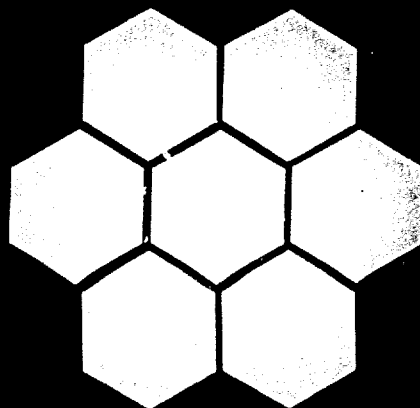


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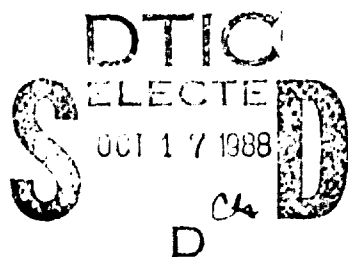


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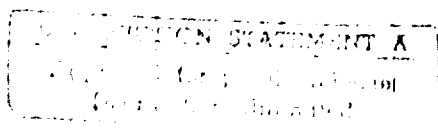
ELECTRICAL DEGRADATION IN CERAMIC DIELECTRICS



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PREPARED BY:
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Professor M. P. Harmer



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I. INTRODUCTION

This report, which represents Part I of a two part sequence, will deal with research related to the mechanism of electrical degradation of ceramic dielectrics, with an emphasis on the role of solid state chemistry and microstructure. The work has been carried out on BaTiO_3 , both doped and undoped, prepared to have precisely controlled compositions. The report takes the form of four independent sections, one of which has appeared as a publication, and two others will be submitted in the near future.

It is generally accepted that the leakage current in BaTiO_3 -based dielectrics is predominantly electronic, but that there is a small, underlying ionic component related to oxygen vacancies. A gradual shift in the distribution of oxygen vacancies during voltage-temperature stress results in a redistribution of charge that causes an accelerating increase in the electronic leakage current to the point that the device can be considered to have failed. Thus it is essential to identify the major electronic charge carrier, and to determine the magnitude of the ionic conductivity and how it is affected by the composition and processing. These were the factors addressed during the period of this report. Brief summaries of the four sections are as follows:

1. Acceptor Solubility in BaTiO_3 in Reducing Atmospheres

As previously reported, it was noted early in this program that samples that had been vacuum hot-pressed rather than sintered in air

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ABSTRACT

This report describes a continuation of an investigation of the mechanism of electrical degradation of ceramic dielectrics based on BaTiO_3 . The emphasis has been on the application of defect chemistry and electron microscopy in order to correlate degradation behavior with compositional and microstructural effects. The report is in four parts that deal with 1) an explanation for the earlier observation that samples that had been densified in a vacuum hot-press were unusually stable against voltage-temperature stress, 2) a simplified technique for determining the ionic contribution to the electrical conductivity, 3) an identification of the major charge carrier for the bulk leakage current, and 4) an investigation of the role of Mn in BaTiO_3 .

1. It has been found that the solubility of acceptor impurities is strongly suppressed during densification in highly reducing atmospheres. The residual gases in the vacuum hot-press are in equilibrium with graphite heating elements and dies, and is extremely reducing. Under these circumstances, the high concentration of oxygen vacancies caused by reduction suppresses the solubility of acceptor impurities. After reoxidation the corresponding concentration of compensating oxygen vacancies is strongly reduced, and the samples are correspondingly more stable against degradation. Support for this explanation was obtained by measurements of the equilibrium conductivities and the ionic transport numbers. After annealing treatments in air that resulted in substantial grain growth, the impurities were reincorporated into the lattice, and the normal acceptor-doped behavior was restored.

2. It is shown that the absolute value of the ionic conductivity and the ionic transport number under equilibrium conditions can be obtained by analysis of the total equilibrium electrical conductivity measured as a function of oxygen partial pressure. The results are in excellent agreement with the much more cumbersome concentration cell technique, which gives only the fractional ionic contribution. The absolute value of the ionic conductivity is required for correlation with degradation behavior.

3. Doped and undoped samples of BaTiO_3 were equilibrated under a variety of temperature-oxygen pressure combinations in order to vary the trapped hole and oxygen vacancy concentrations independently. It was found that the leakage currents followed the trapped hole concentration, and were independent of the oxygen vacancy concentration. It is concluded that the bulk leakage current is carried primarily by holes.

4. The effect of Mn on the degradation behavior, Curie temperature, crystal structure, microstructure, and equilibrium conductivity of BaTiO_3 has been studied. The behavior is complex, and depends on concentration level and processing conditions, but, in general, Mn behaves as an acceptor impurity and appears to substitute only on the Ti site. It was previously suggested that the less acceptor-doped behavior observed for Mn-doped samples densified in reducing atmospheres might be due to incorporation of divalent Mn on Ba sites, where it would be subsequently oxidized to the trivalent state and behave as a donor impurity. In view of the finding that the solubility of acceptor impurities is suppressed by densification in highly reducing atmospheres, as described above, it seems more likely that the effect on solubility is the reason for the observation.

stress. The behavior of the sample with the higher leakage current is characteristic of a sample sintered in air, while the other sample was vacuum hot-pressed and then reoxidized at 1000°C in air. It was subsequently found that the same improved behavior could be achieved by pressureless sintering in the hot-press, so the effect seems to result from exposure to the atmosphere of the hot-press rather than from reduced porosity or finer grain size. In a later study of the ionic contribution to the conductivity of BaTiO_3 by means of the oxygen-concentration-cell technique, it was observed that the emf generated across a hot-pressed sample was much less than that across a sample sintered in air. All of these observations are consistent with a reduction in the extrinsic oxygen vacancy concentration in the samples processed in the highly reducing atmosphere of the vacuum hot-press, and this could result from a suppression of the solubility of acceptor impurities. It will be shown that this is indeed the case, and that the normal acceptor-doped behavior can be restored only by annealing treatments that result in significant grain-growth.

EXPERIMENTAL

All BaTiO_3 powder used in this study was prepared via a liquid-mix process which is described elsewhere (4,5). Polycrystalline specimens were obtained either by hot-pressing at 1200°C under 40 MPa pressure in a graphite die, or by cold pressing and sintering at 1400°C in air. The high temperature equilibrium electrical conductivity was measured at 1000°C as a function of oxygen pressure by means of a standard four-probe dc technique (1). Leakage currents of disk-shaped samples

were unusually stable against electrical degradation. It has now been determined that this effect is due to the suppression of the solubility of acceptor-type impurities in highly reducing atmospheres. Because the dissolution of an acceptor and reduction both result in the formation of oxygen vacancies, there is a common-ion effect. Under highly reducing conditions, the vacancy concentration caused by reduction becomes so high that it pushes the dissolution reaction for acceptor impurities backwards, reducing their solubility. This was confirmed by measurement of the equilibrium electrical conductivity, which showed that such samples were less acceptor-doped than those sintered in air, and measurement of the ionic transport number which showed a lower ionic conduction. When samples were annealed in air under conditions that led to substantial grain growth, the impurities were dissolved into the structure, and the normal acceptor-doped behavior was restored. All of the results were consistent with a reduction of the solubility of naturally-occurring acceptors in undoped BaTiO_3 by about an order of magnitude. The resulting reduction in the concentration of extrinsic oxygen vacancies caused these samples to be much more resistant to electrical degradation.

2. Ionic Transport Numbers from Equilibrium Conductivities

Information on the ionic conductivity, its temperature dependence, and the way it is affected by composition, processing, and microstructure are essential for an understanding of the mechanisms of electrical degradation. The traditional technique for studying ionic

conductivity in mixed conductors is the oxygen concentration cell. The sample is sandwiched between gaseous atmospheres having two different oxygen contents, and the emf of the concentration cell is measured. However, in addition to being a cumbersome procedure, this technique gives only the fraction of the current carried by ions, not the absolute value of the ionic conductivity. The latter is needed for correlation with degradation behavior. It is shown that both the absolute value and the fractional contribution can be obtained by deconvolution of the total equilibrium conductivity measured as a function of the oxygen partial pressure. This is possible because the functional dependences of all of the charge carrying species on the oxygen activity are known for these systems. The technique has been applied to BaTiO_3 , SrTiO_3 , CaTiO_3 , and LiNbO_3 , and the results are shown to be in excellent agreement with the concentration cell technique.

3. The Major Charge Carrier in BaTiO_3

For studies of the time dependence of the leakage current during voltage-temperature stress, it is important to know the identity of the major charge carrier. The possible candidates are electrons, holes, and oxygen vacancies. When equilibrated in oxygen-rich atmospheres, e.g. air, BaTiO_3 is an oxygen-excess, p-type semiconductor. When cooled to ambient temperatures it is an insulator, and would be expected to still be p-type. The magnitude of the ionic currents under these conditions has not been accurately known. In a series of controlled equilibration experiments, BaTiO_3 samples were prepared to have different trapped hole

concentrations at constant oxygen vacancy content, and different vacancy concentrations at constant trapped hole content. The leakage currents were found to follow the hole content and to be independent of variations in the vacancy concentration. Thus it is concluded that bulk leakage currents are predominantly carried by holes.

4. Properties of Mn-Doped BaTiO₃

Mn is a very common additive to BaTiO₃-based dielectrics, and seems to be beneficial for a variety of properties, including stability against electrical degradation. For this reason the effects of Mn on the defect chemistry and electrical properties have been studied. Previous reports that Mn lowers the temperature of the hexagonal to cubic transition were confirmed. Thus for Mn concentrations above about a percent, the paraelectric hexagonal phase was obtained. From microstructural observations and from the effect on the equilibrium conductivity, Mn appears to substitute only for Ti in the perovskite structure, and behaves as a normal acceptor impurity. It had been observed that the acceptor effect was greatly reduced when the samples were densified in a vacuum hot press. We initially suggested that under reducing conditions the Mn was divalent, and that this larger cation partially substituted on Ba sites. After reoxidation, the Mn would become trivalent and would behave as a donor. In view of the effect of reducing atmospheres on the solubility of acceptor impurities, as described in Section 1. above, it seems more likely that the observed behavior is due to a suppression of the Mn solubility under highly

reducing conditions, rather than to a change of its location in the lattice.

AWARDS RELATED TO THIS RESEARCH

1. Ceramographic contest, American Ceramic Society, Cincinnati, 1985.

Transmission Electron Microscopy: Third prize, H. M. Chan, M. P. Harmer, A. Bhalla, and L. E. Cross for "Ordered Microdomain in PST".

2. Ceramographic Contest, Annual Meeting, American Ceramic Society, Chicago, 1986.

Second prize, Z. Wang, H. M. Chan, and M. P. Harmer, "In-situ Observations of Ferroelectric Domain Motions in BaTiO_3 ".

3. D. M. Smyth, Edward C. Henry Award of the Electronics Division of the American Ceramic Society for the most significant contribution to the electronic ceramic literature published by the society during the preceding ten years, 1987.

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1. D. M. Smyth, "Effect of Impurities on Electrical Conductivity of Capacitor Dielectrics", Microstructure and Properties of Ceramics Materials, Proceedings of the First China-U.S. Seminar, T. S. Yen and J. A. Pask, Eds., Science Press, Beijing, PRC, 339-409 (1984).
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10. Y. Sakabe, T. Takagi, K. Wakino, and D. M. Smyth, "Dielectric Materials for Base-Metal Multilayer Ceramic Capacitor", Adv. in Ceramics, 19, 103-115 (1987).
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12. M. P. Harmer, H. M. Chan, and D. M. Smyth, "Compositional Control of Ceramic Microstructures: An Overview", Proc. Mat. Res. Soc. Symp., 60, 125-134 (1986).
13. Z. Q. Zhuang, M. P. Harmer, D. M. Smyth, and K. E. Newnham, "The Effect of Octahedrally-Coordinated Calcium on the Ferroelectric Transition in BaTiO_3 ", Proc. Sixth IEEE Int. Symp. on Application of Ferroelectrics, 122-125 (1986).

14. D. M. Smyth, "Ternary-Oxide Systems", *Advances in Ceramics*, 33, 339-350 (1987).
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18. E. K. Chang, A. Mehta, and D. M. Smyth, "Ionic Transport Numbers from Equilibrium Conductivities", in *Electro-Ceramics and Solid-State Ionics*, H. L. Tuller and D. M. Smyth, Eds., The Electrochem. Soc.: Pennington, NJ, 1988, pp. 35-45.

RELATED PRESENTATIONS

1. August 31, 1984, "The Defect Chemistry of CaO-Doped BaTiO₃", Y. H. Han, M. Lal, X.-W. Zhang, and D. M. Smyth, 10th Intern. Symp. on the Reactivity of Solids, DiJon, France.
2. September 15, 1984, "Electrical Characterization of Transition Metal Oxides", AMP, Inc. (D. M. Smyth).
3. October 12, 1984, "Unravelling the Mysteries of BaTiO₃", DuPont, Wilimington, DE. (M. P. Harmer).
4. October 30, 1984, "Solubility of BaO in BaTiO₃", Y. H. Hu, M. P. Harmer, and D. M. Smyth, Electronics Division Meeting, American Ceramic Society, Paper No. 25-E-84P.
5. November 6, 1984, "Microstructural Relationships with Electric Degradation of Dielectrics Based on BaTiO₃", D. M. Smyth, Second U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Williamsburg, VA.
6. December 17, 1984, "Electronic Ceramics - An Overview", AMP Inc., Harrisburg, PA (M. P. Harmer).
7. February, 1985, "Domain Configurations in BaTiO₃", Penn State University, University Park, PA (M. P. Harmer).
8. February 14, 1985, "The Chemistry of Ferroelectric Oxides", J. T. Baker, Phillipsburg, NJ. (D. M. Smyth)
9. March, 12, 1985, "Composition, Microstructure, and Electrical Properties of Ceramic Dielectrics", University of Pennsylvania, Department of Materials Science and Engineering (D. M. Smyth).
10. May, 1985, "Effect of Compensating Defects on Grain Growth in Ceramic Systems", H. Chan, M. P. Harmer, and D. M. Smyth, Annual Meeting of American Ceramic Society, Cincinnati, OH.
11. May 7, 1985, "Impurity Defect Compensation and Grain Growth Inhibition in Ceramic Systems", H. Chan, M. P. Harmer, and D. M. Smyth, Annual Meeting of the American Ceramic Society, Cincinnati, OH.
12. October 9, 1985, "Degradation Mechanisms in Ceramic Dielectrics", M. P. Harmer, and D. M. Smyth, ONR Contractors Meeting, Penn State University.
13. October 15, 1985, "Rare Earth Additions to BaTiO₃", K. Takada, E. Chang, and D. M. Smyth, Electronics Div., American Ceramic Society, Orlando, FL.

14. October 16, 1985, "The Effect of Charge Carrier on Electrical Degradation of BaTiO_3 ", H. H. Hu, M. P. Harmer, and D. M. Smyth, Electronics Div., American Ceramic Society, Orlando, FL.
15. November 8, 1985, "The Effect of Impurities on the Electrical Properties of BaTiO_3 ", a seminar at North American Phillips, Briarcliff Manor, NY (D. M. Smyth).
16. December 3, 1985, "Compositional Control of Ceramic Microstructures", M. P. Harmer, H. M. Chan, and D. M. Smyth, Materials Research Society Meeting, Boston, MA.
17. April 29, 1986, "Erbium-Doped BaTiO_3 ", K. Takada and D. M. Smyth, 88th Annual Meeting, American Ceramic Society, Chicago, IL.
18. April 29, 1986, "Effect of Octahedrally-Coordinated Calcium Ions on the Ferroelectric Transition of BaTiO_3 ", Z. Zhuang, M. P. Harmer, and D. M. Smyth, 88th Annual Meeting, American Ceramic Society, Chicago, IL.
19. May 5-26, 1986, A series of eight seminars on impurity effects in BaTiO_3 and on the defect chemistry of LiNbO_3 , Qinghua University, Beijing; Xian Jiaotong University, Xian, and Hanzhong University Wuhan, People's Republic of China (D. M. Smyth).
20. July, 1986, "The Effect of Impurities on the Electrical Conductivity of BaTiO_3 ", Dow Chemical Co., Midland, MI. (D. M. Smyth).
21. July, 1986, "Electrical Conductivity in Ceramics: A Review", Ceramic Microstructures '86: Role of Interfaces, Berkeley, CA. (D. M. Smyth).
22. July, 1986, "Microstructures of High Dielectric Constant Materials", Ceramic Microstructures '86, Berkeley, CA (M. P. Harmer).
23. September, 1986, "Ternary Oxide Systems", Third International Workshop on Non-stoichiometric Compounds", University of Keele, England (D. M. Smyth).
24. November, 1986, "Trivalent Impurities in BaTiO_3 ", K. Takada, R. Y. Lee, S. R. Witek, and D. M. Smyth, poster, Third U.S.-Japan Seminar on Dielectric and Piezoelectric Ceramics, Toyama, Japan (D. M. Smyth).
25. November, 1986, "The Effects of Impurities in Ceramic Dielectrics", Murata Manufacturing Co., Kyoto, Japan (D. M. Smyth).

26. November, 1986, "The Effects of Impurities in Ceramic Dielectrics", NEC, Kawasaki, Japan (D. M. Smyth).
27. December, 1986, "Degradation Mechanisms in Ceramic Dielectrics", M. P. Harmer and D. M. Smyth, ONR Contracts Conferences, Pennsylvania State University, University Park, PA.
28. July, 1987, "Defects and Electrical Properties in Perovskites", Gordon Conference, Plymouth, NH, invited (D. M. Smyth).
29. September, 1987, "Ionic Transport in Ceramic Dielectrics", E. K. Chang, A. Mehta, and D. M. Smyth, Second U.S.-China Symposium on Advanced Ceramics, NBS, Gaithersburg, MD (invited).
30. September, 1987, "Equilibrium Conductivity for ER-Doped BaTiO_{3y} ", K. Takada, H. Ichimure, and D. M. Smyth, Sixth Meeting on Ferroelectric Materials and Their Applications, Kyoto, Japan.
31. October 22, 1987, " SrTiO_3 Grain-Boundary-Layer Capacitor Material", L.-T. Li, Y.-Y. Tang, X.-W. Zhang, and H.-P. Zhou, and D. M. Smyth, Symposium on Electro-Ceramics and Solid-State Ionics, Electrochemical Society, Honolulu, HA.
32. October 22, 1987, "Positron Annihilation in Calcium-Doped BaTiO_3 ", L.-T. Li, X.-W. Zhang, D. M. Smyth, and Y.-J. He, Symposium on Electro-Ceramics and Solid-State Ionics, Electrochemical Society, Honolulu, HA.
33. October 22, 1987, "Ionic Transport Numbers from Equilibrium Conductivities", E. K. Chang, A. Mehta, and D. M. Smyth, Symposium on Electro-Ceramics and Solid-State Ionics, Electrochemical Society, Honolulu, HA.
34. October 31, 1987, "Defect Equilibria in Perovskite Oxides", Chapman Conference on Perovskites, American Geophysical Union, Bisbee, AR, invited (D. M. Smyth).
35. May 5, 1988, "Diffusion in Polycrystalline Alkaline Earth Titanates", E. P. Butler, H. Jain, and D. M. Smyth, 90th Annual Meeting, American Ceramic Society, Cincinnati, OH.
36. June 4, 1988, "Ionic Transport in Ceramic Dielectrics", Department of Electronic Engineering, Xian Jiaotong University, Xian, People's Republic of China (D. M. Smyth).
37. March, 1987, "Impurities and Electrical Conductivity in BaTiO_3 ", Alfred University, Alfred, NY (D. M. Smyth).
38. April, 1987, "Effect of Humidity and Microstructure on Electrical Degradation of Barium Titanate", V. Bheemineni, M. P. Harmer, and D. M. Smyth, a poster, 89th Annual Meeting, American Ceramic Society, Pittsburgh, PA.

SECTION 1

ACCEPTOR SOLUBILITY IN BaTiO_3 IN REDUCING ATMOSPHERES

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39. April, 1987, "Thermally Stimulated Currents in LiNbO_3 ", A. Mehta and D. M. Smyth, a poster, 89th Annual Meeting, American Ceramic Society, Pittsburgh, PA.
40. June, 1987, "Ionic Transport in BaTiO_3 ", Philips Forschungs-laboratorium, Aachen, West Germany (D. M. Smyth).

ACCEPTOR SOLUBILITY IN BaTiO_3 IN REDUCING ATMOSPHERES

V. Bheemineni, E. K. Chang, M. Lal, M. P. Harmer, and D. M. Smyth

INTRODUCTION

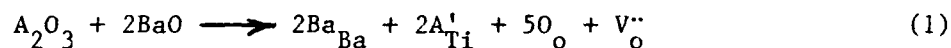
The defect chemistry of BaTiO_3 has been studied extensively, and is quite well understood (1-3). It has been shown that the behavior of undoped BaTiO_3 is strongly influenced by the naturally-occurring impurity content. The most abundant metallic impurities have lesser ionic charges than the species they replace in the perovskite structure, e.g. Na^+ or K^+ for Ba^{++} , and Fe^{+3} or Al^{+3} for Ti^{+4} (1). Therefore, they behave as acceptor impurities and are compensated by doubly-charged oxygen vacancies. Reduction of BaTiO_3 leads to the formation of oxygen vacancies and free electrons. Since oxygen vacancies result from both reduction and acceptor dissolution, it can be anticipated that there will be an interaction between the two processes under equilibrium conditions. In this paper it will be shown that the solubility of acceptor impurities is greatly reduced when BaTiO_3 is processed in a strongly reducing atmosphere.

This investigation was initiated during a study of the degradation of the insulation resistance of BaTiO_3 subjected to severe voltage-temperature stress. It was observed that the leakage current was lower, and more stable with time, for samples that had been densified in a vacuum hot-press than for samples that were pressureless sintered in air. This is illustrated in Fig. 1, where the leakage current is plotted as a function of the time of voltage-temperature

with non-fitted platinum electrodes on both sides were measured with a field of 4 KV/cm at 100°C and 200°C.

RESULTS AND DISCUSSION

Undoped BaTiO_3 invariably contains a net excess of naturally-occurring acceptor-type impurities, since the natural abundances of potential donor-type impurities are extremely low (1). The acceptor impurities are compensated by oxygen vacancies; a general incorporation reaction for a small trivalent impurity A^{+3} that substitutes for Ti^{+4} can be written as follows



The acceptor impurities and their compensating oxygen vacancies are the major defects except under highly reducing conditions. The reduction reaction creates free electrons as well as additional oxygen vacancies



and results in an n-type conductivity that increases with decreasing oxygen pressure, $P(\text{O}_2)$, at temperatures where the material can equilibrate with the surrounding atmosphere. At higher $P(\text{O}_2)$, some of the extrinsic oxygen vacancies are filled, along with the creation of holes



and this results in p-type conduction that increases with increasing $P(O_2)$. The two conduction regimes are separated by a minimum in the conductivity as a function of $P(O_2)$, at the point where the conduction is due solely to intrinsic ionization across the band gap. The conductivity minimum occurs at the oxygen pressure where the electron and hole conductivities are equal, and when this condition is combined with the mass-action expressions for the oxidation and reduction reactions, Eqs. (2) and (3), and the condition of charge neutrality, $[A'] = 2 [V''_O]$, the pressure at the minimum, $P(O_2)^0$, can be expressed as

$$P(O_2)^0 = 4 \left(\frac{\mu_n}{\mu_p} \right)^2 \frac{K_{red}}{K_{ox}} \frac{1}{[A']^2} \quad (4)$$

where μ_n and μ_p are the electron and hole mobilities, and K_{red} and K_{ox} are the mass-action constants for the reduction and oxidation reactions (2). Thus the conductivity minimum moves to lower $P(O_2)$ by two orders of magnitude for each order of magnitude increase in the acceptor concentration, and the position of the minimum at a given temperature is a convenient measure of the relative concentration of acceptor impurities. A simplified defect diagram for $BaTiO_3$ with two different acceptor contents is shown in Fig. 2. It should be noted that the pressure dependence of the electron concentration changes from $-1/4$ to $-1/6$ with decreasing $P(O_2)$ as it crosses the acceptor impurity level. This occurs when the reduction reaction becomes the major source of defects, and the condition of charge neutrality changes to $n = 2 [V''_O]$, i.e. the acceptor impurity content becomes negligible by comparison.

The equilibrium conductivities at 1000°C are shown in Fig. 3 for two samples of undoped BaTiO_3 , one sintered in air, and the other hot-pressed. While the hot-pressed sample is heavily reduced when removed from the apparatus, it quickly equilibrates with the gas atmospheres during the conductivity measurements. The conductivities essentially follow the electron and hole lines as shown in Fig. 2. The conductivity minimum for the sintered sample is at about 10^{-4} atm, while for the hot-pressed sample it is at about $10^{-1.5}$ atm. From Eq. (4), this indicates that the acceptor content of the hot-pressed sample is about 20 times less than that of the sample sintered in air. The conductivities do not change with time at 1000°C, indicating that the concentration of dissolved acceptor impurities remains constant during the several hours required for the measurement. This is in accord with the very low diffusivities of cations in the perovskite lattice; once the acceptor content is established during the densification process, it remains fixed. While the change to a logarithmic $P(\text{O}_2)$ dependence of $-1/6$ is just starting to occur at the lowest $P(\text{O}_2)$ of 10^{-15} atm for the sintered sample, it takes place at about 10^{-7} atm for the hot-pressed sample. It should be remembered that this change in slope takes place as the electron concentration crosses the acceptor concentration level. The difference in the conductivity levels at which the change in slope occurs is also consistent with about an order of magnitude difference in dissolved acceptor concentrations.

It is assumed that the undissolved acceptor impurities remain in the grain boundaries of the polycrystalline material. They cannot enter

the lattice by diffusion, but can be incorporated during any subsequent grain-growth. Since the hot-pressed material has very small grains ($\sim 1-2 \mu\text{m}$), it is possible to obtain substantial grain-growth (to $\sim 20-40 \mu\text{m}$) by a subsequent anneal at 1400°C . The equilibrium conductivities of a hot-pressed sample, and of a sample that was hot-pressed and then annealed at 1400°C in air, are compared in Fig. 4. The conductivity profile of the latter sample is virtually identical to that of a sample sintered in air, indicating that the acceptor content in solid solution has been restored to that characteristic of equilibration in air during the grain-growth process.

When undoped BaTiO_3 is sintered in the hot-press without the application of pressure, the conductivity profile is the same as that of a hot-pressed sample. This indicates that the effect is due to the atmosphere in the hot-press, and not to any differences in porosity or grain size. In order for the reducing atmosphere to suppress the solubility of the acceptor impurities through the application of Le Chatelier's Principle to the incorporation reaction, Eq. (1), the reduction must result in a substantial increase of the total oxygen vacancy concentration above that due to the acceptors alone. This means that the conductivity profile at the densification temperature must be well into the region where the conductivity is proportional to $P(\text{O}_2)^{-1/6}$. This condition is fulfilled in the vacuum hot-press used in this study. The apparatus uses resistively heated graphite heating elements, and the samples are hot-pressed in a graphite die. Thus the gas phase is in equilibrium with solid carbon at the densification

temperature. At the hot-pressing temperature, 1200°C, it is estimated that the oxygen partial pressure is about 10^{-26} atm.

In the highly reducing atmosphere characteristic of the vacuum hot-press, both the electron and the oxygen vacancy concentrations are proportional to $P(O_2)^{-1/6}$. When this is combined with the mass-action expression for the acceptor incorporation reaction, Eq. (1), it is easily shown that the solubility of singly charged acceptor centers varies as $P(O_2)^{1/12}$, while a similar treatment for doubly charged acceptor centers shows that their solubilities will vary as $P(O_2)^{1/6}$. While such acceptor impurities as Al^{+3} substituted for Ti^{+4} , or the alkali metal ions substituted for Ba^{+2} , should always be singly charged centers, Fe and Mn are divalent under highly reducing conditions (6), and should be doubly charged centers. The evidence is that the total acceptor content is drastically reduced, so it is not a matter of suppressing the solubilities of doubly charged centers while the singly charged centers are unaffected. This was confirmed by an investigation of deliberately doped samples. The results for Al and Mn doped $BaTiO_3$ are shown in Fig. 5, where conductivities are shown for both hot-pressed and hot-pressed and air-annealed samples. The solubilities of both impurities were suppressed by the atmosphere in the hot-press, and were restored by grain-growth in air.

It has been shown that Ca^{++} is a very effective acceptor in $BaTiO_3$ when $(Ba + Ca)/Ti > 1$ (7). In that case up to 1.5% Ca^{++} can be forced onto Ti-sites where it acts as a doubly charged acceptor, $Ca_{Ti}^{''}$. However, when such samples were sintered in the hot-press, there was no

evidence for suppression of the acceptor content. While rather surprising at first glance, this behavior can be rationalized. Compared with an acceptor impurity like Al^{+3} with a solubility of about 0.1%, it will require a lower $P(\text{O}_2)$ by a factor of 10^6 to affect the solubility of an acceptor with a solubility of 1%, when the impurities are at their nominal saturation levels in both cases. (Actually, when the more soluble acceptor is doubly charged and the less soluble one is singly charged, the factor is 10^8 .)

In a related investigation, the ionic contribution to the conductivity of BaTiO_3 was studied by the oxygen-concentration-cell technique (8). The details will be published elsewhere, but it is of interest to note here that the ionic conductance in hot-pressed samples was less than 10% of that for samples sintered in air. Since it is generally accepted that ionic conduction in BaTiO_3 is due to the movement of oxygen vacancies, this is further confirmation of the suppression of the solubility of acceptor impurities. Once again, the results are consistent with a decrease in solubility by about an order of magnitude.

The response of BaTiO_3 to severe voltage-temperature stress, as shown in Fig. 1, is also consistent with the proposed model. Through control of added impurity contents and of the temperature and $P(\text{O}_2)$ of equilibration, samples have been made in which the oxygen vacancy content was varied at constant hole concentration and the hole concentration was varied at constant oxygen vacancy content (9). It was found that the leakage current levels followed the hole concentration,

not the vacancy content. This led to a model in which the leakage current is due to holes, but where there is an underlying ionic contribution that is small in comparison, but which leads to a gradual redistribution of mass and charge that eventually causes the hole current to increase to ultimate failure. The hole current results from a very small amount of ionization of holes that are primarily trapped at acceptor centers at the test temperatures. The concentration of trapped holes is a function of the stoichiometric excess of oxygen. Since the hot-pressed samples have barely moved into the oxygen-excess region after equilibration in air, they have a very small concentration of trapped holes, and therefore, lower leakage currents, as seen in Fig. 1. Since the hot-pressed samples also have a smaller concentration of extrinsic oxygen vacancies, the ionic conduction that leads to degradation of the insulation resistance is also reduced. As seen in Fig. 1, they can withstand stress for longer times before the leakage current begins to rise. After such samples were annealed in air to promote grain growth, the leakage currents and degradation behavior were comparable to those of samples that had been sintered in air in the first place.

A possible alternative explanation for the observed behavior could be that impurities that normally occupy Ti-sites as acceptors are induced to occupy Ba-sites instead, where they would be either isovalent (divalent ions), or act as donors (trivalent ions). However, this does not appear to be likely. In a study of the incorporation of trivalent ions as a function of their ionic radii, only Y^{+++} and Er^{+++} were found to be able to occupy either site, depending on the Ba/Ti ratio, to such

an extent that the defect chemistry was significantly affected (10). Attempts to influence the choice of site by these impurities by sintering in a reducing atmosphere were unsuccessful, so it should not be expected that impurities with more definite site preferences could be affected by the oxygen activity during sintering.

CONCLUSIONS

When compared with samples that have been sintered in air, undoped and acceptor-doped BaTiO_3 that have been densified under severely reducing conditions show the following properties:

1. Lower leakage currents
2. Slower degradation rates under voltage-temperature stress.
3. Less ionic conduction
4. Displacement of the equilibrium conductivity minima to higher $P(\text{O}_2)$
5. Extension of the region where the equilibrium conductivity varies as $P(\text{O}_2)^{-1/6}$ to higher values of $P(\text{O}_2)$

After being annealed in air such that extensive grain growth occurs, the properties of these samples revert to those of samples that have been sintered in air.

For the undoped samples described here, comparisons of the shift of the conductivity minima, the conductivity levels at which the $P(\text{O}_2)$ dependence changes, and the amount of ionic conduction are all

consistent with a reduction in the acceptor content of the hot-pressed samples by a factor of 10-20.

The requirements for the observed suppression of the solubility of acceptor impurities are as follows:

1. The atmosphere during densification (or grain growth) must be reducing enough to create a concentration of oxygen vacancies that is large compared with that which results from the acceptor impurity content. These vacancies can then push the impurity incorporation reaction, Eq. (1), toward the left according to Le Chatelier's Principle.
2. The impurity content must be close enough to the solubility limit in air, so that the solubility limit under reducing conditions is exceeded.

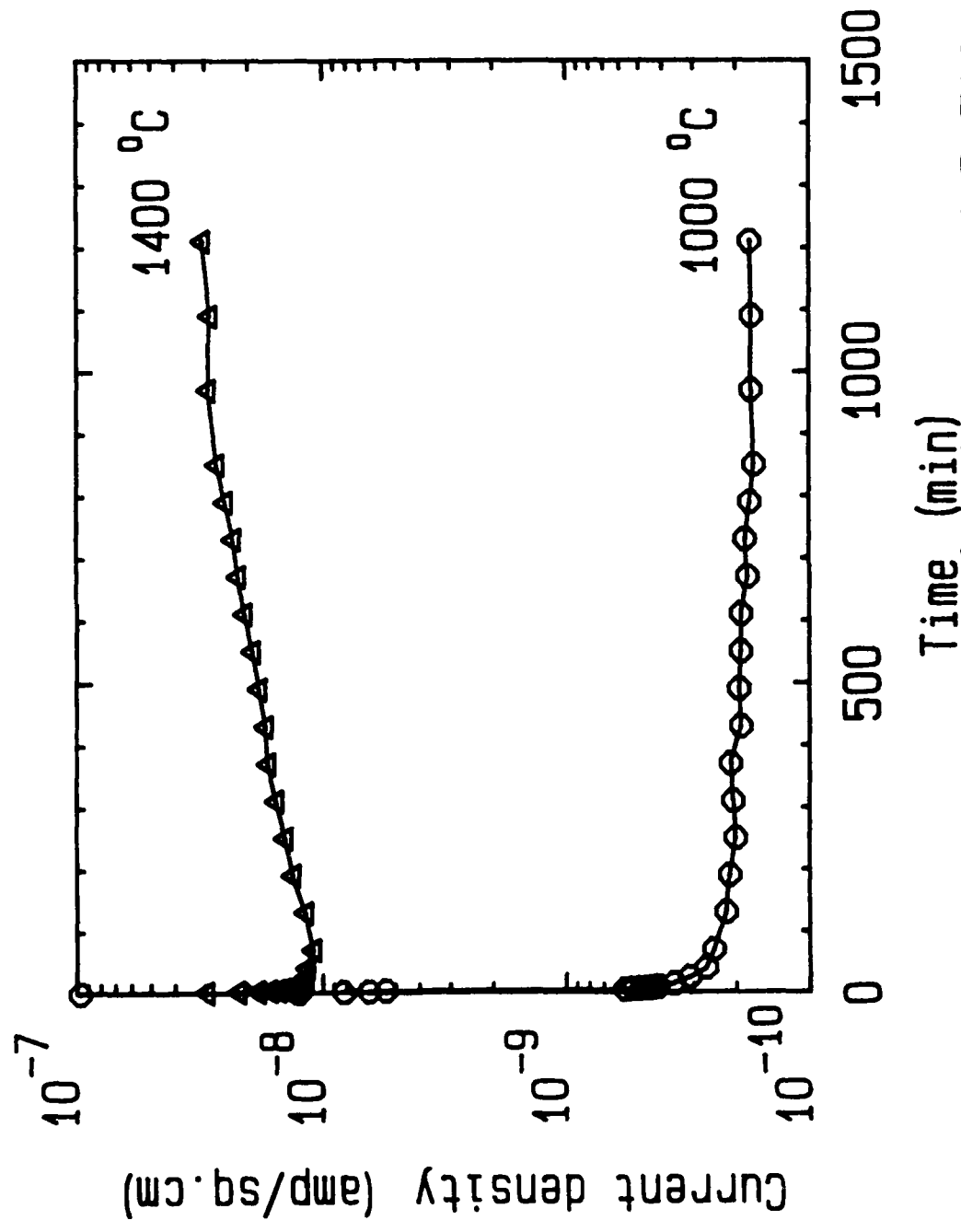
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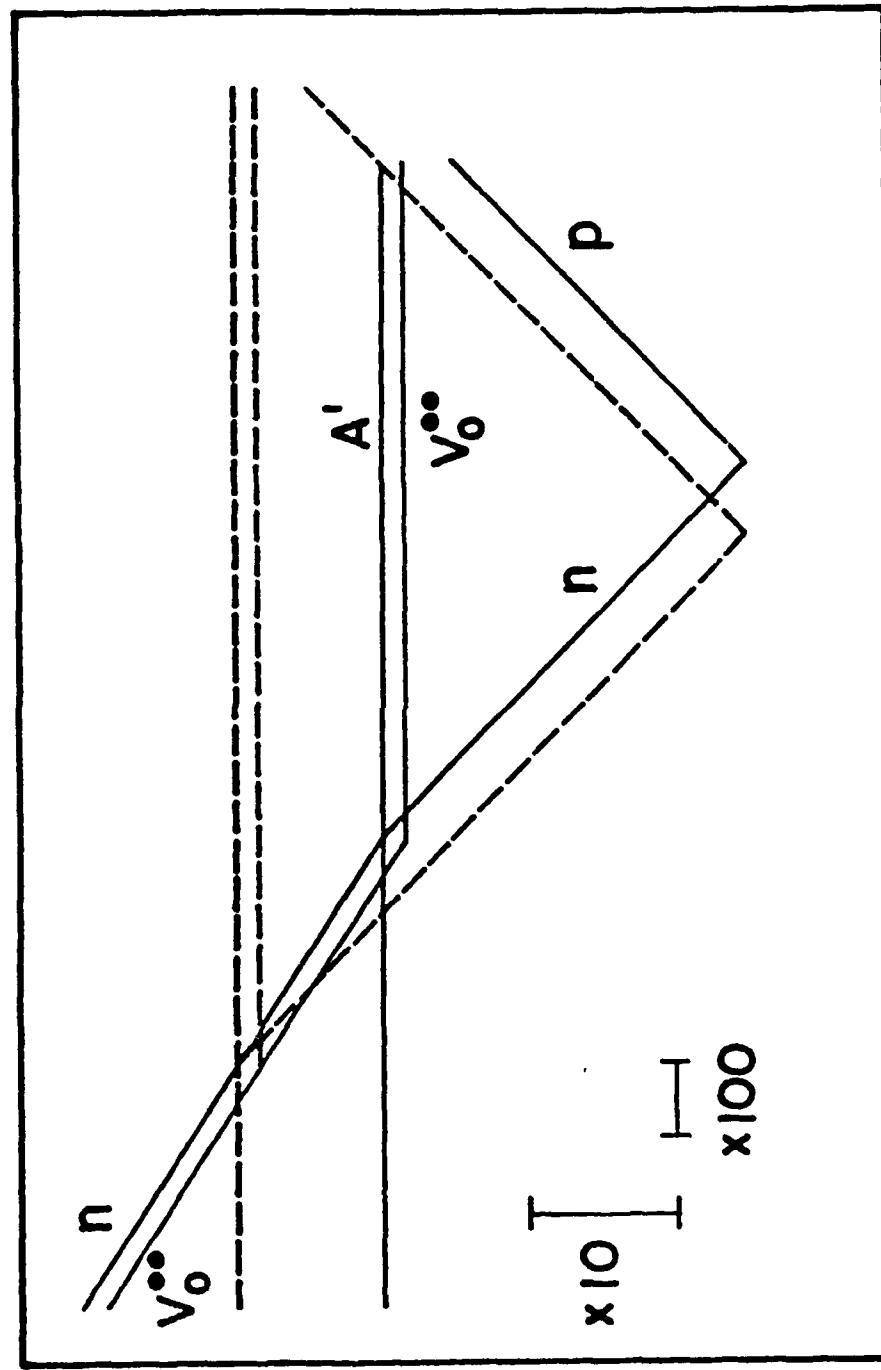
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FIGURE CAPTIONS

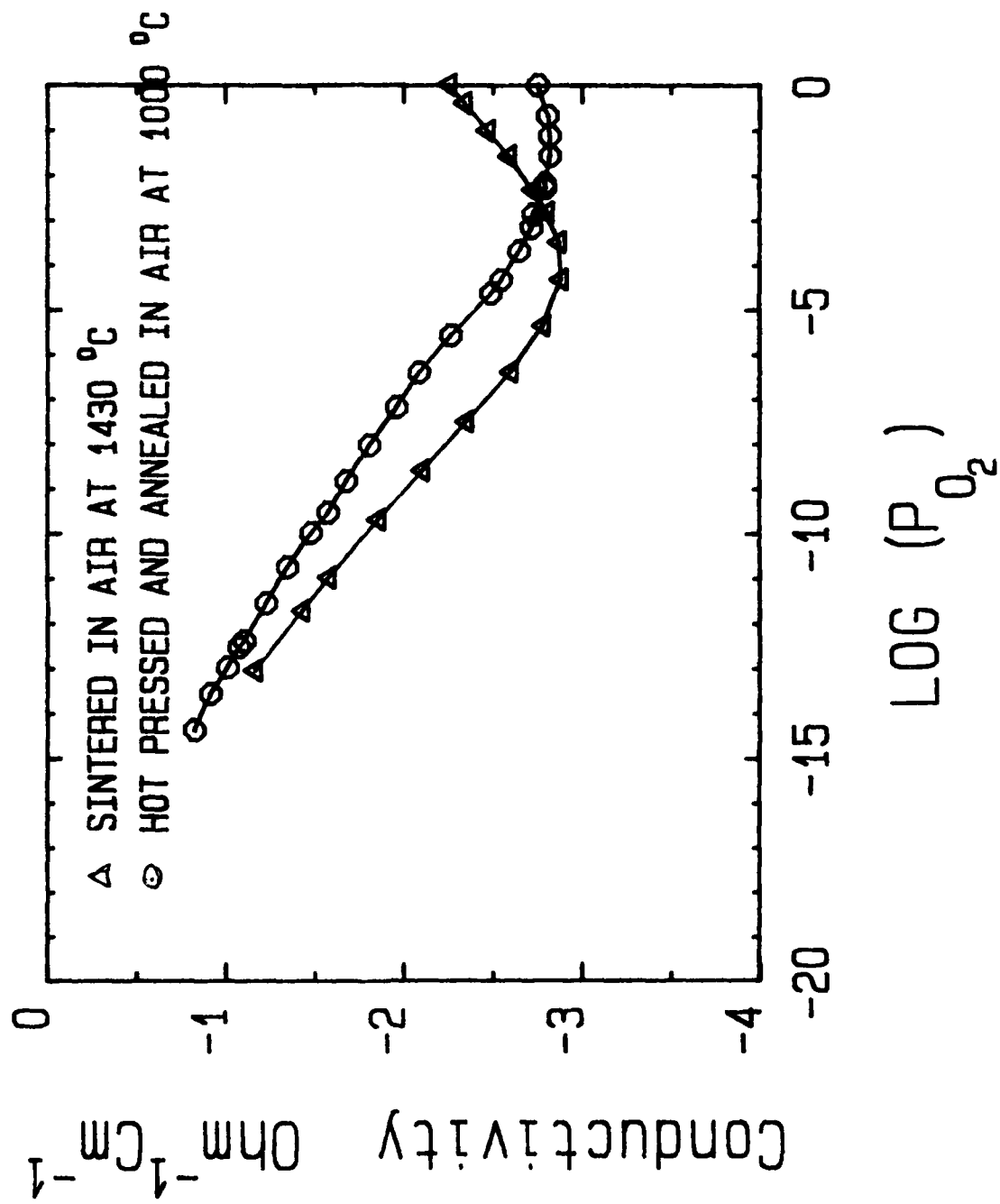
1. Leakage current vs. time at 4 KV/cm at 100°C for undoped BaTiO₃. Both samples were hot-pressed and then annealed in air at the indicated temperatures. The sample annealed at 1400°C behaves very much like a sample sintered in air.
2. A schematic diagram of defect concentrations in BaTiO₃ as a function of oxygen partial pressure. The dashed lines represent a sample with a higher acceptor concentration.
3. The equilibrium conductivities at 1000°C for hot-pressed and sintered samples.
4. The equilibrium conductivities at 1000°C of hot-pressed samples annealed in air with (1400°C) and without (1000°C) grain-growth.
5. The equilibrium conductivities at 1000°C for acceptor-doped samples that were hot-pressed and then annealed in air with (1400°C) and without (1000°C) grain-growth.

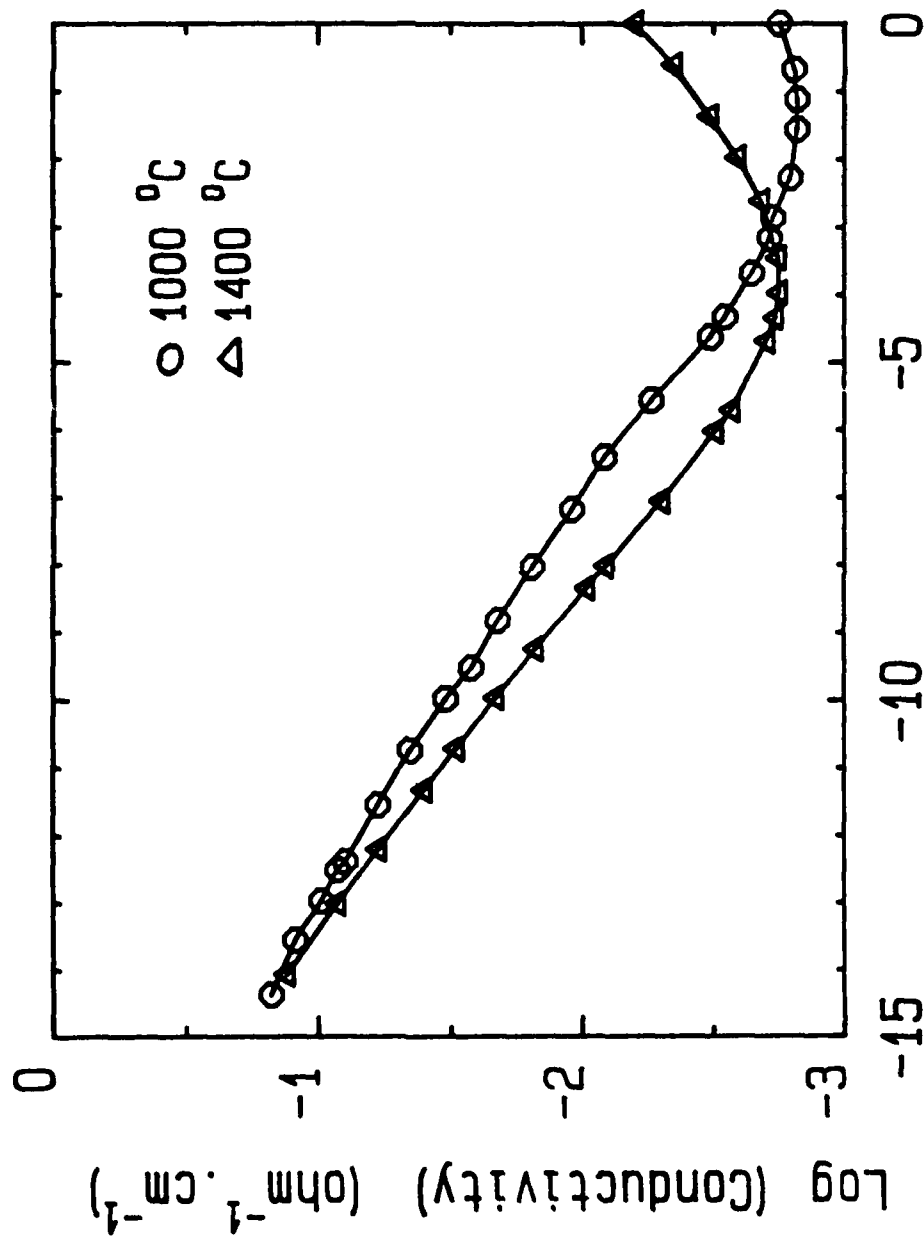


Leakage current of hot pressed BaTiO₃ after annealing at 1000 °C and 1400 °C.

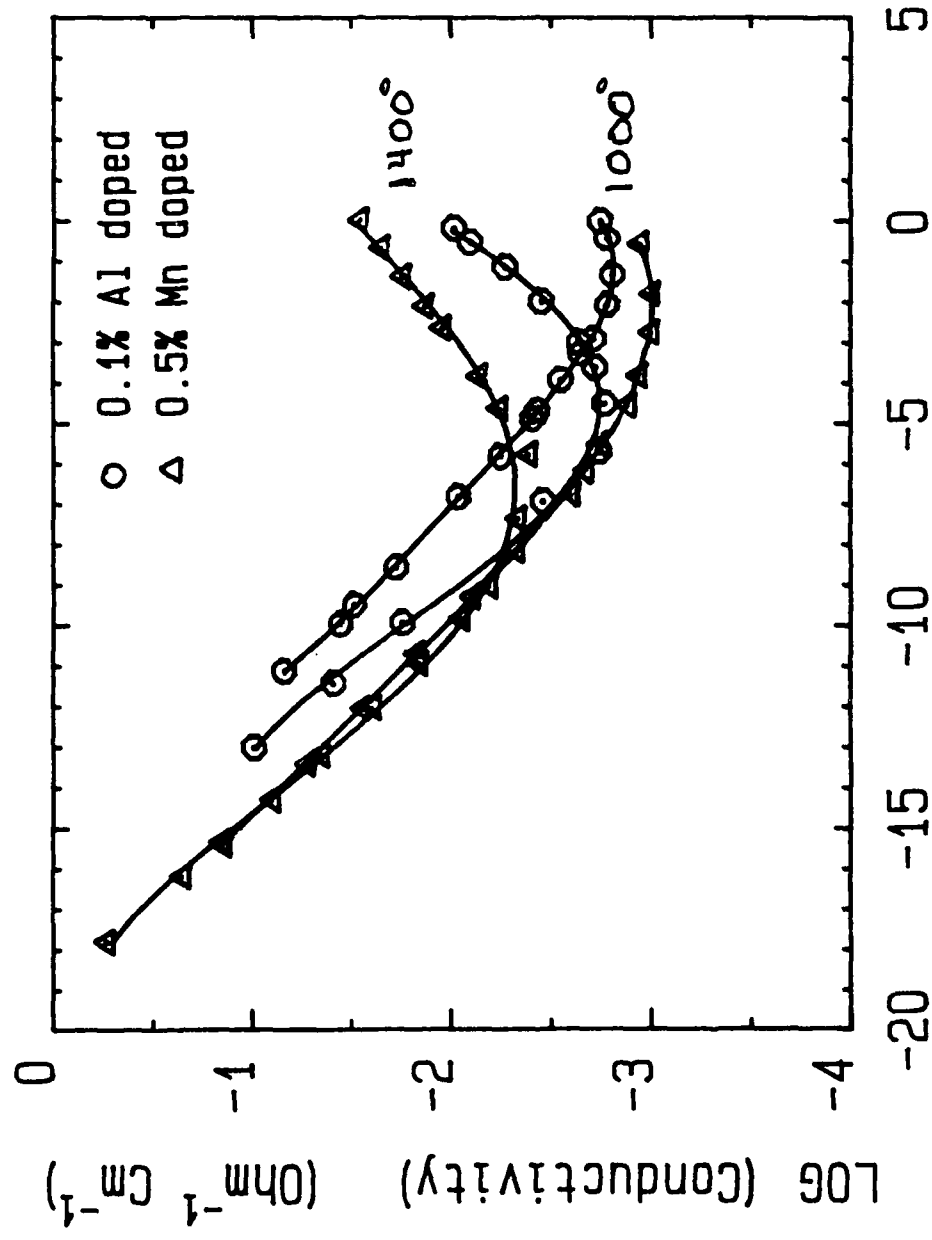


LOG RELATIVE P_{O_2}





Log (Oxygen partial pressure)
Conductivity profiles of BaTiO₃
annealed at 1000 °C, and 1400 °C.



Conductivity of acceptor doped BaTiO_3 at 1000 °C

SECTION 2

IONIC TRANSPORT NUMBERS FROM EQUILIBRIUM CONDUCTIVITIES

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ABSTRACT

It is shown that in many cases it is possible to separate the electronic and ionic contributions to the total conductivity from measurements of only the total conductivity under equilibrium conditions. The requirement is that the two components must have different, and known, dependences on the nonmetal activity, i.e., the oxygen partial pressure in the case of oxides. The procedure is demonstrated for acceptor-doped BaTiO_3 and SrTiO_3 , and for CaTiO_3 with different Ca/Ti ratios. The results are shown to predict accurately the behavior of oxygen concentration cells, the traditional, but more cumbersome, technique for obtaining ionic transport numbers.

INTRODUCTION

In principle, all oxides are mixed conductors, but for many applications either the ionic or the electronic contribution can be neglected. In some cases, however, the minority contribution can be of major importance, as in the formation of oxide films by the thermal oxidation of a metal, where the rate of film formation may be determined by whichever type of conduction is smallest. In the case of oxides used as insulators, very small ionic contributions to the total conductivity may represent a mechanism for ultimate failure; capacitor dielectrics are a particularly good example of such a situation. Thus it is of importance to be able to separate the ionic and electronic components, even in cases where one of them may be much smaller than the other.

The earliest technique for measuring the ionic contribution to conduction in solids was developed by Tubandt (1). This involves measurement of the weight changes of the anode and cathode after the passage of a dc current in an electrolytic cell in which the material of interest serves as the electrolyte. The weight loss of the anode, and weight gain of the cathode, ideally equal, compared with the chemical equivalency of the total charge passed, gives the ionic charge passed and thus the ionic conductivity. While simple in principle, the technique requires that the electrodes be ideal sources and sinks for the mobile ion, and that both electrodes separate cleanly from the electrolyte layer after the passage of current. Moreover, the technique is not sensitive to very small

absolute values of the ionic conductivity. A more commonly used technique is the measurement of the emf of an appropriate concentration cell in which the material again serves as the electrolyte, e.g. an oxygen concentration cell in the case of oxides. This technique gives the ionic transport number, t_i , the fraction of the total current carried by ions. In order to obtain the magnitude of the ionic conductivity, it is also necessary to measure the total conductivity. In this paper, it will be shown that in cases where the defect chemistry is sufficiently well-defined, both the ionic conductivity and the ionic transport number can be obtained from just the total equilibrium electrical conductivity measured as a function of oxygen activity. The concentration cell measurement is then not necessary.

Since the total conductivity of a transition metal oxide may be a function of oxygen activity, the transport number may also be a variable. Ideally, one would like to measure the emf of the concentration cell between two closely-spaced oxygen activities, in order to obtain the transport number for a well-defined situation, but the accuracy of the measurement is thereby decreased since the emf is correspondingly smaller. It is an extremely tedious task to make enough measurements to get an accurate picture of the transport number as a function of oxygen activity. This can be obtained in detail by a proper analysis of the total equilibrium conductivity. The results of this technique have been checked by comparison with concentration cell measurements, using a procedure that gives an overall view of the transport number with a minimum of experimental manipulation.

Oxygen Concentration Cells

The emf of an oxygen concentration cell is given by

$$E = \frac{1}{nF} \int_{\mu(O_2')}^{\mu(O_2'')} t_i d\mu(O_2) \quad (1)$$

where $\mu(O_2)$ is the chemical potential of oxygen, and the single and double primes denote the two sides of the cell. F is the Faraday constant and n is the number of electrons exchanged per chemical unit, 4 in the case of O_2 . When t_i is an unknown function of $\mu(O_2)$, the integral cannot be solved explicitly. A common approximation involves the removal of t_i from the integral as an average transport number, $\bar{t}_i$, representative of the interval of oxygen activity used in the cell.¹ With this approximation and the substitution of $\mu(O_2) = \mu^0(O_2) + RT \ln P(O_2)$, the integrated form of the emf can be written as

$$E = \frac{\bar{t}_i RT}{4F} \ln \frac{P(O_2'')}{P(O_2')} \quad (2)$$

The hazards of this approach are illustrated by published results on some acceptor-doped alkaline earth perovskites, where it was found that $\bar{t}_i$ either increased or decreased with temperature, depending on the oxygen activities used in the cells (2). One can bracket a specific oxygen activity with converging pairs so as to obtain the value of $\bar{t}_i$ extrapolated to zero activity difference, but that is an extremely tedious way to obtain a complete picture of transport number as a function of oxygen pressure and temperature. An alternative approach is based on the differential form of Eqn. (1), where $\bar{t}_i$ is obtained from the slope of a plot of E vs. $\ln P(O_2'')$ with $P(O_2')$ fixed at 1 atm (3). For most applications, the absolute value of the ionic charge motion is needed, and to obtain this the transport number must be combined with the total conductivity, also measured as a function of oxygen activity.

Analysis of the Total Equilibrium Conductivity

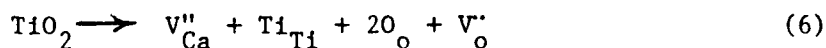
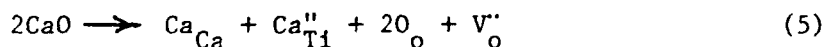
If the total conductivity consists of significant electronic and ionic components that have different functional dependences on the oxygen activity, and if those dependences are known, it is possible to separate the two components by deconvolution of the shape of the total conductivity as a function of oxygen activity. This can be conveniently illustrated with conductivity measurements made on the alkaline earth titanates, $BaTiO_3$, $SrTiO_3$, and $CaTiO_3$. The equilibrium conductivities for all three of these compounds can be related to a Kröger-Vink diagram of the type shown in Fig. 1 (4,5,6). This shows the concentrations of the various defect species as a function of oxygen activity at constant temperature. The dominant defects over most of the experimental range are the naturally occurring acceptor impurities (such as Fe, Al, Na) and the compensating oxygen vacancies. The conductivities are predominantly determined by the sum of the electron and hole contributions, and thus display a characteristic minimum near the oxygen activity where the concentrations of the two electronic carriers are equal. If the oxygen vacancies are sufficiently mobile to make a significant contribution to the total charge transport, this will be most apparent in the vicinity of the conductivity minimum. As shown schematically in Fig. 2, the result will be a raising and flattening of the minimum. An example of this is shown in Fig. 3, which compares the equilibrium conductivities of undoped and acceptor-doped $BaTiO_3$. The higher oxygen vacancy concentration in the acceptor-doped material results in a much larger ionic contribution to the conductivity, and a corresponding change in the level and shape of the conductivity minimum. Of course the minimum is also shifted toward lower oxygen activities in a predictable way (7).

An analysis of the defect chemistry of the titanates indicates that the electron and hole concentrations near the conductivity minimum vary as $P(O_2)^{-1/4}$ and $P(O_2)^{+1/4}$, respectively (4,5). Since the oxygen vacancy concentration is fixed by the acceptor impurity content in that region, their concentration is invariant with oxygen activity. Thus the total conductivities for oxygen activities above and below the minima can be approximated as

$$\sigma_T^a = \sigma_i + \sigma_p^o P(O_2)^{1/4} \quad (3)$$

$$\sigma_T^b = \sigma_i + \sigma_n^o P(O_2)^{-1/4} \quad (4)$$

where σ_i is the ionic conductivity, σ_p^o and σ_n^o are the hole and electron contributions at $P(O_2) = 1$ atm, and σ_T^a and σ_T^b are the total conductivities above and below the minimum, respectively. The contribution of the minority electronic carrier is neglected in these expressions, so they do not apply for the region very close to the minimum. Thus a plot of the total conductivity vs. $P(O_2)^{+1/4}$ for data above the minimum should give a straight line with a slope of σ_p^o and an intercept of σ_i . A plot of the total conductivity vs. $P(O_2)^{-1/4}$ for data below the minimum should give a straight line with a slope of σ_n^o and an intercept of σ_i . If the analysis is correct, and if the data are sufficiently accurate, the two plots should give the same intercept, which corresponds to the ionic conductivity. Examples of such plots are shown in Figs. 4, 5, and 6 for undoped and acceptor-doped $BaTiO_3$ and $SrTiO_3$, and for $CaTiO_3$ with various Ca/Ti ratios. The intercepts are the same for plots from both sides of the minimum for all three materials, and the magnitudes of the conductivities change as expected with composition. In the case of $CaTiO_3$, there is a significant solubility for both excess CaO and excess TiO_2 with the formation of compensating oxygen vacancies, and this causes an increase in the ionic conductivity:



The transport numbers can then be obtained for any oxygen activity by dividing the ionic conductivity by the total conductivity at that activity. Examples for $BaTiO_3$ are shown in Fig. 7; the shape of these curves is obviously just the inverse of the shapes of the conductivity curves in this case. Thus the absolute value of the ionic conductivity, and precise values of the transport numbers as a

function of oxygen activity, are obtained from a measurement only of the total conductivity as a function of the oxygen activity. There is no averaging of the transport numbers as in the case of the concentration cell measurements.

Concentration Cell Measurements

For the cases just described, the correspondence of the intercepts for plots made from both sides of the conductivity minima supports the validity of the approach. In addition, the results for acceptor-doped BaTiO_3 have been compared with concentration cell measurements. An incremental technique was used to show the contribution of ionic transport to the total emf of the cell. The oxygen pressure was fixed at one atmosphere on one side of the cell, and the partial pressure was reduced in increments on the other side. The stepwise increase in the emf was then compared with the value predicted by the values of t_1 determined from the conductivity plots. As an example, each order of magnitude decrease in the oxygen partial pressure on one side of the cell can contribute a maximum additional 63.2 mv at 1000°C. The fraction of this value that is actually observed is the average transport number over that increment of oxygen activity. The solid line in Fig. 8 shows the predicted build-up of the emf as the oxygen activity is progressively decreased on the variable side of the cell. The data points are the observed emf values. The agreement is quite satisfactory. In essence, the transport numbers determined by two totally independent techniques are in good agreement. Similar correspondence has been found for measurements on LiNbO_3 single crystals; the details will be published elsewhere. In this case, only the oxygen-deficient, n-type region is accessible for $P(\text{O}_2) < 1 \text{ atm}$, so that confirmation by comparison with results obtained from the p-type side of a conductivity minimum is not possible. Thus it was particularly satisfying to obtain good agreement with the results of concentration cell measurements.

The Temperature Dependence

Ionic conduction is invariably a thermally-activated process, so it decreases with decreasing temperature in the usual Arrhenius behavior. The temperature dependence of t_1 , however, depends on the relative temperature dependences of the ionic and electronic components. In the case of BaTiO_3 , the p-type and n-type electronic components decrease with decreasing temperature with activation energies of 0.46 and 2.95 eV, respectively, while the ionic conductivity decreases with an activation energy of 1.1 eV (4,7). Thus t_1 decreases with decreasing temperature in the p-type region in the high range of $P(\text{O}_2)$ values, but increases in the n-type region in the lower range of $P(\text{O}_2)$. This is demonstrated in Figure 7. These results explain why it was previously observed that the transport

numbers for highly acceptor-doped perovskites can either increase or decrease with temperature, depending on the range of oxygen pressures used in the concentration cells (2). It is also clear why the conductivity minima become increasingly flat and shallow with decreasing temperature; the electronic minima are dropping with an activation energy that is half of the band gap, $3.4/2 = 1.7$ eV in the case of BaTiO_3 , and the t_i is thus becoming larger at the minima.

Comparison with Previous Results

Previously reported results on similar materials have given various values of $\bar{t}_i$, and even temperature dependences with different signs. These apparent discrepancies become understandable when the experimental conditions are correlated with our results. Concentration cell measurements were made on both single crystalline and ceramic BaTiO_3 by Glower and Heckman (8). They used oxygen pressures in the range 0.01-1 atm, and temperatures in the relatively low range of 100-500°C. They could detect no ionic contribution in undoped, flux-grown single crystals. This is not surprising because of the lack of enhancement of the oxygen vacancy content by the addition of acceptor dopants, and for these crystals grown from a KF flux, the accidental acceptor content may be compensated by the incorporation of the appropriate amount of F^- as a donor dopant. On the other hand, for a crystal containing 0.1 atomic % Fe, an acceptor impurity, the ionic transport increased from about 6% to over 50% as the temperature was decreased from 475° to 105°C. With a ceramic sample, $\bar{t}_i$ increased from 7% to 100% as the temperature decreased from 540° to 250°C. These temperature dependences are in the opposite direction from those we report above for a similar range of oxygen pressures. This is because our temperature range was much higher, 700-1000°C, where the temperature dependence of the electronic component is determined by the enthalpy of the oxidation reaction. The samples are equilibrating with the gaseous atmosphere, and the holes are all free to conduct. In the lower temperature range, the holes begin to trap out at the acceptor sites as the material gradually changes from a semiconductor to an insulator. The materials are no longer chemically equilibrating, and the temperature dependence of the electronic contribution is determined by the trapping energy, which is about 1 eV, very similar to the activation energy of the ionic conduction. Results obtained by Payne on ceramic BaTiO_3 containing "proprietary additives" indicated values for $\bar{t}_i$ of about 0.6 for a similar range of oxygen pressures and temperatures of 250, 200, and 150 C° (9). It is remarkable that reliable results can be obtained at the low temperatures used in these studies. In both cases, however, the validity of the measurements was indicated by demonstrating that when the gas atmospheres on either side of the sample were reversed, the emf was of similar magnitude and opposite sign.

Takahashi made concentration cell measurements on several highly doped perovskites, e.g. $\text{CaTi}_{0.7}\text{Al}_{0.3}\text{O}_{3-x}$ and $\text{SrTi}_{0.9}\text{Al}_{0.1}\text{O}_{3-x}$, in the temperature range 600-1100°C (2). He found values for t_i of 0.1 to 0.7, increasing with increasing temperature, when the gas atmospheres were air and pure oxygen. When the gases were H_2 with 18-32 torr of H_2O vs. pure oxygen, the values were higher, 0.7-0.9, and decreased with increasing temperature. These results are in general agreement with ours. For the higher oxygen pressures, there is substantial hole conduction which has a relatively modest temperature dependence, while for the broader range of oxygen activities, the region of minimum electronic conduction is included, where the temperature dependence is determined by the band gap. Similar results have been reported by Browall and Muller for $\text{LaAl}_{0.85}\text{Mg}_{0.15}\text{O}_{2.925}$ in an air/oxygen cell at 440-690°C, and for oxygen pressures in the 10^{-14} - 10^{-17} atm range at 830-980°C (10).

SUMMARY

When both electronic and ionic carriers make significant contributions to the equilibrium electrical conductivity, and when their dependences on the nonmetal partial pressure are different and are accurately known, it is possible to separate the two contributions by analysis of the curvature of the pressure dependence of the total conductivity. This gives the partial electronic and ionic conductivities, and the transport number, as a function of temperature and nonmetal activity, from measurement only of the total conductivity. The values are specific for each experimental condition, and are not averaged over some composition range as is implicit in the concentration cell technique.

ACKNOWLEDGEMENT

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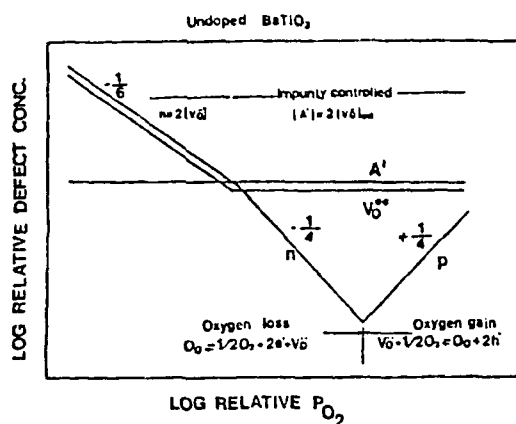


Fig. 1. Schematic representation of the concentrations of the major ionic and electronic defects as a function of oxygen activity at constant temperature for an undoped or acceptor-doped alkaline earth titanate.

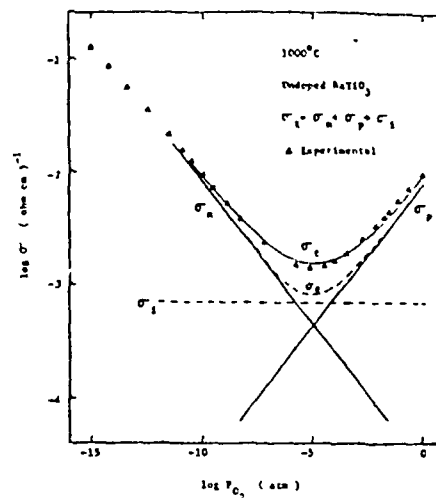


Fig. 2. The effect of a $P(\text{O}_2)$ -independent component of ionic conduction on the shape of the minimum in the total equilibrium conductivity as a function of $P(\text{O}_2)$.

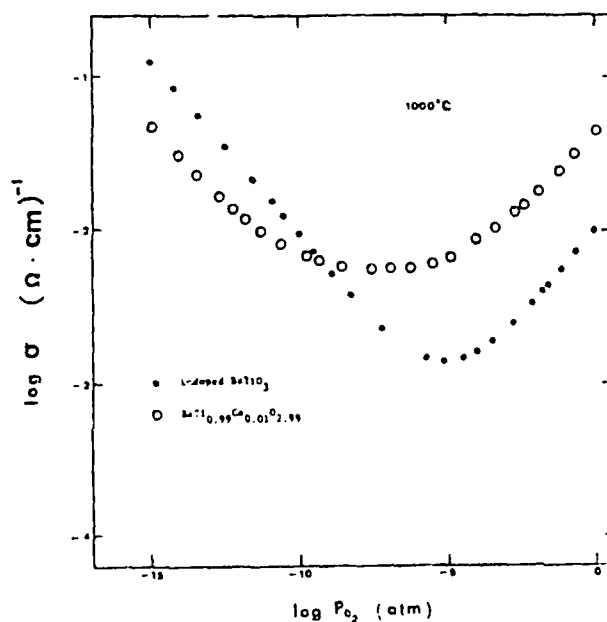


Fig. 3. The change in shape and conductivity level of the conductivity minimum in undoped and acceptor doped BaTiO_3 at 1000°C.

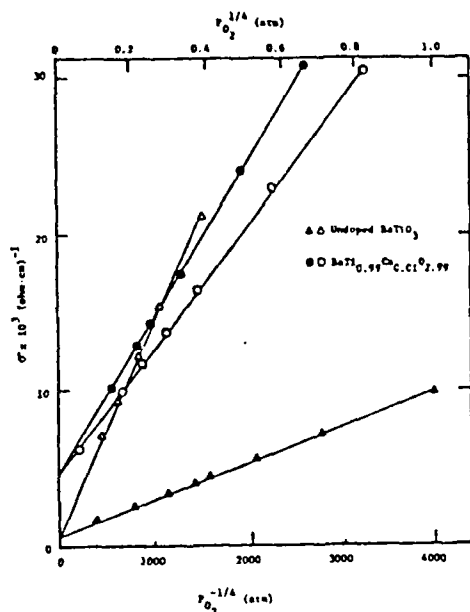


Fig. 4. Plots of the total equilibrium conductivity vs. $P(O_2)^{\pm 1/4}$ for undoped and acceptor-doped BaTiO₃ at 1000°C. The solid symbols refer to the p-type side and the upper abscissa, while the open symbols refer to the n-type side and the lower abscissa.

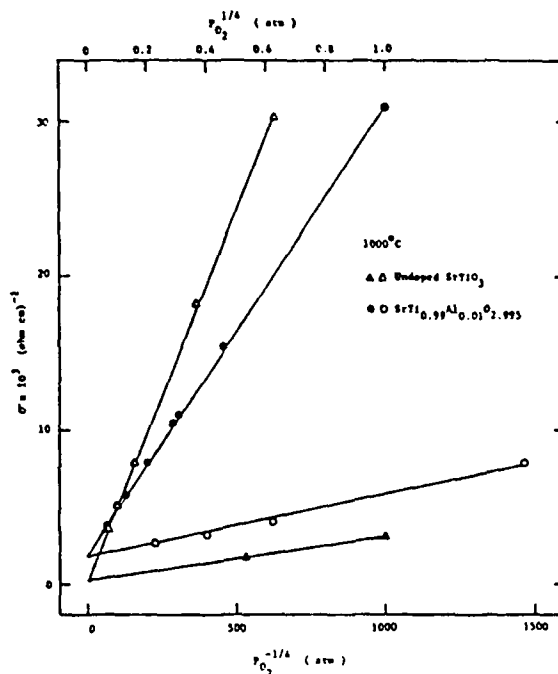
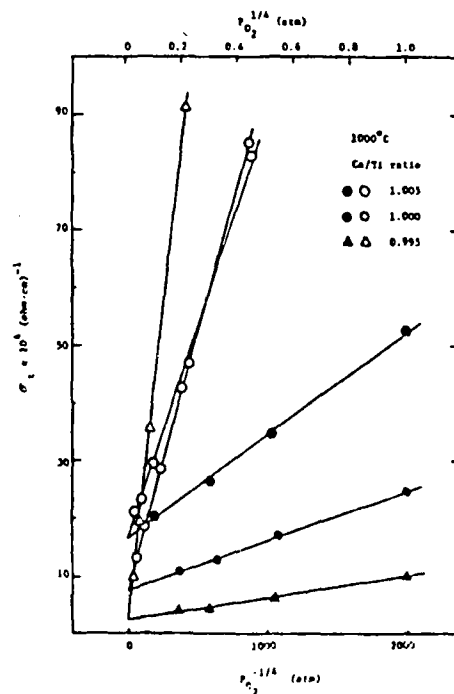


Fig. 5. SrTiO₃: same conditions and symbols as in Fig. 4.

Fig. 6. CaTiO₃: same conditions and symbols as in Fig. 4. Samples are undoped and have Ca/Ti = 1.005, 1.000, and 0.995.



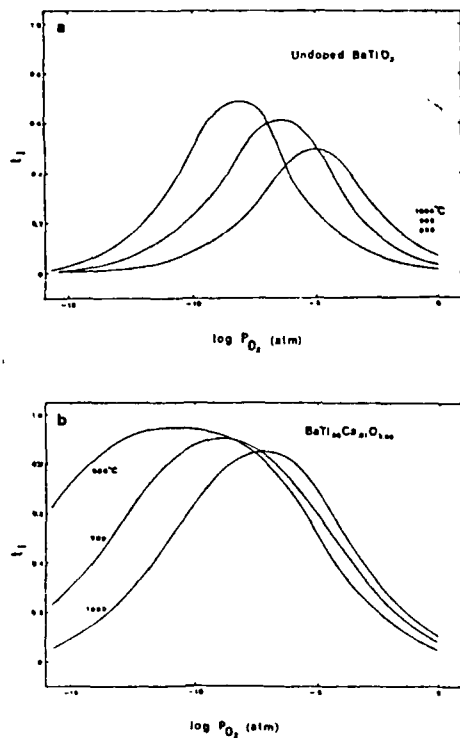


Fig. 7. The transport number of undoped (a) and acceptor-doped (b) BaTiO₃ as a function of $P(O_2)$ at 800°, 900°, and 1000°C.

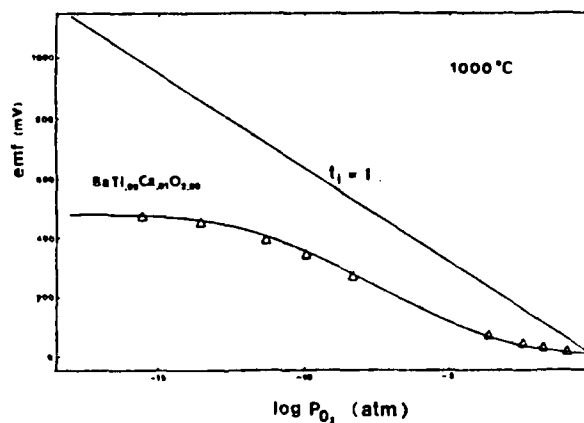


Fig. 8. Comparison of the emf of an oxygen concentration cell for acceptor-doped BaTiO₃ at 1000° (the symbols) with the values derived from the equilibrium conductivity (the solid line). $P(O_2)$ was fixed at 1 atm on one side of the concentration cell, and was varied on the other side. The line $t_i = 1$ would be expected for 100% ionic conduction.

SECTION 3

THE MAJOR CHARGE CARRIER IN BaTiO_3

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THE MAJOR CHARGE CARRIER IN BaTiO_3

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ABSTRACT

Dielectric degradation is conventionally characterized by measurement of the leakage current as a function of time during imposition of voltage-temperature stress. In the case of ceramic dielectrics such as BaTiO_3 , the principal carrier of the leakage currents has not been clearly identified. Electrons, holes, and oxygen vacancies have been suggested. Undoped and acceptor-doped samples of BaTiO_3 have been equilibrated at combinations of temperature and oxygen partial pressure so that the hole and oxygen vacancy concentrations could be controlled independently. The leakage current levels were found to follow the hole concentrations, suggesting that holes are the primary charge carriers for these compositions.

INTRODUCTION

When subjected to sufficient voltage-temperature stress, the leakage resistances of ceramic dielectrics based on BaTiO_3 degrade with time, and this is an important mode of device failure. Many such capacitors prove to be perfectly stable under rated use conditions, indicating that defect-free dielectrics can resist

degradation when properly formulated and used within their design limitations. Due to the structural complexity and close spatial tolerances of multilayer capacitors, however, the ideal, defect-free device is not always achieved. Pores, inclusions, electrode delaminations, and other mechanical defects cause the adjacent dielectric to be subjected to local fields above the design level, with the result that the intrinsic degradation process is accelerated. This can lead to failure in individual devices. Thus the intrinsic degradation mechanism is still of importance with regard to capacitor reliability.

The steady increase in leakage associated with the degradation process indicates that the field distribution within the dielectric is changing. The appearance of characteristic colors adjacent to the anode and cathode is further support for local compositional changes (1). It is universally conceded that this is due to a field-driven transport of oxygen vacancies, V_O , that leads to a distortion of the space charge distribution. It has even been suggested that the leakage current itself is primarily due to oxygen vacancies (2). This paper describes a series of experiments designed to identify the principal charge carrier involved in the leakage current.

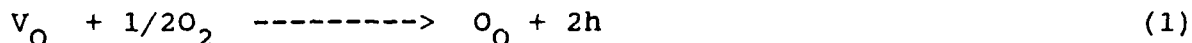
EXPERIMENTAL

Fine-grained $BaTiO_3$ powders were prepared by the liquid-mix

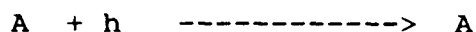
process (3,4), a modification of a process developed by Pechini (5). Impurity additions are homogeneously incorporated in precisely known amounts, and the Ba/Ti ratio is accurately determined. Samples were pressed into disks in a 1.27 cm steel die with a pressure of 276 MPa. Electrodes were applied in the form of unfluxed Pt paste that was fired in air at 1000° C.

RESULTS AND DISCUSSION

Electrons, holes, and oxygen vacancies are the most likely candidates for the principal charge carriers in BaTiO₃. Undoped and acceptor-doped BaTiO₃ is known to be a p-type conductor when in equilibrium with an oxidizing atmosphere above 600° C (6,7). This arises from a partial filling of extrinsic oxygen vacancies that are present due to either the naturally-occurring or added acceptor impurity content (6,8,9)



The defect notation is that of Kroger and Vink(10). As the material is cooled toward room temperature, it gradually becomes an insulator as the holes are trapped by the acceptor impurity centers



(2)

Under these circumstances, it is difficult to see how the bulk conductivity of the material could be n-type. There is, however, the possibility of ionic conduction due to the oxygen vacancies. Measurements of the ionic transport number by means of oxygen concentration cell experiments seem to indicate values approaching unity for temperatures near 200° C, and in one case, the ionic contribution is increasing with decreasing temperature (11,12). A small contribution to the equilibrium conductivity of BaTiO₃ measured at 700-1000° C has been identified that is independent of the oxygen partial pressure, increases with the extrinsic oxygen vacancy concentration, and is thermally activated with an activation energy of 106 kJ/mol (1.1 eV). It has been suggested that this is oxygen vacancy conduction (6,7). Because the activation energies observed for the leakage currents of ceramic capacitors are very close to this value, it has been proposed that the leakage currents are also primarily due to oxygen vacancies (2). In order to be able to interpret degradation behavior in terms of composition, it is important to clarify this question of the principal charge carrier.

The oxygen vacancy content of BaTiO₃ is controlled by the acceptor impurity content, except under the most severely reducing conditions. The hole concentration depends on the temperature,

$P(O_2)$, and the acceptor concentration. It is thus possible to vary the vacancy and hole concentrations independently, by means of the known dependences of the defect concentrations on the equilibration conditions. Samples were prepared so that the degradation currents could be compared for the following conditions:

1. As a function of the hole concentration at constant vacancy concentration and equilibration temperature. This was accomplished by equilibrating an undoped sample at two different values of $P(O_2)$. The vacancy content was determined by the naturally occurring acceptor impurity content.

2. As a function of the vacancy concentration at constant hole concentration and equilibration temperature. This was accomplished by equilibrating an undoped and an acceptor-doped sample at different values of $P(O_2)$ chosen to give the same hole concentration.

3. As a function of equilibration temperature at constant hole and vacancy concentrations. This was accomplished by equilibrating two undoped samples at two different temperatures at values of $P(O_2)$ chosen to give the same hole concentration.

In all of these samples, the hole concentration refers to the relative level of p-type conductivity as measured at the

equilibration temperature. At the temperatures of the degradation experiments, the holes are mostly trapped at the acceptors as shown in Equation (2). The equilibration was carried out at rather low temperatures, usually 600°C , where the process takes several hours and the compositions can be quenched-in by normal furnace cooling.

Comparisons of the degradation currents for the three cases are shown in Figures 1-3, respectively. In Figure 1, the hole concentrations differed in the two samples by a factor of 25. The degradation current levels differ by a similar factor, with the higher hole concentration giving the higher current. This suggests that the current is carried primarily by holes. In Figure 2, the vacancy concentrations differed by a factor of about 15. The degradation current starts out at about the same level, but soon begins to rise rapidly for the sample having the higher vacancy content. This illustrates the role of the oxygen vacancy in contributing to the degradation process, but the similarity of the initial currents indicates that the vacancies are not contributing significantly to the predegradation current. The results shown in Figure 3 exhibit only normal sample-to-sample scatter, demonstrating that the equilibration temperature itself has no influence on the current levels.

CONCLUSIONS

These results indicate that the predegradation currents follow the hole concentration (actually the concentration of ionizable acceptor centers) and not the vacancy concentration. Thus for undoped and acceptor-doped BaTiO_3 , the leakage currents seem to be primarily carried by holes. There have been reports of negative thermopowers, indicative of electronic conduction, for some commercial ceramic capacitors (13). Many dielectric formulations have large excess concentrations of donor impurities, such as Nb, that serve as grain-growth inhibitors and also suppress the oxygen vacancy concentration to improve stability. The conduction mechanism may be quite different in these materials.

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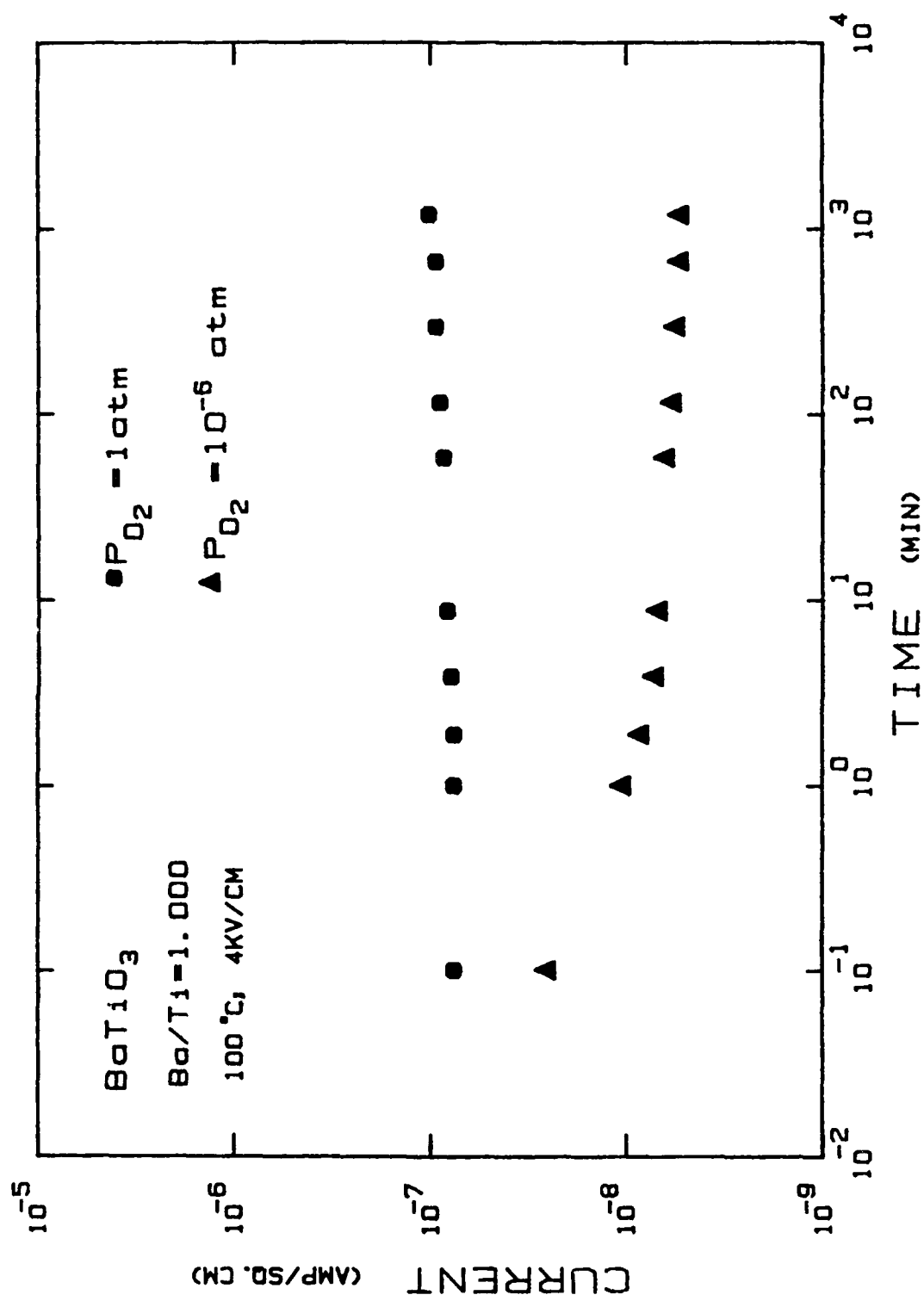
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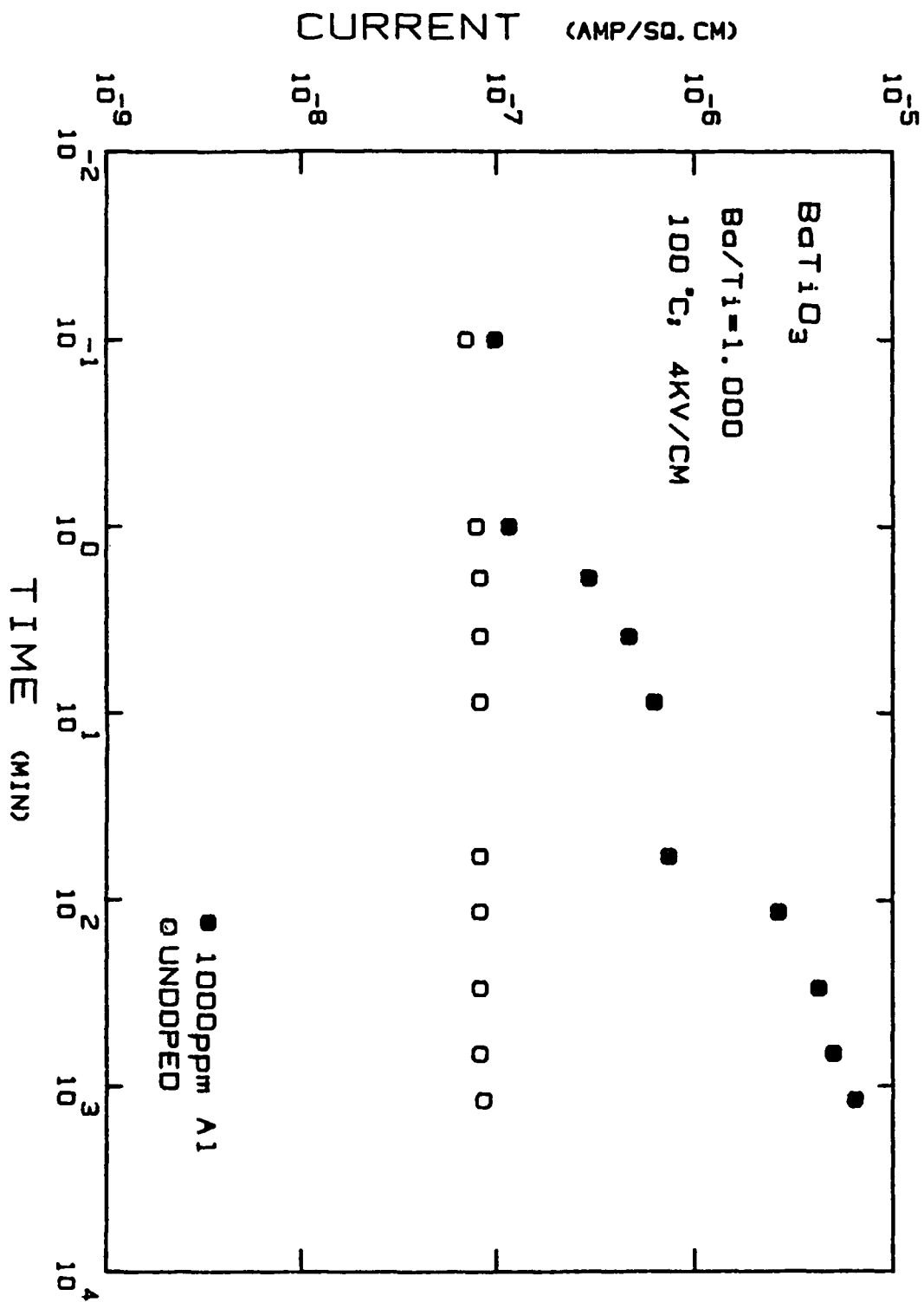
FIGURE CAPTIONS

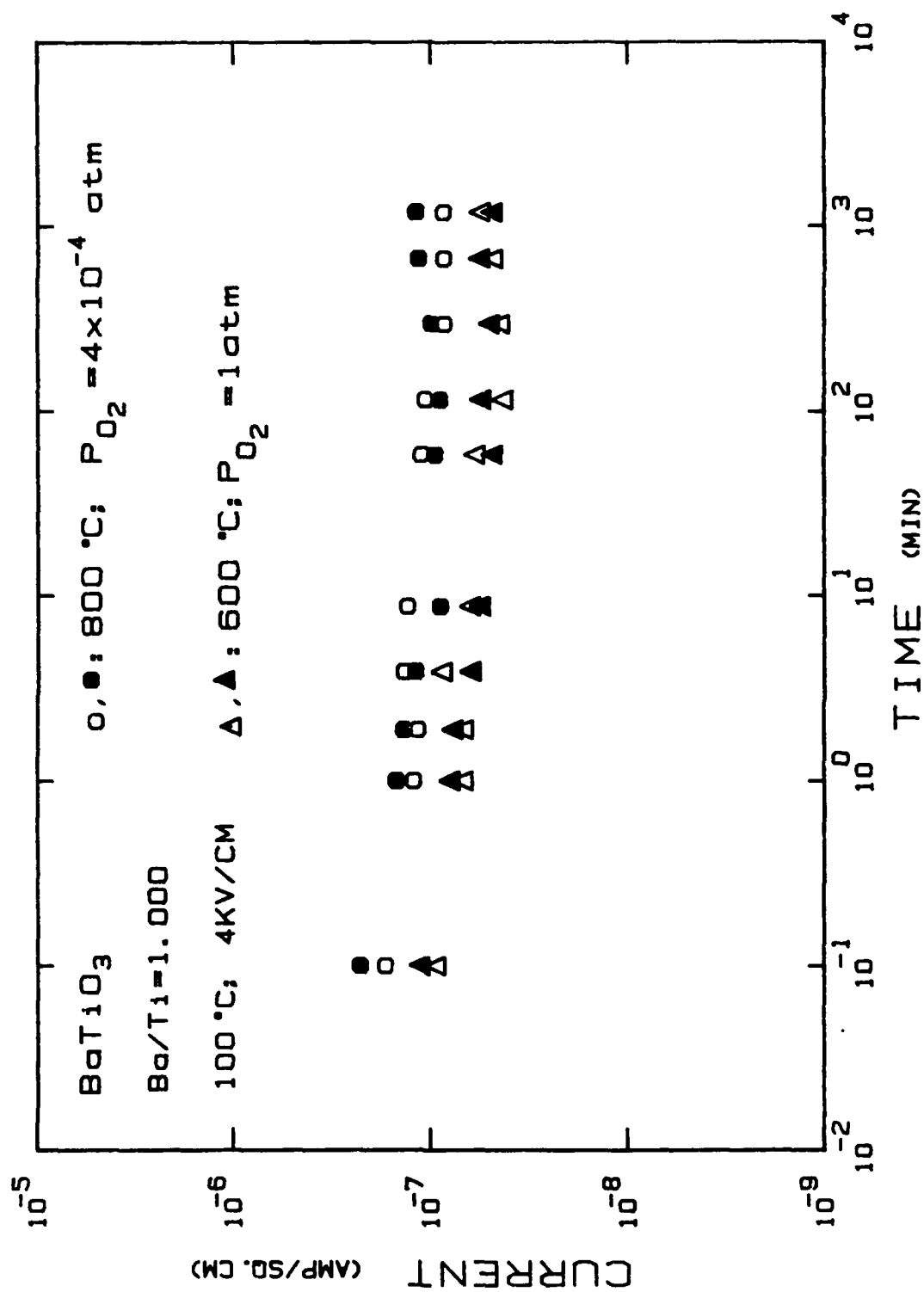
1. The leakage current as a function of time for undoped BaTiO_3 equilibrated at 600°C at 10^5 , ■ , and 10^{-1} , ▲ , Pa oxygen partial pressure.

2. The leakage current as a function of time for undoped BaTiO_3 equilibrated at 600°C and 10^5 Pa, □ , and for BaTiO_3 doped with 1000 ppm Al equilibrated at 600°C in air, ■ .

3. The leakage current as a function of time for undoped BaTiO_3 equilibrated at 600°C and 10^5 Pa, ▲ , and at 800°C and 40 Pa, □ ■ .







SECTION 4

PROPERTIES OF Mn-DOPED BaTiO_3

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PROPERTIES OF Mn-DOPED BaTiO_3

V. Bheemineni, M. P. Harmer, and D. M. Smyth

INTRODUCTION

In the manufacture of multilayer ceramic capacitors, it is advantageous to sinter the devices in a reducing atmosphere so that Ni electrodes can be used instead of the much more expensive noble metals. However, BaTiO_3 loses its insulating properties when reduced, and it becomes a semiconductor. It has been shown that when BaTiO_3 is doped with acceptor-type impurities (cations of lesser charge than the host cations they replace), it will remain insulating after exposure to moderately reducing atmospheres (1). The severity of the reducing atmosphere that can be tolerated depends on the concentration of acceptors in the lattice and on their charge. Multilayer capacitors have been successfully prepared with Ni electrodes using this technique (2), and Mn is one of the acceptor impurities that have been studied extensively.

Past investigations of Mn-doped BaTiO_3 have shown that Mn lowers the cubic-hexagonal transition temperature by as much as 200°C (3). Sintering above the transition temperature results in the nonferroelectric hexagonal form of BaTiO_3 . The hexagonal structure reverts to the cubic form with Mn precipitating out as MnO during annealing in sufficiently reducing atmospheres (4). Mn also decreases the Curie temperature, and this has been attributed to the creation of

oxygen vacancies when the Mn occupies the Ti-site (5,6). A higher resistivity for Mn-doped BaTiO_3 (compared to undoped BaTiO_3) after annealing in air or reducing atmospheres has been reported by previous investigators (4,5,7,8). It has been suggested that treatment in air causes a change in the valence of the Mn and leads to the trapping of holes by trivalent Mn (5), while the effect of the reducing atmosphere has been attributed to the extension of the oxygen-excess, p-type behavior to lower oxygen pressures (8). The presence of tetravalent Mn under oxidizing conditions and divalent Mn under reducing conditions has been confirmed by EPR studies and thermogravimetric measurements (8-13).

In this investigation, microstructure, electrical degradation, Curie point shift, and the high temperature equilibrium conductivity have been studied as a function of Mn concentration and Ba/Ti ratio. The purpose was to determine the incorporation mechanism of Mn, and to study its effect on the electrical degradation of BaTiO_3 .

EXPERIMENTAL

BaTiO_3 powder was prepared by the liquid-mix technique (14). Mn was added as MnCO_3 powder along with BaCO_3 or by dissolving MnCO_3 in citric acid. "Ba-excess" and "Ti-excess" samples were prepared with compositions of the type $\text{BaTi}_{1-x}\text{MnO}_3$ and $\text{Ba}_{1-x}\text{MnTiO}_3$, respectively, with x values of 0, 0.001, 0.005, 0.01, 0.02, and 0.05. Specimens in the form of disks with 13 mm diameter and 0.7 mm thickness were used to study leakage current and Curie point shift. Rectangular bars (15.5 x

6.7 x 1.5 mm) were used for the measurement of the high temperature equilibrium conductivity.

Specimens were sintered in air, or in CO-CO₂ atmospheres with oxygen partial pressures of 10⁻¹⁰ atm as measured by a stabilized zirconia sensor. After sintering in the reducing atmosphere, samples were annealed in air at 1000°C for one hour. All of the samples were sintered at 1420°C for 2.5 hours, except when the formation of a liquid phase made it necessary to sinter at a lower temperature (1375°C for three hours). The equilibrium conductivity was measured as a function of oxygen partial pressure at 1000°C by a 4-point dc technique (15). For measurement of the Curie temperature and leakage currents, a nonfritted Pt paste was fired on disk specimens to form electrodes. For the degradation studies, the leakage currents were measured continuously for up to 20 hours, after the application of 4 Kv/cm at 100 or 200°C. The Curie points were measured at 1 Khz with a field of 10 V/cm and a heating/cooling rate of 2 degrees/min.

RESULTS

Figure 1 shows the microstructure of BaTi_{0.95}Mn_{0.05}O₃ and Ba_{0.98}Mn_{0.02}TiO₃ sintered in air. As can be seen from the micrographs, the Ba excess composition is a single phase material and the Ti excess composition has had some liquid phase. In fact, all of the Ba excess compositions, irrespective of the sintering atmosphere, are single phase materials. The uniformity of chemical composition from grain to grain

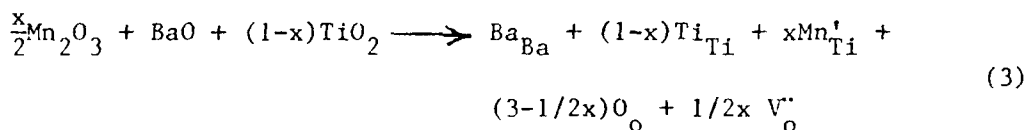
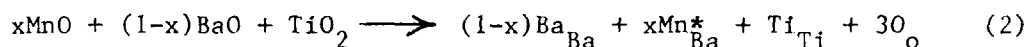
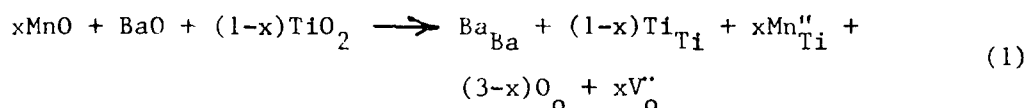
was confirmed with electron microprobe analysis. For Ti excess compositions, a liquid phase of low average atomic number appears at 1% Mn concentration. At 0.5% and below, it is hard to confirm the presence or absence of liquid phase using SEM. Microprobe analysis of the solidified liquid phase gave a Ba/Ti Ratio of 1/2.5 and as shown in Figure 2 is rich in Mn. The concentration of Mn in the liquid phase varied with the level of doping. Table 1 summarizes the microstructures of all compositions studied.

The hexagonal phase is the predominant phase at 1% or higher Mn concentration when both Ba and Ti excess compositions are sintered in air. Reducing conditions favor formation of the hexagonal phase even at the 0.5% doping level. One specimen of Ti excess composition with 2% Mn was sintered at 1250°C and was found to retain some tetragonal BaTiO_3 . In general higher temperatures and lower oxygen pressures favor formation of the hexagonal polymorph.

Figures 3a and 3b show small Curie point shifts with increasing Mn concentrations for both Ba and Ti excess compositions. All compositions shown were sintered in air at 1420°C. The Ti excess composition with 1% Mn has a small Curie peak while at higher doping levels the material is paraelectric. The Ba excess composition with 1% Mn has only a trace amount of the ferroelectric phase. At higher Mn levels, the material is completely paraelectric.

at lower temperatures where perovskite structure is (partly) retained show larger shifts in Curie point. The change in Curie point depends on the amount of Mn incorporated into the perovskite lattice. This is not in agreement with the results of Burn (4) which shows no Curie point shift when sintering and subsequent annealing is done in air. The sintering atmosphere does not seem to have any effect on the Curie point. Contrary to the observations of Herbert (3), sintering in a reducing atmosphere does not eliminate the hexagonal phase.

Mn can be incorporated into BaTiO_3 lattice by substituting for Ti in the following manner depending on the oxidation state of Mn:



Tetravalent Mn, being isovalent with Ti in BaTiO_3 , does not create any charged defects but trivalent and divalent Mn act as acceptors and the resulting charge imbalance is compensated by oxygen vacancies. Due to this increase in oxygen vacancy concentration, electron concentration in the n type region (of the defect diagram) decreases and hole concentration in the p type region increases. As a result the oxygen partial pressure, at which the hole and electron concentrations are

Figures 5a, 5b, and 5c show results of leakage current experiments in the form of log-log plots of leakage current density against time. At 100°C, the current levels for undoped and 0.5% Mn doped specimens are comparable. The 0.1% Mn doped specimens have higher leakage current than the specimen of undoped BaTiO_3 . At 200°C, the undoped specimen has degraded after a few minutes while the 0.5% doped samples remain stable at the end of 20 hours. The 1% and 2% Mn doped specimens were the most stable compositions investigated. The equilibrium log resistivities are tabulated in Table 4. A "*" denotes a degraded specimen. In the same box, the top number is log resistivity at 100°C and the bottom number is the same at 200°C.

DISCUSSION

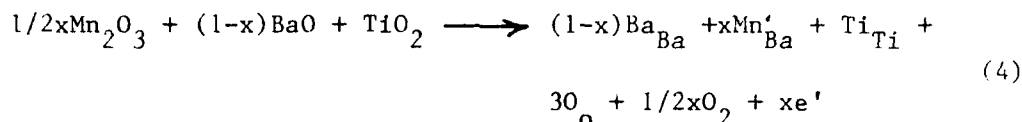
The stabilization of hexagonal phase by Mn at higher concentrations and higher sintering temperatures (as shown by the crystal structure and dielectric constant measurements) is in agreement with the work of Ainger and Herbert (2). As can be seen from the data in Table 2, specimens sintered at lower temperatures retain (at least partly) cubic structure.

The change in Curie point is small for all samples sintered at higher temperatures. It is possible that in the case of the Ti excess samples only a small portion of the Mn is in the perovskite lattice. When tetragonal and hexagonal forms coexist, a great majority of the Mn may be in the hexagonal phase which is paraelectric. Samples sintered

Figure 3c shows Curie point shifts for 2% and 0.5% Mn doped samples that were hot-pressed in reducing atmospheres at 1250°C and annealed in air at 1000°C. These samples were subsequently annealed at 1400°C and the data for them is included in Figure 3c. As can be seen there is a large shift in Curie point prior to annealing the samples in air at 1400°C. After annealing, the 0.5% sample has a Curie point of 127°C, whereas the 2% sample has changed to the non-ferroelectric hexagonal form. Table 2 summarizes the crystal structures, Curie points and maximum dielectric constants for the compositions sintered in air and in CO-CO₂ mixtures.

Figures 4a and 4b show the equilibrium electrical conductivity at 1000°C. The locations of the conductivity minima for Ba excess and Ti excess samples (Figure 4a) are almost identical at the same Mn concentration. The conductivity minima for undoped, 0.1% and 0.5% Mn doped specimens occur at log(oxygen partial pressure) of -4, -5.75, and -6.5, respectively. Profiles (Figure 4b) for specimens sintered in reducing atmospheres up to 0.5% Mn concentrations have their conductivity minima shifted to higher oxygen partial pressures. The Ba excess sample with 1% Mn and the Ti excess sample with 2% Mn, both sintered at 1250°C in a reducing atmosphere, have their conductivity minima shifted to lower oxygen partial pressure, but the Ti excess sample with 1% Mn behaves similar to undoped BaTiO₃. The equilibrium electrical conductivities are summarized in Table 3.

equal and the conductivity has its minimum value, decreases. If Mn occupies Ba site as a trivalent cation then,



Mn'_{Ba} acts as a donor and the resulting material is a semiconductor. This incorporation of Mn in BaTiO_3 determines the electron concentration and makes it independent of the oxygen partial pressure in the extrinsic region. The effect of the occupation site of Mn on the conductivity versus oxygen partial pressure plot is shown in Figure 6.

The results of the equilibrium conductivity measurements for all compositions sintered in air show a shift of the conductivity minimum towards lower oxygen partial pressure. From this observation, it can be concluded that Mn acts as an acceptor and therefore is either in trivalent or divalent state on the Ti lattice site. This is also substantiated by the presence of liquid phase present in Ti excess compositions and its absence in Ba excess compositions. The failure to detect liquid phase in Ti excess samples with 0.5% Mn may well be due to the inadequacy of the SEM technique in detecting small amount of liquid phase.

Ti excess composition with 1% Mn has a conductivity profile similar to that of undoped barium titanate. This may be due to Mn occupying both Ba and Ti site (and thus leading to self compensation) or due to most of the Mn being expelled into the Ti rich liquid phase or both.

oxygen vacancy concentration results in reduced solubility of acceptor impurities provided that solubility limit is exceeded (17). This leads to acceptor impurities being expelled from bulk of grains to grain boundary areas. As the net acceptor content of the lattice decreases, the conductivity minimum shifts to higher oxygen partial pressures (18) just as in the case of 0.1% and 0.5% Mn doped BaTiO_3 . For higher concentrations of Mn doping, expulsion of dopants does not occur. This may be due to variation in solubility product among slightly doped and heavily doped barium titanate.

Evidence (17) points to expulsion of impurities being the correct choice to explain the shift of conductivity minimum to higher oxygen pressures (Figure 4b). Undoped BaTiO_3 sintered in a reducing atmosphere shows a similar conductivity profile. Upon annealing at 1400°C , the conductivity profile returns to that of undoped BaTiO_3 sintered in air (Figure 7). This is explained on the basis of expulsion of accidental acceptor impurities from the lattice. When the sample was annealed in air at 1400°C , the impurities are redissolved into the lattice. Computer simulation studies by Lewis and Catlow (19) indicate self compensation as being unfavorable. This and the assumptions made make occupation of Ba site by Mn a less reasonable choice.

The majority charge carriers prior to breakdown in BaTiO_3 are thought to be holes even though it is the migration of oxygen vacancies that leads to eventual failure (11,15,20). As acceptor impurities lead to higher hole concentration, they should give higher leakage currents

For Ti excess compositions with 0.1% and 0.5% Mn sintered in a reducing atmosphere, it appears that some type of donor type impurity is beginning to compensate for the background acceptor impurity. This may be rationalized in one of two ways. The first one is that Mn occupies a Ba site and acts as a donor (Mn being in trivalent state). The second rational is that Mn, along with other accidental background impurities, is being expelled from the perovskite matrix into grain boundary areas upon sintering in reducing atmosphere.

Mn on Ba Site

Since the background impurity is of the order of only 100 to 200 ppm, it may be that at least some of the Mn is on the Ba lattice site and that some of it may be in trivalent state. In the light of the difference in the ionic radii of Ba (1.5A) and trivalent Mn (0.785A), it seems unlikely that Mn^{3+} goes into Ba lattice site. But Mn may have entered the Ba lattice site as divalent Mn (ionic radius 0.97A) under reducing conditions at higher sintering temperatures and may have then been oxidized to Mn^{3+} subsequently. [Yttrium and Erbium both with ionic radius of 0.89A are able to occupy both Ti and Ba site depending on the Ba/Ti ratio (16).] Once Mn enters one or other lattice site, it may be difficult to displace it at lower temperatures. Solubility of Mn on Ba site may be small. This may explain the similarity of 0.1% and 0.5% Mn doped samples in reducing atmosphere.

Expulsion of Impurities

When $BaTiO_3$ is sintered in a severely reducing atmosphere, oxygen vacancies are created as oxygen leaves the lattice. This increase in

for samples annealed and tested in air. Higher stability of 0.5% Mn doped specimens does not seem to follow the notion that acceptor doped specimens tend to be less stable than undoped BaTiO_3 . Even if Mn is in divalent state and oxidized by trapping holes, the concentration of the holes left behind (and trapped at acceptor centers near room temperature) should be comparable to that of undoped BaTiO_3 . Leakage current measurements (15,21) show that current density is a strong function of sample density and microstructure even though breakdown does not always occur at pores and laminations in the sample (22). The importance of microstructure is illustrated in Figure 8 which shows leakage current measurements of six different samples from the same batch of undoped BaTiO_3 . The reason for the lower leakage currents of 0.5% Mn-doped BaTiO_3 and higher currents of 0.1% Mn doped BaTiO_3 is most likely the variation in microstructure. Experiments on hot pressed Mg doped and Al doped BaTiO_3 (15) show that leakage currents increase as the acceptor concentration increases.

CONCLUSIONS

In air sintered samples, Mn occupies Ti lattice site and acts as an acceptor.

When BaTiO_3 is lightly doped with Mn and sintered in reducing atmosphere, Mn is not accommodated in the lattice but is expelled to the grain boundaries.

Mn doped BaTiO₃, sintered in air, has leakage currents similar to that of undoped BaTiO₃ allowing for scatter due to microstructure.

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Table 1. Microstructure of Mn doped Barium Titanate.

		Mn content				
		0.1%	0.5%	1%	2%	5%
AIR	Ba xcess	S	S	S	S	S
AIR	Ti excess	S	S	M+L	M+L	M+L
REDUCING ATM.	Ba excess	S	S	S	S	-
REDUCING ATM.	Ti excess	S	S	M+L	M+L	-

S --> Single Phase Material

M+L --> Matrix Phase + Liquid Phase

Composition of Liquid Phase: Ba/Ti ratio=1/2.5

Table 2. Crystal Structure, Peak Dielectric Constant and Curie point.

Comp. and Atm.	Temp. C	Mn content				
		0.1%	0.5%	1%	2%	5%
Ba excess comp. Sintered in AIR	1420	T 12000 (128)	T 12000 (128)	H 325 (123)	H -	H -
	1375	T	T	H	H	-
	1250	T	T	H+T 7200 (121)	H+T 2800 (118)	-
Ti excess comp. Sintered in AIR	1420	T 9200 (129)	H -	H -	H -	H -
	1375	T	T 10000 (125)	T+H 2500 (126)	H -	H -
	1250	T	T	T+H 3700 (121)	T+H 3100 (122)	H -

Table 2. Crystal Structure, Peak Dielectric Constant and Curie point. (continued from previous page)

	Temp. C	Mn content				
		0.1%	0.5%	1%	2%	5%
Ba excess comp. Sintered in REDUCING atm.	1420	H+T 3200 (128)	H+T 2100 (123)	H	H	-
	1375	-	-	H	H	-
	1200	-	-	T 10000 (120)	T+H 6800 (117)	-
Ti excess comp. Sintered in REDUCING atm.	1420	T+H 6500 (129)	T+H 2300 (129)	-	-	-
	1375	-	-	H	H	-
	1200	-	T+H 7000 (122)	T+H 4400 (124)	T+H 4700 (129)	-

T denotes Tetragonal structure.

H denotes Hexagonal structure.

Numbers enclosed in perenthesis are curie points in C.

Table 3. Equilibrium Conductivity at 1000 C.

		Mn content				
		0.1%	0.5%	1%	2%	5%
AIR	Ba excess	A	A	A	-	-
AIR	Ti excess	A	A	A	-	-
REDUCING ATM.	Ba excess	D	-	A	A	-
REDUCING ATM.	Ti excess	D	D	U	A	-

A --> Acceptor type
 D --> Doner type
 U --> Same as undoped

Table 4. Log(Electrical Resistivity) Under 4KV/cm Stress.

		Mn content				
		0%	0.1%	0.5%	1%	2%
AIR	Ba excess	13	10.8	13	14.4	13.6
		*	*	11	12.0	11.5
AIR	Ti excess	-	9.8	12.1	13.1	13.6
			*	10.8	12.2	11.4
REDUCING ATM.	Ba excess	-	-	-	-	11.1
						10.0
REDUCING ATM.	Ti excess	-	12.2	13.5	-	14.8
			-	-		13.4

Top number in box is resistivity at 100 C.
 Bottom number in box is resistivity at 200 C.
 A * denotes a resistivity of 1M ohm-cm or less.



10 MICRONS
5% Mn (Ba EXCESS)

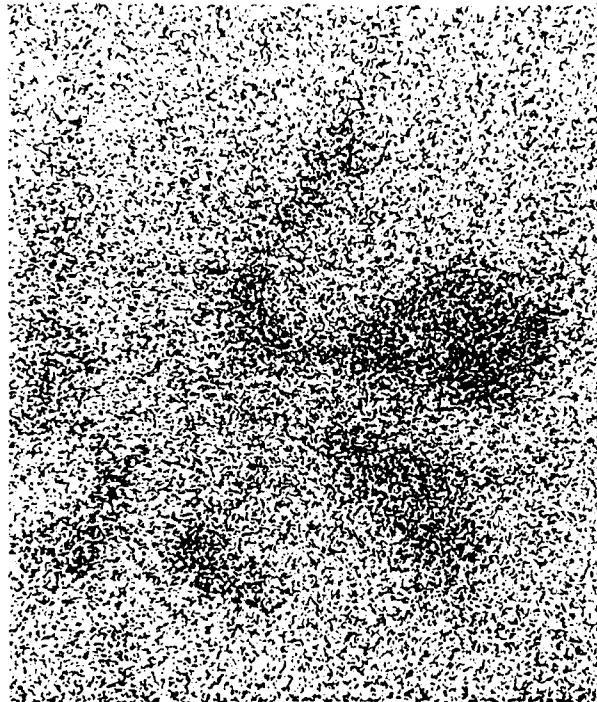


50 MICRONS
2% Mn (Ti EXCESS)



Mn X-RAY MAP
2% Mn (Ti EXCESS)

10 MICRONS



Ba X-RAY MAP
2% Mn (Ti EXCESS)

10 MICRONS

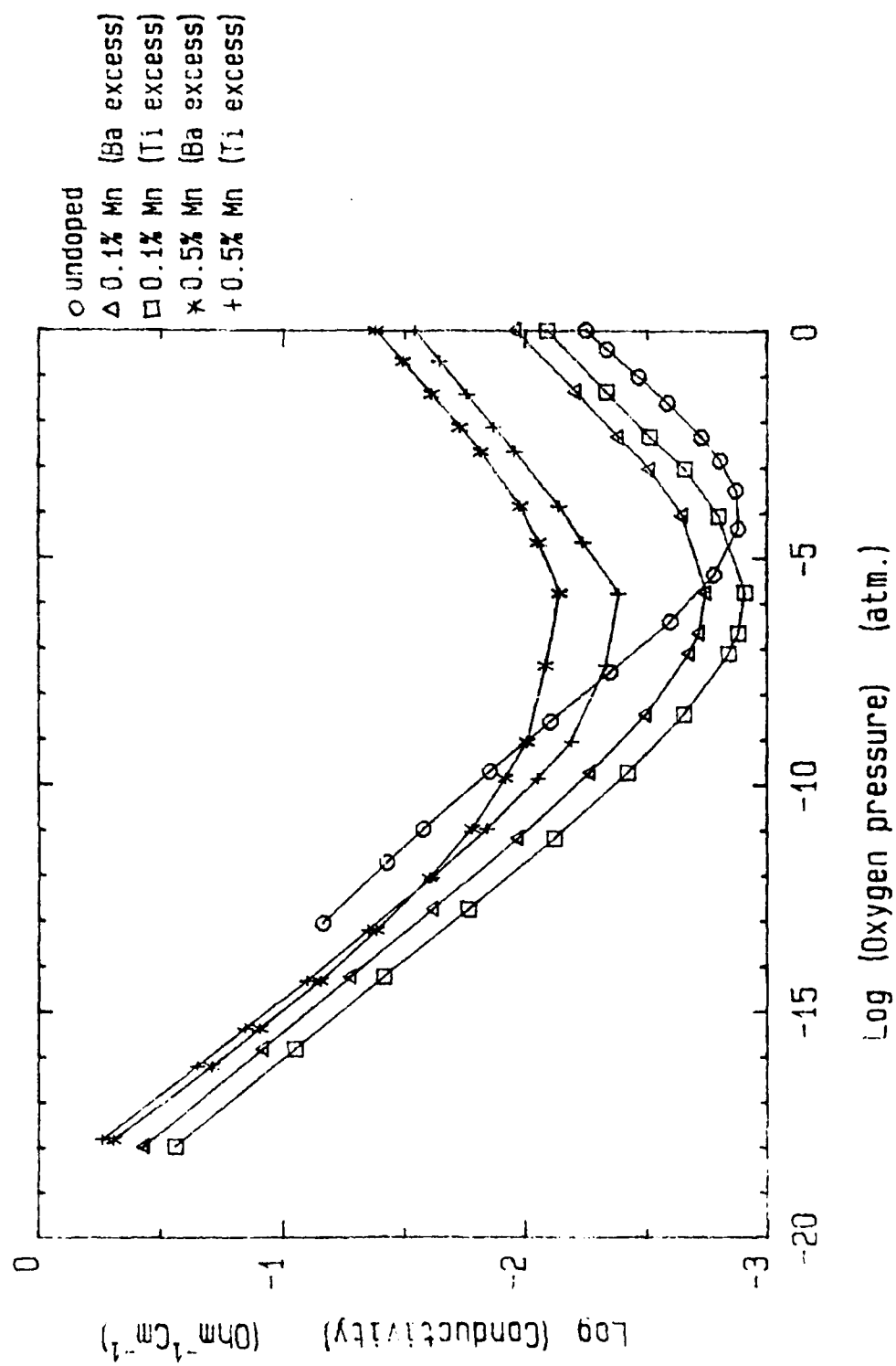


Figure 4(a). Conductivity data of samples sintered in air

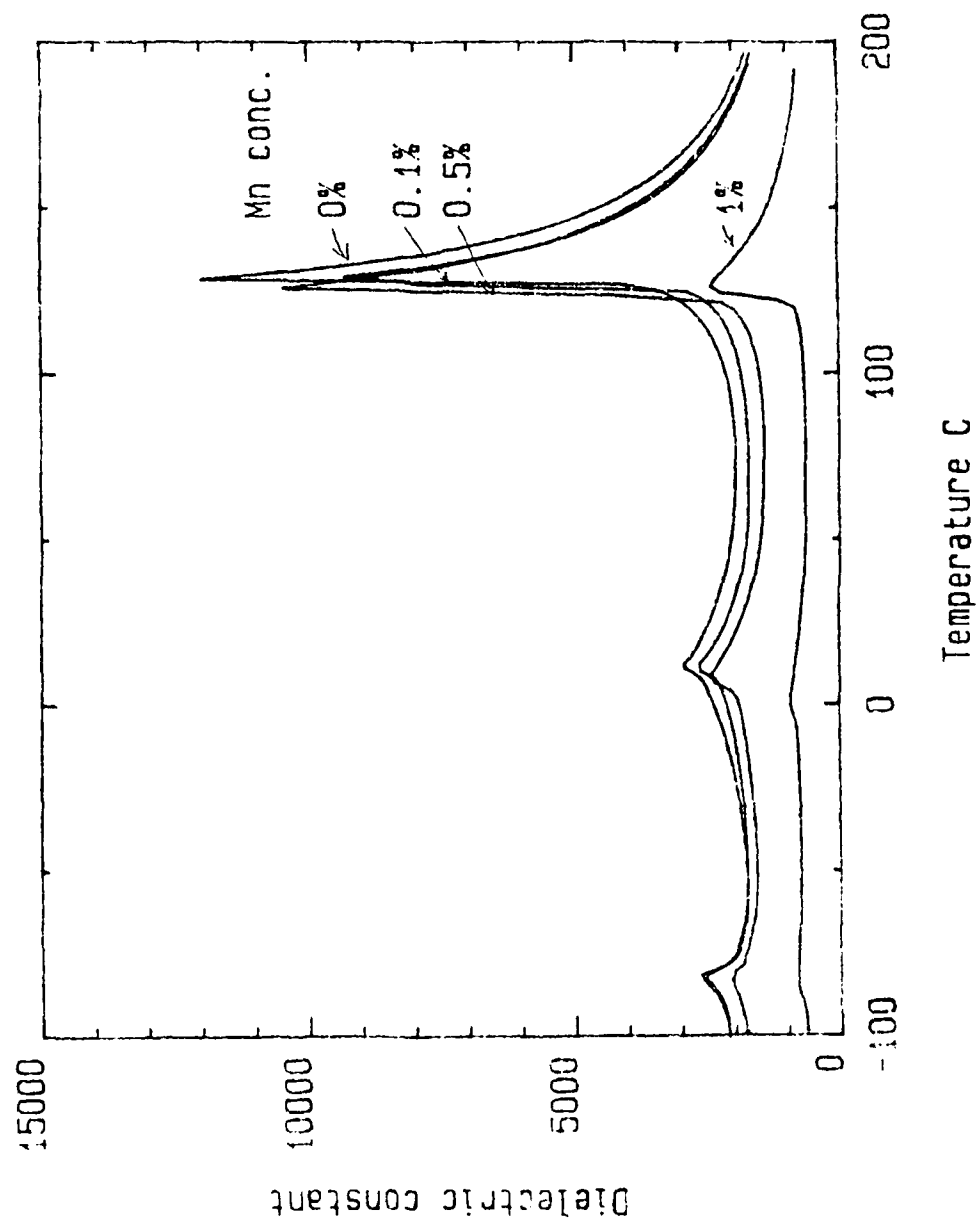


Figure 3(b). Dielectric constant vs Temp. for Ti excess samples.

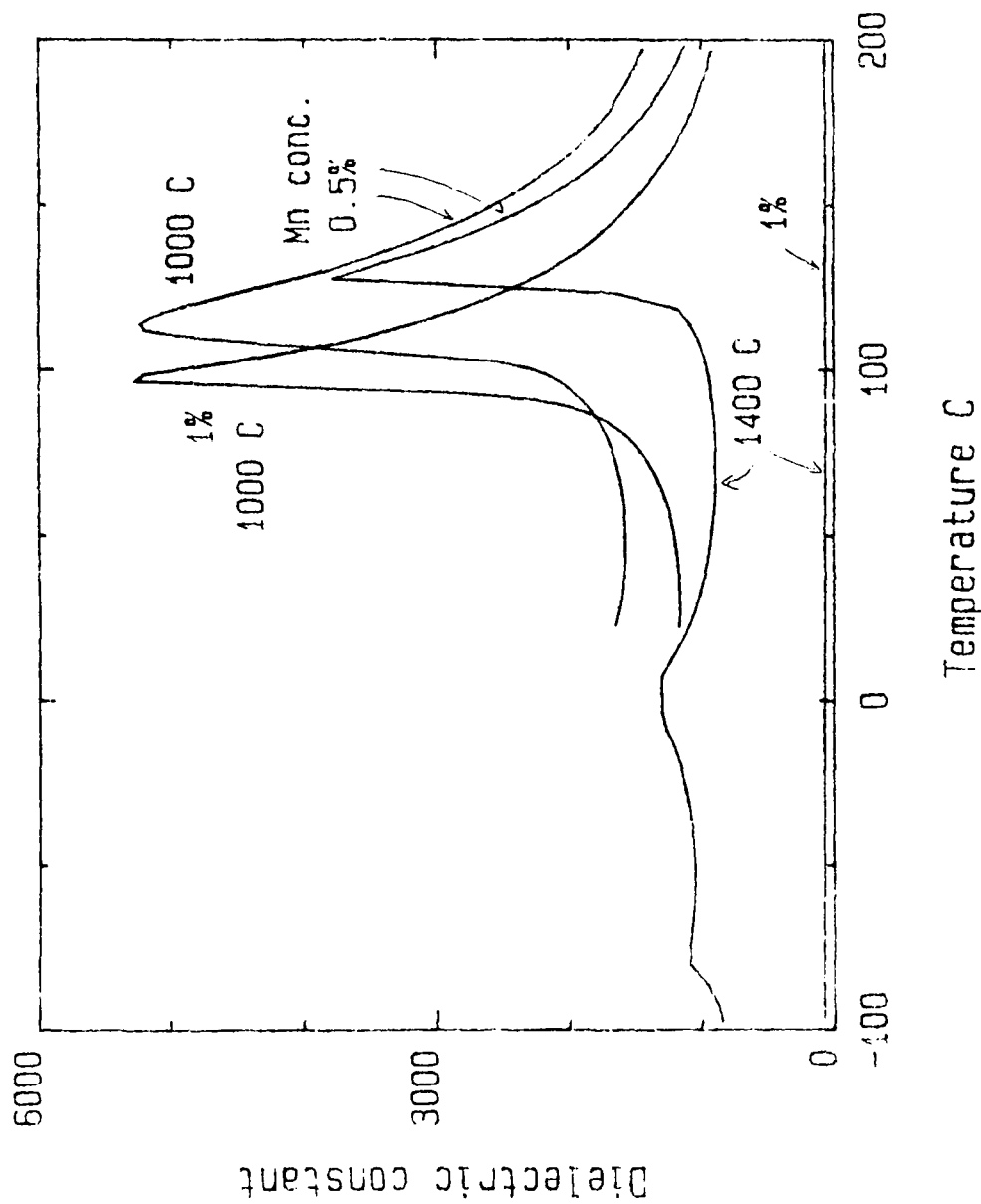


Figure 3(c). Dielectric constant vs Temp. for hot-pressed samples annealed at 1000 C and at 1400 C in air.

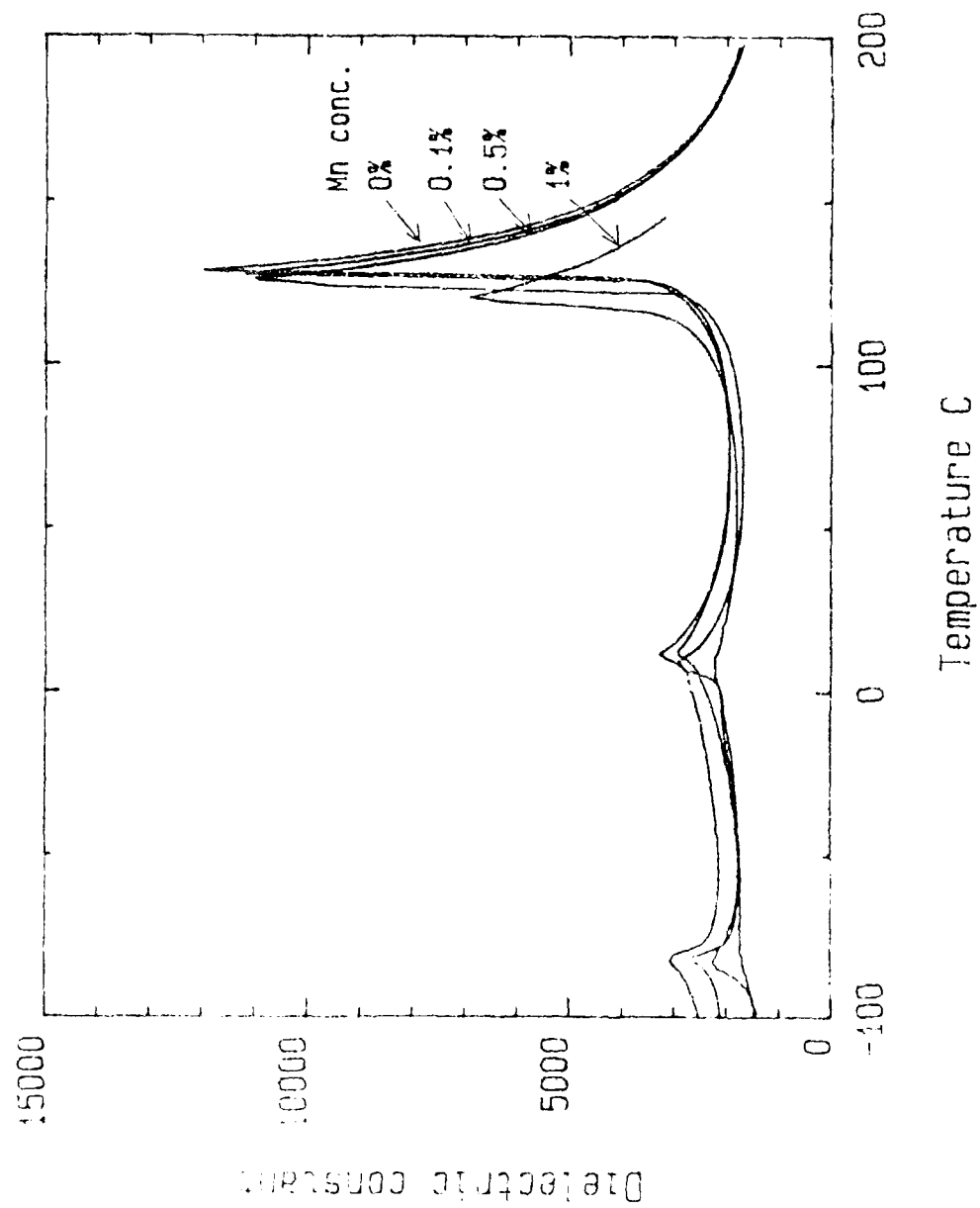


Figure 3(a). Dielectric constant vs temperature for Ba excess samples.

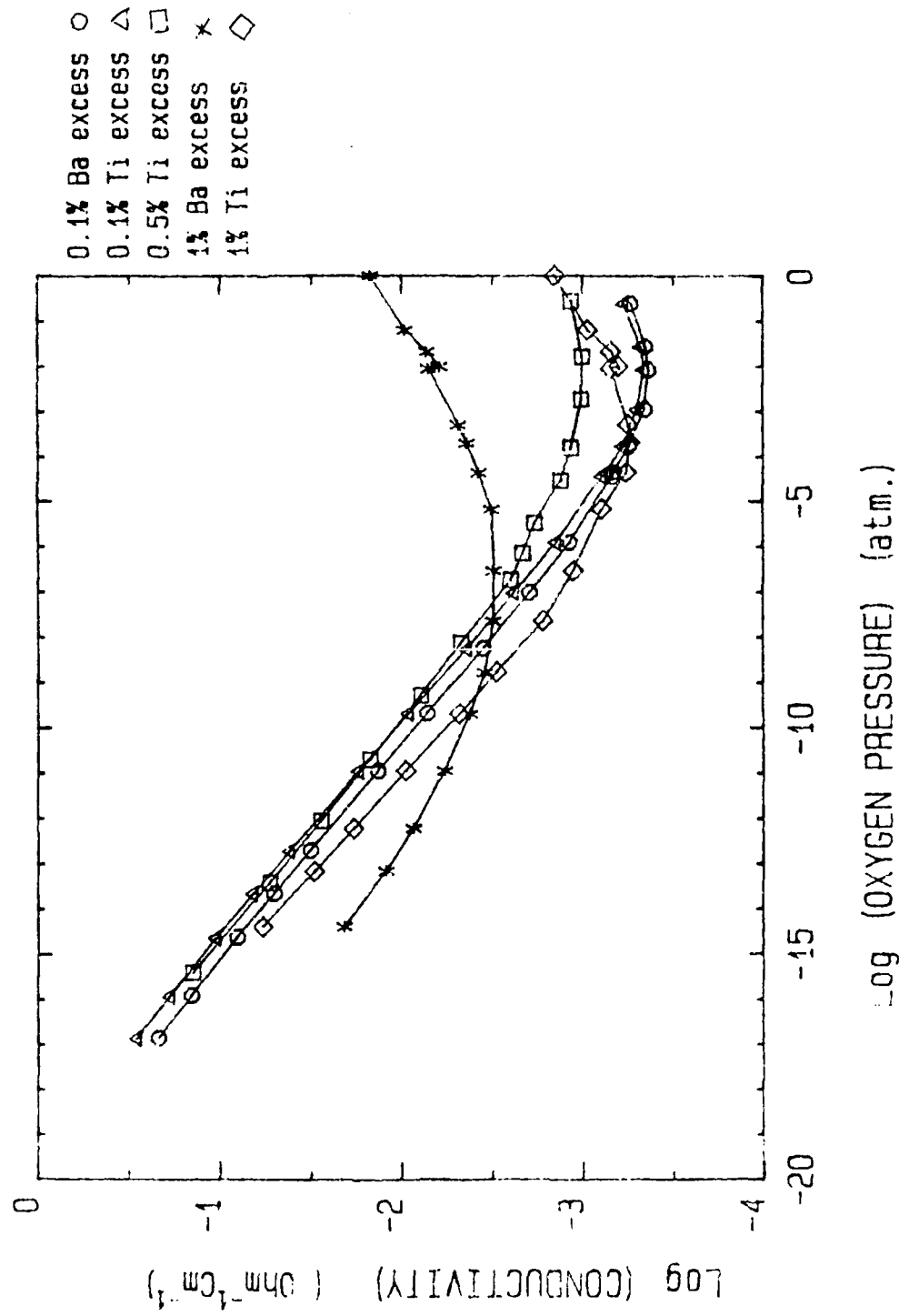


Figure 4(b). Conductivity data of samples sintered in reducing atmosphere

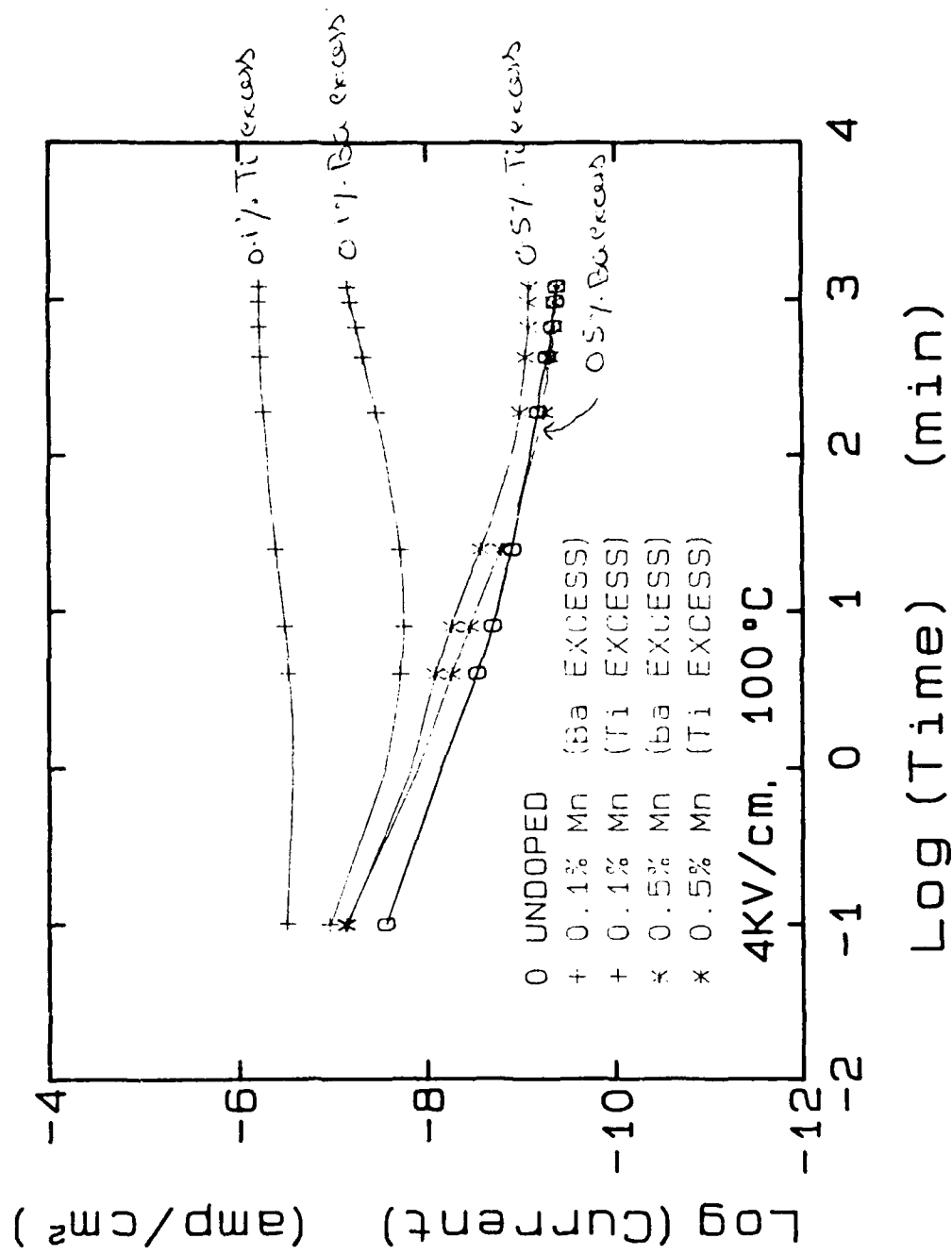


Figure 5(a) Leakage currents of Mn doped BaTiO_3 at 100°C

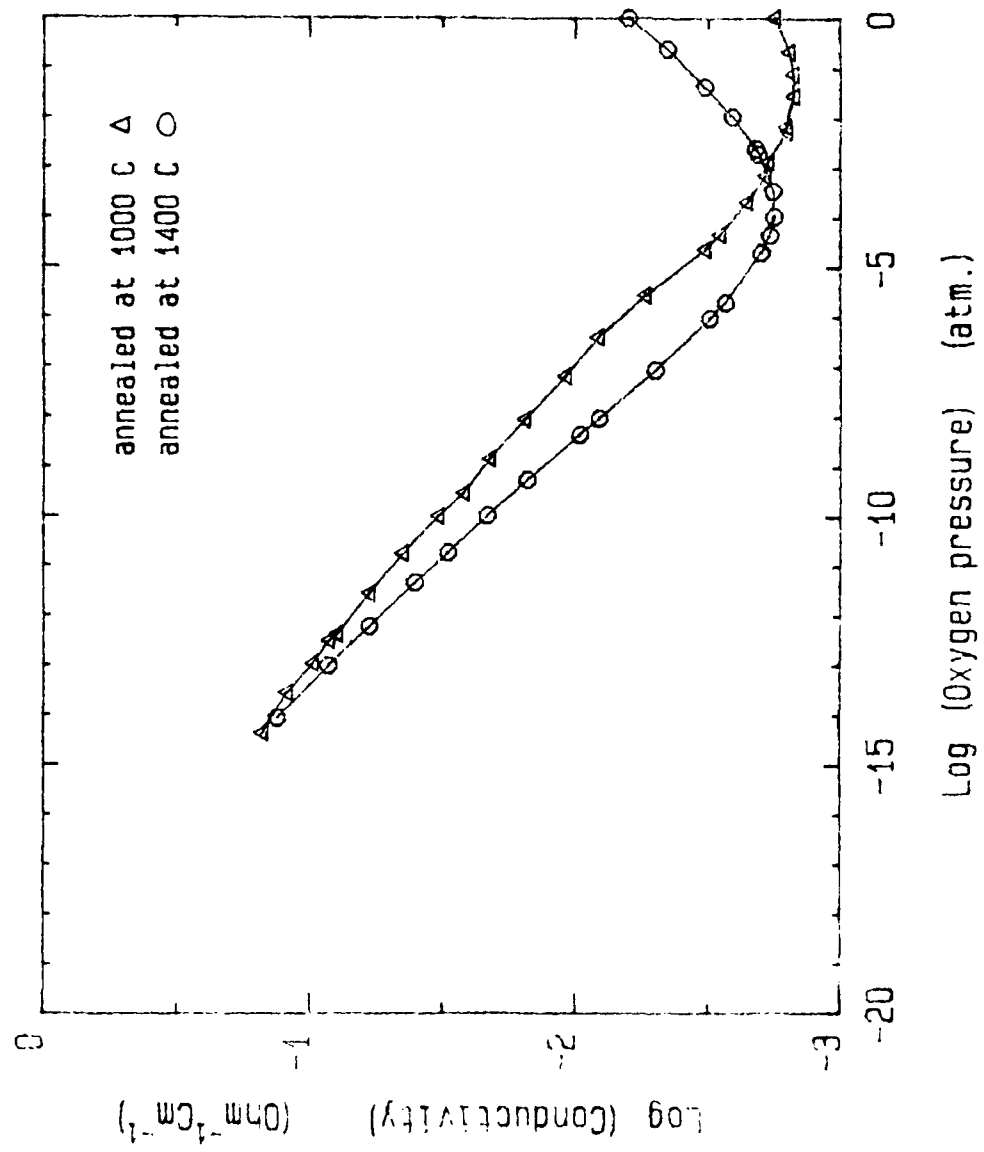
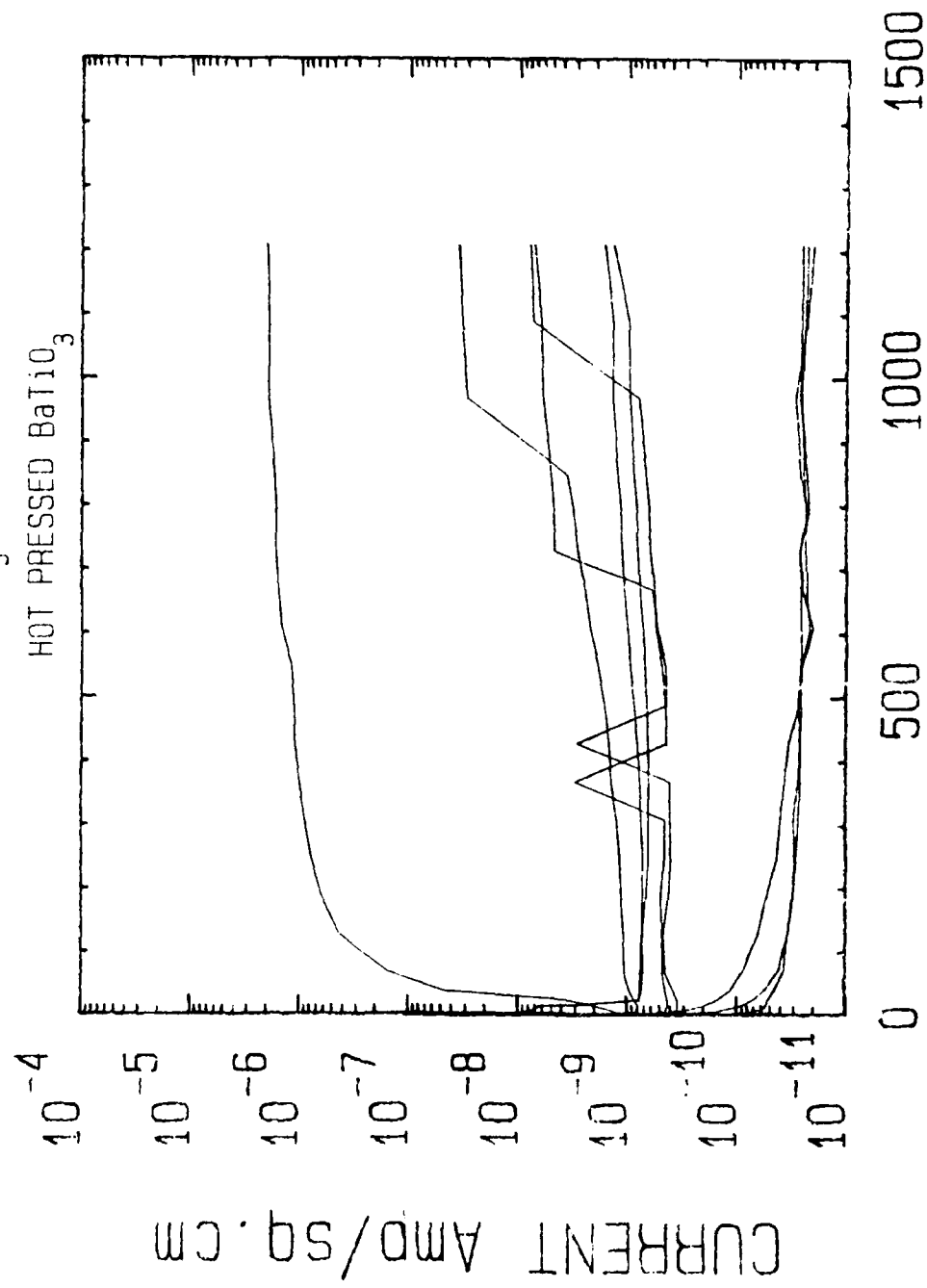
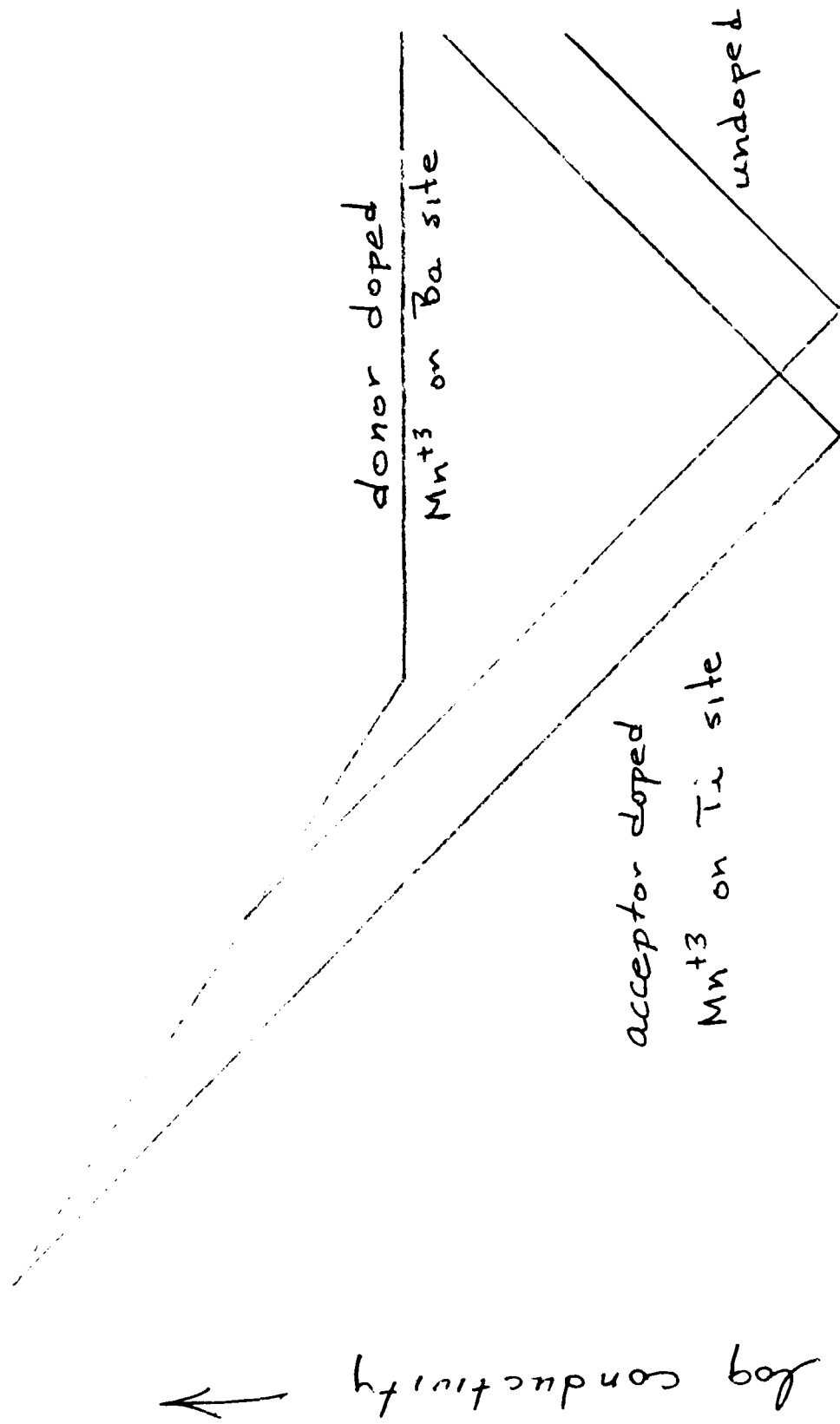


Figure 7. Conductivity profiles for hot-pressed undoped BaTiO_3 annealed at 1000 C (Δ) and at 1400 C ($\circ$).

BaTiO₃ SINTERED WITHOUT PRESSURE
HOT PRESSED BaTiO₃



TIME in Min



$\log P_{O_2} \rightarrow$

Fig. 6 Effect of occupation site on equilibrium

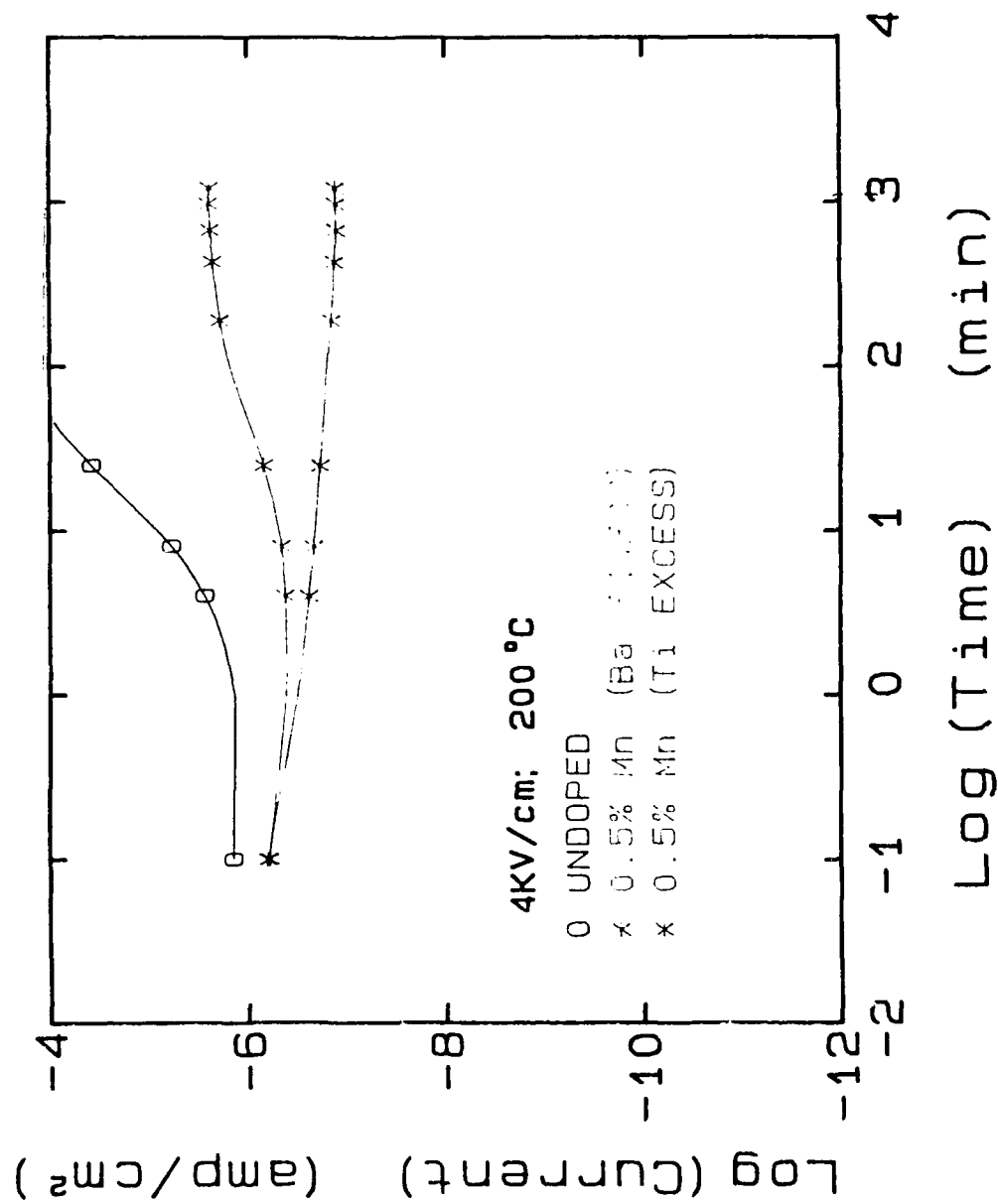


Figure 5(c) Logarithmic current-time curves for undoped and Mn-doped BaTiO_3 at 4KV/cm and 200°C.

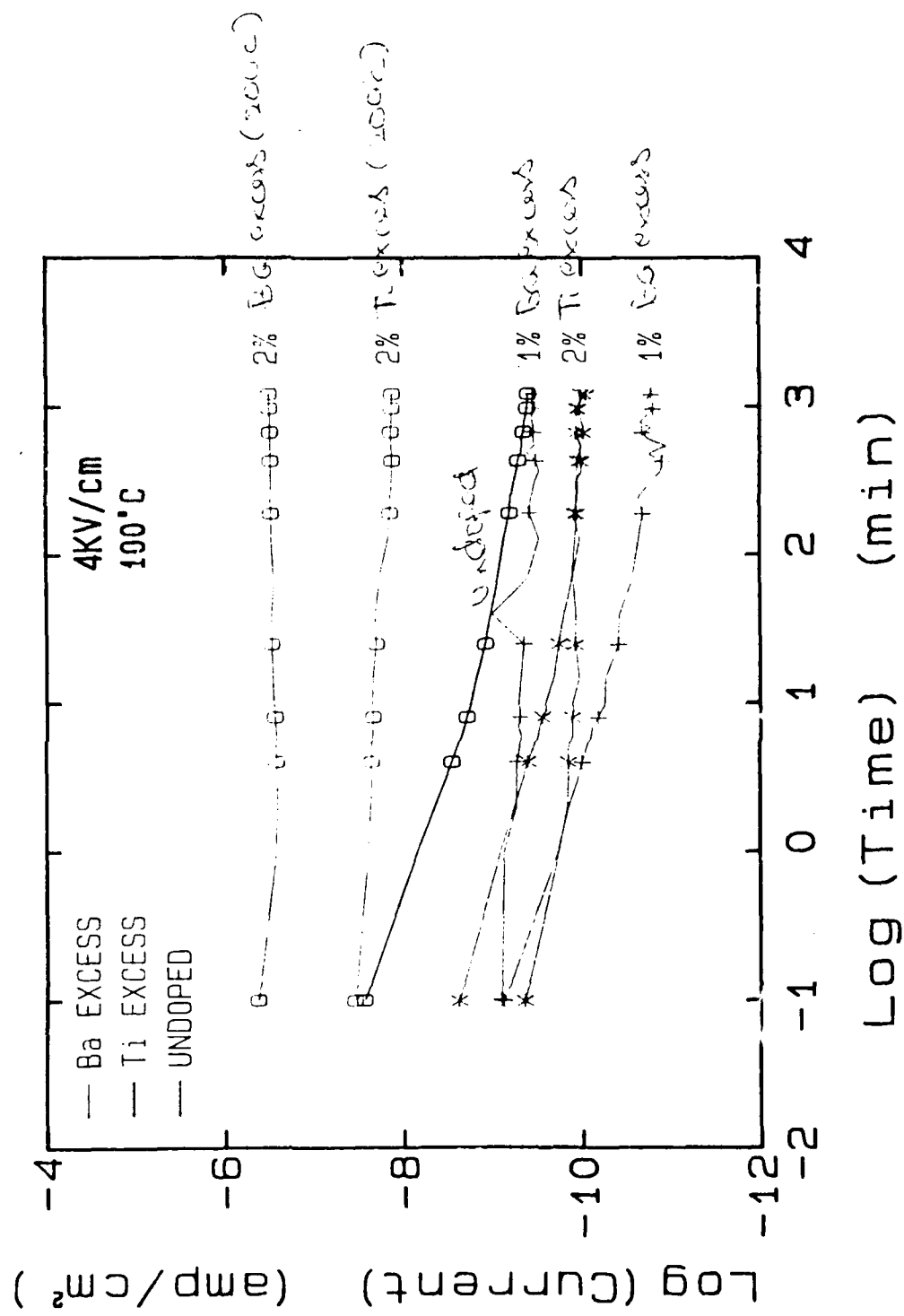


Figure 5(b) Log (Current) vs Log (Time) of Undoped BaTiO₃ at 100°C & 4KV/cm