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Dielectric properties of donor-doped polycrystalline $SrTiO_3$

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Various donor dopants such as Y^{3+} and Nb^{5+} were incorporated in $SrTiO_3$ in amounts $\leqslant 2.5$ mol % during sintering in air at 1450° C for $\leqslant 15$ h. Dense ceramic materials with grains of optimum uniformity and largest size were obtained when the cation stoichiometry was adjusted to allow for charge compensation of the donor ions by strontium vacancies. For donor levels $\gtrsim 0.3$ mol %, the dielectric constant measured at 25° C and 1 kHz was up to two orders of magnitude higher than that of undoped strontium titanate. The increase in permittivity, however, was dependent on grain size, was influenced by the method of electrode application, and was suppressed by the presence of $\lesssim$ 0.1 mol % Mn in the ceramic. These observations, together with data obtained from electrical measurements at other temperatures and frequencies, were consistent with interpretation of the anomalously high dielectric constant as a boundary-layer effect resulting from semiconducting grains and weakly insulating grain-surfaces. It is suggested that donor doping influences the electrical properties of $SrTiO_3$ mainly by increasing the volatility of oxygen from the grains during sintering, and by decreasing the rate of re-oxidation during cooling.

1. Introduction

Donor-doped polycrystalline strontium titanate exhibits interesting and useful dielectric properties. For example, doping $SrTiO_3$ with several mol% bismuth [1–3], or trivalent rare-earth ions [4–6] has been found to result in relaxor behaviour with significantly increased permittivity. This effect, in which the dielectric properties are sensitive to frequency in a certain temperature range, has usually been attributed to intrinsic ionic polarization enhanced by the distortion accompanying incorporation of the donor ions in the crystal lattice.

Also, semiconducting strontium titanate obtained by heating donor-doped material in atmospheres of low oxygen content is used as a basis for manufacturing boundary-layer capacitors. In this technology [7–9], thin, and therefore high capacitance, dielectric layers are produced by impregnating the grain boundaries with various "oxidizing agents" to make them insulating while maintaining conductivity in the grains. Materials of this type have dielectric properties that depend on frequency according to Maxwell–Wagner theory [10], in which important parameters include the conductivity and size of the crystalline grains.

In the present work the influence of donor-doping on the conductivity and size of the grains has been examined for strontium titanate sintered in atmospheres of various oxygen partial pressures. The experimental data for materials sintered in air suggest an explanation of the dielectric relaxation observed in this and in earlier work in terms of interfacial polarization at grain boundaries.

2. Experimental details

2.1. Materials

Undoped $SrTiO_3$ powder was prepared from reagent-grade $SrCO_3$* and high-purity ($\gtrsim$99.9%) TiO_2†. Stoichiometric amounts of the powders

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* J. T. Baker Chemical Co, Phillipsburg, New Jersey, USA.
† Toho Titan Co, Japan.

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were blended in distilled water, dried and then calcined at 1200°C in air for several hours. Comminution of the calcined powder to an average particle size of 1.0 to 1.5 μm was accomplished without significant contamination by jet-milling. TiO_2 assay of the strontium titanate indicated a Sr/Ti ratio of 1.00 ± 0.005. Donor doping was accomplished by blending with the pre-made $SrTiO_3$, oxides or carbonates of one of the following elements: Y, Ho, La, Nd, Ce, Bi, Sb, Nb, Ta, W. Stoichiometry was adjusted by also adding TiO_2 or $SrCO_3$ along with the donor as discussed presently.

Specimens approximately 10 mm × 10 mm × 0.5 mm were made by the doctor-blade technique. These were preheated in air at 750°C for 0.5 h to remove organic binders and then sintered either in air, nitrogen, or mixtures of CO and CO_2 at 1450° C for up to 15 h in platinum-lined alumina boats, and cooled at a rate of about 45° C min^{-1}. Oxygen partial pressures were calculated from gas-equilibrium thermodynamic data, or were measured using a zirconia oxygen-sensor positioned in the hot-zone of the furnace. In some instances, the atmosphere was changed after the sintering period and the samples were withdrawn from the hot-zone of the furnace under conditions that were more oxidizing, or more reducing.

Electrical contact was made to the ceramic plates either by painting with In–Ga alloy, or by applying electrode paste which was fired on. The electrode paste was made by blending silver or silver–palladium alloy (70 wt % Ag) with small, carefully measured amounts of bismuth oxide and copper oxide powders in an organic binder system. Silver pastes were fired on at 900°C, and those containing the Ag–Pd alloy at 1100°C.

2.2. Measurements

Electrical measurements were made in the temperature range −55 to 125°C. The capacitance (yielding effective permittivity), and dissipation factor ($\tan\delta$) of materials with dielectric properties were measured in the frequency range 10^2 to 10^5 Hz using an HP-4274A LCR meter. Insulation resistance was determined by monitoring leakage current with a Keithley 610B electrometer at various applied voltages. The conductivity of semiconducting materials was measured using a four-point probe with tungsten carbide tips* applied directly to the ceramic surface.

3. Results

3.1. Influence of stoichiometry

Donor levels of 0.2 to 0.6 mol % were added to $SrTiO_3$ without stoichiometric compensation in some preliminary experiments. Firing at 1450°C in air resulted in porous bodies for large cation donors (e.g. Y^{3+}), while for small cation donors (e.g. Nb^{5+}) a dense polycrystalline ceramic was obtained with a wide range of grain sizes. This situation was characteristic of the sintering behaviour of high-purity $SrTiO_3$ having, respectively, a stoichiometric excess or deficiency of large cations over small cations.

In further experiments with yttrium, additions of TiO_2 were made according to the following compensation schemes:

$$(1-x)\text{SrTiO}_3 + \frac{x}{2}(\text{Y}_2\text{O}_3 + 2\text{TiO}_2) \qquad (1)$$

or

$$(1-\tfrac{3}{2}x)\text{SrTiO}_3 + \frac{x}{2}(\text{Y}_2\text{O}_3 + 3\text{TiO}_2). \qquad (2)$$

Relatively high donor levels ($\gtrsim$ 1 mol %) were used to magnify the differences between Schemes 1 and 2, while remaining within the expected solubility range. Samples with stoichiometry adjusted according to Scheme 1 were marginally dense with small grains (1 to 2 μm) when fired for 2 h at 1450°C. On the other hand, dense material, with relatively large uniform grains ($\simeq$ 25 μm), indicative of good solution of the yttrium, was obtained with Scheme 2. As postulated for other donor dopants on the basis of density and X-ray diffraction measurements [1, 3–6], this method of stoichiometry adjustment allows for solution of $Y_{2/3}TiO_3$ with charge balance being maintained by the formation of large cation vacancies (V_{Sr}) in the crystal lattice, according to the formula

$$\text{Sr}^{2+}_{1-3x/2}(\text{V}_{\text{Sr}})_{x/2}\text{Y}^{3+}_x\text{TiO}_3.$$

Consequently, stoichiometry was adjusted according to this procedure for trivalent ions expected to occupy strontium (A) sites, with a corresponding formula being used for pentavalent ions occupying titanium (B) sites, e.g. for Nb^{5+}

$$\text{Sr}_{1-x/2}(\text{V}_{\text{Sr}})_{x/2}\text{Nb}^{5+}_x\text{Ti}_{1-x}\text{O}_3,$$

or in compositional terms

$$(1-x)\text{SrTiO}_3 + \frac{x}{2}(\text{Nb}_2\text{O}_5 + \text{SrO}). \qquad (3)$$

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*Alessi Industries, Costa Mesa, California, USA.

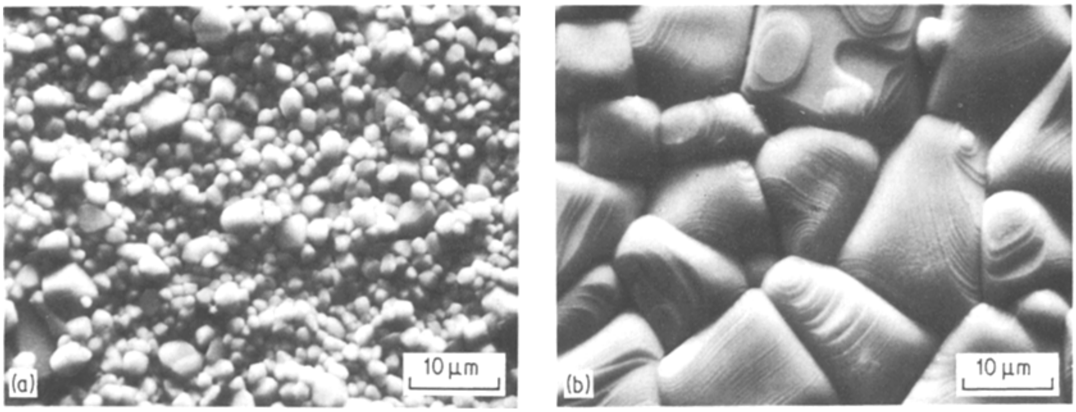

Figure 1 Microstructure of $SrTiO_3$ doped with 1 mol% antimony oxide and sintered 2 h at 1450° C in air. Stoichiometry was adjusted assuming incorporation of Sb^{3+} (a), or Sb^{5+} (b).

Similarly, for a hexavalent dopant (i.e. W^{6+}), the equivalent mode of stoichiometric compensation was

$$Sr_{1-x}(V_{Sr})_xW^{6+}_xTi_{1-x}O_3$$

and

$$(1-x)SrTiO_3 + xWO_3 \quad (4)$$

i.e. no additions of TiO_2 or $SrCO_3$ were needed. Densification with good grain development and solution of the donor in the $SrTiO_3$ grains was usually achieved when these procedures for compensating the cation stoichiometry were adopted. There were some donors, however, for which the actual valence state was unclear for the sintering conditions used, e.g. Sb and Bi. For these donors the stoichiometry was adjusted first on the assumption of large cation substitution (Sb^{3+}, Bi^{3+}), and then on the assumption of substitution as small cations (Sb^{5+}, Bi^{5+}). By comparing the microstructures illustrated in Fig. 1a and b for antimony doping, and in Fig. 2a and b for bismuth doping, it was deduced that the donors were incorporated as Sb^{5+} and Bi^{3+}.

Although the stoichiometry could be adjusted sufficiently to distinguish the likely mode of accommodation of the donor, precise control of stoichiometry was difficult if the donor had any volatility. Also, there was a measure of uncertainty in the Sr/Ti ratio of the $SrTiO_3$ being used, even though it was relatively close to unity (1.00 ± 0.005) for material made by powder processing. For these reasons the stoichiometry was occasionally fine-tuned by trial and error when trying to optimize the composition for size and uniformity of grains for a given sintering condition.

For $SrTiO_3$ of less precise Sr/Ti ratio or lower purity than that used in the present work, it is usually not possible to make valid inferences about how the donor is incorporated in the lattice from the effect of addition of $SrCO_3$ or TiO_2 on grain size. Nevertheless, for such materials, which

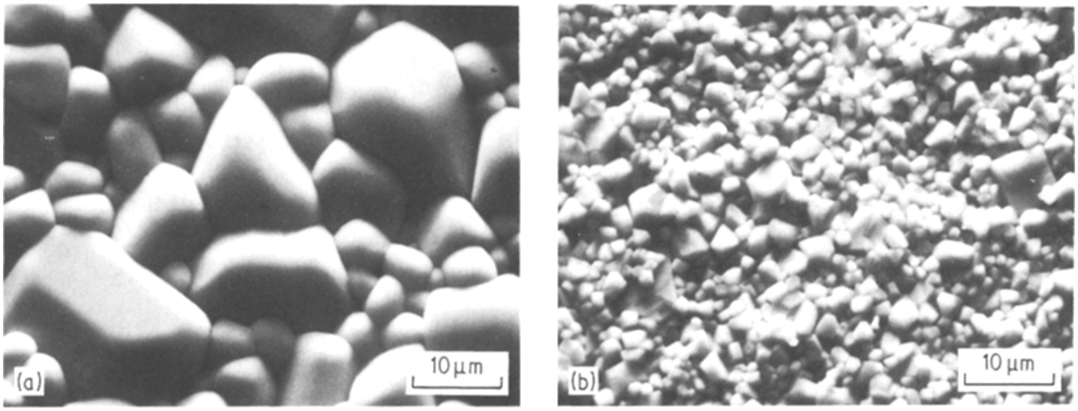

Figure 2 Microstructure of $SrTiO_3$ doped with 1 mol% bismuth oxide and sintered 2 h at 1450° C in air. Stoichiometry was adjusted assuming incorporation of Bi^{3+} (a), or Bi^{5+} (b).

includes most commercial $SrTiO_3$, a microstructure of large uniform grains can normally be obtained by adjusting the stoichiometry entirely empirically.

3.2. Influence of donor level on grain size and dielectric constant

Specimens were prepared doped with yttrium in increasing amounts up to 2.5 mol% and fired in air (1450° C; 15 h). Capacitance measurements at 1 kHz were then made with In–Ga contacts, and the apparent dielectric constant (K_a) at room temperature was calculated in the usual manner from the thickness of the sample and the electrode area. Typical behaviour is illustrated in Fig. 3 which shows a sudden rise in K_a from 320 with no donor to about 18 000 for donor levels in the range 0.75 to 1.0 mol%; this is followed by a gradual decrease in K_a at higher donor levels. Also shown in Fig. 3 is the change in approximate maximum grain size with donor level which follows a trend similar to that of K_a.

Specimens sintered for 2 h rather than 15 h generally had smaller grain sizes, as might be expected, but also had lower values of K_a. On the other hand, larger grain sizes and values of K_a could sometimes be achieved if the stoichiometry was adjusted slightly by trial and error as discussed above. This is illustrated in Fig. 4 which shows data for samples in which the stoichiometry for a

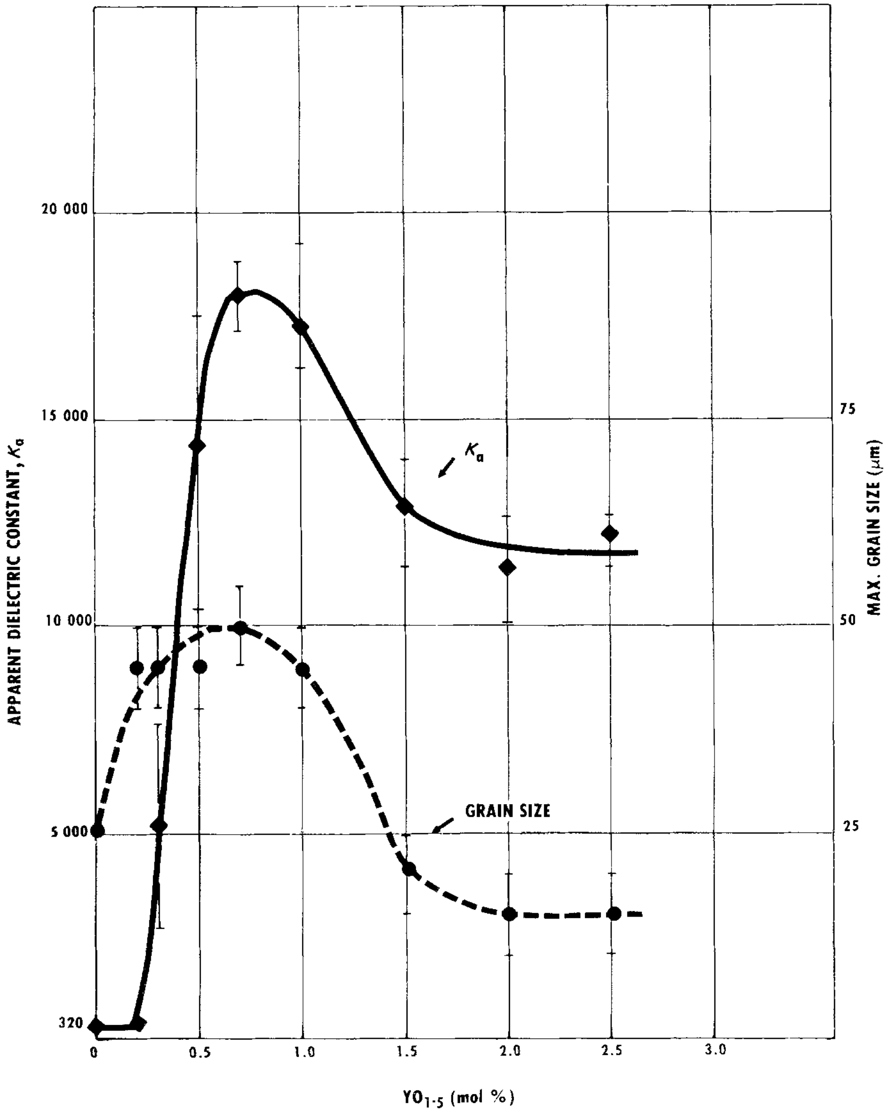

Figure 3 Influence of yttrium content on the dielectric constant and grain size of $SrTiO_3$ sintered 15 h in air at 1450° C. (In–Ga electrodes, 25° C, 1 kHz.)

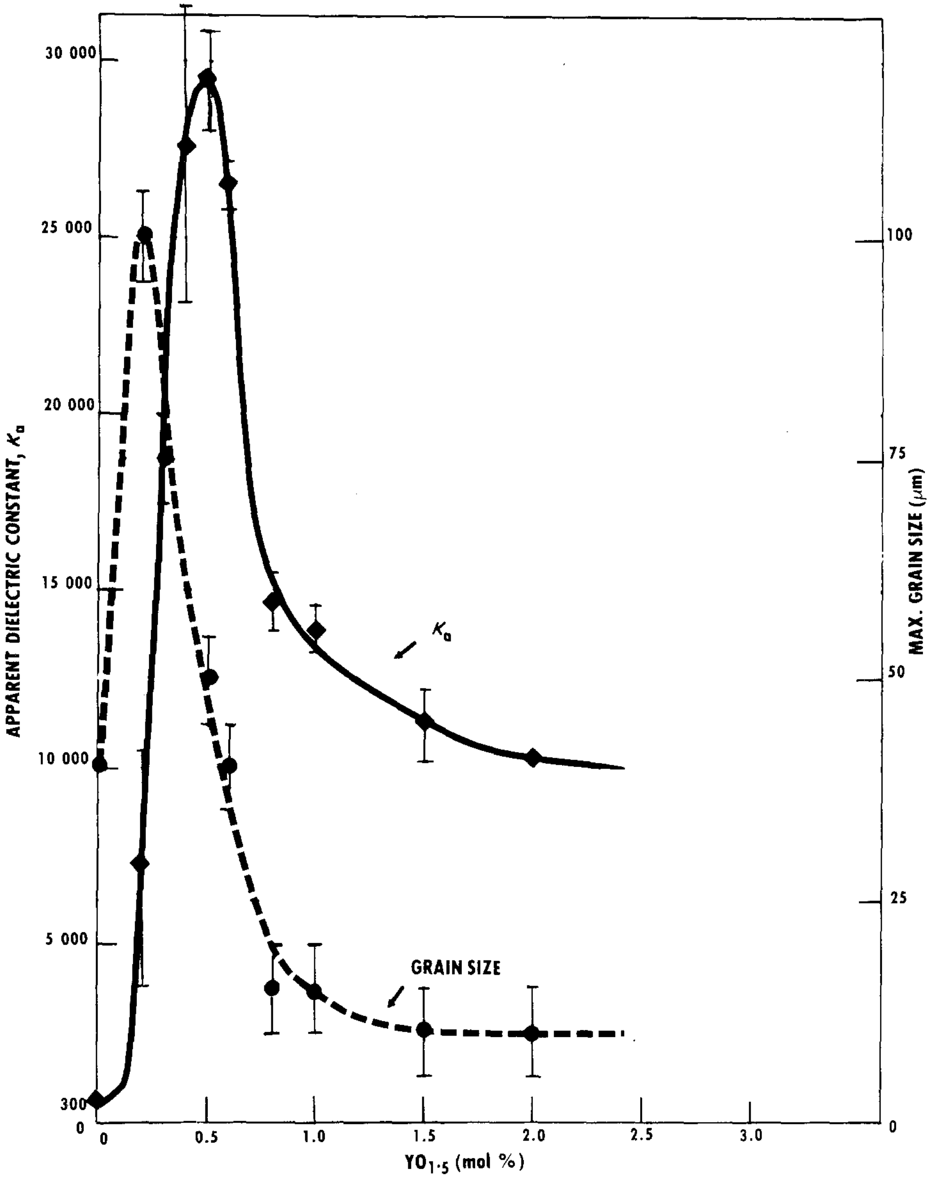

Figure 4 Influence of yttrium content on the dielectric constant and grain size of $SrTiO_3$ with adjusted stoichiometry sintered 15 h in air at 1450° C. (In–Ga electrodes, 25° C, 1 kHz.)

given donor level was adjusted according to Scheme 2 except that 0.5 mol % TiO_2 was omitted from each composition.

A few experiments with samples of different thickness yielded similar values of apparent dielectric constant, indicating that the increase in K_a produced by donor doping was a bulk rather than a surface effect such as a (Schottky) barrier formed between a metal electrode and a semiconducting ceramic. However, the observed correlation between increasing dielectric constant and increased grain size was strongly suggestive of a grain-boundary-layer effect. In such a situation an increasing apparent permittivity results from a decrease in the number of grain boundaries in series as the grain size increases. In addition, the colour of the ceramic usually changed from a rose-pink to a dark grey-green when the donor level was sufficiently high to produce a significant increase in K_a. This also suggested the possibility that the grains might be semiconducting.

3.3. Resistivity

Measurements of the electrical resistance of the ceramic plates with In–Ga electrodes applied, revealed relatively low values of d.c. resistivity (e.g. $\simeq 10^6\,\Omega$cm) in materials with high apparent dielectric constant. However, as indicated in Table I, these values could be increased by cooling the ceramic in oxygen instead of air after sintering or, more effectively, by firing on silver electrodes at 900° C (2 h soak). Even higher values of resistivity, especially at higher field strengths, were achieved by adding small amounts (e.g. 5 wt %) of a mixture of 90 wt % Bi_2O_3 and 10 wt % Cu_2O to the silver electrode paste.

Although the use of bismuth oxide, copper oxide, or their mixtures for improving the resistance of boundary-layer capacitors is well documented [7–9], these oxides have usually been applied to the surface of a semiconducting ceramic and then heated at some elevated temperature near 1100° C, before applying electrodes. As also observed in such cases, however, the oxides were found to penetrate the grain boundaries (e.g. [11–13]), apparently producing an intergranular layer of increased resistivity [13].

These observations tended to support the hypothesis that the high dielectric constants resulted from boundary-layer behaviour in which the grain boundaries are partially reoxidized during cooling in air. Also given in Table I are details for samples cooled in nitrogen ($p(O_2) \simeq 10^{-4}$ atm) which showed characteristic boundary-layer properties when silver electrodes were fired on. Differences in the apparent dielectric constant in Table I can be attributed to variations in the total thickness of the boundary layers within the plates.

Because the measurements of resistivity in Table I were bulk values, i.e. including both grains and grain boundaries, they are designated as ρ_a, the apparent resistivity. Measurements of the resistivity of the grains alone was not attempted because the usual four-probe technique for avoiding contact resistance was not practicable for grains $\simeq 50\,\mu$m in diameter. Instead, the four-probe technique was used for bulk resistivity measurements on unelectroded plates that had been sintered and cooled under various low oxygen partial pressures. It was hoped that these measurements would at least approximate the grain resistivities if significant reoxidation of the grain boundaries were prevented. As shown in Fig. 5, typical semiconductor behaviour was found in all cases, i.e. increasing resistivity with decreasing temperature [14–16]; the activation energy (0.15 ± 0.02 eV) was the same within experimental error for each set of data. An attempt was made to estimate the grain resistivity at 25° C for air-sintered material by extrapolation of the data for resistivity against oxygen partial pressure during sintering, but the value obtained ($\simeq 10^3\,\Omega$cm) was considered too tenuous. Metallic-type conductivity, for which the resistivity of reduced titanates is found to increase with temperature [15, 16], was not observed for the materials and oxygen partial pressures used in the present work. This has a bearing on the interpretation of relaxor behaviour, as discussed presently.

3.4. Other donors

Similar results were obtained when various other donor dopants were used instead of yttrium, provided that sufficient dopant was used and stoichiometry was adjusted appropriately to produce good grain development during sintering. Some examples are listed in Table II.

TABLE I Influence of cooling atmosphere and electroding procedure on dielectric properties at 25°C and 1 kHz (0.4 mol % Y, sintered in air).

Cooling atmosphere*	Electrode	K_a	*Resistivity, ρ_a (Ωcm)	
			100 V cm^{-1}	1 kV cm^{-1}
Air	In–Ga	35 000	5×10^6	–†
Air	Ag	32 000	7×10^9	–†
Air	Ag + Bi_2O_3/Cu_2O	25 000	4×10^{11}	3×10^{11}
O_2	In–Ga	24 000	1×10^8	–†
O_2	Ag	23 000	2×10^{10}	–†
O_2	Ag + Bi_2O_3/Cu_2O	19 000	4×10^{11}	8×10^{11}
N_2	In–Ga	–†	5×10^2	–†
N_2	Ag	117 000	4×10^8	–†
N_2	Ag + Bi_2O_3/Cu_2O	48 000	2×10^{11}	2×10^{10}

*Cooling rate approximately 45° C/min.
†Not measurable (voltage not sustained).

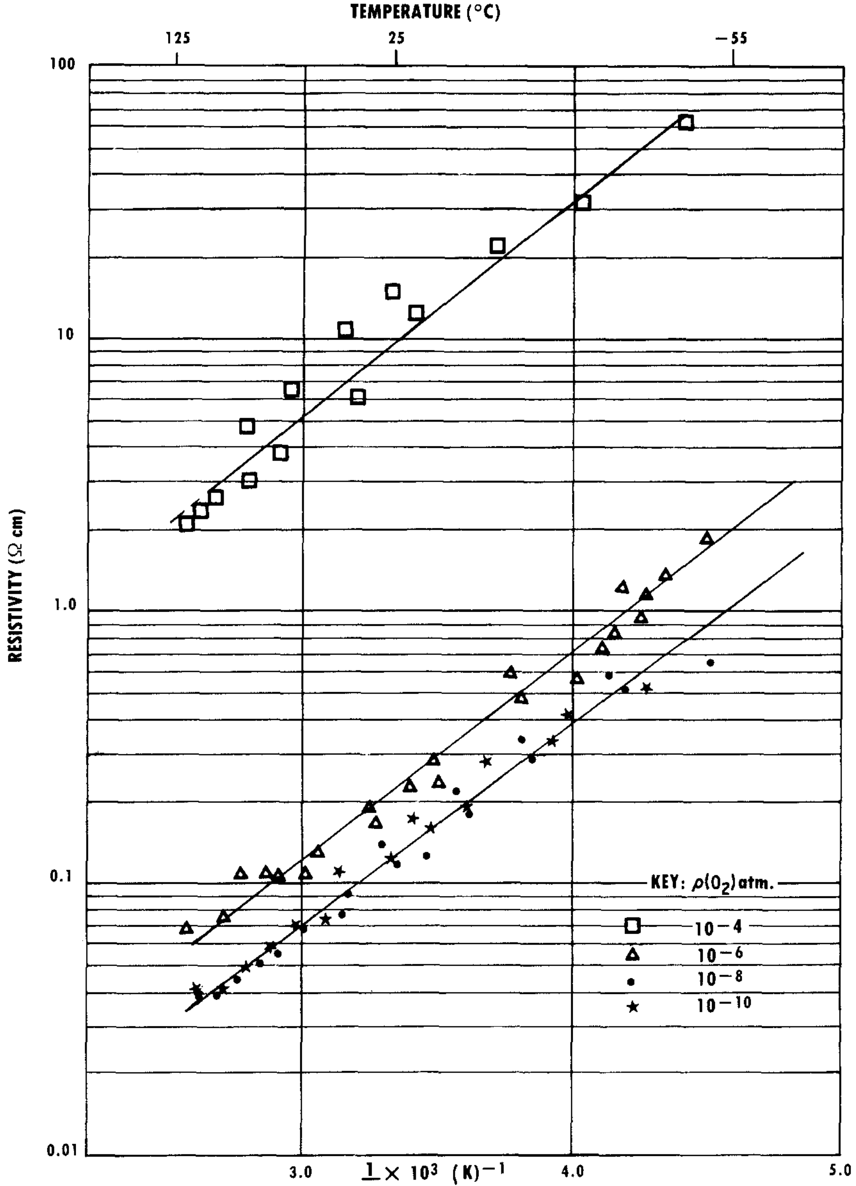

Figure 5 Resistivity of $SrTiO_3$ doped with 1 mol% $YO_{1.5}$ and sintered 15 h at 1450° C in atmospheres of various oxygen partial-pressures.

Grain development was relatively poor in the case of Ce^{3+} doping when fired in air and the material was brown rather than grey-green; nevertheless, enhanced permittivity was measured for cerium, a finding which differed from the work of Johnson *et al.* [5]. Better grain growth was observed when cerium-doped material was sintered in nitrogen rather than air. Electron-probe microanalysis indicated essentially complete incorporation of the cerium into the grains in both cases. It is possible, however, that in the case of sintering in air, some of the cerium was present as Ce^{4+} so that stoichiometry adjustment on the assumption of Ce^{3+} would have been inappropriate, leading to poorer grain development.

Grain growth was not influenced significantly by firing in nitrogen instead of in air for materials that had donors with stable valence states (e.g. Y^{3+}); however, sintering in atmospheres of low oxygen content was avoided for donors that could be readily reduced to the metallic state (e.g. Bi, Sb).

Although there were some differences in the properties of materials doped with different donors, they could have resulted from variations in

TABLE II Electrical data for polycrystalline $SrTiO_3$ doped with 1 mol% donor and sintered in air

Donor*	Approximate maximum grain size (μm)	K_a at 25° C	Resistivity† (Ωcm at 1 kV cm^{-1})
Ho^{3+}	50	19 000	1×10^{12}
La^{3+}	35	11 000	1×10^{12}
Nd^{3+}	50	10 000	1×10^{12}
Ce^{3+}	20	5000	1×10^{12}
Ce^{3+} (sintered in N_2)	50	23 000	7×10^{11}
Bi^{3+}	20	7000	2×10^{12}
Bi^{5+}	2	300	5×10^{13}
Nb^{5+}	55	14 000	6×10^{11}
Ta^{5+}	50	11 000	5×10^{11}
Sb^{5+}	90	20 000	8×10^{11}
W^{6+} (0.5 mol%)	50	13 000	1×10^{12}

*Assumed valence state for stoichiometry adjustment.
†Ag–Pd electrodes with Bi_2O_3/Cu_2O.

sintering behaviour and microstructure, and from variations in the amount of liquid phase absorbed by the grain boundaries during electroding, rather than from any intrinsic differences in polarizability.

3.5. Influence of acceptors

Because Al_2O_3 is a common impurity in commercial $SrTiO_3$, it was of interest to examine the effect of small alumina additions on the increased permittivity produced by donor doping. Allowing for the change in stoichiometry, the alumina appeared to neutralize some of the donor, at least for alumina additions up to approximately 0.5 mol%. If the donor level was near the minimum required for increased permittivity (Figs. 3 and 4), then the ceramic was light coloured with K_a close to that normally observed for $SrTiO_3$ ($\simeq 300$). A return to dark colour and increased K_a was achieved by increasing the amount of donor with appropriate stoichiometry adjustment. It was concluded that when Al_2O_3 was present, some of the donor was neutralized, being compensated both in charge and stoichiometry by Al^{3+} ions on titanium sites, e.g. as

$$Y_{Sr}^{\cdot}Al_{Ti}'O_3$$

instead of by strontium vacancies and extra TiO_2 (Scheme 2).

Quite a different behaviour was observed in the case of additions of manganese oxide which were found to eliminate the high permittivity of air-sintered material, even when present in amounts $\lesssim 0.1$ mol%. This is illustrated in Fig. 6 which shows a gradual decrease in K_a from approximately 26 000 with no manganese, to 260 with 0.1 mol% Mn, for materials doped with 1.0 mol% Y and electroded with In–Ga. Also shown in Fig. 6 is the sharp rise in dielectric loss during the transition from anomalously high to normal values of K_a.

Other possible acceptor dopants (e.g. Ga, Fe, Mg, Cr, Co, Ni) behaved more like Al than Mn in that if they reduced K_a at all, a significant reduction was seen only when the acceptor was present in relatively large amounts, or when minimum donor levels were used.

On the basis of these observations, it is difficult to explain the effect of Mn on neutralization of the donor as seemed to be the case for Al. In addition, it seems unlikely that small additions of manganese could have such a marked effect on any ionic polarization mechanism.

3.6. Temperature and frequency characteristics

Changes in capacitance and loss angle with temperature and frequency are shown in Fig. 7a and b for donor-doped $SrTiO_3$ cooled in nitrogen and oxygen, respectively (electroded with Ag + Bi_2O_3/Cu_2O, see Table I). The general trend of decreasing capacitance (or K_a) with increasing temperature (e.g. at 10^5 Hz in Fig. 7a) is similar to that normally seen for undoped $SrTiO_3$, except that some frequency dispersion was observed for donor-doped materials. The dispersion was more evident in the material cooled in oxygen, which exhibited frequency dependence of capacitance and loss angle in two regions: one at high frequencies at the lower temperatures ($\lesssim -55°$ C), and the other at low frequencies at temperatures above about 25° C. Frequency dispersion at the higher temperatures was relatively slight for the sample cooled in nitrogen, and the low temperature dispersion was not visible. Data for samples cooled in air were, as might be expected, intermediate in behaviour between the samples cooled in N_2 or O_2.

Frequency dispersion was magnified considerably in samples that contained small amounts of Mn. This is illustrated in Fig. 8 for two of the Mn-containing materials represented in Fig. 6, but electroded for ease of handling with Ag + Bi_2O_3/Cu_2O instead of In–Ga. Data are shown for 0.02 and 0.05 mol% Mn (both with 1 mol% Y); note the scale differences between Figs. 7 and 8. As can be seen in Fig. 8b, frequency dispersion disappears when the material reverts to normal (low) K_a values (e.g. $T < 0°$ C), and increased values of K_a

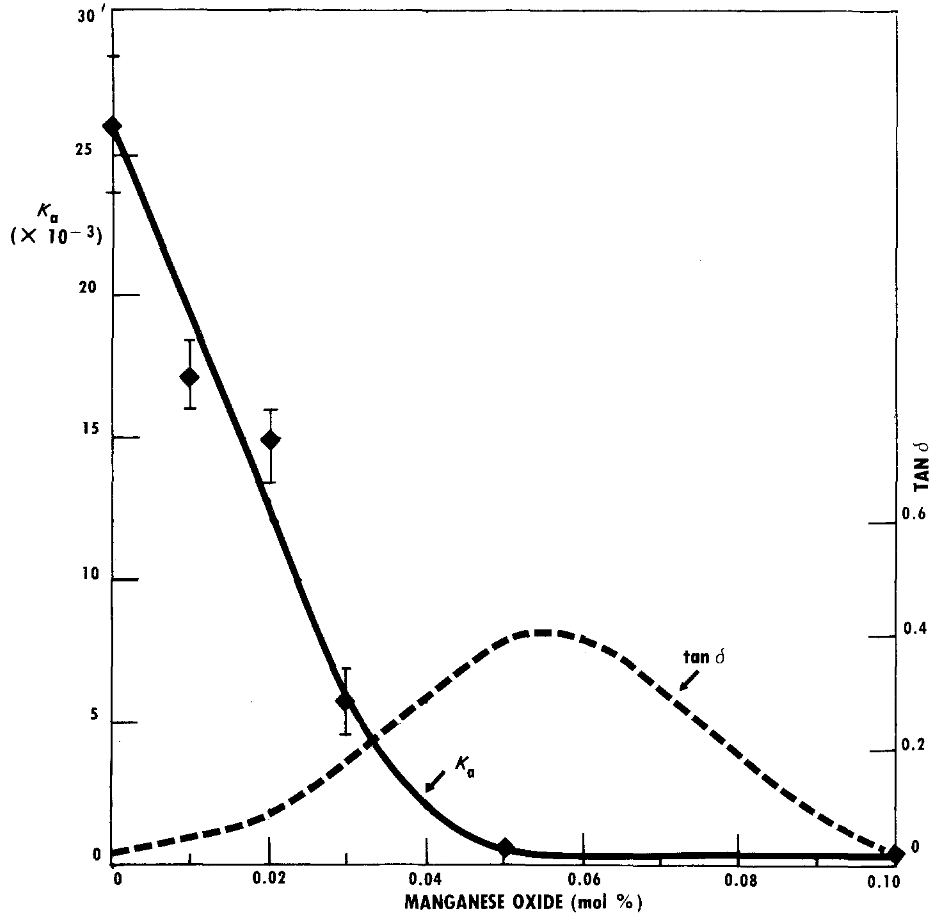

Figure 6 Influence on dielectric properties of manganese oxide additions to $SrTiO_3$ doped with 1 mol% $YO_{1.5}$ and sintered 15 h at 1450° C in air. (In–Ga electrodes, 25° C, 1 kHz.)

appear only at higher temperatures, accompanied initially by very high losses, starting at the lower frequencies.

4. Discussion

4.1. K_a

The experimental results can be explained in terms of barrier-layer behaviour in a ceramic material consisting of semiconducting grains, partially re-oxidized grain-surface layers, and highly resistive grain-boundary regions. The equivalent circuit of such a material is depicted in Fig. 9a, where the subscripts G, O and B refer to grain core, oxidized layer, and grain boundary, respectively. As discussed in Section 3.3, the oxidized surface layers are weakly insulating after normal sintering in air but the resistivity of the grain-boundary regions can be increased by impregnation with various low-melting oxides, such as Bi_2O_3–Cu_2O mixtures.

As shown in Table III, an estimate of the elec-

TABLE III

Impedance × unit area × reciprocal thickness* (Ωcm)	Frequency (Hz)			
	10^2	10^3	10^4	10^5
lR_B	10^{13}–10^{14}	10^{13}–10^{14}	10^{13}–10^{14}	10^{13}–10^{14}
lX_B	$\simeq 6 \times 10^7$	$\simeq 6 \times 10^6$	$\simeq 6 \times 10^5$	$\simeq 6 \times 10^4$
mR_O	6×10^8–8×10^9	6×10^8–8×10^9	6×10^8–8×10^9	6×10^8–8×10^9
mX_O	6×10^7	6×10^6	6×10^5	6×10^4
nR_G	–	–	–	–
nX_G	6×10^7	6×10^6	6×10^5	6×10^4

*l, m, n are the reciprocal thicknesses of the dielectric in each case.

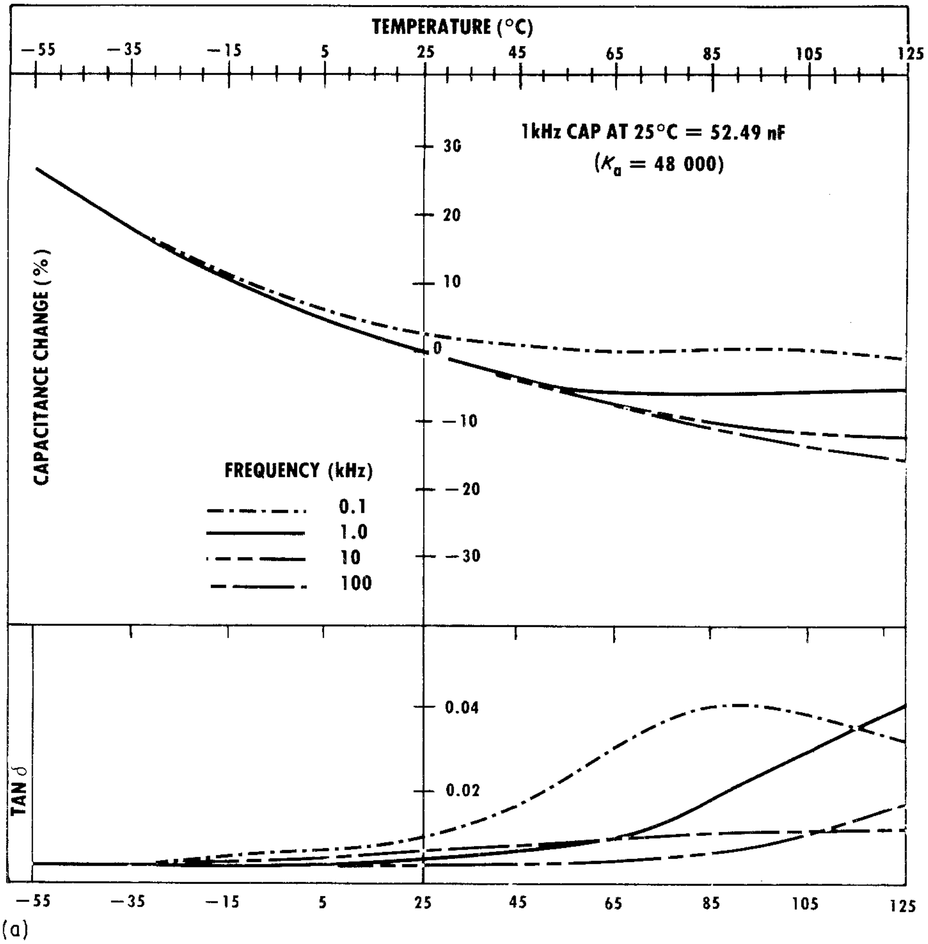

Figure 7 Dependence of capacitance and dielectric loss on temperature and frequency for donor-doped $SrTiO_3$ sintered in air (see text) but cooled in nitrogen (a), or oxygen (b).

trical impedance (for unit area) of each part of the circuit can be made from the known dielectric constant of $SrTiO_3$ ($\simeq 300$), the apparent dielectric constant (K_a), and the resistivities contained in Table I, assuming cubic grains for simplicity.

Although the resistance of the grains, R_G, could not be obtained for air-sintered materials, it was possible to estimate R_O from the resistivity measured with In–Ga electrodes for samples cooled in air and oxygen, and R_B could be estimated from the resistivities measured with Ag + Bi_2O_3/Cu_2O electrodes. This was accomplished using the relationship $R = \rho \times t$, for unit area, where t is the total thickness of the appropriate barrier-layer calculated from the values of K_a in Table I. It was also possible to estimate the actual thickness of the barriers by taking into account the number of grains across each sample (~ 10)*.

Similarly, the reactive impedance of each part of the circuit is given by $X = 1/\omega C$, or $t/\omega K\epsilon_0$ for unit area. Although the actual dielectric constant, K, of the intergranular layer is not known, it can be assumed that it is similar to, or possibly less than, that of the grain cores, i.e. $\lesssim 300$ [12, 13].

Each segment of the circuit in Fig. 9a behaves mainly as a resistor for $R \ll X$, or as a capacitor for $R \gg X$. Lossy capacitor behaviour is obtained for $R \sim X$. Consequently, for materials electroded with Ag + Bi_2O_3/Cu_2O the circuit simplifies to that of Fig. 9b. In addition, if there is little re-oxidation of the grain surface during cooling, as for material cooled in nitrogen, then the circuit

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*Such calculations gave a value of 0.2 to 0.3 μm for both the average thickness of the intergranular layer, and for the average thickness of the oxidized layer on each side of a grain.

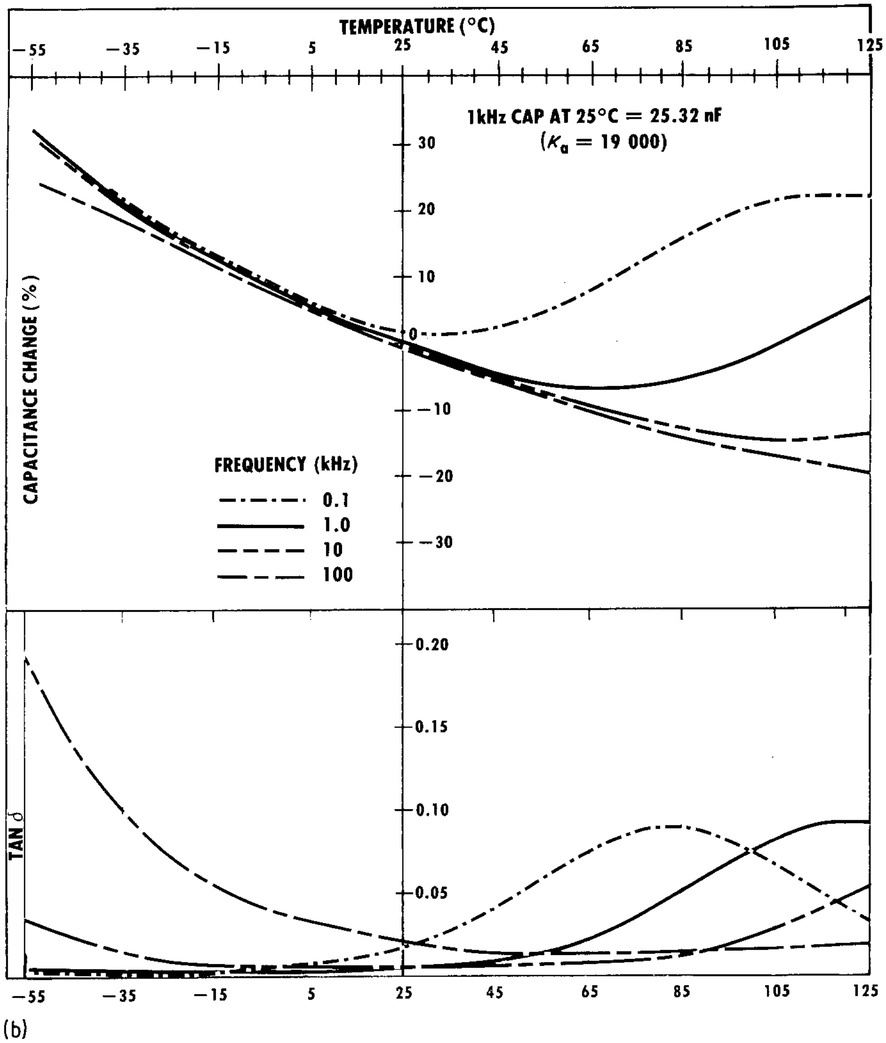

Figure 7 continued.

reduces further to that of Fig. 9c. This assumes that the grain-boundary impregnation and electroding are done at sufficiently low temperatures (e.g. 900° C) to avoid the formation of an appreciable re-oxidation layer in the grain surfaces by diffusion into the grains of either atmospheric oxygen or the impregnant.

The numbers in Table III indicate that R_O approaches X_O at low frequencies so that some dispersion can be expected from the surface layers. Dispersion at higher frequencies can occur if R_O decreases with increasing temperature, as is usual for ceramic dielectrics. This behaviour fits the dispersion at temperatures above 25° C, observed in material cooled in oxygen (Fig. 7b), and for that with the 0.02 mol % Mn addition (Fig. 8a). Similar characteristics observed by others [4] can also be explained this way.

For the grain cores, little dispersion is expected for frequencies $\lesssim 10^5$ Hz when $\rho_G \ll 6 \times 10^4\, \Omega$cm. The equivalent circuit then reduces to that in Fig. 9d, at least for materials without appreciable surface re-oxidation, and high values of K_a will be obtained with low losses. On the other hand, in situations for which $R_G \gg X_G$, the material will have normal (i.e. low) values of K_a (Fig. 9e); this is most likely to occur at low temperatures because of the temperature dependence of ρ_G (Fig. 5). However, as the resistivity of the grain cores decreases with increasing temperature, and R_G approaches X_G, increased values of K_a will be observed, initially with high values of tan δ, starting first at low frequencies. This condition is illustrated in Fig. 8b, for a sample with the grain resistivity increased by the addition of Mn. In appropriately donor-doped $SrTiO_3$, without Mn

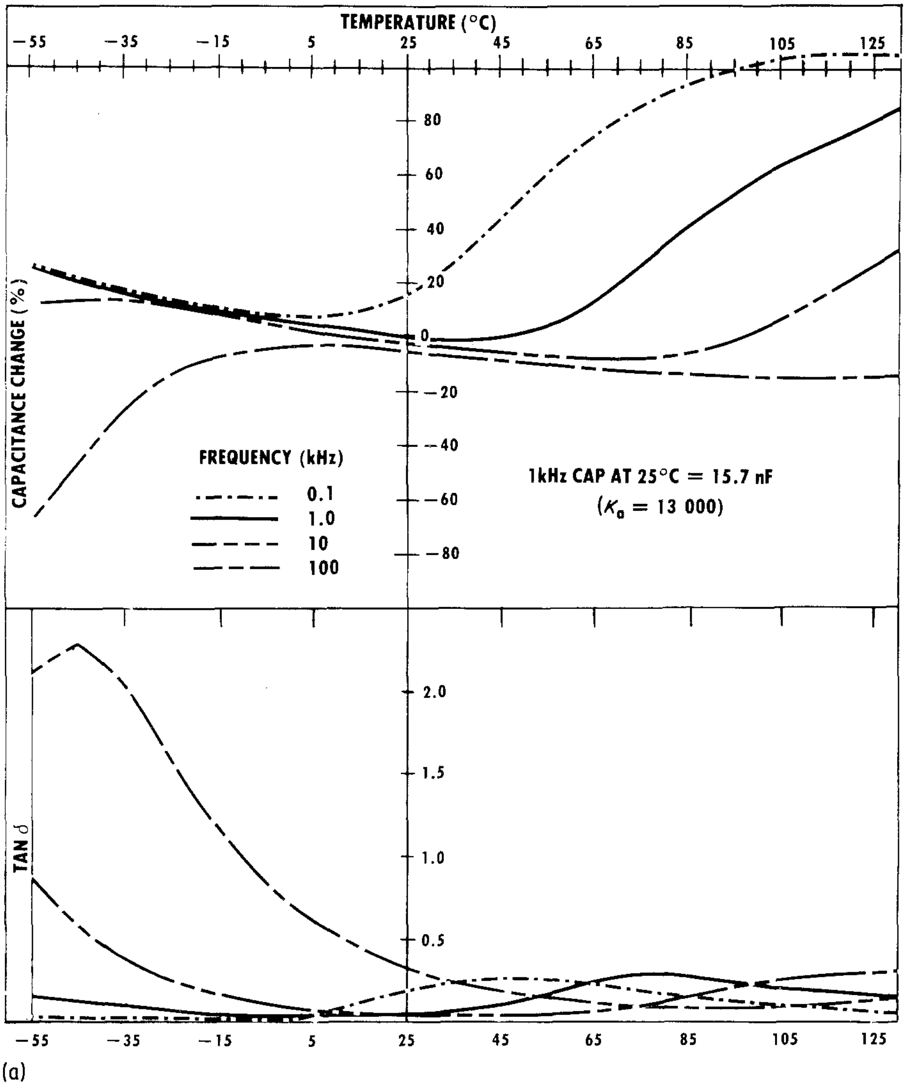

Figure 8 Influence of manganese oxide additions on the dependence of capacitance and dielectric loss on temperature and frequency, for donor-doped $SrTiO_3$ sintered and cooled in air (see text): with 0.02 mol% Mn (a), or 0.05 mol% Mn (b).

additions, the grain resistivity will not normally reach a sufficiently high value to produce dispersion of this type except at very low temperatures. However, the low-temperature relaxation behaviour previously reported for donor-doped $SrTiO_3$ [1–6] probably resulted from this effect.

4.2. Conductivity of the grains

Although it was not possible to measure the grain conductivity in materials sintered in air, it seems reasonable to assume in view of the experimental results and preceding discussion that, with appropriate doping, resistivities $< 6 \times 10^4\,\Omega$cm were obtained, at least at room temperature (Table III). However, it remains to be explained how this conductivity arises.

It seems that ions which substitute for Sr or Ti with higher charge do not produce an increase in the number of conduction electrons in the usual sense of donor doping, as for example by the compensation scheme

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

For which low-energy donor levels (Ti^{3+}) would result in increased conductivity. On the contrary, the present and previous work points to accommodation of the "donor", at least at levels $\gtrsim 0.2$ mol%, by the creation of strontium vacan-

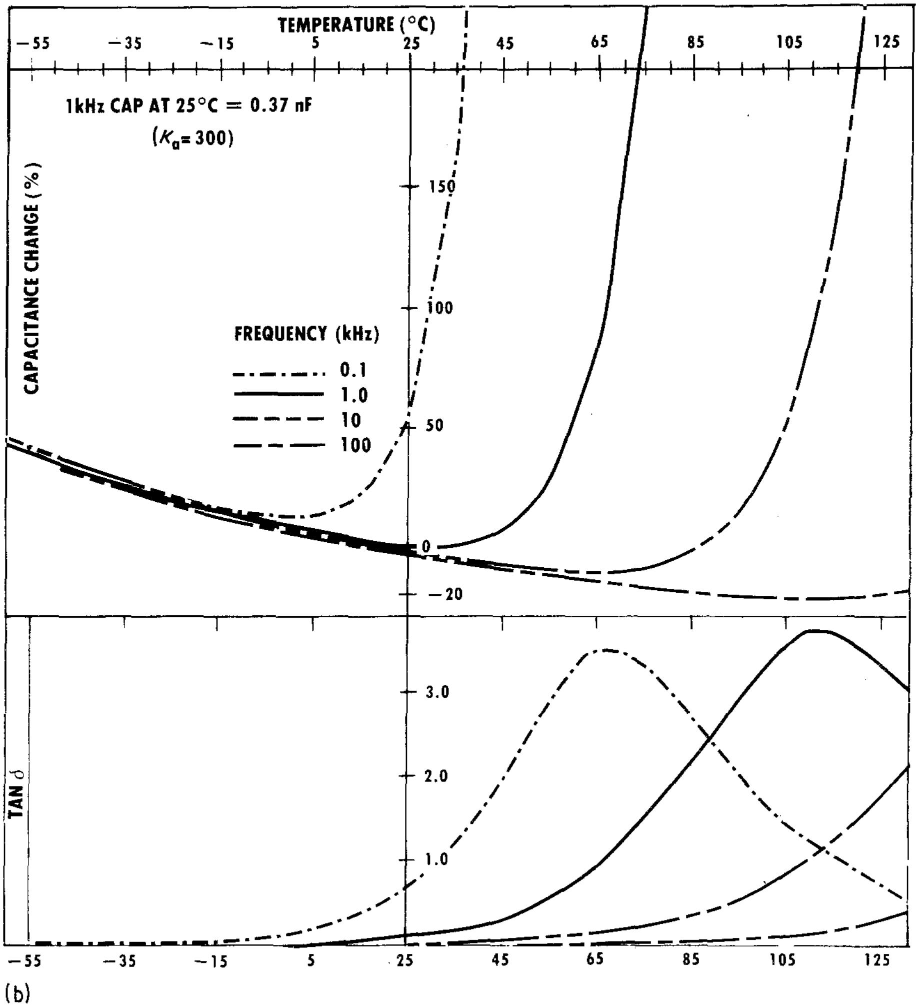

Figure 8 continued.

cies, as discussed earlier, instead of by electronic compensation. The only true donors in $SrTiO_3$, therefore, appear to be oxygen vacancies produced by loss of oxygen from the material at high temperatures, i.e. with customary notation:

$$O_0 \leftrightarrows V_0^{\cdot\cdot} + 2e' + 1/2O_2.$$

Nevertheless, the oxygen vacancy concentration can be strongly influenced by "donor" doping. For example, it has been shown that the defect chemistry of even very high-purity $SrTiO_3$ is dominated by "acceptor" impurities and that these impurities are electrically compensated by oxygen vacancies [17, 18]. These "extrinsic" oxygen vacancies do not produce donor electrons but permit electro-migration of oxygen ions under high fields [19], and high rates of oxygen diffusivity at elevated temperatures [20]. In general, doping with small amounts of "donor" is found to reduce these effects significantly, probably because the impurities are neturalized by a donor–acceptor compensation mechanism, as discussed earlier, instead of by oxygen vacancies.

Reduction of $SrTiO_3$ by heating at elevated temperatures in atmospheres of low oxygen content normally results in intrinsic oxygen vacancies in both donor-doped and in undoped $SrTiO_3$. It can be expected that the number of intrinsic oxygen vacancies will depend not only on the temperature and oxygen partial pressure, but also on the number and nature of the lattice defects already present in the material. For example, for a given temperature and oxygen partial pressure, less oxygen loss might be expected from a material with an already high (extrinsic) oxygen vacancy concentration. Indeed, in undoped $SrTiO_3$ significant conductivity was obtained only after heating in quite strong reducing conditions e.g. $p(O_2) \leqslant$

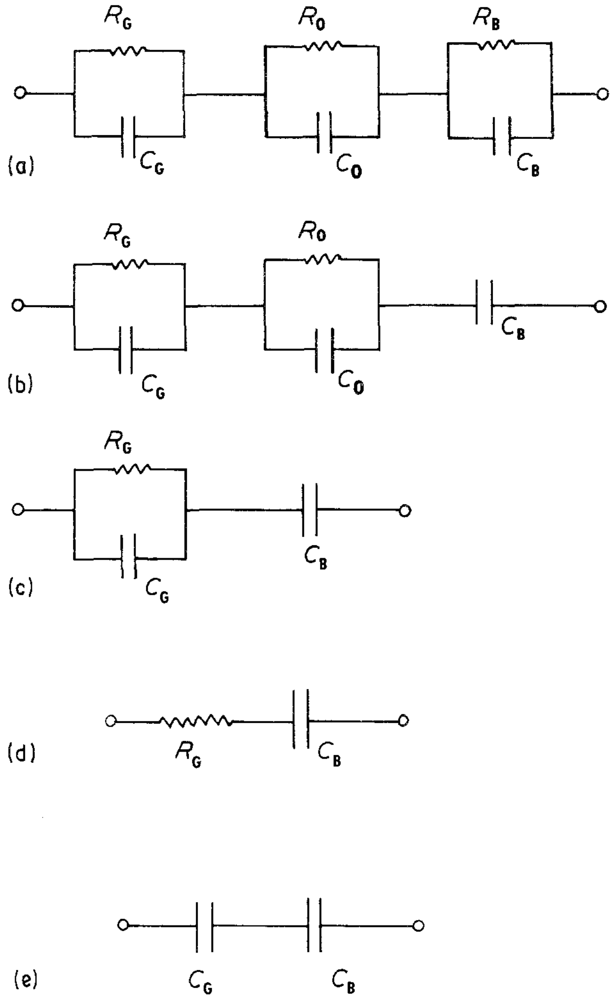

Figure 9 Equivalent circuits for boundary-layer capacitors.

10^{-10} atm at 1450° C. Conversely, a higher oxygen loss might be expected from a material with a high concentration of cation (Sr) vacancies. Such an argument has also been suggested recently to account for the behaviour of donor-doped $BaTiO_3$ [21], and could explain why donor-doped $SrTiO_3$ sintered in atmospheres of relatively high oxygen partial pressure such as air, could become conducting. Barrier layers, albeit weak ones, can then be expected to result in donor-doped $SrTiO_3$ if sufficient oxygen loss occurs during sintering, and then some re-oxidation of the grain surfaces is allowed to take place during cooling. In fact, if the grains are made conducting unequivocally by sintering in a slightly reducing atmosphere and then cooled under oxidizing conditions, properties similar to air-fired materials are obtained except for slight differences in frequency dispersion.

Grain growth during sintering was an important feature of the materials described in the present work. Not only did large grains lead to increased values of the apparent dielectric constant, but the conductivity attained in the grains during sintering and the amount of re-oxidation that took place on cooling were probably also influenced by grain size. During sintering it is likely that oxygen is lost mainly from the surface of the original ceramic powder ($\simeq 1.5\,\mu$m average diameter). Thus, oxygen vacancies can be readily incorporated within the grains during grain growth instead of by diffusion of oxygen out of the grains. Moreover, reoxidation during cooling would be minimized both by the reduction in grain surface area and by the increased diffusion path in materials with large grains, as well as by the diminished diffusivity of oxygen resulting from donor-doping.

Finally, the influence of manganese can be explained in terms of trapping of the conduction electrons associated with intrinsic oxygen vacancies within the grains, e.g.

$$\mathrm{Mn_{Ti}} + e' \rightarrow \mathrm{Mn'_{Ti}}$$

or

$$\mathrm{Mn'_{Ti}} + e' \rightarrow \mathrm{Mn''_{Ti}},$$

where $\mathrm{Mn_{Ti}}$, $\mathrm{Mn'_{Ti}}$ and $\mathrm{Mn''_{Ti}}$ are $\mathrm{Mn^{4+}}$, $\mathrm{Mn^{3+}}$, and $\mathrm{Mn^{2+}}$ ions on titanium sites. The ability of Mn to modify the conductivity of titanates by changes in valence has been noted previously [22, 23] and could account for the strong effect of very small manganese additions.

5. Conclusion

Donor-doped polycrystalline $\mathrm{SrTiO_3}$ was sintered in air under conditions conducive to grain growth during densification. Anomalously high values of dielectric constant (K_a) in the range 5000 to 30 000 were measured for donor levels exceeding about 0.3 mol %. This was the case whether the donor was a trivalent ion substituting for $\mathrm{Sr^{2+}}$, or was a pentavelent or hexavalent ion substituting for $\mathrm{Ti^{4+}}$, provided that the cation stoichiometry was adjusted to allow for charge compensation by strontium vacancies.

Substantial increases in the dielectric permittivity of $\mathrm{SrTiO_3}$ following doping with bismuth oxide, or with various rare-earth oxides, have been reported previously but were generally of lower magnitude and were attributed to ionic relaxor behaviour. In the present work, however, the observed dependence of K_a on grain size and on the method of appying electrodes pointed to a boundary-layer effect. This interpretation was supported by the relatively low d.c. resistivity measured for materials with high values of K_a, and by the observation that the presence of manganese in amounts ~ 0.1 mol % would suppress the permittivity to that usual for $\mathrm{SrTiO_3}$, even for donor levels $\gtrsim 1$ mol %.

An explanation of the increased dielectric constant, and of the dependence of K_a on temperature and frequency observed in this and earlier work, has been suggested in terms of boundary layers of partially re-oxidized surface layers on semiconducting grains. Although it could not be proved that the grains were semiconducting, the grain resistivity was estimated to be $< 6 \times 10^4$ Ωcm at 25° C and to decrease with increasing temperature with an activation energy of 0.15 ± 0.02 eV. It is believed that the semiconductivity results from donor electrons associated with loss of oxygen from the grains during sintering and can be suppressed by manganese ions in the grains acting as electron traps. Donor-doping appears to increase the oxygen loss during sintering and retard reoxidation during cooling.

Useful dielectric materials were obtained when their d.c. resistivity was increased by means of the grain-boundary impregnation technique used in boundary-layer capacitor technology.

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