

Dielectric loss of oxide single crystals and polycrystalline analogues from 10 to 320 K

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Abstract

The key factors influencing microwave dielectric loss are examined. A comparison is made between single crystals and polycrystalline analogues. Measurements of the temperature dependence of microwave dielectric losses in various materials are reported, for temperatures between 20 and 300 K. Single crystal and polycrystalline TiO₂, LaAlO₃, MgO and Al₂O₃ are considered. The temperature dependence of dielectric losses of certain single crystals (MgO and Al₂O₃) are found to be in good agreement with the theory of intrinsic losses for temperatures above 100 K. At lower temperatures losses due to defects and grain boundaries dominate. The absolute value of the loss predicted by theory is considerably lower than measured values. © 2001 Published by Elsevier Science Ltd. All rights reserved.

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1. Introduction

Dielectric materials with very high quality factor Q can be used as compact resonators for application in microwave communications. High quality single crystals always display lower loss than polycrystalline analogues but the precise reasons for this are not always obvious.¹

In this paper measurements of microwave dielectric losses in both single crystal and polycrystalline materials are presented. The losses are characterised in terms of the loss tangent $\tan\delta = \epsilon_I/\epsilon_R$, where ϵ_I and ϵ_R are the imaginary and real part of the dielectric constant respectively. The quality factor Q is then given by $Q = 1/\tan\delta$. A dielectric resonator technique was used to measure $\tan\delta$ of TiO₂, LaAlO₃, MgO and Al₂O₃ for temperatures in the range 20–300 K at microwave frequencies. We also compare the measurements for single crystals with the theory of intrinsic dielectric losses developed by Gurevich and Tagantsev.² The theory calculates losses due to the interaction of the electromagnetic field with the phonon system of the crystal, and has previously been found to agree well with experimental measurements on the temperature dependence of sapphire³ for temperatures above approximately 100 K.

The comparison with the theory for single crystals constitutes the first step towards an understanding of loss mechanisms in polycrystalline materials, for which a theory is not at present available.

2. Experimental technique and materials preparation

Single crystals were obtained from ESCETE BV, The Netherlands. Polycrystalline samples were prepared using high purity oxide materials. Al₂O₃ and TiO₂ preparation is described in Refs. 4 and 5. LaAlO₃ was prepared using La₂O₃ and Al₂O₃ and MgO was prepared using MgO powder. The powder was pressed in a 13 mm stainless steel die set and sintered in air at temperatures between 1400–1650 °C depending on composition. All sintered discs were near full density with diameter and height of approximately 10 mm and 4 mm, respectively.

The Q was measured at approximately 3–10 GHz by a resonant cavity method using the TE₀₁₈ mode. The sample was placed in an oxygen-free copper cavity on a 4 mm high low loss quartz spacer. The surface resistance of the copper was calculated from the Q of the TE₀₁₁ resonance of the empty cavity to allow the results to be corrected for the loss due to the cavity walls.⁶ The TE₀₁₈ mode was examined using a vector network

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analyser (Hewlett Packard HP8720C) with 1 Hz resolution. The polycrystalline discs were measured in the “as-fired” condition, i.e. without surface preparation such as polishing. Low temperature measurements were performed by placing the cavity on the cold head of a closed cycle Gifford McMahon cooler (“Workhorse”, Cryophysics, Abingdon, UK). We also refer to work carried out on several single crystals by Krupka et al.⁷ who used the HE₁₁₁, HE₂₁₁, TE₀₂₁ as well as the TE₀₁₁ modes. There is considerable advantage in this if the effect of crystal anisotropy is to be investigated. In our measurements, the principal concern is the comparison of polycrystalline ceramics with single crystal analogues.

3. Theory of intrinsic dielectric losses

Intrinsic dielectric losses are the losses in perfect crystals due to the interaction of the a.c. electric field with the phonon system of the crystal. A complete theory of intrinsic dielectric losses has been developed by Gurevich and Tagantsev.²

Several phonon processes contribute to intrinsic losses in a dielectric, their importance depending on the a.c. field frequency, the temperature range and the symmetry of the crystal under consideration. In particular, loss mechanisms are different in the case of a crystal with a centre of inversion symmetry [centrosymmetric crystal (CS)] from the case of a crystal without one (non-centrosymmetric crystal). In this paper we consider CS crystals, in which losses are generally lower than in non-CS ones. For CS crystals losses are due to two-phonon and three-phonon processes.

Gurevich and Tagantsev² have discussed separately the case in which the sample temperature is much lower than the Debye temperature of the crystal ($T \ll \Theta_D$) and the one in which the temperature is of the same order or higher than the Debye temperature ($T \sim \Theta_D$). In the former temperature range one is allowed to consider the interaction of the electromagnetic field with the acoustic phonon system only. In the latter, the optical branches also need to be taken into account.

At low temperatures ($T \ll \Theta_D$), in CS crystals, the two-phonon losses are strongly influenced by the sym-

metry of the crystal. This is due to the stringent restriction on the range of quasi-momentum values k of the acoustic phonons that participate in the absorption process. The result of this is that crystals belonging to different symmetry groups have very different temperature and frequency dependencies of $\tan\delta$ (see Table 2 of Ref. 2). For crystals with uniaxial anisotropic permittivity such as Al₂O₃ and TiO₂ the temperature and frequency dependency of $\tan\delta$ are different in the directions parallel and perpendicular to the c -axis. For most crystals, temperature dependencies of $\tan\delta \propto T^4$ or T^5 can be found. This is the case for sapphire, for example, for which the theory predicts $\tan\delta \propto T^5$. This was verified experimentally by Braginsky³ in the temperature range 100–300 K (the Debye temperature of sapphire is $\Theta_D = 1047$ K). The three-phonon losses at low temperatures give $\tan\delta \propto T^7$. In most cases these losses are usually negligible with respect to two-phonon losses, but can become dominant in certain frequency ranges due to a greater range of available k values which can participate in the absorption process. Estimates of the loss tangent, from consideration of the mean lifetimes of acoustic phonons and first-order estimates of the change in the inter-atomic force constants in the presence of an electric field are given by

$$\tan\delta = \frac{\eta\omega(kT)^5}{\varepsilon'\rho v^5\hbar^2(k\Theta)^2} \quad (1)$$

for hexagonal symmetry and

$$\tan\delta = \frac{\eta\omega^2(kT)^4}{\varepsilon'\rho v^5\hbar(k\Theta)^2} \quad (2)$$

for rhombohedral or cubic symmetry

η is a dimensionless anharmonicity parameter ranging between 1–100 (we have used 100), ω is the angular frequency, k is Boltzmann's constant, T is absolute temperature, ρ is the density of the dielectric, ε' is the relative permittivity, v is the sound velocity, Θ is the Debye temperature.

In Table 1 the properties of the materials under question are presented. The Debye temperatures of materials are obtained from several sources including Ref. 8. For

Table 1
Properties and predicted losses for crystals assuming a measurement frequency of 10 GHz and measurement temperature of 300 K

Crystal	Structure	Young's modulus E GPa	Density ρ kg/m ³	Relative permittivity ε'	Θ_D (K)	Wave velocity v (m/s)	Tan δ theory	Tan δ experiment
Al ₂ O ₃	Hexag	400	3970	10	1047	10,000	8×10^{-8}	1×10^{-5}
MgO	Cubic	250	3580	9	946	8355	1.5×10^{-10}	1×10^{-5}
TiO ₂	Tetrag	289	4260	89 $\perp c$, 173// c	760	8 250	7×10^{-10} , 4×10^{-10}	1.4×10^{-4}
LaAlO ₃	Cubic	235	6520	25	720	6000	9×10^{-9}	3.5×10^{-5}

LaAlO₃ the source for Debye temperature and wave speed (v) is Ref. 9). The wave speed for MgO, is calculated from $v = (E/\rho)^{1/2}$ using data in ref 9, where E is the elastic modulus and ρ is the density. E for MgO and Al₂O₃ is from Ref. 10 and E for TiO₂ from Ref. 11. The different values for the relative permittivity of TiO₂ are taken from Grant¹² but no anisotropy variations in the elasticity and hence the wave velocity were considered. Actual measurement frequencies are those noted in the text and $\tan\delta$ has been scaled on the assumption that Qf is constant. As the measured frequency is fairly close to 10 GHz the error in this assumption is small.

For sample temperatures in the range $T \sim \Theta_D$, optical phonon modes are excited by anharmonic absorption which decay into acoustic phonons. The temperature dependence of the losses does not depend on the crystal symmetry and is typically of the type $\tan\delta \propto T$ for two-phonon processes and $\tan\delta \propto T^2$ for three-phonon processes. The frequency of the e.m. field determines which of the two processes prevails. This is in agreement with the results of the early experimental study by Stolen and Dransfeld¹³ on alkali halides. The latter have Debye temperatures around 100–200 K, so that range of measurements satisfies $T \sim \Theta_D$.

We note that a model of intrinsic dielectric losses developed by Sparks et al.^{14,15}, is frequently used in the analysis of experimental results (see, for example, Ref. 29). This model calculates the dielectric losses due to lifetime broadened two-phonon processes. The model, developed for the alkali halides, is found to agree well with the earlier results of Stolen and Dransfeld.¹³ The application of the model for materials which are not alkali halides, however, poses some problems. Firstly, the model cannot describe losses at temperatures much lower than the Debye temperature, i.e. predict the steep temperature dependencies observed, for example, in sapphire. Secondly, it does not take into account three-phonon processes and as such is applicable only in limited frequency ranges. The theory developed by Gurevich and Tagantsev² includes the result of Sparks et al. (see pages 731–732 of Ref. 2), and is also able to describe the role of other processes such as acoustic and quasi-Debye losses. On these grounds we have chosen to use the Gurevich and Tagantsev model.

3.1. Experimental results and comparison with theory of intrinsic dielectric losses

Before we examine the temperature dependence experiments, it is worth considering the essential differences between single crystals and polycrystalline ceramics. In all cases we consider losses in the range ~ 1 –20 GHz, i.e. well below infra-red. It is well worth mentioning that losses have been examined in the far infra-red¹⁶ but always extrapolate to values well below

experimental data taken at 1–20 GHz.¹⁷ Wersing¹⁸ has distinguished three mechanisms for microwave absorption.

3.1.1. Losses in ideal crystals

This is treated in detail by Gurevich and Tagantsev.² Here crystal symmetry is a key factor and has been discussed briefly above.

3.1.2. Losses in real crystals

Here we consider good single crystals in which there are defects such as interstitials or vacancies, dislocations etc. Such defects will affect both the absolute value of the loss for a given temperature and will also affect the temperature dependence of the loss. Losses due to different types of defect display different frequency and temperature dependence. The effect of oxygen vacancies on the dielectric loss of polycrystalline TiO₂ has been examined by Templeton et al.⁵ (exactly the same arguments will apply to single crystal rutile). They found that very pure TiO₂ sintered to high density displayed very poor $\tan\delta$ of approximately at 300 K. On cooling, the pure TiO₂ showed a dramatic reduction in the $\tan\delta$ at around 100 K and this was interpreted as carrier freeze-out. In order to prevent the reduction of Ti⁴⁺ to Ti³⁺ the pure TiO₂ was doped with 2+ and 3+ ions with ionic radii in the preferred range 0.5–0.95 Å. The $\tan\delta$ at 3 GHz of such materials was reduced considerably and dropped smoothly as a function of temperature from 6×10^{-5} at 300 K to a value of 5×10^{-6} at 15 K.

3.1.3. Losses in polycrystalline ceramics

Here we may distinguish a wide variety of factors which may influence loss. On the basis of experiments we have carried out it is possible to suggest a very tentative hierarchy of defects which contribute to the loss. Here we ignore the effect of random crystallite orientation. However, we note that in TiO₂ for example the anisotropy in the ϵ_r is very large ($\epsilon_r/c = 173\epsilon_r \perp c = 89$).¹⁹

3.2. Impurities

The effect of even minor amounts of impurity can reduce the Q significantly. In polycrystalline alumina there is a dramatic decrease in the Q with the addition of alkalies and metallic impurities and a far smaller effect on the Q with the addition of silica as seen in Table 2. Interestingly, the Q can be increased by the addition of TiO₂ to values in excess of 50,000 at 10 GHz.²⁰ The exact reason for this is unclear but in TEM samples, it is observed that there is an increase in the dislocation density in the TiO₂ doped alumina suggesting that there is stored energy within the samples. Stress effects can affect the dielectric loss considerably. In lead based perovskite ferroelectrics applied pressure reduces

Table 2
Effect of impurities on the Q of dense sintered alumina at 10 GHz

Dopant	Level (ppm wt)	Q_u (10 GHz)	Level (ppm wt)	Q_u (10 GHz)
K ₂ CO ₃	100	ND ^a	500	6500
Na ₂ CO ₃	100	2000	500	ND
SiO ₂	100	33,000	500	25,000
Fe ₂ CO ₃	100	4000	500	950
TiO ₂	100	48,000	500	50,000
Control Al ₂ O ₃	0	40,000	0	

^a ND, not determinable.

the $\tan \delta$ at room temperature.²¹ The effect of pressure on microwave dielectric materials is the subject of further research. We have also observed how the presence of certain additives can maintain low $\tan \delta$ in TiO₂ by preventing the creation of oxygen vacancies as noted above.

3.3. Porosity

The pore volume in polycrystalline alumina plays a critical role in determining the $\tan \delta$. Penn et al show that even small amounts of porosity considerably reduce the $\tan \delta$ and suggested Eq. (3) which provided a good fit to their experimental data on polycrystalline alumina as shown in Fig 1.

$$\tan \delta = (1 - P)\tan \delta_0 + A'P \left(\frac{P}{1 - P} \right)^{\frac{2}{3}} \quad (3)$$

The data were fitted to this model to give $\tan \delta_0 = 1.565 \times 10^{-5}$ and $A' = 9.277 \times 10^{-3}$. Eq. (3) is a good fit to the data and gives a full density $\tan \delta$, which is higher than that of a single crystal. This is expected as even in a fully dense ceramic there will be sources of loss, e.g. random grain orientation and grain boundaries that are not present in a single crystal. It is not unreasonable to consider that the loss may be related to

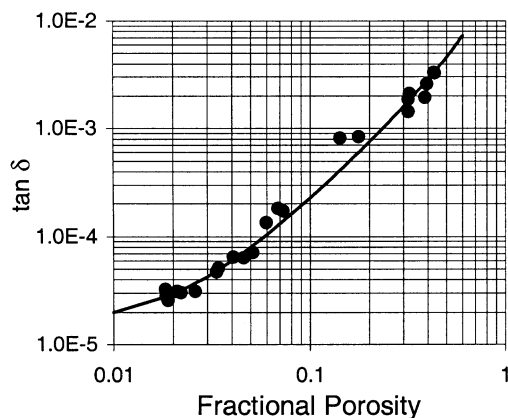


Fig. 1. Effect of porosity on the $\tan \delta$ of polycrystalline alumina at 300 K and 10 GHz taken from Ref. 22. Fitted curve is Eq. (3).

the surface area of the porosity as the structure of the alumina at the surface of a pore is in a different environment to the alumina within the matrix. Mackrodt^{23–25} has shown, for example, that the presence of a free surface (such as a pore) leads to a relaxation of the crystal lattice.

3.4. Grain size

The effect of grain size in polycrystalline dielectrics is anomalous. In alumina the $\tan \delta$ increases as the grain size increases, but in polycrystalline TiO₂ there is no influence of grain size on $\tan \delta$ as seen in Figs. 2a and b. This conflicting behaviour may be responsible for the conflicting views on the relationship between grain size and loss in the literature.²²

3.5. Grain boundaries

It is generally the case that any impurities are swept to the grain boundaries by diffusion. At the grain boundaries there may be relaxation of space charges or dipoles. The two-phonon acoustic and quasi-Debye can

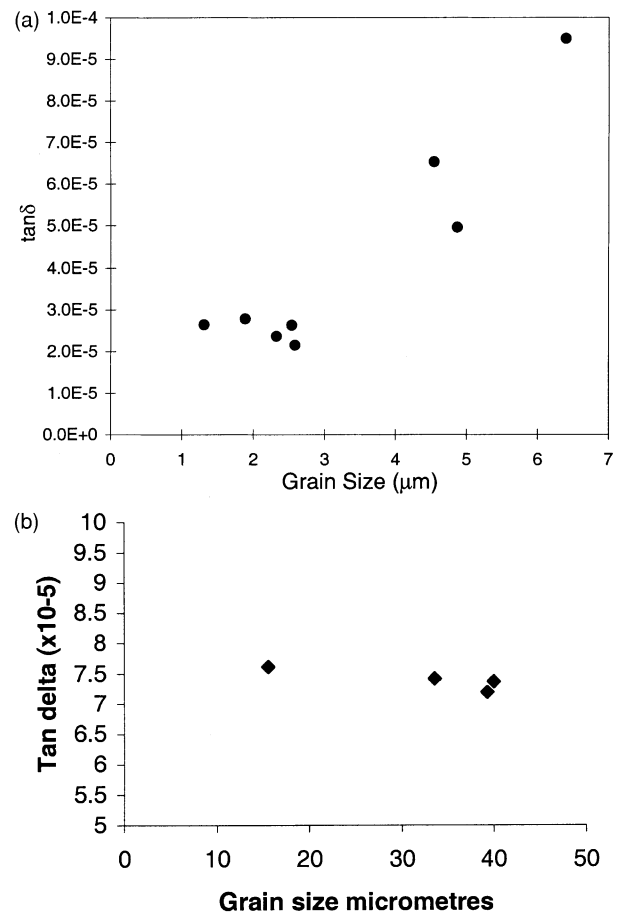


Fig. 2. (a) Effect of grain size on $\tan \delta$ of alumina (300 K and 10 GHz) Ref. 22; (b) Effect of grain size on $\tan \delta$ of polycrystalline TiO₂ at 3 GHz and 300 K. From Ref. 30.

occur at the grain boundaries due to relaxation of the conservation of quasi-momentum rules and a breakdown of time-reversal symmetry.^{26,27}

4. Comparison of the temperature dependence of single crystals and polycrystalline analogues

TiO₂: the results of measurements of $\tan\delta$ for single crystal (See also Ref. 28 and polycrystalline TiO₂ are presented in Fig. 3. Surprisingly, the losses are very similar for the two samples and it is not clear at present why this is the case. The intrinsic losses in the single crystal can be modelled in terms of the theory of Gurevich and Tagantsev. The Debye temperature of TiO₂ is $\Theta_D = 760$ K. The temperature range of our measurement therefore includes both a region where $T \ll \Theta_D$ (approximately 20–100 K) and one where $T \sim \Theta_D$ (approximately from 100 K to room temperature). We now discuss the predictions of the theory in both these regions and compare them with the experimental result for the single crystal. For the frequency we are considering, $f = 3$ GHz, the theory predicts $\tan\delta \propto T^2$ for $T \sim \Theta_D$. A curve with this temperature dependence fitting the experimental curve at the highest temperature point is shown in the figure, in the range 100–300 K. The single crystal experimental plot decreases with temperature slower than the theoretical curve, and is found to be fitted by $\tan\delta \propto T^\alpha$ with $\alpha = 1.6$. For $T \ll \Theta_D$ the theory predicts $\tan\delta \propto T^4$, as can be derived from Table 2 of Ref. 2 using the fact that the symmetry group of TiO₂ is D_{4h} and that in our experiment the microwave field was perpendicular to the c-axis of the crystal.

MgO: the experimental results for single crystal and polycrystalline MgO are shown in Fig. 4. Magnesium oxide has a Debye temperature $\Theta_D = 946$ K. The temperatures in our range of measurement approximately satisfy the inequality $T \ll \Theta_D$, and we can compare the experimental result with the low temperature theory of

Gurevich and Tagantsev. MgO has a cubic NaCl-type lattice and belongs to the O_h symmetry group. From Table 2 Ref. 2, we see that two-phonon processes for this symmetry group give a dependence of the dielectric losses of the type: $\tan\delta \propto \omega^2 T^4$. A curve $\tan\delta \propto T^4$ fitting the point of highest temperature in the single crystal plot is shown in Fig. 4. The agreement between theory and single crystal measurement is excellent in the region 200–300 K. The dielectric loss in the polycrystalline material is about one order of magnitude higher, but shows a temperature dependence similar to that of the single crystal. At temperatures below 200 K the extrinsic losses dominate.

We conclude that the $T \ll \Theta_D$ theory of Gurevich and Tagantsev² describes the temperature dependence of the losses in MgO well over a limited frequency range. The theory does not give the correct absolute value for the loss.

LaAlO₃: in Fig. 5 results for lanthanum aluminate (LaAlO₃) are shown. The microwave absorption in single crystals of LaAlO₃ has been thoroughly investigated in a paper by Zuccaro et al.²⁹ In that paper it has been shown that plots of $\tan\delta$ versus T for this material are characterized by a peak around $T = 70$ K. We find the

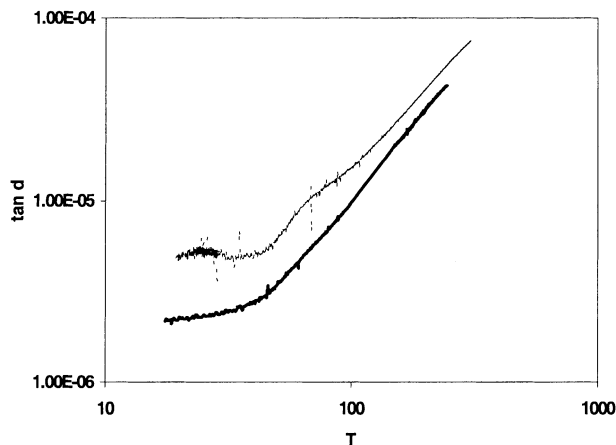


Fig. 3. Temperature dependence of $\tan\delta$ of polycrystalline (upper curve) and single crystal TiO₂ (lower curve) at $f = 3$ GHz.

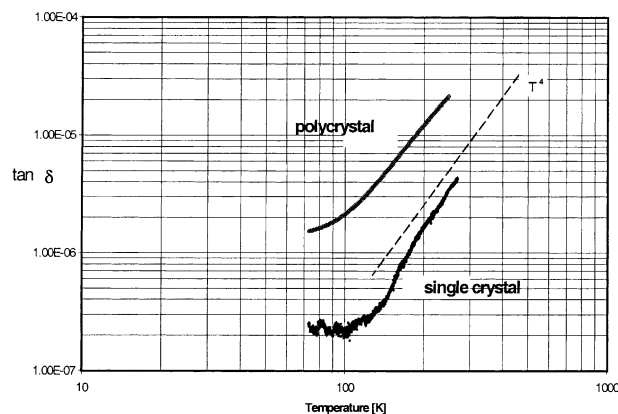


Fig. 4. Temperature dependence of $\tan\delta$ of MgO at $f = 7.5$ GHz.

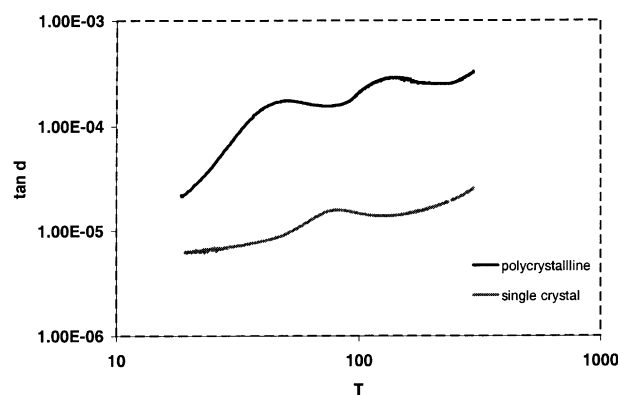


Fig. 5. Temperature dependence of $\tan\delta$ of polycrystalline ceramic (upper curve) and single crystal (lower curve) LaAlO₃ at $f = 7.3$ GHz.

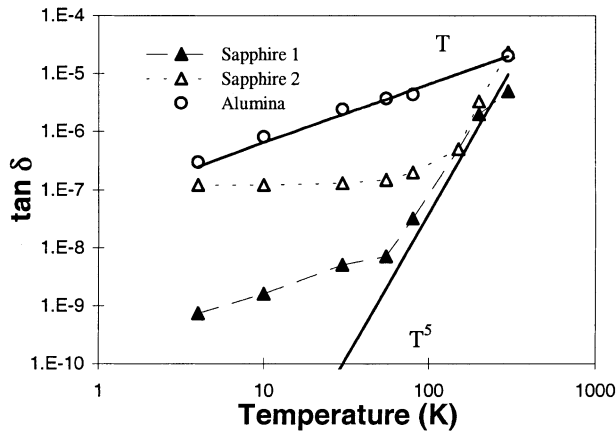


Fig 6. Temperature dependence of Al_2O_3 at 10 GHz. Single crystal data from Ref. 3.

same behaviour in our experiment, as can be seen in Fig. 5.

The peak in the plot of $\tan\delta$ has been explained in Ref. 29 due to relaxation of dipoles associated to defects in the crystal, and the classic Debye formula for dipole relaxation processes has been used to model the experimental results.

$$\tan\delta_D \approx \frac{\omega \exp(-Ea/kT)}{1 + \omega^2 \exp(-Ea/kT)^2} \quad (4)$$

In addition, in some of the single crystal samples considered in Ref. 29 a second peak in the $\tan\delta$ plot was present at higher temperatures (centered at about $T=200$ K). Our plot for the polycrystalline material shows a similar behaviour.

Al_2O_3 : The temperature dependence of the $\tan\delta$ for Al_2O_3 is shown in Fig. 6. Aluminium oxide has been the subject of considerable study in single crystal form, e.g. Refs. 2, 3 and 7. The loss of single crystal sapphire at 300 K is only a factor of two smaller than that for high quality polycrystalline alumina ($\tan\delta=1 \times 10^{-5}$ and 2×10^{-5} , respectively). However the temperature dependence of single crystals over the range $\sim 300\text{--}80$ K is approximately T^5 as predicted by Gurevich et al.² This is in the region $T \ll \theta$. Below ~ 80 K extrinsic losses dominate and the losses are proportional to T . The temperature dependence of polycrystalline alumina $\propto T$ over the entire measured range of temperature. The consequence of this is that at a temperature of 80 K there are more than two orders of magnitude difference in the losses between polycrystalline alumina and single crystal sapphire.

5. Conclusions

The dielectric loss of a series of single crystals and polycrystalline analogues has been examined over a

temperature range of approximately 10–300 K. An investigation of losses in dielectric materials examined the effect of impurities, porosity, grain size and grain boundaries. All can influence the loss profoundly. The effect of vacancies was observed to be quite considerable in the case of TiO_2 for example. Substantial differences are observed in the temperature dependence of the $\tan\delta$ of the materials. Single crystals of Al_2O_3 and MgO (with higher Debye temperatures) agree well with the theory of Gurevich et al.² over a portion of the temperature range (300 to ~ 80 K). Single crystals of TiO_2 and LaAlO_3 with lower Debye temperatures do not agree well with the theory and exhibit quasi-Debye losses. LaAlO_3 in both single crystal and polycrystalline form exhibits certain peaks in the relaxation which are well described by theory. The temperature dependence of TiO_2 in both single crystal and polycrystalline form display remarkably similar characteristics both in temperature dependence and in the absolute value of the loss. Similarly, the temperature dependence for both single crystal and polycrystalline MgO is very similar although the absolute value of the loss between the two forms is significantly different. In Al_2O_3 the temperature dependence of the $\tan\delta$ between 300 to 80 K is $\sim T^5$ for the single crystal, quite different in comparison with the polycrystalline sample where the loss is proportional to temperature. The polycrystalline ceramics studied here always exhibit greater losses than single crystals but in high quality ceramics the differences can be small. In TiO_2 the difference between single crystals and polycrystalline ceramics is small over the entire temperature range of the experiment. At room temperature MgO and alumina ceramics possess losses which are only a factor of around two higher than their single crystal analogues. The research indicates that it is possible to manufacture polycrystalline ceramic dielectrics with remarkably low loss. We can achieve this by a systematic classification of the various factors influencing the loss. Further research is required to isolate the relative influence of crystallite orientation and the relative influence of grain boundaries in polycrystalline dielectric ceramics.

Acknowledgements

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