

Sintered alumina with low dielectric loss

Neil McN. Alford^{a)} and Stuart J. Penn

School of Electrical, Electronic and Information Engineering, South Bank University, 103 Borough Road, London SE1 0AA, United Kingdom

(Received 23 April 1996; accepted for publication 7 August 1996)

Low dielectric loss materials are required for applications in radio-frequency and microwave communications. Aluminium is the second most abundant element in the Earth's crust and aluminium oxide (alumina) is one of the commonest ceramics. Single crystals of aluminium oxide, i.e., sapphire, possess one of the lowest dielectric losses of any material. Polycrystalline alumina has a higher loss due to extrinsic factors. The dielectric loss of sintered alumina is studied in an attempt to determine the causes of extrinsic loss. Impurities are shown to play an important role, but the microstructure also is a key factor. High-purity aluminas, sintered to near theoretical density, are found to display very low loss, $\tan \delta = 2.7 \times 10^{-5}$ at 10 GHz. Doping alumina with titanium dioxide was found to reduce the $\tan \delta = 2 \times 10^{-5}$. © 1996 American Institute of Physics. [S0021-8979(96)00922-X]

I. INTRODUCTION

Aluminium oxide (alumina) Al_2O_3 is used as a ceramic packaging material because of its high thermal conductivity, suitable dielectric constant, and low dielectric loss. Most of the properties of so-called "high-purity" alumina, e.g., thermal expansion, thermal conductivity, elastic modulus, melting point, Poisson's ratio, and dielectric constant, fall within fairly narrow limits for different samples from a wide range of sources. The dielectric loss, however, is highly variable from sample to sample varying over several orders of magnitude. It is this issue that we address and in particular we show that the dielectric loss of sintered materials can approach that measured in single crystals.

Dielectric loss is conventionally described by the imaginary component of the permittivity, or by $\tan \delta$, the ratio of the imaginary to the real part of the permittivity. The loss is also sometimes expressed in terms of the quality factor Q which in the absence of other sources of loss $= 1/\tan \delta$. The Q values quoted in this article are corrected for other sources of loss, e.g., the copper walls of the resonator, so that $Q = 1/\tan \delta$. This work is concerned with the cause of dielectric loss and how it can be reduced. Losses fall into two categories: intrinsic and extrinsic. Intrinsic losses are dependent on the crystal structure and can be described by the interaction of the phonon system with the ac electric field. The ac electric field alters the equilibrium of the phonon system and the subsequent relaxation is associated with energy dissipation.^{1,2} A fundamental review of the theory of intrinsic losses is presented by Gurevich.² These intrinsic losses set the lower limit of losses found in pure "defect-free" single crystals. Extrinsic losses are associated with imperfections in the crystal structure, e.g., impurities, microstructural defects, grain boundaries, porosity, microcracks, random crystallite orientation. It is clear from our experiments, and those of others, that the loss in sintered ceramics is limited by these extrinsic factors. The huge differences in microstructure and perfection between single-crystal sapphire and

polycrystalline alumina are clear indicators why the conventional wisdom has assumed the impossibility of achieving a dielectric loss approaching that of single-crystal counterparts in the sintered materials. It is of general interest to examine the potential of polycrystalline ceramics and alumina is an excellent model.

A single crystal is made from a melt and the melting point of alumina is 2072 °C. Sintering a ceramic involves taking a fine powder of the material, pressing it into the desired shape, and then heating it to temperatures less than their melting point (usually about 75% of the melting point). In an effort to reduce surface energy, the powders sinter together, reducing surface area until the porosity is reduced substantially or entirely. The sintering process involves less expensive capital equipment and is less energy intensive. For example, a single crystal of alumina in cylindrical form is around 10 000 times more expensive than an identically shaped sintered alumina. Single-crystal sapphire supplied by ESCETE measured in our laboratory has a $\tan \delta$ of 1×10^{-5} .

The lowest claimed dielectric loss in sintered alumina at room temperature (≈ 25 °C) and microwave frequencies was by Woode *et al.*³ who measured a $\tan \delta$ of 4.3×10^{-5} ($Q = 23\,356$) at approximately 9 GHz. This value was a significant improvement over earlier studies, e.g., Molla *et al.*,⁴ who measured $\tan \delta = 3 \times 10^{-4}$ ($Q = 3333$). However, in comprehensive studies on very pure alumina, Molla, Heidinger, and Ibarra^{5,6} and Kobayashi and Katoh⁷ recorded low losses in the region $\tan \delta = 2 \times 10^{-5}$. Molla and co-workers⁵ suggested that these losses were intrinsic in origin. Woode *et al.*³ noted that purity alone was a poor indicator of the dielectric loss tangent. In order to verify this statement we have measured several so-called high-purity aluminas with varying degrees of impurities present. In contrast, it was found that purity does appear to influence the Q ; however, although an impure alumina always gives a poor Q , a very pure alumina is not a guarantee of a high Q . Both high purity and the correct processing are required for a high Q . It must be pointed out that the pure alumina may be purposely doped with certain elements in order to assist the sintering process. It is therefore vital that these additions do not adversely in-

^{a)}Electronic mail: alfordn@vax.sbu.ac.uk

fluence the Q . For example, aluminas with high levels of impurities such as alkali salts (particularly sodium) are seen to possess a higher dielectric loss. Also, metallic impurities might be expected to reduce Q and this is observed in the studies of the impure alumina powders discussed below.

II. EXPERIMENT

To investigate the difference between high-purity powders, ceramic pucks were produced from a range of commercially available high-purity powders. The powders were pressed in a 13-mm-diam stainless-steel die press at a pressure of 100 MPa. The pressed samples were sintered in air at 1550 °C for 300 min. The sample density was measured by noting the sample mass and dimensions. The dielectric constant and dielectric loss were measured at 9 GHz using a parallel-plate resonator (modified Hakki–Coleman⁸) technique. To reduce the influence of the copper plates on the Q measurement the dielectric sample is placed in the gap between the copper plates on a 4-mm-high, 10-mm-diameter disk of low-loss quartz. The sintered alumina samples were also approximately 10-mm-diam, 4-mm-thick disks. The $TE_{01\delta}$ mode was examined using a Hewlett–Packard HP8719C vector network analyzer with 1 Hz resolution. All dielectric measurements were carried out at room temperature in air at a relative humidity of approximately 30%. No special precautions were taken to prevent the adsorption of water to the sample surface which might be expected to have an adverse effect on the dielectric loss. The disks were measured in the “as-fired” condition, i.e., without surface preparation such as polishing. The loss measurements are presented in terms of the Q factor, i.e., $(\tan \delta)^{-1}$. The effect of the copper plates on the Q was corrected for using the Itoh–Rudokas model.⁹ Great care was taken to ensure that the sample Q was measured correctly. In order to test the measurement equipment a range of ceramic dielectric resonator materials from different manufacturers (Morgan Matroc, Tekelec, Murata) were tested. In all cases the sample Q which was measured agreed closely with the manufacturer’s measurements. These samples generally possessed a higher dielectric constant so that in practice the experiment was more straightforward due to the fact that more of the electromagnetic field is confined in the sample. In alumina, with a dielectric constant of approximately 10, care must be taken to avoid radiation losses and this was achieved by carefully adjusting the distance between the gaps between the copper plates and the sample. A major factor was to ensure parallelism of the copper plates with respect to the sample as only a few microns misalignment can have an adverse effect on the Q . Results have been confirmed using a cavity resonator technique. Table I shows the impurity analyses from the powder manufacturers of powders A–E and also gives the sintered density and measured Q at 9 GHz. The major impurities consist of Na, Mg, Si, Fe, Ca, and Cu. All the powders used were commercial alpha alumina powders with similar surface areas. Other alumina powders were also tested which had surface areas of approximately $1 \text{ m}^2 \text{ g}^{-1}$. The sintered density of these powders was too low for meaningful comparisons to be made.

TABLE I. Chemical analyses (ppm) and surface areas of aluminum oxide powders used. Sintered density and Q at 9 GHz is also shown.

Impurity (ppm)	Powder				
	800	300	600	20	6
Na ₂ O	800	300	600	20	6
MgO	400	1000	1800	16	5
SiO ₂	400	400	400	85	18
Fe ₂ O ₃	300	100	200	29	11
CaO	200	40	300
SO ₃
CuO	13	4
Surface area ($\text{m}^2 \text{ g}^{-1}$)	7	5	3	5–10	9–16
Density (%)	97.8	98.2	79.2	98	99
Q (at 9 GHz)	3500	1000	4500	37 000	35 000

An increased level of impurities in the alumina powders was observed to cause a deterioration in the Q . Indeed, in some less pure aluminas tested the Q was so poor as to be unmeasurable. The two purest aluminas gave the highest Q but the purest alumina, alumina E did not achieve the highest Q and this may be due to a powder surface area effect which has a large influence on the manner in which the powders sinter. The effect of porosity on the dielectric loss was also checked and found to have a very significant effect. Alumina D was chosen and sintered at temperatures between 1000 and 1550 °C for 5 h in order to vary the final density. Figure 1 shows the effect of sample density on the Q and demonstrates the extreme importance of microstructure in determining the extrinsic loss. The theoretical density of alumina was taken as 3.97 Mg m^{-3} and the correlation coefficient between Q and density was $r=0.87$, which is significant at the 99.9% confidence level. Because of the variation in Q with density we have compared samples with varying levels of impurity at near-theoretical density. At the highest density the Q was found to be 37 000. The microstructure of the samples with varying porosity is seen in Figs. 2(a) and 2(b). The difference in microstructure is clearly seen in terms of grain size and porosity. We also measured the dielectric constant of the aluminas and found that it behaved much as expected decreasing as pore volume increased and followed a Maxwell mixture law¹⁰ fairly closely.

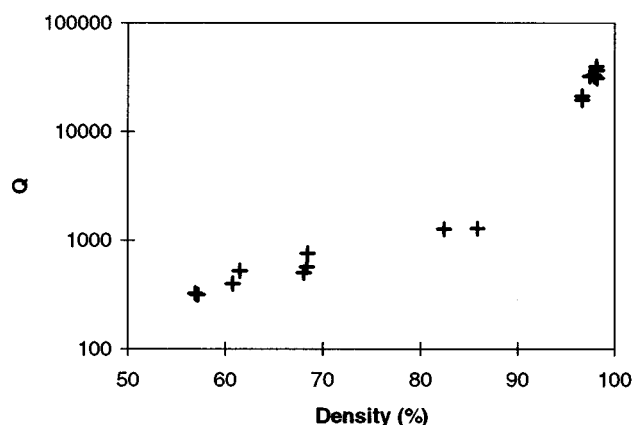


FIG. 1. The effect of density on the Q at 9 GHz of polycrystalline alumina.

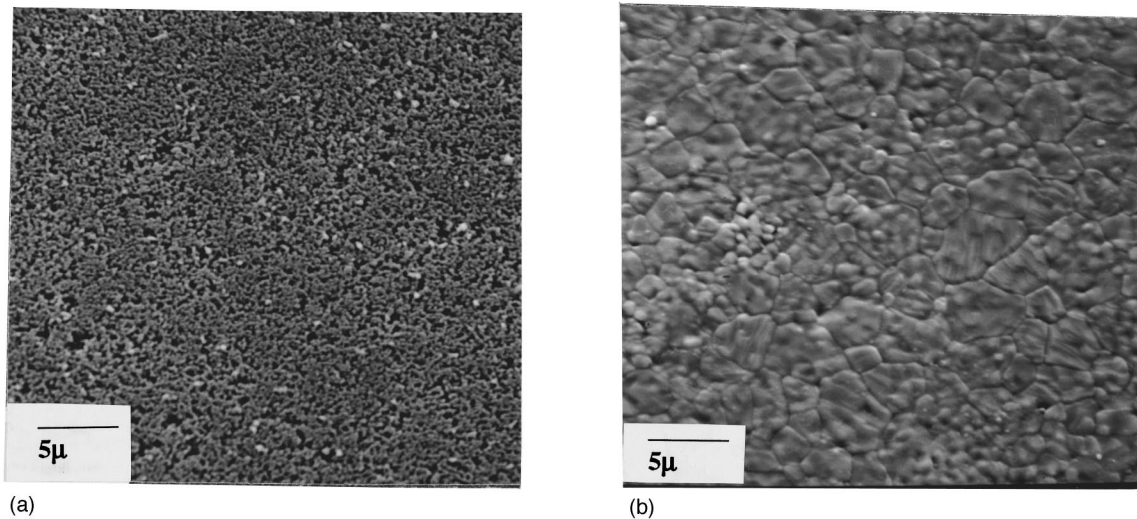


FIG. 2. Scanning electron micrograph showing variation in microstructure with density: (a) alumina sintered at 1100 °C, 5 h, 40% porosity; (b) alumina sintered at 1550 °C, 5 h near full density.

In the second series of experiments a high-purity alumina (alumina D) was doped with titania, TiO_2 . The addition of TiO_2 to sapphire single crystal has been noted by Heidinger¹¹ where he examined sapphire in which 0.02 wt % TiO_2 was added to the melt. The $\tan \delta$ of the Ti:sapphire at 300 K was not improved over an undoped single crystal made by the Czochralski technique and a single crystal made by the Bridgeman technique at 145 GHz. The $\tan \delta$ at this frequency of all three of the single crystals was approximately 2×10^{-4} ; however the TiO_2 doping level was lower in comparison with the levels reported below. In the following experiments, the TiO_2 was added to the alumina by thoroughly mixing TiO_2 powder with the alumina powder. The addition of TiO_2 influences the sintering temperature at which the material achieves high density and for this reason the aluminas doped with TiO_2 were sintered at 1500 °C. The results of doping the alumina with TiO_2 on the Q are shown in Fig. 3 and Table II. It is seen that the Q increases to a maximum of 50 300 at a doping level of 0.5 wt % TiO_2 ; this is about 50% of the Q of a high-quality single crystal.

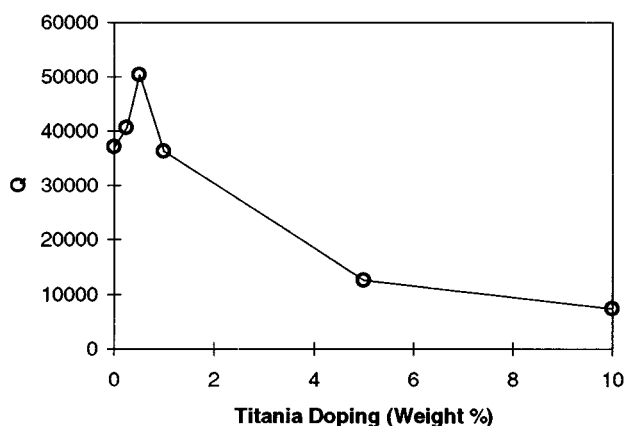


FIG. 3. The effect of TiO_2 doping on the Q of alumina at 9 GHz.

Samples of TiO_2 sintered in air to full density display a very low Q (1500) compared with that of a single crystal of TiO_2 which had a measured Q of 7000. Pure stoichiometric TiO_2 is white in color, the ceramics sintered in air show a darkening to a brown-tan color, this being due to the fact that TiO_2 is easily reduced.¹²⁻¹⁴

The samples of alumina doped with titania display a bluish tinge and a slight darkening from their usual white color and this may be due to a stoichiometric deficiency of oxygen.¹⁴ It might be expected that doping with TiO_2 would reduce the Q due to the inclusion of a high-loss component and possible reduction of the oxide. The fact that there is an enhancement in the Q is surprising and it is not clear at present whether the TiO_2 plays an active role in reducing the loss or whether the addition of TiO_2 has simply improved the microstructure by acting as a sintering aid. The microstructure of the 0.5 wt % TiO_2 doped alumina is shown in Fig. 4 where it is seen that the grain size varies between 2 and 10 μm . The grain structure is quite different in comparison with the undoped alumina which achieved near-theoretical density at 1550 °C [Fig. 2(b)] requiring a higher temperature compared with the TiO_2 -doped alumina which achieved near-theoretical density at 1500 °C (Fig. 4). The 0.5 wt % TiO_2 -doped alumina shown in Fig. 4 possesses a slightly larger grain size than the undoped alumina shown in Fig. 2(b) even though the sintering temperature was lower suggesting that the TiO_2 has indeed acted as a very effective sintering aid. Energy-dispersive x-ray analysis revealed that

TABLE II. Effect of TiO_2 dopant on the Q of alumina at 9 GHz.

TiO_2 (wt %)	Q
0	37 000
0.25	40 599
0.5	50 310
1	36 170
5	12 650
10	7 376

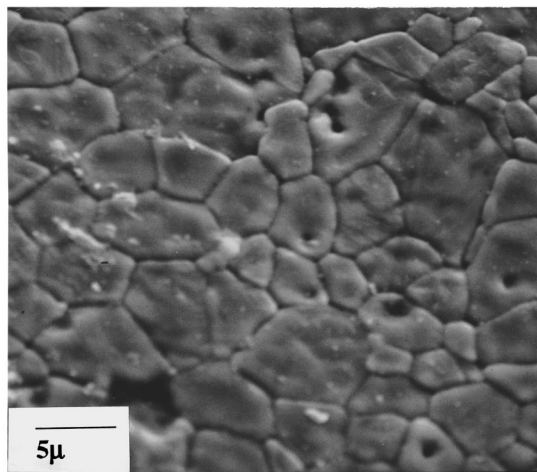


FIG. 4. Scanning electron micrograph of sintered alumina doped with 0.5% TiO₂ sintered at 1500 °C, 5 h.

the Ti is located in discrete grains at the triple points of the alumina grains. Transmission electron microscopy performed on 12 of these grains further indicates that the Al:Ti ratio is very close to of 2:1 suggesting that aluminum titanate, Al₂TiO₅, has formed. The samples appear highly strained as seen in Fig. 5 where the presence of dislocation loops is clearly seen. It is possible that the strain present in the sintered samples has a direct effect on the dielectric loss; however, this is the subject of further study. The 10 wt % TiO₂-doped alumina grain morphology is entirely different consisting of larger, rounded, and equiaxed grains due to the presence of larger amounts of aluminum titanate.

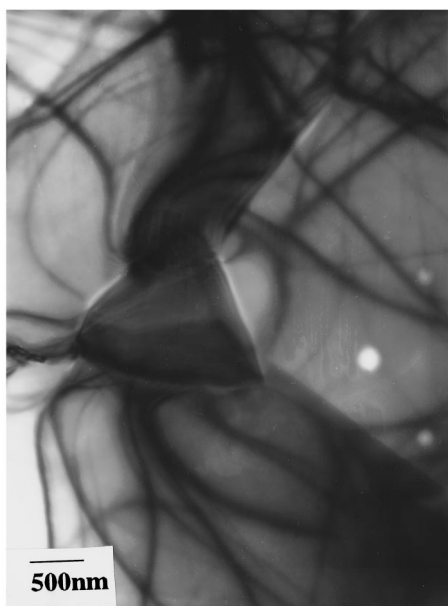


FIG. 5. Transmission electron micrograph showing aluminum-titanate-rich region at the triple point of alumina grains and the presence of dislocation loops. Marker is 500 nm.

Substituting Nb and Y for Ti also produces an enhanced Q but Zr did not alter Q indicating that at least certain elements close to Ti in the periodic table when used as a dopant do not increase loss and indeed could even reduce the loss; however, in these doping experiments Q was found to be extremely sensitive to the sintering regime. The reasons for the reduction in dielectric loss with the addition of TiO₂ are not fully understood; however the possibilities are: first, that the reduction of the titanium oxide is responsible; second, that the presence of strain due to TiO₂ addition is a major factor; or, finally, that the addition of the TiO₂ has simply acted as a sintering aid and has improved the overall microstructure of the samples.

III. CONCLUSIONS

In conclusion, we have shown that high-purity polycrystalline sintered alumina can achieve low dielectric loss. Doping the alumina with titania, TiO₂, has produced a material with an exceptionally low dielectric loss at room temperature and at microwave frequencies approaching that of sapphire single crystals. Low-temperature measurements are currently in progress and indicate that significant further reduction in the loss is achievable. Further experiments are in progress involving the use of superconducting shields at low temperature and the indications in preliminary experiments are that there is a considerable enhancement in the Q at cryogenic temperatures.

ACKNOWLEDGMENTS

Thanks are due to John Gallop of NPL and Tony Centeno and Jonathan Breeze of Matra Marconi Space for useful discussions. Special thanks are due to Norbert Klein of KFA Jülich for carrying out measurements at cryogenic temperatures the results of which are due to be reported. We are indebted to Kevin Schrapel and Mike Reece at Queen Mary and Westfield College, London for x-ray and TEM analysis. This work is supported in part by an EPSRC grant.

- ¹V. B. Braginsky and V. S. Ilchenko, Phys. Lett. A **120**, 300 (1987).
- ²V. L. Gurevich and A. K. Tagantsev, Adv. Phys. **40**, 719 (1991).
- ³R. A. Woode, E. N. Ivanov, M. E. Tobar, and D. G. Blair, Electron. Lett. **30**, 417 (1994).
- ⁴J. Molla, A. Ibarra, J. Margineda, J. M. Zamarro, and A. Hernandez, IEEE Trans Instrum. Meas. **42**, 817 (1993).
- ⁵J. Molla, R. Heidinger, and A. J. Ibarra, Nucl. Mater. **212–215**, 1029 (1994).
- ⁶A. Ibarra, R. Heidinger, and J. Molla, J. Nucl. Mater. **191–194**, 530 (1992).
- ⁷Y. Kobayashi and M. Katoh, IEEE Trans. Microwave Theory Tech. **33**, 586 (1985).
- ⁸B. W. Haki and P. D. Coleman, IEEE Trans. Microwave Theory Tech. **8**, 402 (1960).
- ⁹D. Kajfez and P. Guillon, *Dielectric Resonators* (Artech House, Zürich, 1986).
- ¹⁰W. D. Kingery, H. K. Bowen, and D. R. Uhlmann, *Introduction to Ceramics* (Wiley, New York, 1976), Vol. 2.
- ¹¹R. Heidinger, J. Nucl. Mater. **212–214**, 1101 (1994).
- ¹²M. Reece and R. Morrell, J. Mater. Sci. **26**, 5566 (1991).
- ¹³R. G. Betsch, H. L. Park, and W. B. White, Mater. Res. Bull. **26**, 613 (1991).
- ¹⁴F. A. Grant, Rev. Mod. Phys. **31**, 646 (1959).