

ELECTRICAL PROPERTIES OF CERIUM DOPED BARIUM TITANATE

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ABSTRACT

Barium titanate (BaTiO_3) and cerium (Ce) doped barium titanate samples with general formula $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ (where $x = 0.0, 0.1, 0.2, 0.3$, and 0.4) were prepared by solid-solid ceramic method at the sintering temperature of 1250°C . I-V characteristics of pure and Ce-doped BaTiO_3 show ohmic behavior with two distinct slopes. At the higher voltage region receptivity of the samples is of the order of $10^7 \Omega\text{-cm}$. The dc receptivity variation of BaTiO_3 with temperature shows a transition from tetragonal to cubic structure at about 120°C . The Curie temperature of $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ decreases linearly with the increase of Ce.

INTRODUCTION

Barium titanate (BaTiO_3), a ferroelectric ceramic having perovskite structure with tetragonal symmetry, possesses relatively high dielectric constant and electro-optic coefficient. BaTiO_3 ceramics have a strong piezoelectric effect⁽¹⁾. In addition they are mechanically rugged and rather insensitive to temperature and humidity. Therefore, these ceramics find wide applications in devices such as microphone, ultrasonic and underwater transducer, spark generators, etc.

Highly Ce^{3+} -doped BaTiO_3 ceramic materials have been described as having promising dielectric properties, such as relatively high permittivity and high endurance. They can be used as materials for the production of multilayer ceramic capacitors.⁽²⁾ Cerium can exist in two oxidation states, $4+$ and $3+$. It can be incorporated into the BaTiO_3 perovskite lattice substituted in both existing oxidation states. In oxidation state $4+$, it enters the BaTiO_3 lattice at the Ti^{4+} sites, whereas in oxidation state $3+$, it is incorporated at the Ba^{2+} sites. When cerium enters BaTiO_3 at Ba^{2+} sites in oxidation state

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3+, it acts as donor and therefore incorporation requires the formation of effectively negatively charged compensating lattice defects (ionized cation vacancies, electrons). The site where cerium enters the BaTiO₃ lattice, as well as the donor charge compensation mechanism (when it is incorporated at Ba sites), depends on the firing atmosphere and on the starting composition.⁽³⁻⁶⁾

When BaTiO₃ is sintered in air together with CeO₂ and an excess amount of TiO₂, CeO₂ partially reduces and cerium enters the BaTiO₃ lattice as a donor at the Ba sites. The excess charge in highly Ce³⁺-doped BaTiO₃ is compensated by the formation of ionized vacancies at Ti sites.^{2,3} The solubility limit of solid solution Ba_{1-x}Ce_x³⁺TiO₃ is highly temperature dependent, $x = 0.04$ at 1200°C and $x = 0.08$ at 1400°C.⁽⁶⁾ At a temperature with a low oxygen partial pressure, CeO₂ is totally reduced. Consequently cerium is dissolved in BaTiO₃ in oxidation state 3+, independently of the starting composition. In contrast to most of the rare-earth elements, which are stable in air in oxidation states 3+, cerium is the most stable one in oxidation state 4+. There is a spontaneous polarization on cooling BaTiO₃ below the Curie point T_c due to changes in the crystal structure. The paraelectric cubic phases are stable above 130°C with the center of positive charges (Ba²⁺ and Ti⁴⁺ ions) coinciding with the center of negative charge (O²⁻). On cooling below the Curie point T_c , a tetragonal structure develops where the center of Ba²⁺ and Ti⁴⁺ ions are displaced relative to the O²⁻ ions, leading to the formation of electric dipoles. Spontaneous polarization develops the net dipole moment produced per unit volume for the dipoles pointing in a given direction.⁽⁷⁾

In this study Ba_{1-x}Ce_xTiO₃ samples were prepared and the dc electrical resistivity was investigated. The observed results are discussed in this paper.

EXPERIMENTAL

The materials used in the preparation of experimental samples with analytical grade were barium oxide (BaO), titanium dioxide (TiO₂), and cerium oxide (CeO₂). All the materials were procured from local market. Thus a set of samples of Ba_{1-x}Ce_xTiO₃ ceramics where $x = 0.0, 0.1, 0.2, 0.3$, and 0.4 were prepared using solid-solid ceramic reaction method. The samples were tablet size with a diameter of 0.6 cm and a surface area of 0.28 cm². The dc resistance of samples was measured by using two-probe method.

The resistance was measured as a function of temperature during heating and then the receptivity was calculated using the formula

$$p = \left(\frac{V_s}{V_F} \right) \left(\frac{A}{d} \right) R_F$$

where A , the cross-sectional area of the sample; d , the length separating the contacts; V_s , the voltage measured across the sample; V_F , the voltage measured across the fixed resistance, and R_F , the standard fixed resistance.

RESULTS AND DISCUSSION

(i). *Current-voltage (I-V) characteristics* : The I-V characteristics curves of $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ (where $x = 0.0, 0.1, 0.2, 0.3$, and 0.4) is shown in Fig. 1. It is observed that the increase of current is linear. That is current-voltage characteristics of the samples obey $I \propto V^n$ law with two distinct slopes. In the lower region, slopes of the curves fall between $0.50 < n < 0.94$. Above 10V, the slopes of the curves the between $1.23 < n < 1.37$. The value of n in the lower region varies much from sample to sample whereas it does not vary much in the higher voltage region. It is seen that the I-V behavior is consistent in the higher voltage region. Thus, in the higher voltage region the slope is close to unity which is an ohmic behavior.⁽⁸⁾

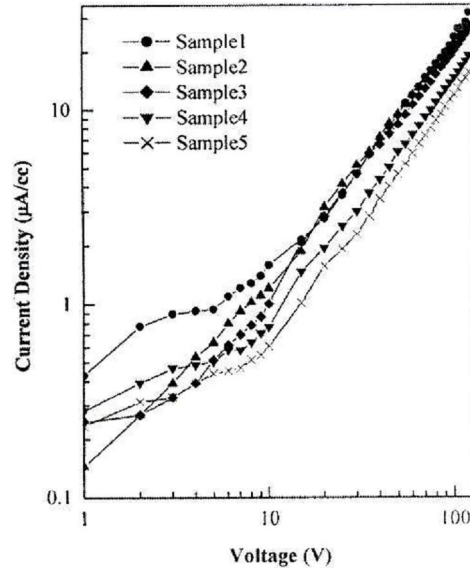


Fig. 1. Comparison of I-V characteristics of $\text{Ba}_{1-x}\text{TiO}_3$ ($x = 0.0, 0.1, 0.2, 0.3$ and 0.4).

In the higher voltage region ($>10\text{V}$), for lower amount of Ce doping in $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ ($x = 0.0, 0.1, 0.2$) the resistivity remains almost same whereas it decrease for $x = 0.3$ and 0.4 .

(ii). *Temperature dependence of resistivity* : In Fig. 2(a), it is seen that the dc resistivity of BaTiO_3 increases with the temperature up to 120°C and then decreases. It indicates a transition from tetragonal to cubic in the BaTiO_3 structure.^(1,8) At the transition temperature the resistivity of BaTiO_3 is found to be about $2.068 \times 10^7 \Omega\text{-cm}$.

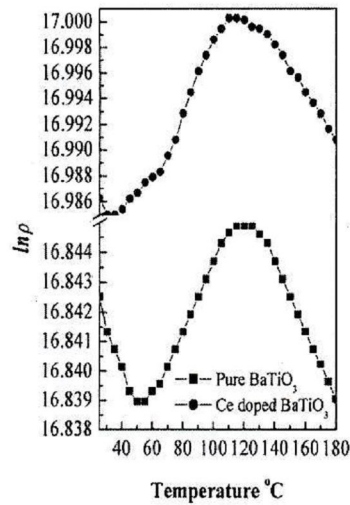
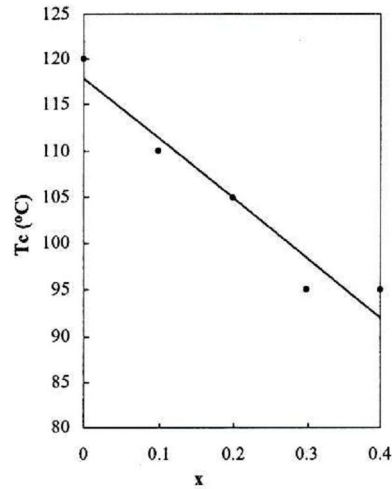
With the increase of Ce-dopant in $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ the resistivity of the samples show the same characteristics and the transition temperature linearly decreases as shown in Fig. 2(b). The calculated values of resistivity of different samples are shown in Table 1.

TABLE 1.

CHANGE OF TRANSITION TEMPERATURE WITH DOPING CONCENTRATION.

| Sample No. | Value of X in $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ | Resistivity at room temperature $\Omega\text{-cm}$ | Transition temperature (T_c) $^{\circ}\text{C}$ | Resistivity at the transition temperature $\Omega\text{-cm}$ |
|------------|--|--|---|--|
| 1 | 0.0 | 2.06×10^7 | 120 | 2.068×10^7 |
| 2 | 0.1 | 2.39×10^7 | 110 | 2.41×10^7 |
| 3 | 0.2 | 1.96×10^7 | 105 | 1.957×10^7 |
| 4 | 0.3 | 1.21×10^7 | 95 | 1.213×10^7 |
| 5 | 0.4 | 2.22×10^7 | 95 | 2.218×10^7 |

It is observed that BaTiO_3 has the highest transition temperature. While as Ce is doped in BaTiO_3 , the transition temperature decreases and the lowest transition occurred at 95°C for $x = 0.4$. Hwang and Han⁽⁹⁾ found similar result when $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$ ($x = 0.005, 0.01$, and 0.02) was studied with temperature in the oxygen partial pressure, $P(\text{O}_2)$, and composition. They reported that there is a significant shift of T_c to lower temperatures when Ce^{3+} is incorporated into Ba^{2+} sites up to 2.0 mol%. In the present work the shift of the transition temperature to lower temperature values supports an incorporation of Ce^{3+} into Ba^{2+} sites.

Fig. 2(a). Temperature dependence of resistivity of pure and Ce-doped BaTiO_3 .Fig. 2(b). Change of transition temperature due to doping concentration in $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$.

The change in the resistivity of these ceramics at Curie temperature indicates that either the mobility of the majority charge carriers decreases at the tetragonal to cubic

transition or that the number of charge carriers in the conduction band decreases at the transition temperature.⁽⁸⁾ A possible cause for a mobility decrease would be a narrowing of the conduction band due to the change in the crystal symmetry accompanying the tetragonal \rightarrow cubic transition.

CONCLUSIONS

The current-voltage characteristics of the samples obey $I \propto V^n$ law with two distinct slopes. The I-V behavior is ohmic in the higher voltage region. In the higher voltage region the resistivity remains almost same for lower amount of Ce doping whereas current is dependent on Ce for its higher amount.

The resistivity exhibits a transition around the temperature of 120°C where the crystal structure changes from tetragonal to cubic. As the amount of Ce increases in $\text{Ba}_{1-x}\text{Ce}_x\text{TiO}_3$, the transition temperature shifts to a lower value.

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