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High resistivity $BaTiO_3$ ceramics sintered in $CO–CO_2$ atmospheres

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A barium titanate ceramic containing 13.5 mol % calcium zirconate was doped with up to 3 mol % of oxides of various metals that were considered likely on the basis of ionic size and valence to enter the small cation lattice with charge less than 4+. It was hoped in this way to compensate electrically for loss of oxygen during sintering in $CO–CO_2$ mixtures, so as to obtain high resistivity dielectrics and allow the use of base metal electrodes in a monolithic capacitor. Doping with approximately 0.5 mol % Mn, Co, or Mg produced the highest resistivities, and dielectrics with nickel electrodes and relative permittivity up to 10 000 were obtained with resistivity in excess of 10^{12} Ω cm at room temperature. When the doped ceramic sintered in contact with nickel, the grain structure and permittivity-temperature characteristics depended on the oxygen partial pressure of the sintering atmosphere, apparently influenced by dissolution of Ni into the ceramic.

1. Introduction

Barium titanate, and the modifications that are commonly used as high permittivity dielectrics in ceramic capacitors, have a resistivity $\gtrsim 10^{12}$ Ω cm when sintered in oxidizing atmospheres such as air. If sintering takes place in an atmosphere of lower oxygen content, the resistivity may be as low as 10 Ω cm [1] because loss of oxygen from the titanate lattice results in n-type conductivity through partial reduction of the titanium ions (Ti^{4+}) to the trivalent state. Under certain conditions, however, the presence of cations that can substitute for Ti^{4+} with lower valence (i.e. acceptors) will compensate electrically for loss of oxygen and thereby inhibit an increase in conductivity when sintering is carried out in reducing atmospheres [2, 3]. Monovalent cations substituting for Ba^{2+} should also compensate for loss of oxygen, though there is no confirmation of this in the literature.

Barium titanate ceramics that retain high resistivity after sintering in atmospheres of low oxygen content are very desirable for use in multilayer capacitors because electrodes of a base metal can be used instead of platinum or palladium [4]. The extent to which such ceramics have been developed is reported in the patent literature [5-7] but very little basic information is available on the properties of acceptor doped barium titanate ceramics fired in reducing atmospheres.

In the present work a $BaTiO_3–CaZrO_3$ composition popular as a high permittivity dielectric was studied. Efforts were made to identify the most efficient reduction-inhibiting dopant and the optimum concentration, for atmospheres sufficiently reducing that the ceramic could be fired with base metal electrodes.

2. Experimental

2.1. Materials

The barium titanate was prepared from equal molar amounts of reagent grade $BaCO_3$* and high purity TiO_2†. The calcium zirconate was "electronic grade" material‡ containing approximately 2.1 (mol) % Al, 2.1 % Si and 0.2 % Ti as principal impurities. High permittivity solid solutions with $BaTiO_3$ can be obtained up to 20 mol % $CaZrO_3$, with Curie points decreasing from that of barium titanate, at about 130° C, to near room temperature with increasing calcium zirconate content [8]. The amount used in the present work was 13.5 mol %. The overall Al and Si contamination levels were, therefore, both approximately 0.28 % (0.03 wt %).

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‡ Transelco 117, Transelco Inc, Penn Yan, N.Y.

Up to 3 mol % of oxides of the following elements were tried as reduction-inhibiting dopants: Cr, Mn, Fe, Co, Ni, Mg, Zn, Al, Ga, Li. These elements are all capable of having a valence < 4 with similar ionic size to Ti^{4+}. Acceptor substitutions for Ba^{2+} were not attempted because the oxides of elements with suitable ionic valence and size are either easily reduced (Ag, Cu) and, therefore, poorly reactive with barium titanate in reducing conditions, or are volatile (Na, K, Cs, Rb).

2.2. Procedures

First an essentially qualitative survey of the effectiveness of the various additives in preventing reduction was carried out using pressed discs (1.2 cm in diameter). Discs that had no open porosity after firing were electroded with an air-drying silver preparation.

When the most suitable dopants and concentration levels had been narrowed down, "thick-film" capacitors were prepared by screen printing. These capacitors had an active dielectric approximately 75 μm thick and 10 mm² in area and were made in the same way as those described elsewhere [9] but the electrodes were nickel, and air-dry silver electrode terminations were used.

Sintering of the discs or thick-films was accomplished by heating for 2 h at 1350°C, or in a few cases at 1300°C, in a controlled atmosphere furnace. The wire-wound (Pt–40% Rh) heating element contained a 4 cm i.d. alumina tube both ends of which extended from the furnace and were closed with removable gas-tight fittings. Samples, placed in a platinum-lined alumina boat, were pushed into the hot zone of the furnace by means of a thin alumina rod attached to the boat, and which could slide through a water-cooled O-ring union in one of the end fittings. Maximum temperature was reached in 20 min, and the boat could be pulled out of the hot zone after the sintering period and cooled in about the same time. The oxygen partial pressure was adjusted by regulating the proportions of CO_2 and CO in mixtures flowing through the furnace at approximately 9 litres per hour, a rate sufficient to avoid separation of the gases by thermal diffusion [10]. Discs were sintered in a CO_2–CO mixture of 6:1. The electroded thick-films were fired in various atmospheres with CO_2/CO ratios in the range 22.5 to 0.35.

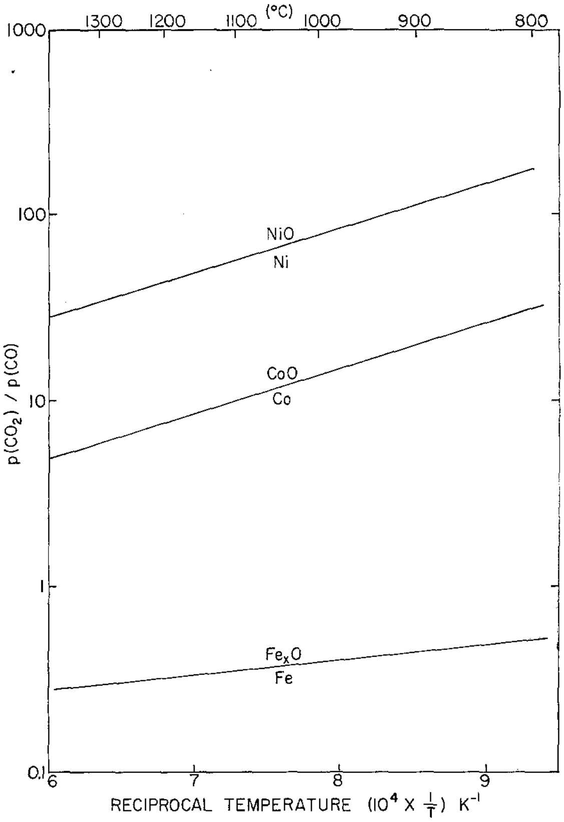

Figure 1 Metal-metal oxide equilibria in CO_2–CO atmospheres [10, 11, 12].

At 1350°C, CO_2/CO ratios less than about 30:1 ($\simeq 10^{-6}$ atm O_2) are effective in protecting nickel from oxidation [11, 12], with smaller ratios being required for possible alternative electrode metals, e.g. Co, Fe (Fig. 1). Since the CO_2/CO mixtures were sufficiently oxidizing to burn carbon [12], organic binders were removed from the ceramic without prefiring, and with negligible influence on the oxygen partial pressure for the flow rate used.

3. Results and discussion

3.1. Sintering and acceptor action

Discs of the $BaTiO_3$–$CaZrO_3$ mixture with no dopant added were porous after firing in CO_2–CO at 1350°C for 2 h. Dense ceramics could be obtained by adding 1.5 mol % TiO_2, or more, but grey-black material with resistivity $\lesssim 10^6$ Ω cm resulted. However, all of the acceptor dopants tried, except Ni, Zn, Al and Li, improved densification, about 0.5 mol % being sufficient to eliminate any open porosity. Furthermore, all the dense materials had resistivity $\gtrsim 10^9$ Ω cm.

The ability of barium titanate ceramics to densify at 1350°C is often dependent on the amount of liquid phase that forms during sintering [13]. Barium dititanate melts below 1350°C so that excess TiO_2, and additives that substitute for Ti or react to form eutectics, usually aid densification. In the firing atmosphere used for the discs, the NiO dopant was probably mostly reduced to the metal during the sintering process and as such would be relatively insoluble in the ceramic. Aluminium, zinc and lithium oxides would not be reduced [12] but apparently do not readily substitute for Ti or form phases that aid sintering in the titanate ceramic studied. On the other hand, lithia-doped barium titanate with excess TiO_2 has been found to resist reduction [14].

No significant enhancement of resistivity was detected on increasing the dopant concentration to more than 0.5 mol %. Larger amounts of dopant had the effect of suppressing the high permittivity characteristics of the material, except in the case of Ga_2O_3 for which a high permittivity material with a sharp Curie peak at 43°C was obtained up to at least 2.4 mol %. As will be discussed presently, the low permittivity resulted from the formation of mixed phases. It seems that Ga had a higher solubility in the $BaTiO_3$–$CaZrO_3$ solid solution than the other dopants, but it happened to be one of the least effective in producing high resistivity.

Resistivities were in the range 10^9 to 10^{12} Ω cm, the efficacy of the various dopants increasing in the order Fe, Ga, Cr, Mg, Co, Mn, suggesting that divalent ions produced the best results. The effectiveness of the dopants was very much diminished, however, when added together with extra TiO_2. It is suspected that with excess TiO_2 a major portion of the dopant remains in the intergranular "sintering phase". Consequently, for barium titanate ceramics that contain an excess of small cations to large cations, additional large cations (Ba, Ca, etc.) may be needed to reduce the amount of sintering phase and allow dissolution of the dopant into the perovskite lattice [7].

Although the amount of dopant found to be most suitable was determined principally by the sintering characteristics of the $BaTiO_3$–$CaZrO_3$ composition chosen for the study, 0.5 mol % dopant can be expected to be roughly sufficient to compensate for oxygen lost from the titanate lattice during sintering. Data for oxygen lost from barium titanate reduced in hydrogen ($BaTiO_{3-x}$) indicate a maximum loss given by $0.0036 \leqslant x < 0.0073$ in the tetragonal state [15]. Assuming a similar figure for the $BaTiO_3$–$CaZrO_3$ solid solution, such a loss could ideally be compensated by 0.36 to 0.73 mol % divalent ions substituting for Ti^{4+}, or twice the amount of a trivalent substitute.

3.2. Dependence of permittivity on firing conditions

Measurements of the dependence of permittivity on temperature of nickel electroded thick-films containing 0.5 mol % MnO indicated that the position of the permittivity peak depended on the atmosphere present during sintering (Fig. 2). For materials sintered at 1300°C, peaks were broader and permittivities generally lower than those obtained by firing at 1350°C. Thick-films electroded with Ni but doped with Co or Mg instead of Mn showed a similar dependence of permittivity on the oxygen partial pressure present during firing. The permittivity versus temperature curves suggest a transition from a mixed phase system for the higher oxygen partial pressures (cubic barium titanate solid solution plus calcium zirconate solid solution [8]) to a relatively homogeneous single phase system for the low oxygen partial pressures (tetragonal barium titanate solid solution). This interpretation is supported by the microstructure of the materials which showed increased grain growth with decreasing oxygen partial pressure, within the range of oxygen partial pressures used (Fig. 3).

Since no comparable dependence of permittivity on firing atmosphere was observed for ceramic material electroded after sintering it appeared that, for the thick films, the oxygen partial pressure was controlling dissolution of Ni into the ceramic during firing. Electron probe microanalysis of materials fired at 1350°C indicated that, although Ni was barely detectable ($\lesssim$ 0.04 mol %) for an atmosphere of 10^{-10} atm O_2 ($CO_2/CO = 0.35$), a Ni content of 0.30 ± 0.04 mol % was found distributed throughout ceramic fired in 10^{-7} atm O_2 ($CO_2/CO = 11$). For oxygen partial pressures close to the Ni–NiO equilibrium (e.g. 10^{-6} atm at 1350°C) the electrodes dissolved almost entirely in the ceramic during firing.

The fact that a small addition to the ceramic, whether it be Ni or some other transition metal or Mg [16], can have such a large effect on the permittivity characteristics of the material

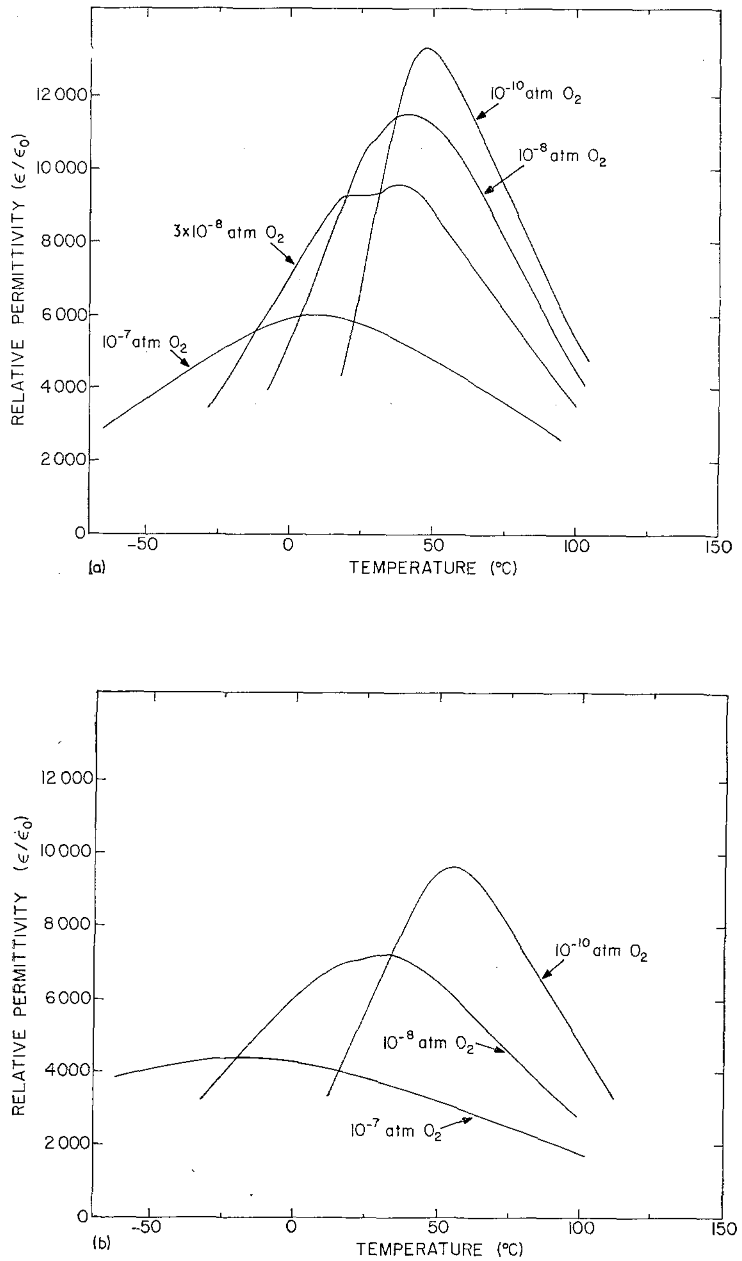

Figure 2 Dependence of permittivity on temperature for thick-films of Mn doped $BaTiO_3$–$CaZrO_3$ ceramic sintered under various oxygen partial pressures at 1350°C (a), and at 1300°C (b).

usually results not from substitution in the titanate lattice, as sometimes suggested, but by inhibiting solid solution of the $CaZrO_3$. If the additive forms an intergranular titanate phase in a composition where there is close overall stoichiometry in large and small cations, then the major phases become excess in large cations (Ba, Ca), a situation that has been found to retard homogenization.

3.3. Insulation resistance

Room temperature measurements were made of leakage current with 150 V applied ($\simeq$ 20 kV cm^{-1}) and a 2 min charging time. Representative

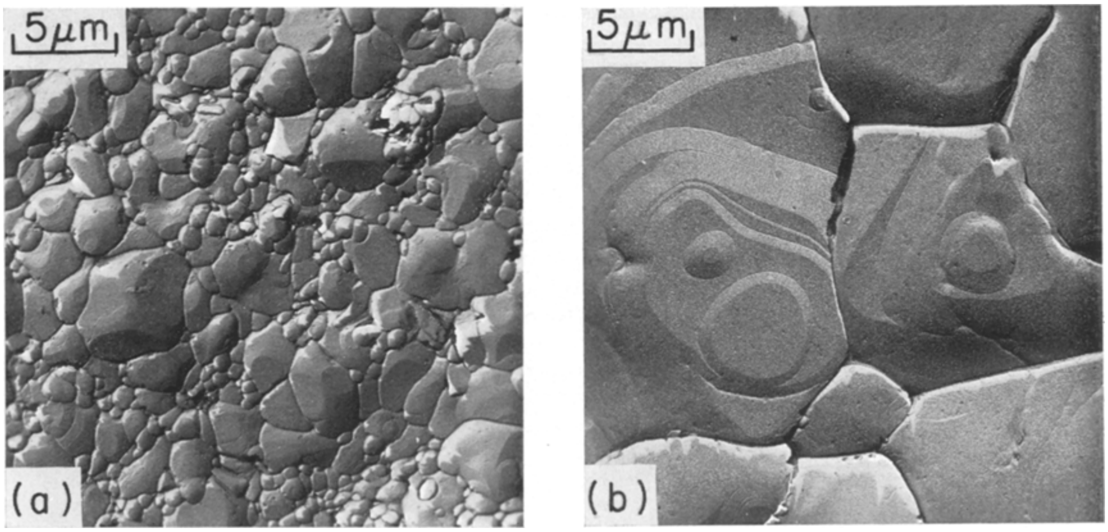

Figure 3 Microstructure of Mn doped $BaTiO_3$–$CaZrO_3$ ceramic sintered at 1350°C (a) with 10^{-7} atm O_2, and (b) with 10^{-10} atm O_2 (× 3000).

data are presented in Table I which includes values of resistance-capacitance (RC) product, a parameter of interest in capacitor applications. In agreement with the preliminary work with discs, resistivities of materials doped with Co or Mg were generally lower than when containing Mn for similar firing conditions. Also in line with undoped titanate ceramics, there was a trend to decreased resistance with increasing firing temperature and with decreasing oxygen partial pressure, although the data were not entirely consistent at the intermediate oxygen partial pressures.

It was found that an increase in resistance could be obtained by a post sintering treatment at lower temperature and/or higher oxygen pressure. Table II shows data obtained for various sintering conditions that were followed by an anneal at 1300°C for 2 h with a CO_2/CO atmosphere of 22.5/1. This "reoxidation" treatment was chosen mainly because units initially sintered under these conditions had shown high resistivity (Table I). Annealing treatments at lower temperatures might have been equally or more effective in increasing the resistance but a higher CO_2/CO ratio could have led to oxidation

TABLE I Room temperature data for nickel electroded thick-films of acceptor doped $BaTiO_3$ + 13.5 mol % $CaZrO_3$

Dopant (0.5 mol %)	Sintering temp. (°C)	Atmosphere		Resistivity (10^{12} Ωcm)	Relative permittivity $\epsilon/\epsilon_0 \equiv k$	RC (ΩF or sec)
		CO_2/CO	$p(O_2)$ atm			
MnO	1300	22.4	10^{-7}	8.4	4 000	3000
	1300	7.1	10^{-8}	2.4	7 300	1550
	1300	0.71	10^{-10}	3.4	6 600	1950
	1350	11.2	10^{-7}	2.5	6 100	1350
	1350	6.1	3×10^{-8}	1.2	9 300	1000
	1350	3.5	10^{-8}	2.1	10 500	1950
	1350	0.35	10^{-10}	0.5	7 300	350
CoO	1300	12.3	3×10^{-8}	1.8	5 100	800
	1350	11.2	10^{-7}	1.3	5 600	600
	1350	6.1	3×10^{-8}	0.2	7 900	150
MgO	1350	6.1	3×10^{-8}	0.2	5 700	120

TABLE II Room temperature data for nickel electroded thick-films of acceptor doped $BaTiO_3$ + 13.5 mol% $CaZrO_3$ annealed after sintering

Dopant (0.5 mol %)	Sintering temp (°C)	Atmosphere		Resistivity (10^{12} Ωcm)	Relative permittivity $\epsilon/\epsilon_0 \equiv k$	RC (ΩF or sec)
		CO_2/CO	$p(O_2)$ atm			
MnO	1300	7.1	10^{-8}	5.3	7 300	3400
	1300	0.71	10^{-10}	7.8	5 300	3650
	1350	6.1	3×10^{-8}	3.6	9 300	3000
	1350	3.5	10^{-8}	5.3	10 200	4800
	1350	0.35	10^{-10}	4.2	5 900	2200
CoO	1350	11.2	10^{-7}	1.8	6 800	1100
	1350	6.1	3×10^{-8}	1.4	7 700	1000
MgO	1350	11.2	10^{-7}	4.0	3 800	1500
	1350	6.1	3×10^{-8}	1.2	5 300	600

of the electrodes. Except for some decrease (≃ 20%) in permittivity of the materials initially sintered at the lowest oxygen partial pressures, the permittivity-temperature characteristics of Fig. 2 were not noticeably affected by the annealing treatment. It was possible, therefore, to select a particular permittivity characteristic by appropriate adjustment of the firing conconditions, and then optimize the resistance with a post-firing anneal or suitable cooling procedure.

The improvement in resistivity obtained by the reoxidation treatment was more pronounced at higher temperatures. Fig. 4 shows the leakage current at 125°C for voltages up to about 300 V (40 kV cm^{-1}) for the Mn doped ceramic fired at 1350°C (Fig. 4a), and at 1300°C (Fig. 4b). While the leakage current clearly increased with

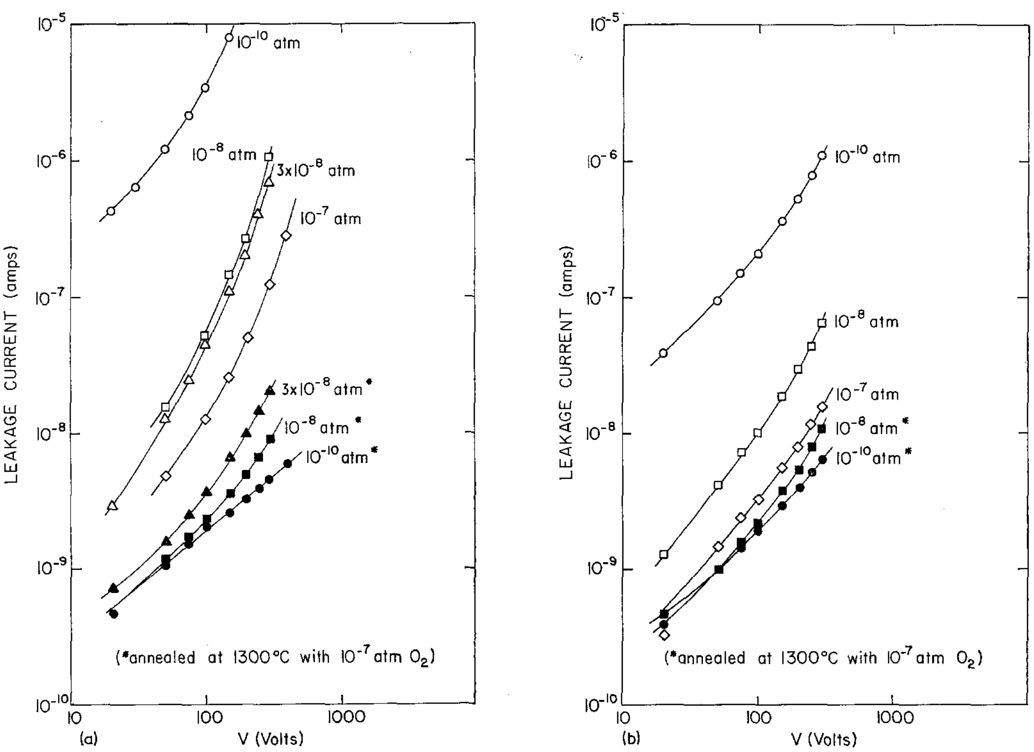

Figure 4 Leakage current at 125°C of Mn doped $BaTiO_3$–$CaZrO_3$ ceramic sintered under various oxygen partial pressures at 1350°C (a), and at 1300°C (b), and effect of annealing.

decreasing oxygen partial during firing for the unannealed materials, the reverse appeared to be true for the annealed materials although here the differences were relatively small. Although the dependence of the current on voltage appears predominantly non-ohmic, it must be borne in mind that in measurements of this type the current does not always achieve an equilibrium value unless long charging times are used, particularly at the lower voltages [17]. Also conductivity at ambient temperatures is usually, at least partially, representative of some non-equilibrium state "frozen-in" during cooling. Nevertheless, the data do illustrate the influence of firing atmosphere and temperature, and the effect of a post-sintering treatment. Lower conductivities following sintering at the lower temperatures and high oxygen partial pressures can be expected because oxygen loss from the ceramic is minimized, particularly if sintering is followed by annealing or slow cooling. The fact that the annealing treatment produced the lowest conductivities in the materials initially sintered at the lower oxygen partial pressures may have been a consequence of the smaller amount of secondary phase, or phases, present in the large grain materials (Fig. 3) which possibly had higher conductivity than the major phase, or which restricted diffusion of oxygen along the grain boundaries.

The nature of the current carriers is not clear. In materials for which the oxygen vacancies are completely compensated by acceptor dopants, the conductivity will be mainly ionic, but if the compensation is not complete, then a significant electronic contribution will be present. Any re-oxidation treatment could be expected to lower both types of conductivity by reducing the number of oxygen vacancies. If compensated oxygen vacancies are filled during annealing or cooling, then either electron holes will be generated, or perhaps more likely, the dopant changes its valence state, for example to Mn^{3+} or Mn^{4+}, in the case of manganese.

3.4. Degradation

An increase in conductivity with time under high fields, often observed in titanate ceramics and generally ascribed to the effects of electrolytic migration of oxygen vacancies, was considerably retarded by the annealing treatment. Resistance to degradation at 125° C followed very closely the trends in conductivity shown in Fig. 4: those materials having the highest conductivities at high voltages showing the earliest signs of an increase in current with time. As shown in Fig. 5 the large grain materials, when annealed after sintering, still had a resistivity of 2×10^{11} Ω cm after 100 h at 125°C with 20 kV cm^{-1} applied. Harwood [18] concluded for TiO_2 doped with manganese that dielectric degradation was inhibited by Mn^{4+} changing to a lower valence in preference to Ti^{4+} changing to Ti^{3+} during oxygen migration, thereby delaying an increase in conductivity. Such a situation could apply in the present work to the annealed materials.

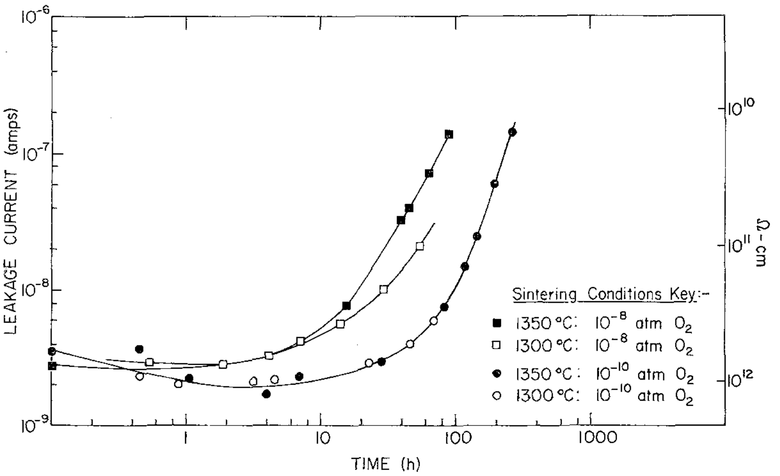

Figure 5 Leakage current versus time at 125°C and 150 V (≃ 20 kV cm^{-1}) for Mn doped ceramic sintered under various conditions and annealed 2 h at 1300°C with 10^{-7} atm O_2.

4. Summary

High permittivity dielectrics in the system $BaTiO_3$–$CaZrO_3$ were obtained following sintering in CO–CO_2 atmospheres in contact with nickel electrodes. Low insulation resistance was avoided by doping the material with 0.5 mol % Mn, Co or Mg. Other dopants such as Cr, Ga or Fe, while inhibiting high conductivity following sintering in reducing atmospheres, were not as effective in producing useful dielectrics. The permittivity-temperature dependence of electroded dielectrics was influenced by the sintering atmosphere when the oxygen partial pressure was close to that for Ni/NiO equilibrium. This appeared to be related to the influence of nickel from the electrodes dissolving in the ceramic during sintering and retarding solid solution of the $CaZrO_3$ in the $BaTiO_3$. Resistivities were higher and resistance to degradation stronger when the dielectrics were annealed under more oxidizing conditions following sintering. The best properties were obtained for dielectrics doped with Mn and sintered in atmospheres with oxygen partial pressure more than three orders of magnitude below that for Ni/NiO equilibrium, provided that they were partially re-oxidized afterwards.

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