 alumina grades is related to a dipolar defect associated to the presence of Mg. The Wesgo AL300 sample does not show this peak, in spite of the fact that the Mg content is similar. This is probably due to the charge compensation by other impurity, perhaps to the large amount of silicon.

3.2. Fe-doped samples

In this work we extend the previous study to the case of iron. In this case a high purity powder (99.99% purity) was used and several amounts of iron were introduced during sintering. Final concentrations (after sintering) of iron, from 20 ppm to more than 600 ppm, were obtained. The dielectric losses as a function of frequency for three different samples are shown in Fig. 4. Contrary to the case of

magnesium, no effect is obtained on the high frequency side. This could be expected a priori because iron appears in alumina as Fe^{3+}, in the site of Al^{3+} and so no dipole is expected to exist.

In this case, the thermal treatment is very important. It is known that Fe^{3+} can be reduced to Fe^{2+} by heating in an atmosphere poor in oxygen [30]. This was checked heating the samples in argon at 1550°C during 24 h. The resulting dielectric loss after this treatment is shown in Fig. 5. It is observed that a very narrow peak appears between 0.1 and 1 GHz. A reduction of loss at low frequency occurs at the same time. In the Wesgo AL995 sample we made the same thermal treatment because its iron concentration (between 350 and 700 ppm) is close to the second doped sample. It can be observed that the height and peak
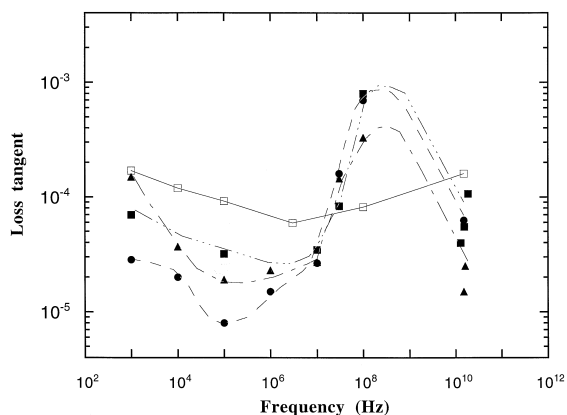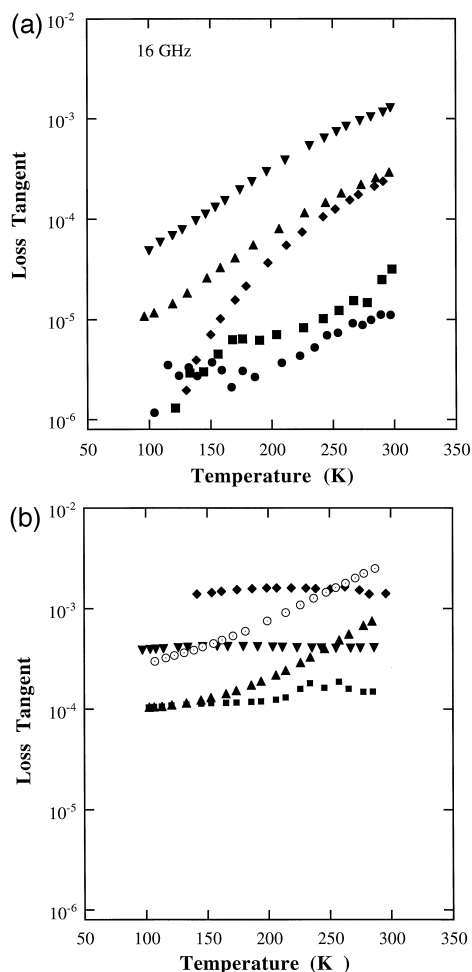

Fig. 5. Frequency dependence of loss tangent at room temperature for the alumina shown in Fig. 4, after a thermal treatment at 1550°C – with 600 ppm of iron (●), with > 600 ppm (▲). Data for W995 sample before (□) and after (■) the same thermal treatment are also included.

Fig. 6. Temperature dependence of loss tangent at 16 GHz for several alumina types: (a) high purity grades – RB92 (♦), BIO (▲), C9999 (■), MM999 (▼) and UC sapphire (●), (b) low purity grades – KA473 (♦), MM995 (▲), W995 (■), MM975 (▼), and C997 (○).

position after this treatment are almost the same that in that sample. The low frequency loss is also reduced.

3.3. Temperature dependence

The dependence of loss tangent with temperature is a useful information for both applied and theoretical research. The loss tangent measured in the several alumina samples when cooling the 15–17 GHz resonant cavity is shown in Fig. 6. It can be observed that two general trends are observed. In a first group we observe a quite important decrease of loss tangent when the temperature decreases. High purity aluminas, MM995 and C997 samples are included in this group. The second one shows only a small decrease of loss tangent (like W995, MM975 and KA473). The large reduction is due to two effects. In very pure materials, like UC-sapphire, previous works indicate that it is mainly due to the narrowing of the very high frequency photon–phonon peak. So, the sharp increase observed at 10^{10} Hz is shifted to higher frequencies, lowering the dielectric loss in this region. The second effect is very well illustrated by samples MM999, MM995 and C997. In these cases, a DL peak exists at frequencies near but below the 15 GHz point. A temperature reduction means that the DL peak shift to lower temperatures [1] leading to a reduction in its high frequency side. This is the expected behavior for a thermally stimulated process. Some activation energies were calculated in a previous work [1] for samples C997 (0.29 eV) and RB92 (0.18 eV) from the shift of the peak with temperature.

Therefore, from an applied point of view it can be said that huge peaks in the frequency spectra will give rise to large variation of loss with temperature due to this peak shift. In the case of high but almost 'flat' loss versus frequency, a lower temperature dependence is observed.

4. Conclusions

An updated database of dielectric properties from a set of commercial aluminas has been presented. An effort has been made in order to be able to measure in as wide frequency range as possible. The curve so obtained provides information useful for many different applications.

The wide spread in dielectric loss between different grades is probably due to differences in impurity content and their chemical state. A discussion of different aspects of impurities has been presented. It is shown for example that the effect of impurities can be maximum for some low concentrations and that adding other impurities can alter drastically the dielectric absorption. Up to now it has only been possible to study two of the more common alumina impurities: magnesium and iron.

In the case of doping with Mg, a dielectric absorption occurs at about 100 MHz. The magnitude of loss is maximum for a concentration near 400 ppm, which is the solubility limit of magnesium in alumina. None of the thermal treatments could change the dielectric spectrum.

On the other hand, doping with iron does not change the dielectric spectrum at high frequency. Only when a thermochemical reduction is done, is a DL peak observed in the 0.1 to 1 GHz range. The comparison with the Wesgo AL995 sample seems to indicate that the same mechanism occurs after a reducing treatment due to its similar amount of iron.

Clearly a systematic study of several impurities can give important knowledge about their influence on alumina and so how to choose the optimal powder.

References

[1] J. Mollá, R. Heidinger, A. Ibarra, J. Nucl. Mater. 212–215 (1994) 1029.
[2] G. Link, R. Heidinger, in: 18th Int. Conf. on Infrared and Millimeter Waves, J.R. Birch, T.J. Parker (Eds.), Proc. SPIE 2104, 1993, p. 150.
[3] R. Moreno, P. Miranzo, J. Requena, J.S. Moya, J. Mollá, A. Ibarra, Ceram. Trans. 21 (1991) 225.
[4] L.H. Rovner, G.R. Hopkins, Nucl. Technol. 29 (1976) 274.
[5] G. P Pells, M. Murphy, J. Nucl. Mater 183 (1991) 137.
[6] S.J. Zinkle, R.H. Goulding, Fusion Materials Semiann. Prog. Rep. DOE/ER-0313/19, 1995, pp. 231–235.
[7] Forschungszentrum Karlsruhe, IMF-1 chemical analysis 360/94, Oct. 1994.
[8] A. Kakimoto, A. Etoh, K. Hirano, S. Nonaka, Rev. Sci. Instrum. 58 (2) (1987) 269.
[9] J. Mollá, A. Ibarra, J. Margineda, J.M. Zamarro, A. Hernández, IEEE Trans. Instrum. Meas. 42 (4) (1993) 817.
[10] V.S. Il'chenko, Sov. Phys. Solid State 31 (1989) 1175.
[11] N.W. Ashcroft, N.D. Mermin, Solid State Physics, ch. 27, Holt-Saunders, Tokyo, 1976.
[12] Y. Kobayashi, M. Katoh, IEE Trans. Microwave Theory Tech. 33 (1985) 586.
[13] N.McN. Alford, S.J. Penn, Appl. Phys. 80 (1996) 6895.
[14] S.J. Penn, N.McN. Alford, A. Templeton, X. Wang, M. Xu, M. Reece, K. Schrapel, J. Am. Ceram. Soc 80 (1997) 1885.
[15] W.R. Tinga, W.A.G. Voss, D.F. Blossey, J. Appl. Phys 44 (1973) 3897.
[16] W.T. Doyle, I.S. Jacobs, J. Appl. Phys 71 (1992) 3926.
[17] H. Looyenga, Physica 31 (1965) 401.
[18] D.A. Bruggeman, Ann. Phys. (Leipzig) 24 (1935) 636.
[19] J.W.S. Rayleigh, Philos. Mag. 34 (1892) 481.
[20] D.E. Aspnes, Am. J. Phys. 50 (1982) 704.

[21] M.C. Wintersgill, Radiat. Eff. Def. Sol. 119–121 (1991) 217.

[22] J.B. Blum, H.L. Tuller, R.L. Coble, J. Am. Ceram. Soc. 65 (1982) 379.

[23] M. Ando, M. Ito, T. Kato, United States patent no. 4.601.990, High-alumina ceramic composition, 1986.

[24] J. Mollá, R. Moreno, A. Ibarra, J. Appl. Phys. 80 (1996) 1028.

[25] J.G.J. Peelen, Materials Science Research, vol. 10, G.C. Kuczynski (Ed.), Plenum, New York, 1975, p. 443.

[26] S.K. Roy, R.L. Coble, J. Am. Ceram. Soc. 51 (1968) 1.

[27] H.W. Wang, C.H. Lee, F.A. Kröger, R.T. Cox, Phys. Rev. B 27 (1983) 3821.

[28] R. Vila, M. Jiménez de Castro, Phys. Rev. 49 (1994) 1696.

[29] P.A. Kulis, M.J. Springis, I.A. Tale, V.S. Vainer, J.A. Valbis, Phys. Status Solidi (b) 104 (1981) 719.

[30] J.J. Krebs, W.G. Maisch, Phys. Rev. B 4 (1971) 757.