

Defect Chemistry of BaTiO₃ Codoped with Mn and Nb

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The effect of Mn and Nb additions on the electrical properties of BaTiO₃ has been studied by means of equilibrium electrical conductivity as a function of temperature, oxygen partial pressure(Po₂) and composition. If the manganese ion is added to the normal Ti site, i.e. BaTi_{1-x}Mn_xO_{3-δ}, the equilibrium conductivity shows strong evidence of acceptor-doped behavior. The conductivity minimum, corresponding to the transition from oxygen excess, p-type behavior to oxygen deficient, n-type behavior with decreasing Po₂, is displaced to lower Po₂ and is broadened and flattened. The partial replacement of Mn ion with Nb decreases the acceptor-doped effect and the total replacement exhibits a typical donor-doped behavior. It was confirmed that unlike undoped or other acceptor-doped samples, for the p-type region, the electrical conductivity follows the 1/6th power dependence of oxygen partial pressure.

Key words : Defect chemistry, Barium titanate, Conductivity, Impurity effects

I. Introduction

The temperature stability of BaTiO₃ based ceramic capacitor is an important material issue for device application. To obtain the moderate temperature coefficient of capacitance(X7R), a metastable core-shell structure is employed by doping some oxide additives, e.g., CoO and Nb₂O₅.¹⁾ Sintering process allows those additives to diffuse into Ti sublattice sites and results in a concentration gradient of additive oxides from grain boundary through center of grain. Manganese oxide as well as niobium oxide is added to modify the temperature behavior of BaTiO₃ ceramic and to expedite sintering rate.²⁾

Osawa and Yoo reported the Po₂ dependence of the electrical conductivity of Mn-doped BaTiO₃ in terms of valence change of Mn ions.^{3,4)} Unlike other acceptor-doped cases, the p-type conductivity at the oxygen activity near stoichiometric composition is proportional to the 1/6th power of Po₂. Defect models for acceptor-doped and donor-doped BaTiO₃ were presented by numerous researchers.⁵⁻¹⁰⁾ Blumenthal^{5,6)} and Smyth⁷⁾ proposed that for currently available purities, there is a net excess of acceptor impurity dominating any type of defect concentration from intrinsic disorder. In other words, undoped materials are no longer free from background acceptor impurities in nature. Acceptor impurities which replace the host ion have a lower ionic charge and are compensated by a corresponding number of oxygen vacancies. Typical acceptor doped Kröger-Vink diagram is illustrated in Fig. 1 in the form of log-log plots of the defect concentration as a function of oxygen pressure, Po₂, at constant temperature. This can be characterized by [A'], [V_O], [e'], [h'] which represent the acceptor im-

purity, oxygen vacancy, electron and electron hole concentration, respectively. The idealized effect of increased acceptor content on the relative defect concentration is shown and the position of minimum moves toward lower Po₂ for increase in acceptor content. The major defect elements of samples doped with manganese ions can be described as Mn_{Ti'} and V_O. The position of the minimum can be used as a convenient parameter for comparing relative acceptor contents of various samples.

An impurity cation having a higher ionic charge than that of the host cation replaced by it is called a donor impurity. The donor impurity bears an effective positive charge relative to the ideal lattice of the host oxide, which is compensated by negatively charged defects, e.g., acceptor impurities, cation vacancies, or electrons. Typical donor impurities in BaTiO₃ include large cations with charge greater than 2 substituting for the Ba ion, e.g., La or Th, and small cations with charge greater than 4

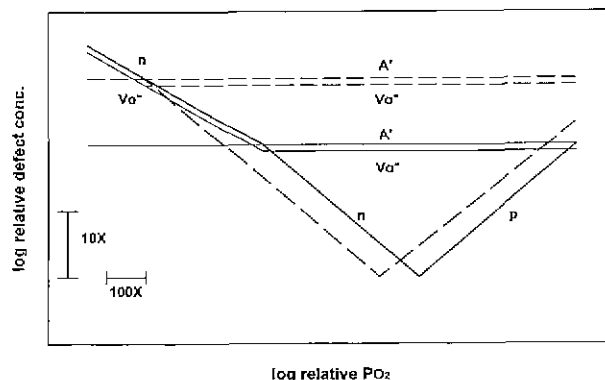


Fig. 1. Idealized defect for BaTiO₃ containing two different levels of acceptor impurities. The dashed line corresponds to the sample with the higher acceptor content.

substituting for Ti, e.g., Nb or Ta.

In this paper we present electrical conductivity measurements on BaTiO₃ doped with Mn or Nb, and codoped with Mn and Nb.

II. Experimental Procedure

Powders were prepared by the liquid mix technique developed by Pechini.¹¹ Each sample composition was prepared by polymerization and calcination of an organometallic solution containing precisely determined amounts of the sample components as described in the previous work.¹² The calcined powders were pulverized into fine powder and pressed into rectangular bars at 1 ton/cm². Holes were drilled through the largest face and 2 cm long platinum wires were inserted through each hole to serve as voltage leads. The samples were sintered at 1350°C for 4 h in air and then furnace-cooled. Platinum paint was applied onto both ends of each sample and fired at 900°C to serve as current leads.

The conductivity was measured with a four-point dc technique, using constant applied current to maintain a voltage drop of ~0.5 V in the temperature range 800° to 1100°C. The desired oxygen partial pressures were obtained from mixtures of N₂-O₂, CO-CO₂ and 0.01%CO premixed N₂-CO₂. The oxygen activity was determined by measurement of the emf of a closed-end tube of stabilized zirconia.

III. Results and Discussion

Fig. 2 shows the typical equilibrium electrical conductivities of undoped BaTiO₃ as a function of oxygen partial pressure, and similar results to previous reports.⁷ The current sample prepared by liquid mix method is assumed to contain about 100 ppm net acceptor impurities. The oxygen deficient n-type region and oxygen excess p-type region are separated by the conductivity minima which correspond to the completely compensated

stoichiometric state, neglecting mobility differences. As the sample is reduced in the n-type region, each oxygen leaving normal oxygen site forms oxygen vacancies and adds 2 electrons to the crystal, while in the p-type region, extrinsic oxygen vacancies due to background acceptor impurity are filled and 2 electron holes for each incorporation of oxygen are formed. At the conductivity minima, intrinsic electronic disorder contributes to electrical conduction and there is no contribution from excess oxygen or deficiency.

Equilibrium electrical conductivities as a function of Po₂ at 1000°C are shown for the Mn-doped samples and an undoped sample in Fig. 3. As the manganese content is increased, the conductivity increases in the p-type region and decreases in the n-type region around the conductivity minimum. This behavior indicates that the oxygen vacancy due to manganese ion retards the reduction reaction at low oxygen pressure and expedites oxidation at high oxygen pressure to fill itself with oxygen. At extremely low Po₂ the conductivities of all samples approach to a single line and the properties become independent of manganese content. The position of the conductivity minimum should move to two orders of magnitude toward lower Po₂ for each order of magnitude increase in acceptor content as described in Fig.1. The shift of conductivity minima to lower Po₂ is in qualitative accord with these expectations.⁹ However, the conductivity is proportional to Po₂^{-1/4} in the n-type region, and Po₂^{-1/6} in the p-type region. The n-type behavior is similar to the previous results⁹ while the p-type region is different from the behavior of undoped and other acceptor-doped BaTiO₃.⁷⁻⁹ The unusual 1/6 th power of Po₂ dependence in the p-type region is due to the variable ionic state of Mn ions. It was reported that Mn ions can change their valence state from tetravalent in the higher Po₂ region to trivalent or divalent in the lower Po₂ region.¹³⁻¹⁵ Osawa³ reported that the Po₂^{1/6} dependence is due to this valence change of Mn, and [Mn_{Ti}'] electrically compensated by [V_O], is sufficiently greater than [A'] and [e'] near the conductivity minimum in the p-

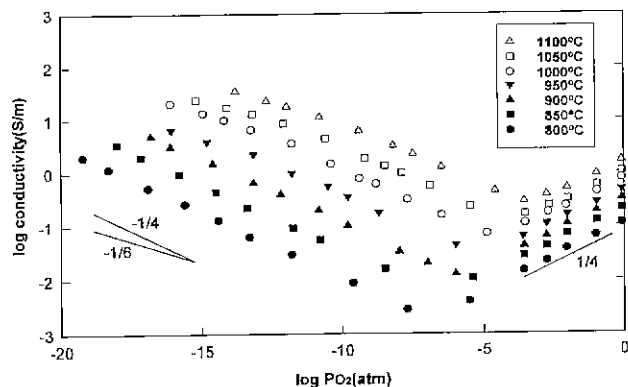


Fig. 2. Equilibrium electrical conductivity of undoped BaTiO₃ (Ba/Ti=1,000). Lines having ideal slopes are indicated for reference.

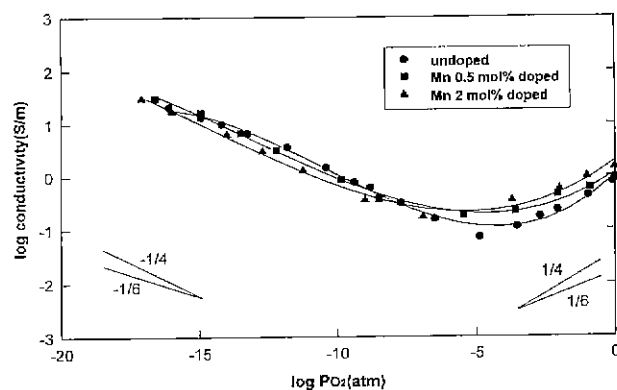


Fig. 3. Equilibrium electrical conductivity at 1000°C of undoped BaTiO₃ and BaTi_{1-x}Mn_xO₃ (x=0.005, 0.02)

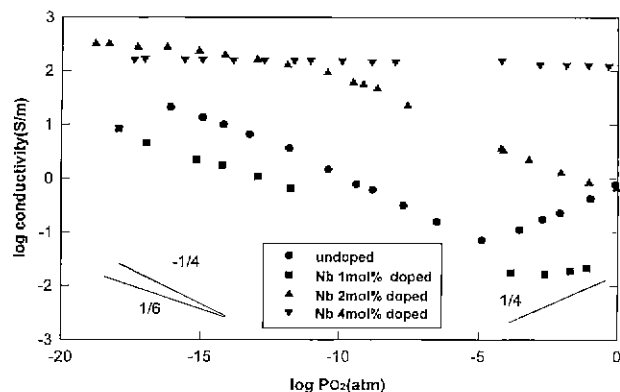


Fig. 4. Equilibrium electrical conductivity at 1000°C of undoped BaTiO_3 and $\text{BaTi}_{1-x}\text{Nb}_x\text{O}_3$ ($x=0.01, 0.02, 0.04$).

type region.

Fig. 4 shows the electrical conductivities of Nb doped and undoped BaTiO_3 as a function of oxygen partial pressure. The p-type region is not observed at any level of Nb doped $\text{BaTi}_{1-x}\text{Nb}_x\text{O}_3$ ($x=0.01, 0.02, 0.04$). As the amount of niobium is increased from 1 to 4 mol%, the electrical conductivities increase all over the Po_2 measured. The samples doped with 1 and 2 mol% show an n-type conductivity behavior: the conductivities increase with decreasing oxygen pressure. However, the conductivities of the sample doped with 4 mol% are independent of oxygen pressure. Undoped BaTiO_3 normally contains net acceptor impurities that are compensated by oxygen vacancies. The amount of net acceptors is assumed to be of the order of 100 ppm which is well below the niobium doping level studied in this work. It was suggested that the replacement of Ti with Nb by less than 0.5 mol% results in an n-type semiconducting material.¹⁰ However, niobium incorporation greater than 1 mol% is compensated by barium vacancies, V_{Ba} and BaTiO_3 becomes insulating.¹⁶ It was reported that the barium vacancies are the major compensating defects formed in 4 mol% Nb-doped BaTiO_3 . In other words, the addition of niobium greater than 0.5 mol% switches the compensating defects from electrons to bar-

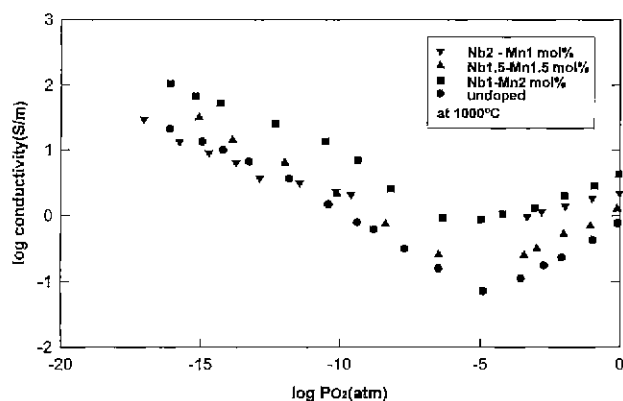


Fig. 5. Equilibrium electrical conductivity at 1000°C of undoped BaTiO_3 and $\text{BaTi}_{0.97}\text{Nb}_{0.03-x}\text{Mn}_x\text{O}_3$ ($x=0.01, 0.015, 0.02$).

ium vacancies.

Codoping experiments were carried out to see if the defects of samples doped with Mn and Nb are compensating each other. Fig. 5 shows the electrical conductivities of $\text{BaTi}_{0.97}\text{Nb}_{0.02}\text{Mn}_{0.01}\text{O}_3$, $\text{BaTi}_{0.97}\text{Nb}_{0.015}\text{Mn}_{0.015}\text{O}_3$, $\text{BaTi}_{0.97}\text{Nb}_{0.01}\text{Mn}_{0.02}\text{O}_3$, and undoped BaTiO_3 as a function of oxygen partial pressure. Unlike the Nb-doped cases shown in Fig. 4, the electrical conductivity shows a typical n-type and p-type characteristic which are separated by conductivity minima. The appearance of p-type behavior with Mn codoping makes the codoped samples insulating. The sample codoped with Mn implies that the positively charged Nb defects are compensated by barium vacancies as suggested by Wu,¹⁶ instead of electronic compensation when doped with less than 0.5 mol% Nb. It supports the net donor-doped composition, e.g., $\text{BaTi}_{0.97}\text{Nb}_{0.02}\text{Mn}_{0.01}\text{O}_3$ exhibits an acceptor-doped behavior.

IV. Conclusions

1. For Mn-doped BaTiO_3 , it is confirmed that the electrical conductivity follows the 1/6th power dependence of oxygen partial pressure at p-type region.
2. For Nb-doped BaTiO_3 , the electrical conductivity shows only n-type behavior.
3. For co-doped BaTiO_3 , the n-type behavior disappears at high oxygen pressure and the donor impurity is compensated by Mn.

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