Electrical properties and ageing characteristics of BaTiO$_3$ ceramics doped by single dopants

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Abstract

BaTiO$_3$ ceramics doped by single dopants of Sm$_2$O$_3$, Ho$_2$O$_3$, Bi$_2$O$_3$, La$_2$O$_3$, CeO$_2$ and Ta$_2$O$_5$, respectively, were prepared and aged in air. The room-temperature resistivity was measured and the relationship between resistivity change versus ageing time was determined. The electrical resistivity of Bi- and Ta-doped samples decreases at the early ageing stage, and then increases with the ageing time; the other doped ceramics display a monotonous increase of the resistivity with ageing time. The electrical properties and ageing characteristics are analyzed by considering interior oxidation and reduction reactions and the electronegativity of the doping elements.
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Keywords: BaTiO$_3$; Electrical properties; Ageing

1. Introduction

Barium titanate with a perovskite lattice structure has been of practical importance for about 50 years because of its attractive electrical properties. The significance of this material is mainly based on the wide variety of applications for which it is used, such as capacitors, positive temperature coefficient thermistors, piezoelectric devises, optoelectronic elements. On the other hand, it has been a large interest in its fundamental behaviors such as electronic transport properties, microstructure and lattice dynamics.[1–4] The various applications have resulted in many scientific studies aiming at preparation and characterization of BaTiO$_3$ ceramics. The stability of the electric properties is important for the practical application. But, in fact, the electrical properties of the elements would deteriorate during operating under various conditions such as electric field, humidity and high temperature, etc. Ageing heat treatment is one way to study the influence of temperature on the stability of the electrical properties of the ferroelectric ceramics. Some researchers have found that the resistivity/time relationship at high temperature continuous load test is different from that of room temperature ageing, and the resistance/temperature charac-

teristics of aged samples are also different from those of reduced or oxidized samples.[5–8] Therefore, a mechanism involving a combination of internal oxidation and reduction reactions was proposed for the ageing characteristics of donor-doped BaTiO$_3$.[8] In the present paper we report some recent results on the single-dopant doped BaTiO$_3$ ceramics aged at 100 and 150 °C in air. The interior oxidation and reduction reactions of the ceramics and the electronegativities of the doping elements are used to explain the doping mechanism and abnormal ageing characteristics.

2. Experimental procedure

BaTiO$_3$ ceramics were prepared by using the raw materials of BaCO$_3$ and TiO$_2$ (>99%, Merck KGaA, Germany) with a molar ratio of 1.00:1.01. The powders are doped by single dopant (Sm$_2$O$_3$, Ho$_2$O$_3$, Bi$_2$O$_3$, La$_2$O$_3$, CeO$_2$ and Ta$_2$O$_5$, respectively) with an amount from 0.1 to 0.6 mol% of dopant ions. Generally, Sm, Ho, Bi and La are elements with a valency of 3, Ce is a quad-valent element and Ta is a penta-valent element. The starting materials were ball milled using in alcohol for 24 h followed by calcination at 1000 °C for 6 h. The powders were then granulated by using polyvinyl alcohol and pressed into pellets with a diameter of 15 mm and thickness of 4 mm. The shape-forming pressure

was 100 MPa. Sintering was performed at 1350 °C for 2 h in air in a box furnace (Model VMK 1800, Linn High Therm GmbH, Germany). The sintered samples were ground to a thickness of about 2.5 mm. Silver paste was then painted on both sides of the sample end surfaces followed by heating at 900 °C for 0.5 h to make an electrode. The room-temperature electrical resistivity of the ceramics was measured by using a standard ohmmeter. The room temperature was 20 °C, which was controlled by an air conditioner. The characteristics of electrical resistivity versus temperature (ρ–T) were studied at a heating rate of about 1 °C/min. The samples were aged in air at temperatures of 100 and 150 °C, respectively. The electrical resistivities of all the samples were measured after different ageing time and cooling over one night. The resistivity change was calculated by the following equation:
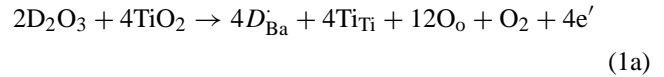
$$\gamma = \frac{\rho - \rho_0}{\rho_0} \times 100\%$$

where ρ_0 is the resistivity before ageing and ρ is the resistivity after ageing.
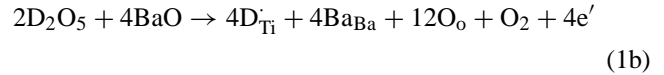
3. Results and discussion

The dopant content dependence of room-temperature resistivity (ρ_{rt}) of the samples is shown in Fig. 1. The ρ_{rt} of the Bi- and La-doped samples decreases monotonously with dopant content. The ρ_{rt} of the other samples decreases with increasing of dopant content at low doping levels, and reaches a minimum value at a certain doping level, then increases with dopant content in the high doping level.
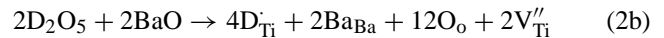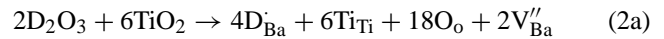
During the sintering process, both tri-valent and penta-valent elements act as donor dopants, but the element with the valency of 3 replaces Ba-site and the penta-valent dopant (Ta) substitutes Ti-site in the grains:[9]

$$2D_2O_3 + 4TiO_2 \rightarrow 4D_{Ba}^{\cdot} + 4Ti_{Ti} + 12O_o + O_2 + 4e' \tag{1a}$$

and

$$2D_2O_5 + 4BaO \rightarrow 4D_{Ti}^{\cdot} + 4Ba_{Ba} + 12O_o + O_2 + 4e' \tag{1b}$$

where D_2O_3 and D_2O_5 are the dopant oxides, $D_{Ba}^{\cdot}$ and $D_{Ti}^{\cdot}$ are the positions that the dopant replaced the Ba- and Ti-sites, respectively, O_o is an oxygen ion at O-site, e' is an electron in the conduction band. The conduction-band electrons increase with the dopant content increases, so, the ρ_{rt} decreases with the rising of donor content in the low doping level. However, when the dopant content is higher than a certain value, the dopant can be compensated by cation vacancies:

$$2D_2O_3 + 6TiO_2 \rightarrow 4D_{Ba}^{\cdot} + 6Ti_{Ti} + 18O_o + 2V_{Ba}'' \tag{2a}$$

$$2D_2O_5 + 2BaO \rightarrow 4D_{Ti}^{\cdot} + 2Ba_{Ba} + 12O_o + 2V_{Ti}'' \tag{2b}$$

or, acted as acceptor to occupy the Ti-site for the tri-valent dopant:

$$D_2O_3 + 2e' \rightarrow 2D_{Ti}'' + 3O_o + V_O \tag{3}$$
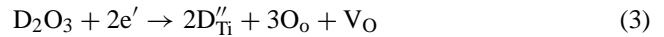
where V_{Ba}' is a barium cation vacancy, V_{Ti}' is a titanium cation vacancy and V_O is an oxygen vacancy in the BaTiO$_3$ perovskite lattice. Therefore, the reactions shown in Eqs. (2a), (2b) and (3) lead to an increasing concentration of cation vacancies and a decreasing concentration of conductor band electrons, resulting in an increase of the resistivity.

For the dopant Ce, it is possible that the dopant was reduced to be Ce^{3+} ion and acted as a donor for Ba-site, or acted as isovalent dopant at Ti-site.[10,11] It cannot produce as much conducting-band electrons as that of tri-valent donor or penta-valent donor at the same doping level. Therefore the Ce-doped samples always show higher resistivity than the other doped materials in present experiment.

Fig. 2 shows the resistivity change with ageing time after ageing in air at 100 °C, where the content of the dopants of Sm, Ho, Bi, La, Ce and Ta are 0.2, 0.3, 0.5, 0.6, 0.3 and 0.3 mol%, respectively. Two types of ageing phenomena can be seen. One, in the samples doped by Sm, Ho, La and Ce, the resistivity increases quickly during the initial ageing stage, and then increases monotonously with ageing time during further ageing. However, another kind of ageing phenomenon is that abnormal ageing characteristics occurred in Bi- and Ta-doped samples: the resistivity change is negative during the initial ageing stage. During the latter ageing stage, the resistivity increases as those of the first type of ageing characteristics.

The results shown in Fig. 2 are obtained when samples are aged at 100 °C which is below their Curie temperature (about 120 °C). In order to compare the ageing characteristics at a temperature higher than the Curie point, 150 °C ageing was
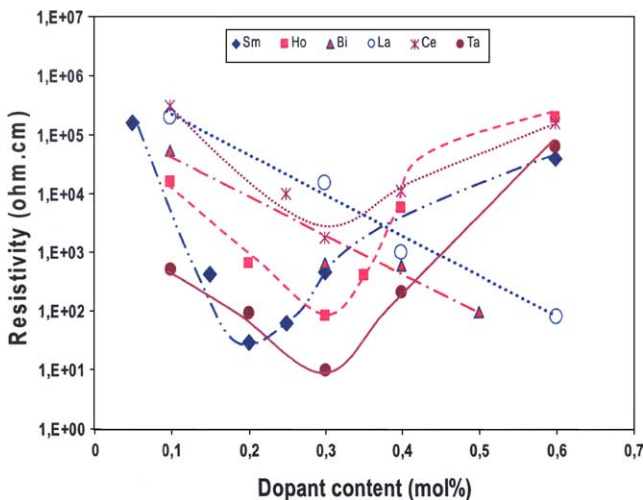

Fig. 1. Dopant content dependence of resistivity in BaTiO$_3$ ceramics.

also performed. Fig. 3 shows the results of samples aged in air at 150 °C. The ageing characteristics are similar to those aged at 100 °C. The differences between the two ageing temperatures are that the time for the decreasing stage and for the quickly increasing stage aged at 150 °C is shorter than that aged at 100 °C, and the resistivity raises faster at the initial ageing stage at 150 °C.

The relationship between electrical resistivity and temperature of samples aged at 150 °C was determined before and after 50-h ageing (shown in Fig. 4). For the samples whose resistivity monotonously increases during ageing such as Ho- and Ce-doped ceramics, both the minimum and the maximum resistivities after ageing are larger than that before ageing (Fig. 4a and b). But the opposite results occurred in the Bi- and Ta-doped samples (Fig. 4c and d, respectively).

The room-temperature resistivity of a PTCR ferroelectric ceramic can be attributed to semiconducting grain interiors, grain boundaries, electrode and the interface between the electrode and the ceramic. It has been established that the grain boundary barrier is the primary contributor to the elec-
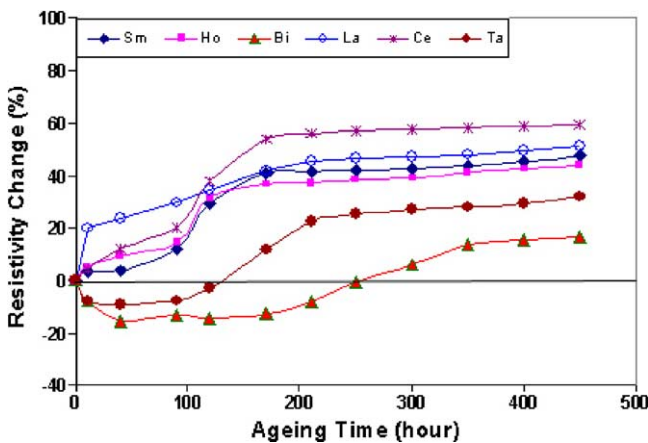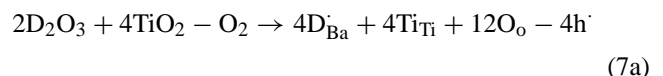

Fig. 2. Resistivity change vs. the ageing time in the samples aged in air at 100 °C, where the content of the dopants of Sm, Ho, Bi, La, Ce and Ta are 0.2, 0.3, 0.5, 0.6, 0.3 and 0.3 mol%, respectively.

Fig. 3. Resistivity change vs. the ageing time in the samples aged in air at 150 °C, the concentrations of dopants are the same as that in Fig. 2.

trical resistance,[12,13] which is in agreement with Heywang's model of treating the potential in deletion region as a Schottky barrier.[14] The oxidation of the electrodes and the oxygen absorption at the grain boundaries may occur during ageing and result in the increase of the room-temperature electrical resistivity.

From the results that the room-temperature electrical resistances of Bi- and Ta-doped ceramics decrease in the initial ageing stage, the oxidation of the electrodes and the oxygen absorption at the grain boundaries cannot be the only reactions during ageing. Some further reaction must have occurred simultaneously. For example, as pointed out by Li et al.[8] the internal reduction reaction has a primary role for the resistivity decrease of aged samples. The detail is described in the following.

Conduction-band electrons formed in the grains, as shown in Eqs. (1a) and (1b). For the tri-valent and penta-valent donors doped samples, respectively. The compensation reaction of cation vacancy occurs at the grain boundaries simultaneously as shown in Eqs. (2a) and (2b). At the same time, the oxygen absorption at the grain boundaries acts as an oxidizing reaction:

$$2TiO_2 + O_2 \rightarrow 2Ti_{Ti} + 6O_O + 2V''_{Ba} + 4h^{\cdot} \qquad (4)$$
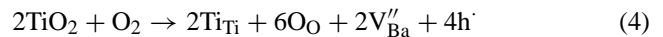
where $h^{\cdot}$ represents the holes contributing to conduction. This reaction is then gradually propagating into the interior of the grains. Combining this reaction with in shown in Eq. (1a), the following result is obtained:

$$2D_2O_3 + 6TiO_2 + E_2$$
$$\rightarrow 4D^{\cdot}_{Ba} + 6Ti_{Ti} + 18O_o + O_2 + 4e' + 4h^{\cdot} \qquad (5)$$
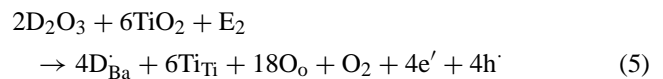
The electron compensation occurs as:

$$4e' + 4h^{\cdot} \rightarrow nil \qquad (6)$$

where nil represents the standard state which is taken as the perfect crystal with all electrons in the lowest available energy states. For the penta-valent dopant, a similar reaction can occur by combining Eqs. (4) and (1b), and the same result as shown in Eq. (6) is obtained. The cation vacancy compensation reaction predominates at the grain boundaries, as described by Eqs. (2a) and (2b), indicating that the concentration of the cation vacancies increases and the electron concentration decreases. Thus the room-temperature resistivity of the aged samples increased.

If the oxygen absorption at the grain boundaries only occurs during ageing, it is impossible to get the result of the aged Bi- and Ta-doped samples. The resistivity decrease must result from some other reaction, which is suggested to be the reduction reactions occurring at grain boundaries. Combining the reactions Eqs. (2a) and (4), (or that of Eqs. (2b) and (4)), the following reactions occur:

$$2D_2O_3 + 4TiO_2 - O_2 \rightarrow 4D^{\cdot}_{Ba} + 4Ti_{Ti} + 12O_o - 4h^{\cdot}$$
$$(7a)$$
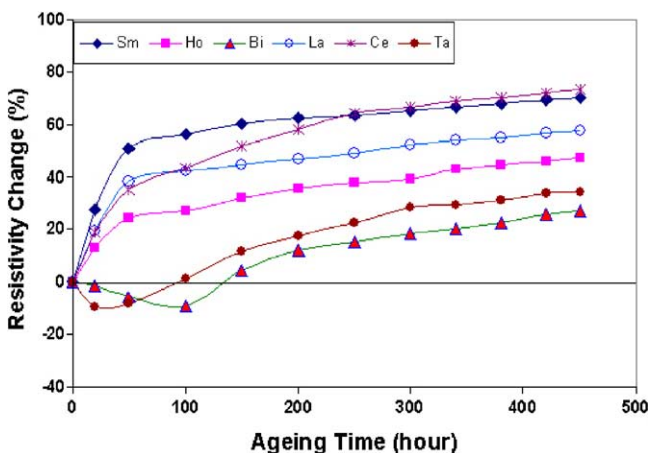
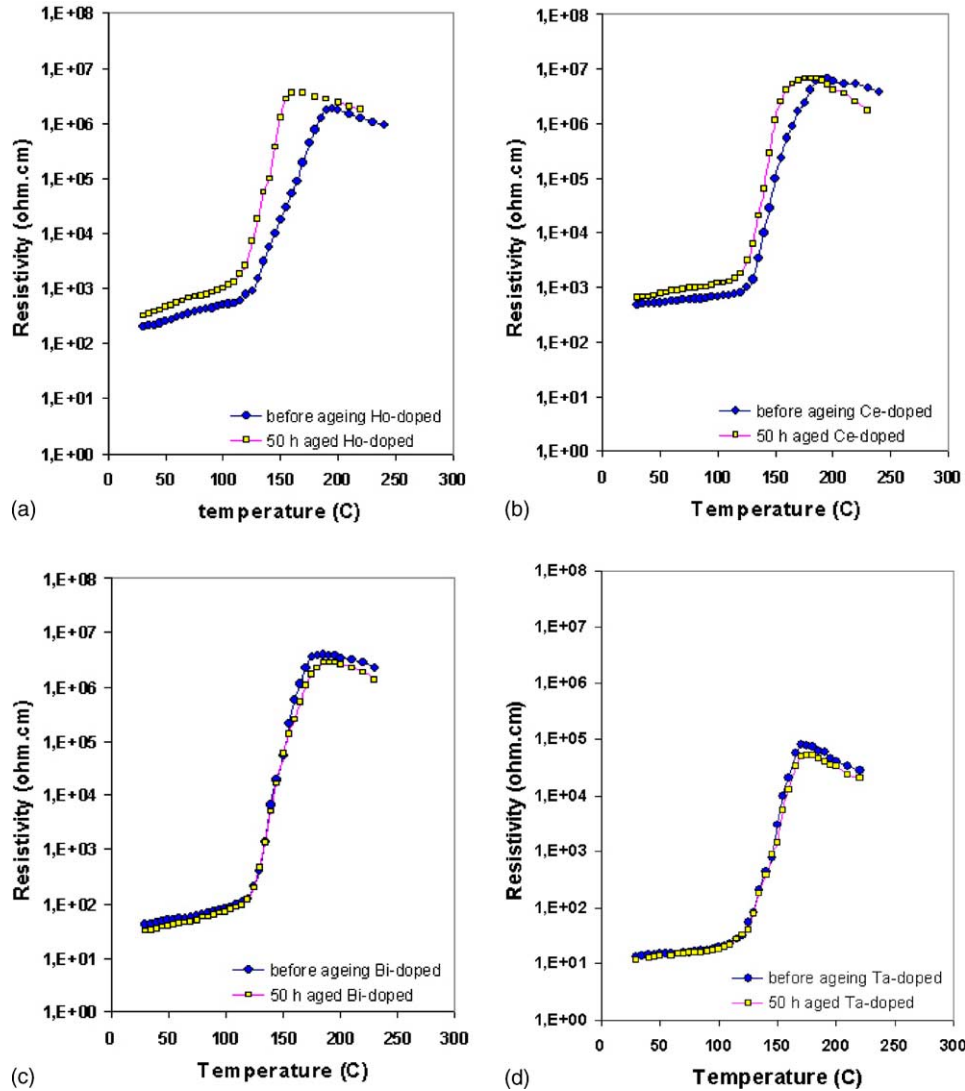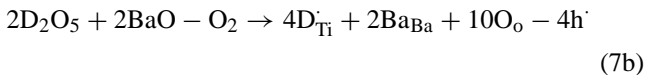Fig. 4. temperature dependence of resistivity of the BaTiO$_3$ ceramics before ageing and being aged at 150 °C for 50 h: (a) 0.3 mol% Ho-doped ceramic, (b) 0.3 mol% Ce-doped ceramic, (c) 0.5 mol% Bi-doped ceramic, (d) 0.3 mol% Ta-doped ceramic.

$$2D_2O_5 + 2BaO - O_2 \rightarrow 4D_{Ti}^{\cdot} + 2Ba_{Ba} + 10O_o - 4h^{\cdot}$$

(7b)

Therefore both of the concentrations of hole for conduction and cation vacancy decrease at the grain boundaries during ageing. This also indicates that the chance of a reaction occurring to a combination of Eqs. (4) and (1a) for trivalent doping, and of Eqs. (4) and (1b) for penta-valent doping, must decrease. Therefore the concentration of conducting electrons increases and the room-temperature resistivity of the aged samples (Bi- and Ta-doped) decreases during the initial ageing stage.

On the other hand, the free electron will be captured by the barium vacancy at the grain boundary during the ferro-electric phase transformation when the samples are heated above their Curie temperature. This electron capturing process should respond the PTCR effect.[9] So the PTCR effect of the ceramics is depended on the concentrations of elec-

trons and the barium vacancies. Because of the combination of oxidation/reduction reaction processes, the number of conduction electrons will be more than in samples with only oxidation, resulting in a maximum resistivity lower than before ageing. This should be the reason for the behavior shown in Fig. 4.

The next question is why the ρ_{rt} decreasing took place in Bi-doped ceramics and Ta-doped ceramics instead of in the others doped ceramics. From the reason for the resistance decrease as described above, the reduction reactions resulting in the forms as shown in Eqs. (7a) and (7b) are the important cause. So the question can aim at the reduction reactions occurred at grain boundaries themselves. It is well known that the electronegativity represents the power of an atom in a molecule to attract electrons. According to the concept, each kind of atom has a certain attracting ability for the electrons involved in a chemical bond. An atom with the higher electronegativity value will always pull the elec-

trons away from the atom that has the lower electronegative, and the electrons is dragged over to the more electronegative atom. The degree of the electron deviation towards the more electronegeative atom is depended on the difference in the electronegativities between the atoms involved. For the tri-valent dopants, the reduction reaction depends on the power between the dopant and the Ti atom to attract electron from oxygen ion. The electronegativities of the atoms of Sm, Ho and La are 1.17, 1.23 and 1.1 in Pauling scale, respectively, which are less electronegative than the Ti atom (1.54). It is more difficult for the atoms of Sm, Ho and La to attract the electrons from oxygen ion than for Ti. Therefore the oxygen ions have much difficulty in forming oxygen molecules. This should be the reason for why the reduction reaction does not occur so easy during ageing. On the contrary, the electronegativity of Bi is 2.02, which is larger than that of Ti. It is possible for the occurrence of the electron polarization to the Bi. So the reduction reaction can easily take place during ageing. For the case of Ta-doped sample, a similar mechanism can also be proposed. Because the penta-valent dopant always substitutes Ti-site, the reduction reaction depends on the electronegativity difference between dopant atom and Ba atom. The electronegativity of Ta is 1.5 and the one of Ba is 0.89. The polarization towards the Ta-site from the oxygen electron may occur, resulting in that the oxygen ions are easier to loss the electron and to form oxygen molecule and the reduction reaction occurs. For the limit dopant content, the reduction reaction cannot occur during the whole ageing period, therefore the ρ_{rt} could not decrease during the whole ageing and increased in the latter ageing stage.

4. Conclusions

1. The room-temperature resistivity in Bi- and La-doped $BaTiO_3$ ceramics decreases with increasing dopant content for the present doping level. The resistivity of $BaTiO_3$ doped with Sm, Ho, Ce and Ta, respectively, decreases with icreasing dopant content in the low doping level, but increases with increasing dopant content in the high doping level.
2. The resistivity of Bi- and Ta-doped samples decreases at the initial ageing stage, and then increase with ageing time; the other doped ceramics display a monotonous increase of the resistance with ageing time.
3. The maximum resistance and the resistance rise rate of the Bi- and Ta-doped samples in the initial ageing stage in PTCR effect become less than that before ageing; The maximum resistance and the resistance rise rate of the other samples become larger than that before ageing.
4. The electrical properties and ageing characteristics are related to interior oxidation and reduction reactions. The electronegativities of the atoms are supposed as a primary factor for the reduction reaction.

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