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Mn-doped polycrystalline $BaTiO_3$

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Barium titanate was doped with $\lesssim 1$ mol % Mn and sintered in air under conditions producing grain growth. Treatment at elevated temperatures in atmospheres of various oxygen partial pressures resulted in changes in crystallographic transition temperatures and in resistivity that seemed to be associated with a change in the valence state of manganese.

1. Introduction

Barium titanate ceramics normally become semiconducting if sintered, or reheated after sintering, in atmospheres of low oxygen content. However, doping with small amounts of ($\lesssim 0.5$ mol%) of certain oxides such as those of Mn or Co has been found to suppress this tendency [1, 2]. It appears that metal ions of appropriate size and with charge less than 4 + can substitute for Ti^{4+} in the titanate lattice and behave as electron acceptors [3, 4]. These acceptors neutralize the donor action of oxygen vacancies that usually form in titanates heated in atmospheres of low oxygen content. The ability of titanate ceramics to maintain high resistivity following such heat treatment is important in the manufacture of ceramic capacitors with base-metal electrodes [1, 2]. During the development of disc capacitors with Cu or Ni electrodes [5], it was observed that the Curie point of a particular Mn-doped barium titanate ceramic was lower by about 12° C when Cu or Ni electrodes were used instead of silver (Fig. 1). The Ag electrodes were fired onto the ceramic in air (at 750° C), whereas the base-metal electrodes were fired in an atmosphere of approximately 10^{-16} atm. O_2 at (900° C). Ceramic samples that were heated without electrodes but under conditions simulating the different electrode firing procedures just described showed the same effect when electrodes of an air-drying silver paint were applied at room temperature. In was apparent, therefore, that the change in Curie point resulted from heat treatment in atmospheres of different oxygen partial pressure, and that interaction of the ceramic with the electrode material was not a factor in this case [2]. A similar effect has been noted by Herbert for barium titanate doped with Co, when heated in hydrogen [1].

In the present work the influence of annealing atmosphere on Mn-doped barium titanate has been studied in some detail and attempts made to explain changes in the crystallographic transition temperatures and differences in the resistivity in terms of the nature and concentration of lattice defects.

2. Materials

The barium titanate used for most of the work was made from reagent purity $BaCO_3$* and high grade ($\gtrsim 99.2\%$) TiO_2†. Some experiments were also performed with $BaTiO_3$ made from the same $BaCO_3$ but with TiO_2 of the highest purity available ($\gtrsim 99.9\%$ TiO_2‡). Manganese carbonate was (wet) mixed with pre-calcined barium titanate in amounts up to 0.5 wt% ($\simeq 1.0$ mol%). In some cases stoichiometry was adjusted by also adding $BaCO_3$. Specimens were prepared in the form of plates approximately 10 mm × 10 mm × 0.5 mm in size by the doctor-blade technique.

Undoped specimens of both grades of barium titanate sintered well with appreciable grain growth when fired in air at 1400° C for 1 to 2 h. Maximum grain sizes were approximately 75 μm

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†"Titanox 1000", N.L. Industries, TAM Div., Niagara Falls, NY, USA.
‡Toho Titan Co., Japan.

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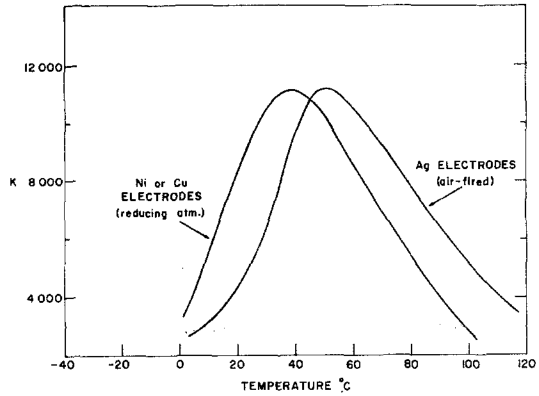

Figure 1 Influence of electrode firing atmosphere on permittivity versus temperature for a commercial Mn-doped barium titanate ceramic [5].

and 125 μm for the lower and high purity materials, respectively. Doping with Mn reduced grain growth in both materials. The effect was slight in the case of the lower purity specimens fired at 1400° C, grain size being reduced to about 25 μm maximum at the highest doping levels (≃1 mol% Mn), but this level of Mn essentially eliminated all growth (i.e. 1 to 2 μm particle size) if the sintering temperature was lowered to 1350° C, even though the material densified well. In the case of the higher purity barium titanate, grain growth was suppressed by as little as 0.25 mol% Mn, even when fired at 1400° C, as illustrated in Fig. 2. Furthermore, grain growth could not be induced by increasing the sintering time and/or temperature, or by adjusting the stoichiometry, without developing appreciable amounts of hexagonal phase.

The amount of Mn incorporated in the grains of the lower purity material was checked by electron probe microanalysis which indicated that at the upper doping levels only about half the Mn entered the grains, with the remainder being retained in a segregated intergranular phase rich in TiO_2. Because of the small grain size, the level of Mn in the grains of specimens sintered without grain growth could not be measured, and it is doubtful in such cases whether the Mn entered the titanate lattice at all.

The only impurity detectable by electron probe analysis was phosphorus, and this was present in the lower purity material only. The phosphorus was segregated in an intergranular phase rich in Ba but was absent from the grains ($\lesssim 0.01\%$). Although it is possible that the presence of phosphorus assisted solution of Mn in the barium titanate during sintering, additional experiments in which Mn was added in the pre-calcination stage indicate that the data presented here are also valid for high purity barium titanate in which the Mn is incorporated in the grains of the material.

3. Experimental

Sintered specimens were annealed at 1000° C for 2 h in CO/CO_2 mixtures producing oxygen partial pressures as low as 10^{-16} atm., as measured by a zirconia probe in the hot-zone of the furnace. Specimens were cooled to room temperature in about 15 min in the same gas used during the annealing period.

Electrical measurements were made by applying an air-drying silver paint to the major faces of the specimens. Crystallographic phase transitions were determined by recording the capacitance change and noting peaks in permittivity as the temperature was increased slowly at about 3° C min^{-1} from −80 to 130° C. Leakage current measurements were made with 100 V applied using a

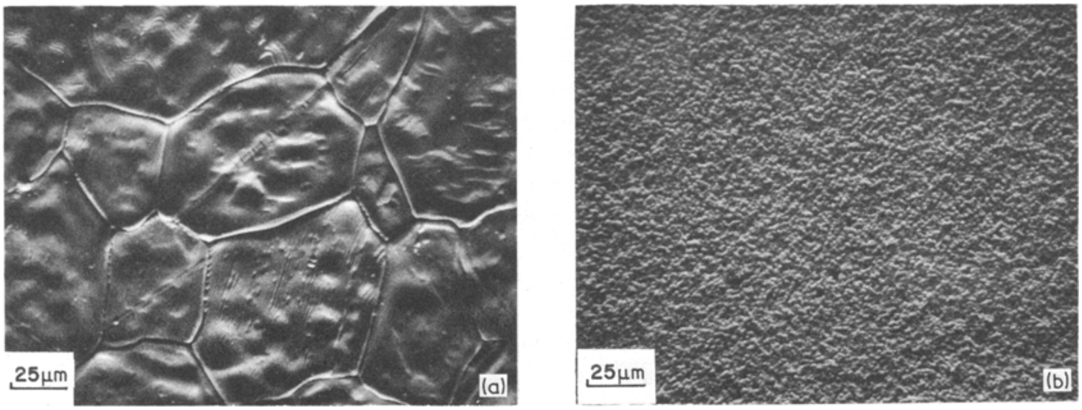

Figure 2 Microstructure of high purity $BaTiO_3$ sintered at 1400° C (a) Undoped; (b) doped with 0.25 mol% Mn.

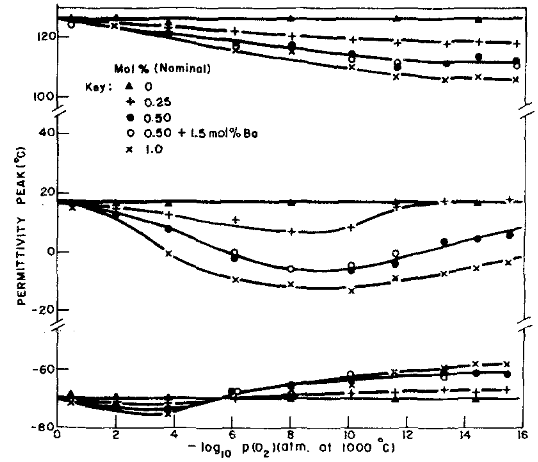

Figure 3 Crystallographic transition points of Mn-doped $BaTiO_3$ after annealing in atmospheres of low oxygen content.

Keithley electrometer (Model 610B). A temperature of 150° C was chosen for the measurements to avoid absorption currents caused by domain reorientation. Conductivity measurements of this type do not give true equilibrium values since they are representative of the defect structure "frozen-in" during cooling from higher temperatures; nevertheless, they are important in practice (i.e. in capacitor applications).

4. Results

4.1. Transition temperatures

The influence of Mn doping on the crystallographic transition temperatures is shown in Fig. 3 for specimens that sintered with grain growth. It can be seen that all three transition temperatures, i.e. cubic–tetragonal ($T_1 \simeq 127^\circ$ C), tetragonal–orthorhombic ($T_2 \simeq 17^\circ$ C), and orthorhombic–rhombohedral ($T_3 \simeq -70^\circ$ C), were influenced by doping with Mn when the material was annealed in atmospheres of low oxygen content. It is worth noting here that the data in Fig. 3 include those of material in which the stoichiometry was adjusted by adding $BaCO_3$. It can be seen that the $BaCO_3$ addition had little if any influence on the transition temperatures, although as will be discussed presently, it did alter the resistivity significantly. Fig. 4a shows that ΔT_1, the shift in T_1 with Mn additions, depended quite linearly on dopant concentration and reached a maximum change close to -40° C per mol% when the oxygen partial pressure was $\lesssim 10^{-12}$ atm. O_2. The changes in the other transitions were more complex (Figs. 4b and c), exhibiting first a decrease in temperature followed by a recovery. The maximum change in T_2 was approximately -60° C per mol%. The change in T_3 ranged from -10° C per mol% to $+20^\circ$ C per mol%.

Specimens of the higher purity material containing Mn (i.e. small grain), and also those of the lower purity material when sintered without grain growth, behaved like undoped barium titanate, the crystallographic transition temperatures being unaffected by the annealing treatments. It seems probable that in such cases the Mn had not

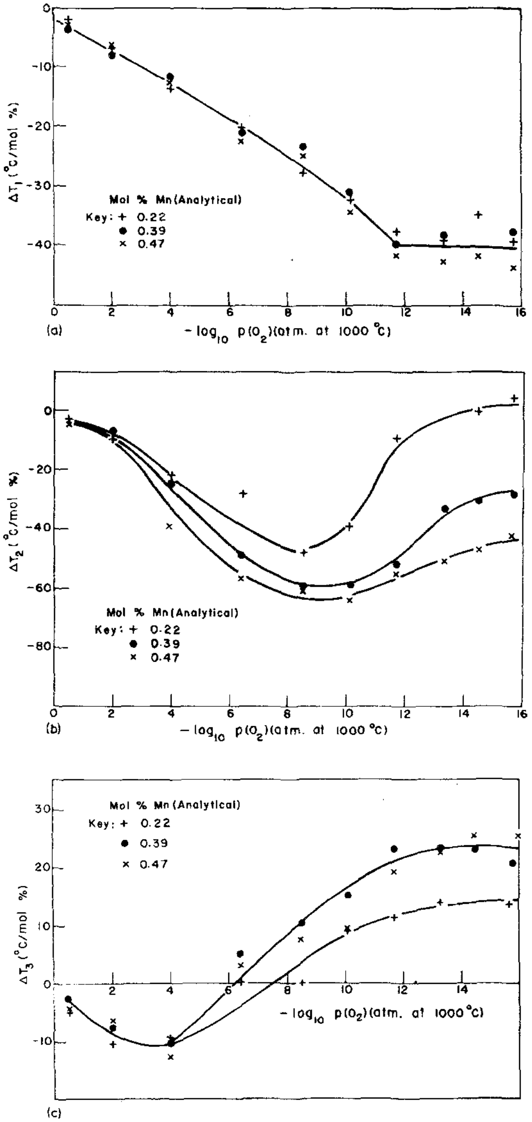

Figure 4 Change in crystallographic transition points of Mn-doped $BaTiO_3$ annealed in atmospheres of low oxygen content (a) tetragonal–cubic, (b) orthorhombic–tetragonal, (c) rhombohedral–orthorhombic.

entered the barium titanate lattice but was present in an intergranular phase.

A few results for other acceptor dopants are shown in Fig. 5 for comparison with those for Mn. The data indicate that T_2 was not influenced significantly by Ga, Co or Ni, but that some changes in T_1 and T_3 were seen compared with undoped barium titanate. Although T_1 and T_3 for Ga or Ni did not vary with annealing atmosphere, it is interesting that, for similar doping levels, the change in T_1 for Ni is about the same as the maximum change for Mn and Co and about twice that for Ga.

4.2. X-ray diffraction

Diffraction peaks occurred at slightly smaller angles when the specimens were annealed in a reducing atmosphere and, although appreciable scatter existed in the *c*-axis values, the data did seem to indicate a lengthening of the *a*-axis and shortening of the *c*-axis to produce a more cubic structure with little change in cell volume. Bois *et al.* [6] reported a decrease in tetragonality produced by oxygen vacancies in (pure) barium titanate annealed in hydrogen. Arend and Kihlborg [7], however, doing similar work, saw no systematic variation in the cell constants of barium titanate due to oxygen deficiency.

4.3. Conductivity at 150° C

Conductivity measurements are shown in Figs. 6a and b. The data seem to follow trends for three separate ranges of oxygen partial pressure. For fairly oxidizing conditions, doping with Mn appears to reduce the conductivity. In the intermediate range, where the conductivity is relatively insensitive to the oxygen pressure of the annealing atmosphere, Mn raises the level of the conductivity "plateau" unless cation stoichiometry is adjusted with extra BaO (Fig. 6b). At low Mn concentration, the manganese extends the plateau region slightly but decreases it at the higher concentrations unless the cation stoichiometry is adjusted. Except in the latter case, annealing at very low oxygen partial pressures results in a sharp increase in conductivity, as is commonly observed with titanates. The importance of cation adjustment in preventing this increase in conductivity has been noted earlier [8].

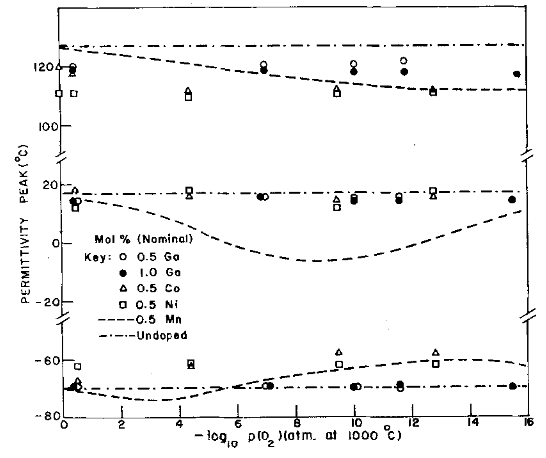

Figure 5 Crystallographic transition points for $BaTiO_3$ doped with Ga, Co and Ni.

5. Discussion

Numerous workers have shown that oxygen is lost from barium titanate when heated in atmospheres of low oxygen content [3, 6, 9]. Hardtl and Wernicke [10], using a dilatometer, observed a decrease in Curie temperature in reduced $BaTiO_3$

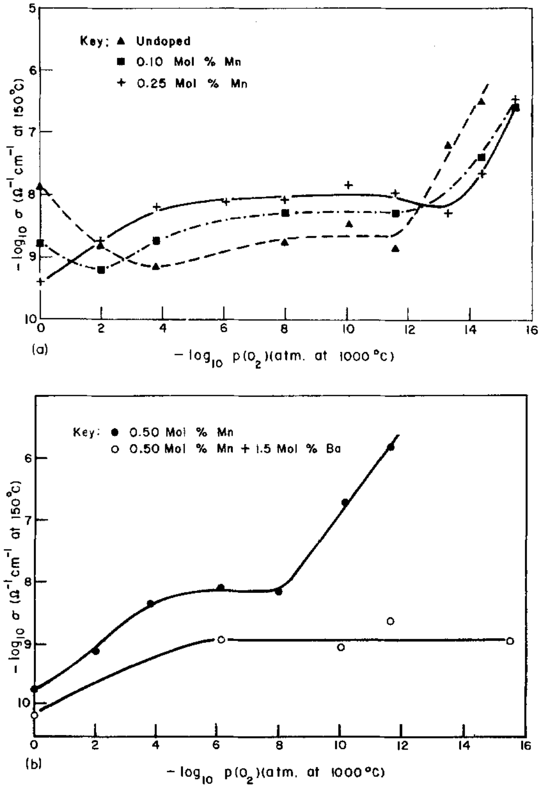

Figure 6 Conductivity at 150° C for Mn-doped $BaTiO_3$ annealed in atmospheres of low oxygen content; (a) low Mn concentrations, (b) 0.50 mol % Mn (nominal) with and without stoichiometry adjustment.

(undoped) of 40 to 50° C for every 10^{20} oxygen vacancies cm^{-3}. Although no decrease in Curie point was observed in the present work for undoped barium titanate, it seems probable that extra oxygen vacancies are built into the lattice by acceptors that are either added intentionally or are present as impurities [4]. In the case of multivalent dopants, the concentration of oxygen vacancies can be expected to change as the valence changes, e.g.

$$\mathrm{BaTi}_{1-x}\mathrm{Mn}_x^{4+}\mathrm{O}_3$$
$$\rightarrow \mathrm{BaTi}_{1-x}\mathrm{Mn}_x^{3+}\mathrm{O}_{3-(x/2)} + (x/4)\,\mathrm{O}_2 \uparrow$$
$$\rightarrow \mathrm{BaTi}_{1-x}\mathrm{Mn}_x^{2+}\mathrm{O}_{3-x} + (x/4)\,\mathrm{O}_2 \uparrow$$

If one assumes that a dopant level of say 1 mol% Mn produces the same number of oxygen vacancies when fully reduced, the Curie point shift ΔT_1 found in the present work is equivalent to $-40°$ C for 1.5×10^{20} oxygen vacancies cm^{-3}, a value similar to that found by Hardtl and Wernicke [10] for undoped but heavily reduced barium titanate.

The Curie point data for the other acceptors can be explained if one assumes the dopants are accommodated in the lattice during sintering in air as follows:

$\mathrm{BaTi}_{1-x}\mathrm{Ga}_x^{3+}\mathrm{O}_{3-(x/2)}$	with $x/2$ oxygen vacancies (uninfluenced by annealing)
$\mathrm{BaTi}_{1-x}\mathrm{Ni}_x^{2+}\mathrm{O}_{3-x}$	with x oxygen vacancies (uninfluenced by annealing)
$\mathrm{BaTi}_{1-x}\mathrm{Co}_x^{3+}\mathrm{O}_{3-(x/2)}$ $\rightarrow \mathrm{BaTi}_{1-x}\mathrm{Co}_x^{2+}\mathrm{O}_{3-x} + (x/4)\,\mathrm{O}_2 \uparrow$	with $(x/2)$ oxygen vacancies initially plus $(x/2)$ when $\mathrm{Co}^{3+} \rightarrow \mathrm{Co}^{2+}$

Thus, ΔT_1 would be similar for Mn, Co and Ni, but Co-doped specimens would be less sensitive to the annealing atmosphere than Mn-doped material, and Ni-doped specimens would be unaffected by the annealing atmosphere, as observed. Similar considerations may apply to some extent to the lower transition temperature (T_3). However, since Mn appeared to be the only dopant influencing the orthorhombic–tetrahedral transition (T_2), it is possible that the particular combination of Mn^{3+} + Mn^{2+} ions de-stabilize the orthorhombic phase at T_2. Similarly a combination of Mn^{4+} and Mn^{3+} might be responsible for the slight de-stabilization of the rhombohedral phase at T_3 for the higher oxygen pressures.

We turn now to the conductivity data, which appeared to show different trends over three separate regions of oxygen pressure. For oxygen pressures $\gtrsim 10^{-4}$ atm. O_2, conductivity increased with increasing $p(\mathrm{O}_2)$, a characteristic of p-type behaviour when oxygen begins to fill impurity related oxygen vacancies, i.e. with conventional symbolism,

$$V_O^{\cdot\cdot} + \tfrac{1}{2}\mathrm{O}_2 \rightleftarrows \mathrm{O}_O + 2h^{\cdot}$$

However if some of these impurities are replaced by Mn during sintering, generation of positive carriers during reoxidation can be avoided by the process

$$2\mathrm{Mn}'_{\mathrm{Ti}} + V_O^{\cdot\cdot} + \tfrac{1}{2}\mathrm{O}_2 \rightleftarrows 2\mathrm{Mn}_{\mathrm{Ti}} + \mathrm{O}_O$$

where $\mathrm{Mn}'_{\mathrm{Ti}}$ and $\mathrm{Mn}_{\mathrm{Ti}}$ are respectively Mn^{3+} and Mn^{4+}. For the middle region of oxygen pressures ($\simeq 10^{-4}$ to 10^{-12} atm. O_2) conductivity may well be mainly (an)ionic as the condition

$$\{\mathrm{Mn}''_{\mathrm{Ti}}\} = \{V_O^{\cdot\cdot}\}; \qquad (\mathrm{Mn}''_{\mathrm{Ti}} \equiv \mathrm{Mn}^{2+})$$

is reached. Any higher titanate phase present in the grain boundaries, however, may produce prematurely the n-type conductivity that is observed for low oxygen pressures. In this case, further oxygen vacancies result in electrons by the process

$$\mathrm{O}_O \rightleftarrows \tfrac{1}{2}\mathrm{O}_2 + V_O^{\cdot\cdot} + 2e'$$

as is observed in undoped barium titanate. This situation will also arise when $p(\mathrm{O}_2)$ becomes sufficiently low to reduce the acceptor dopant to the metallic state.

6. Summary

Differences between the Curie temperature of undoped and acceptor-doped barium titanate appeared to result from a greater number of oxygen vacancies being present in the doped material. The difference in Curie temperature was not influenced by annealing the material in atmospheres of low oxygen content when the dopant valence state remained unchanged (e.g. Ga, Ni) but progressively increased with decreasing oxygen partial pressure for dopants that did change valence state (e.g. Co, Mn). Of the acceptor dopants investigated, only Mn induced any significant changes in the temperature of the orthorhombic–tetragonal transition, so that lattice distortion caused by Mn ions appeared to be a factor in this case.

The near-ambient conductivity of Mn doped barium titanate exhibited characteristics of either p-type, ionic or n-type behaviour, depending on Mn concentration and on the oxygen partial pressure present during pre-annealing. This could also be interpreted in terms of multiple manganese valence states accompanied by changes in the oxygen vacancy concentration.

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