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Dielectric properties of polycrystalline $CaTiO_3$ doped with yttrium oxide

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Y^{3+} was substituted for Ca^{2+} in polycrystalline $CaTiO_3$ in amounts up to 15 at %. Sintering conditions (1450° C, 15 h) were such that grain sizes were $\gtrsim 25\,\mu m$. Stoichiometry was adjusted on the assumption that the excess charge of the dopant was compensated by the creation of calcium vacancies. This assumption was supported by measurements of the Ca/Ti ratio in the grains by electron-probe microanalysis. Unlike yttrium-doped $SrTiO_3$, material sintered in air was light-coloured with no evidence of semiconductivity. On the other hand, when sintering was done in nitrogen, dielectric relaxation characteristic of boundary layers was observed for dopant levels $\gtrsim 1$ mol %. The experimental data support the view that dielectric relaxation in $SrTiO_3$ and $CaTiO_3$ results from semiconducting grains with resistive surface layers and that the semiconductivity arises because oxygen loss from the grains during sintering is increased by "donor" doping.

1. Introduction

The increased permittivity and dielectric relaxation found in earlier work on donor-doped $SrTiO_3$ sintered in air [1] was explained as a boundary-layer effect resulting from semiconducting grains and weakly insulating grain surfaces. It was concluded that the higher charge of the donor ions was compensated by the creation of large cation vacancies (V_{Sr}), e.g. for yttrium:

$$Sr^{2+}_{1-(3x/2)}(V_{Sr})_{x/2}Y^{3+}_{x}TiO_3 \quad (x \lesssim 0.025).$$

In addition, it was suggested that "donor" doping affects the electrical properties of $SrTiO_3$ primarily by increasing the conductivity that results from loss of oxygen from the grains during sintering, and also by decreasing the rate of re-oxidation on cooling. Oxygen vacancies (V_0) result in grain conductivity by the well known reaction

$$O_0 \rightleftarrows \tfrac{1}{2}O_2 + V_0 + 2e'$$

where O_0 represents an oxygen ion in the titanate lattice. This model is extended in the present work and applied to explain the behaviour of Y-doped $CaTiO_3$.

2. Experimental procedure

2.1. Materials and preparation

Undoped $CaTiO_3$ powder was prepared from reagent grade $CaCO_3$† and high purity (≳ 99.9%) TiO_2‡. Equimolar amounts of the powders were blended in distilled water, dried, and then calcined at 1200° C in air for several hours. The calcined powder was comminuted to an average particle size of 2 to 3 μm without significant contamination by jet-milling. Yttrium oxide§ was blended with the $CaTiO_3$ powder together with extra TiO_2 in the ratio (in moles) of $3TiO_2$ to $2YO_{1.5}$. This method of stoichiometry adjustment assumes that the excess charge of the yttrium is compensated by calcium vacancies on incorporation of the

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dopant in the perovskite structure during sintering. Yttrium levels ($YO_{1.5}$) up to 20 mol% $CaTiO_3$ were used. Because extra TiO_2 was also added, the yttrium concentration expressed as at % of calcium lattice sites was lower, e.g. 20 mol% corresponded to the formula

$$Ca_{0.769}(V_{Ca})_{0.077}Y_{0.154}TiO_3.$$

Samples approximately 1 cm × 1 cm × 0.05 cm were made by the doctor-blade technique. They were heated in air at 750° C for 0.5 h to remove organic binders and then sintered in air, or nitrogen ($p(O_2) \sim 10^{-4}$ atm), at 1450° C for 15 h in platinum-lined alumina boats. Cooling to room temperature was done at a rate of $\simeq 45°\,C\,min^{-1}$ in either air or nitrogen at a flow rate of about $10\,l\,h^{-1}$. Electrical contact was made either by painting indium–gallium on the ceramic plates or applying silver electrode paste which was then fired on at 900° C for 2 h. The paste was made from silver powder mixed with a small amount (e.g. 5 wt %) of bismuth oxide and copper oxide in an organic binder system.

2.2. Measurements

Dielectric properties were measured in the temperature range −55 to 125° C. Capacitance (from which the dielectric constant could be calculated) and dissipation factor (tan δ) were measured in the frequency range 10^2 to 10^5 Hz using an HP-4274A LCR meter controlled by an HP-85 computer. In practice, the LCR meter measures the magnitude of the impedance ($|Z|$) and the phase angle (θ). The dissipation factor ($\tan(90-\theta)$) is obtained directly but an equivalent circuit mode, i.e. series or parallel, must be chosen to obtain a value of capacitance. A series mode was used for the present work. Some authors prefer to represent the dielectric constant as a complex quantity but in such cases the real and imaginary components (K', K'') are both functions of two variables ($|Z|, \theta$).

Resistivity was calculated from the leakage current measured with a Keithly 610B electrometer or was determined by the four-point probe technique with the tips applied directly to a sand-abraded surface.

3. Results

3.1. Effect of yttrium content on grain size

The sintering conditions were such that appreciable grain growth took place during densification. Large grain sizes result in an increase in the apparent permittivity in materials with intergranular boundary layers because fewer layers are in series. In addition, it becomes possible to determine the concentration and uniformity of the dopant in individual grains by electron-probe microanalysis. After sintering at 1450° C for 15 h, undoped $CaTiO_3$ had grains $\simeq 100\,\mu m$ in diameter, and the grain size increased with donor-level up to a maximum of about 500 μm for donor levels of 2 to 5 mol%. Grain size decreased to 50 μm or less at donor levels $\gtrsim$ 10 mol%. Thus, compared with $SrTiO_3$ or $BaTiO_3$, $CaTiO_3$ can tolerate relatively high quantities of yttrium without impeding grain growth. For $SrTiO_3$ sintered under the same conditions [1] a maximum grain size of $\simeq 100\,\mu m$ was obtained with 0.3 mol% Y, and grain size decreased to 10 to 20 μm for yttrium levels of only 1.0 to 2.0 mol%. In $BaTiO_3$, grain sizes are reduced to a few microns with Y levels $\gtrsim$ 0.5 mol% [2], as with other donor dopants [3].

3.2. Electron microprobe

Electron microprobe analysis of polished sections confirmed that essentially all the yttrium was incorporated uniformly in the grains after sintering. Also, as shown in Table I, the Ca/Ti ratio in the grains was measured for various dopant levels using the undoped $CaTiO_3$ as a standard. The data support a model of compensation of the dopant by large cation vacancies [1, 4, 5] rather than electronically by the principle of controlled-valency, as is often assumed for donor-doped titanates [6, 7]. For example, if the grains had the composition

$$Ca^{2+}_{1-x}Y^{3+}_{x}Ti^{3+}_{x}Ti^{4+}_{1-x}O_3,$$

then the Ca/Ti ratio would be $1-x$ instead of $1-(3x/2)$, and any excess TiO_2 included in the formulation would be expected to form a second phase in the grain boundaries [8]. A similar argument also applies if compensation is assumed to be by calcium vacancies, but with displaced calcium

TABLE I Electron-microprobe analysis of grains

Yttrium nominal (at %)	Ca/Ti ratio		
	Measured (± 0.015)	V_{Ca} model	Electronic/ shear model
0	1.000(stand.)	–	–
4.6	0.93	0.931	0.954
8.7	0.87(5)	0.870	0.913
15.4	0.77(5)	0.769	0.846

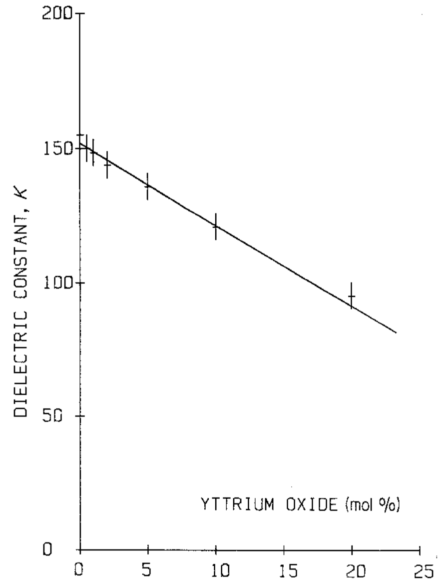


Figure 1 Influence of yttrium oxide on the dielectric constant at 25° C and 1 kHz of $CaTiO_3$ sintered in air (1450° C, 15 h).

oxide present in a shear-structure within the grains [7], i.e. as $Ca_{1-x}Y_xTiO_{3+(x/2)}$.

3.3. Dielectric properties

Specimens of undoped and yttrium-doped $CaTiO_3$ were light coloured following sintering in air at 1450° C, and there was no anomalously high dielectric constant or relaxor behaviour, even for yttrium levels as high as 20 mol%. This is in contrast to earlier work on yttrium-doped $SrTiO_3$ [1] for which apparent permittivities $\gtrsim 10\,000$ were observed for yttrium levels higher than 0.3 mol%. In fact, the dielectric constant of $CaTiO_3$ gradually decreased with increasing "donor" level as illustrated in Fig. 1. This was true regardless of the method of applying electrodes. Furthermore, the dielectric constant was insensitive to frequency, at least in the range 10^2 to 10^5 Hz, and the temperature dependence was similar to that of undoped $CaTiO_3$. Fig. 2 shows typical data, in this case for 10 mol% yttrium. Dielectric losses were low at all temperatures and frequencies with $\tan \delta < 0.01$.

For dopant levels $\lesssim 0.75$ mol%, specimens sintered (and cooled) in nitrogen also were light coloured and had dielectric constants $\lesssim 150$. However, at higher dopant levels the material was dark coloured (grey-green to black) following sintering in nitrogen, and had an anomalously high dielectric constant, K_a, the value of which depended on the method of electrode application (Table II).

The apparent dielectric constant also appeared to be dependent on the grain size, a characteristic of dielectrics with intergranular barrier layers, as

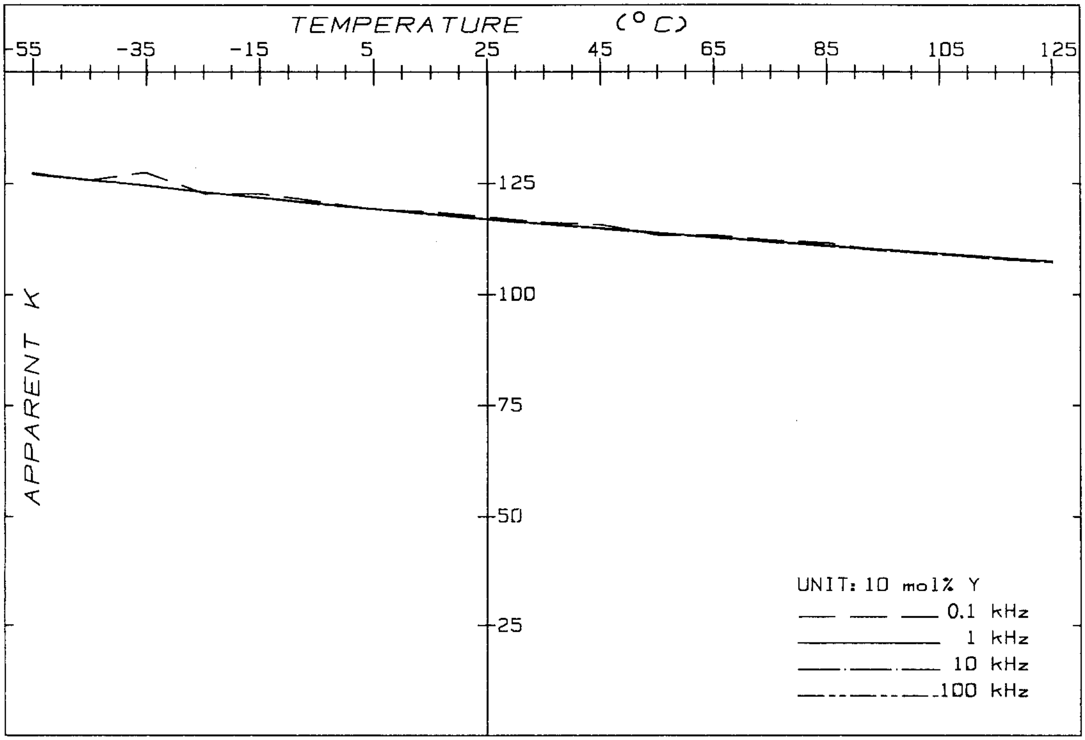


Figure 2 Temperature and frequency dependence of the dielectric constant for $CaTiO_3$ doped with 10 mol% $YO_{1.5}$.

TABLE II Dielectric properties of $CaTiO_3$ doped with 1 mol% yttrium and sintered in nitrogen

Electrode	Apparent permittivity, K_a	Apparent resistivity, ρ_a (Ωcm)	
		100 V cm^{-1}	1000 V cm^{-1}
In–Ga	38 000	*	*
Ag–Bi_2O_3/CuO	1 800	4.0 × 10^{11}	3.6 × 10^{11}

*Voltage not sustained.

mentioned earlier. In addition, materials with a high dielectric constant exhibited relaxor behaviour, as illustrated in Fig. 3 for an yttrium level of 5 mol %. This type of frequency dependence is similar to that observed in donor-doped $SrTiO_3$ [4, 5] except that the strong frequency dependence of K_a occurs at higher temperatures in $CaTiO_3$.

The atmosphere present during cooling from the sintering temperature also influenced the apparent permittivity. Compared with $SrTiO_3$,

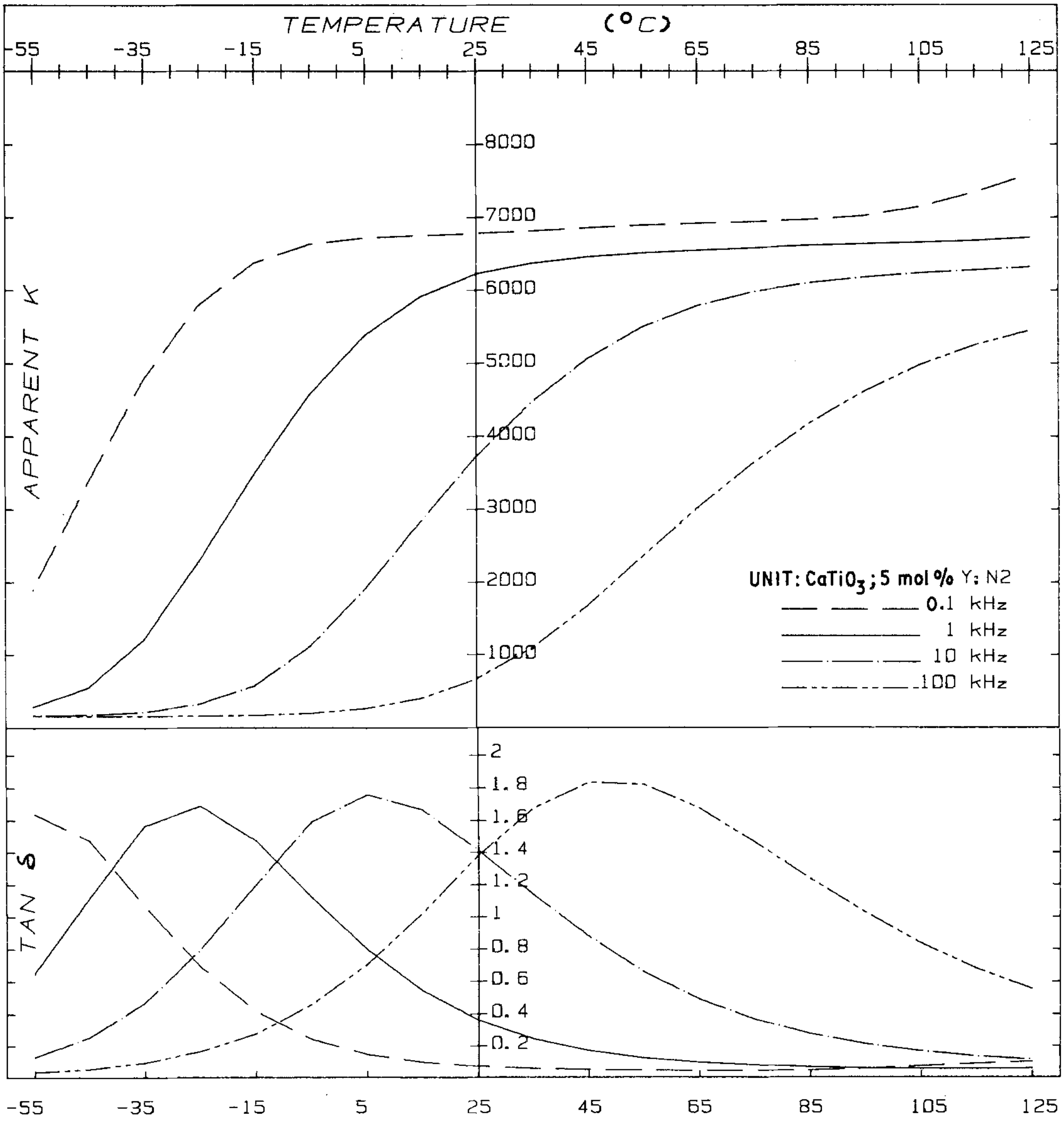


Figure 3 Temperature and frequency dependence of K_a and tan δ for $CaTiO_3$ doped with 5 mol% $YO_{1.5}$ and sintered in nitrogen (1450° C, 15 h).

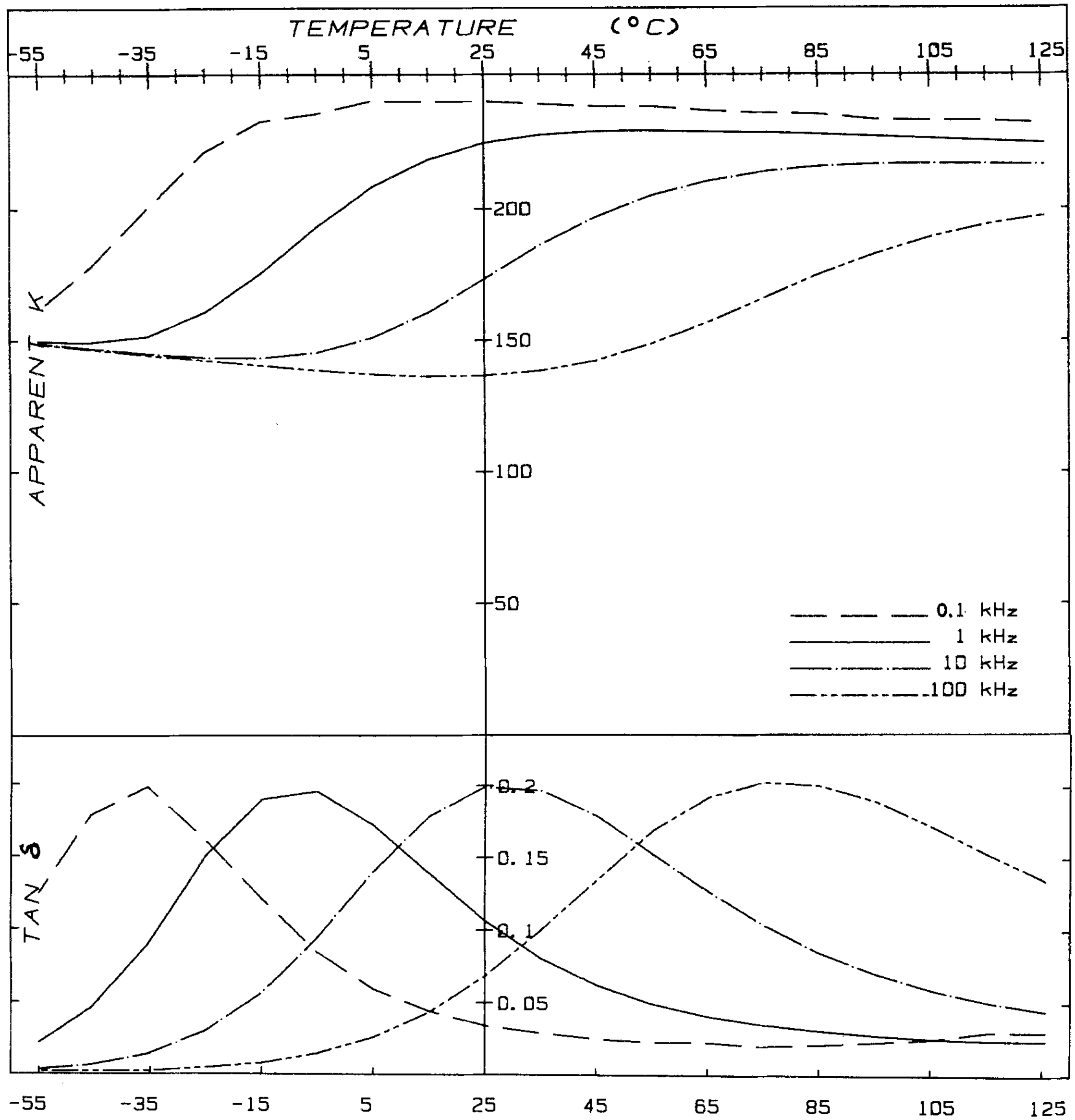
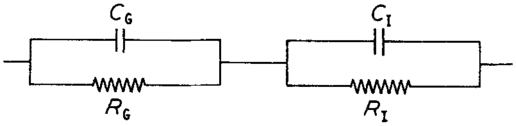


Figure 4 Temperature and frequency dependence of K_a and tan δ for $CaTiO_3$ doped with 5 mol% $YO_{1.5}$ sintered in nitrogen, cooled in air.

yttrium-doped $CaTiO_3$ oxidized quite rapidly and became light-coloured if the nitrogen atmosphere was changed to air during cooling. Reoxidation was not always complete, however, and a slightly elevated dielectric constant with attendant frequency dispersion could result (Fig. 4). It can be seen that in both Figs. 3 and 4, the dielectric constant becomes insensitive to frequency and approaches that typical of $CaTiO_3$ at sufficiently low temperatures.

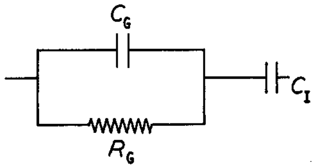
3.4. Analysis of the relaxation

The temperature and frequency dependence of the apparent dielectric constant can be explained in terms of the barrier layer properties of a material with semiconducting grain cores and more insulating areas on the grain surface and between grains [1]. The equivalent circuit of such a material is as follows:



where the subscripts G and I refer to the grain core and the insulating area, respectively. The resistivity of the grain core is established mainly during sintering, and determined by the dopant level and sintering conditions. Re-oxidation during cooling and/or electrode application mostly affects the resistivity of the outer portion of the grain and the grain boundaries. However, the resistivity of the grain cores can also be affected, as was demonstrated by changing the atmosphere to air after sintering in nitrogen.

For materials which are electroded with silver paste containing bismuth and copper oxides [1], the grain boundaries become strongly insulating and, at least for the frequencies of present interest, $R_I \gg X_I$, where X_I is the reactive impedence ($= 1/\omega C$). The circuit then simplifies to that below:



If $R_G \gg X_G$, then the material will have normal dielectric properties typical of $CaTiO_3$, whereas for $R_G \ll X_G$, true barrier layer behaviour will occur with high apparent permittivities. Lossy capacitor characteristics are obtained for $R_G \sim X_G$.

If we consider the case of material with well-insulated grain boundaries with the equivalent circuit above, then it is straight-forward to show from the real and imaginary parts of the total impedance Z that

$$\tan\theta = \frac{1}{\omega C_I R_G} + \frac{\omega C_G^2 R_G}{C_I} + \omega C_G R_G. \tag{1}$$

If we now differentiate with respect to ω to find a minimum in $\tan\theta$ (maximum in $\tan\delta$), then

$$\frac{1}{\omega^2 C_I R_G} = \frac{C_G^2 R_G}{C_I} + C_G R_G \tag{2}$$

or

$$R_G = \frac{1}{\omega}\left(\frac{1}{C_G^2 + C_G C_I}\right)^{1/2}. \tag{3}$$

Assuming cubic grains for simplicity and considering unit area,

$$R_G = \rho L, \quad C_G = \epsilon/L, \quad C_I = \epsilon/t,$$

where L and t are the thickness of the grains and grain-boundary layers, respectively, and ρ is the resistivity of the grains. It is possible that the permittivity of the grains ($\epsilon = K\epsilon_0$) is different from that of the boundary layers following impregnation of the grain boundaries with bismuth and copper oxides [9], but the difference, if any, can be neglected because of the relatively low dielectric constant of $CaTiO_3$.

Substituting for C_G, C_I and R_G in Equation 3

$$\rho = \frac{1}{\omega\epsilon}\left(\frac{t}{L+t}\right)^{1/2}. \tag{4}$$

For a given value of ω, ρ is the value that results in a maximum in $\tan\delta$. Thus, the resistivity of the grain cores can be calculated at the temperatures for which $\tan\delta$ is a maximum at the measuring frequencies (e.g. Figs. 3 and 4). Values of $t/(L+t)$, which is the ratio of the boundary layer thickness to the total thickness of the sample, can be obtained from the ratio of the actual dielectric constant of the ceramic to the apparent dielectric constant, at temperatures for which $R_G \ll X_G$. This was done for the data in Fig. 3 (5 mol% yttrium) and for similar measurements on materials doped with 1.0 and 2.0 mol% yttrium oxide. Data are plotted in Fig. 5, which also contains, for comparison, resistivity measurements made by the four-point probe technique on an unelectroded specimen doped with 5 mol% yttrium.

It can be seen from Fig. 5 that the resistivity calculated from the dielectric relaxation decreased with increasing yttrium level and that the temperature dependence was similar for each dopant level. An activation energy 0.40 ± 0.02 eV was indicated.

Some error might be present in the values of resistivity obtained with the four-point probe below 25° C; at resistivities $> 10^4$ Ωcm it becomes difficult to maintain adequate probe contact with the sample and make accurate current measurements. Nevertheless, the measured resistivities are in very close agreement with those calculated from the dielectric relaxation, particularly at the higher temperatures where the probe measurements are likely to be the most accurate.

Values of the resistivity are intermediate between those typical for many semiconductors (~ 1 Ωcm) and good insulators ($\sim 10^{12}$ Ωcm), and are of similar magnitude to the grain resistivity calculated for air-sintered $SrTiO_3$ relaxors [1].

4. Conclusions

The behaviour of Y-doped $CaTiO_3$ sintered in nitrogen is seen to fit the model used to explain relaxor properties in donor-doped $SrTiO_3$. In this model, sufficient oxygen is lost from the grains during sintering to lower their resistivity to the

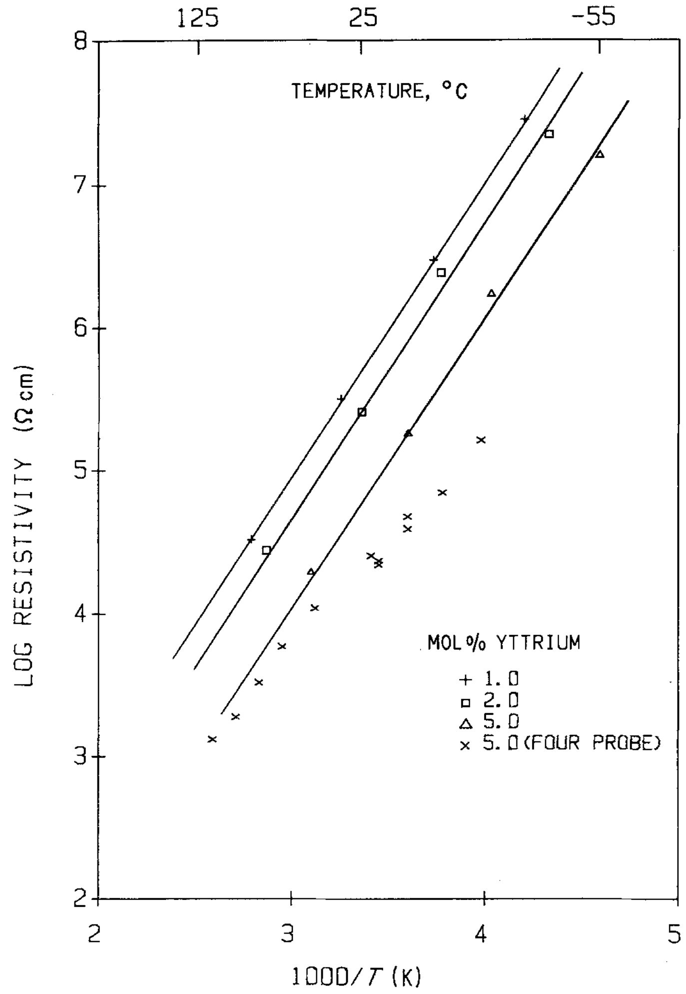


Figure 5 Grain resistivities of Y-doped $CaTiO_3$ sintered in nitrogen (see text).

range 10^3 to 10^6 Ωcm (at room temperature). If the grains are not fully reoxidized before dielectric properties are measured then anomalously high permittivity and relaxor properties will be observed. Reoxidation is slow in donor-doped material, particularly if the grains are large. However, in view of the observed effect of cooling nitrogen-sintered specimens in air, reoxidation appears to take place more readily in donor-doped $CaTiO_3$ than in $SrTiO_3$ or $BaTiO_3$. For example, Wernicke [10] noted that large-grained (100 μm) $BaTiO_3$ doped with 0.5 at % lanthanum remained unoxidized even after several days of heat-treatment (in air) at 1100° C. Similarly, it was found that, whereas undoped $SrTiO_3$ readily reoxidized after being strongly reduced, a dark-coloured ceramic with barrier-layer behaviour was observed for donor-doped $SrTiO_3$, even when cooled from the sintering temperature (1450° C) in oxygen [1]. In addition, while relaxor behaviour has been observed for donor-doped $SrTiO_3$ (e.g. [1, 5]) and $BaTiO_3$ [11] sintered in air, $CaTiO_3$ must be sintered in an atmosphere of lowered oxygen partial pressure to achieve the necessary grain conductivity.

The temperature region at which relaxation in the permittivity is observed depends on the resistivity of the grains and its temperature dependence, because the resistivity increases with decreasing temperature. This temperature dependence is similar for $SrTiO_3$ and $BaTiO_3$ ($\simeq 0.15$ eV) [1, 11], but somewhat stronger for $CaTiO_3$ ($\simeq 0.4$ eV). Consequently, the relaxation phenomena that usually occur below about − 100° C for $SrTiO_3$ [5, 12, 13] and $BaTiO_3$ [11] can be observed above −55° C in $CaTiO_3$.

It is apparent that the main differences in the effect of the "donor" dopant on polycrystalline $CaTiO_3$, $SrTiO_3$ and $BaTiO_3$ are the degree of grain-growth inhibition during sintering and the amount of dopant needed to obtain conductivity in the grains. However, the reasons for these differences cannot be explained satisfactorily at the present time. Small amounts of dopant are believed to eliminate extrinsic oxygen vacancies by neutralizing acceptor impurities [1], but there is no direct evidence that additional amounts of "donor" induce conductivity by the controlled valency principle. In donor-doped $SrTiO_3$ and $CaTiO_3$, which can incorporate relatively large amounts of dopant without preventing grain growth, the experimental results point to compensation of the excess charge of the dopant by cation vacancies. This implies that, in perovskite titanates at least, the conductivity results from oxygen deficiency. This oxygen deficiency will depend on such factors as the temperature and oxygen partial pressure during heat-treatment and the binding energy of the oxygen, which will be determined by the chemical nature of the oxide and the amount of lattice defects. Similar conclusions have been reached by others for donor-doped $BaTiO_3$ [14, 15].

It follows that barrier layers formed during cooling or annealing after sintering result mainly from reoxidation of the grain surfaces. Other explanations, such as diffusion of large cation vacancies into the surface of the grain [3] cannot apply if the donor is already compensated by large cation vacancies. Also, the possibility that the boundary layers result somehow from an increased concentration of dopant at the surface caused by phase segregation during cooling [13] seems unlikely, at least for yttrium in $CaTiO_3$, because of the high solubility and absence of any detectable amount of second-phase. Boundary layers can, of course, result if an appropriate (e.g. liquid) phase segregates during sintering [16], or if the grain boundaries are impregnated with such a phase after sintering [17]. Such boundary layers are likely to have improved voltage-withstanding capability compared with those obtained by gaseous reoxidation, and are thus more useful in capacitor applications.

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