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Effect of ageing on the electrical resistivities of $(Ba_{0.69}Pb_{0.31})TiO_3$ PTCR ceramic thermistors

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Abstract

The electrical resistivity of $(Ba_{0.69}Pb_{0.31})TiO_3$ PTCR ceramic thermistors aged at temperatures of 175, 200, 250 and 300 °C, respectively, were measured. When the samples were aged at temperatures of 175 and 200 °C, room-temperature resistivity decreased at the initial ageing stage, and then increased with the ageing time. The samples displayed a monotonous rise of the room-temperature resistivity when the ageing treatments were performed at 250 and 300 °C. PTCR effects showed different characteristics after different ageing treatments. These ageing characteristics were analyzed by considering interior oxidation and reduction reactions.

Keywords: C. Electrical properties; E. Thermistors; $(Ba_{0.69}Pb_{0.31})TiO_3$; Ageing; Oxidation; Reduction

1. Introduction

Ferroelectricity is a phenomenon which was first discovered in single crystal materials (Rochelle salt) in 1921. A huge leap in the research on ferroelectric ceramics came in the 1950s, leading to the widespread use of $BaTiO_3$-based ceramics in various applications, such as capacitors, piezoelectric transducers, microwave filters, medical diagnostic transducers, positive temperature coefficient of resistivity (PTCR) sensors and switches, ultrasonic motors and so on. The PTCR sensor exhibits an anomalous increase in electrical resistivity near the ferroelectric Curie temperature, which is a grain boundary related phenomenon [1,2]. Many other ferroelectric ceramics have been developed for various operating temperatures, e.g. $(Ba,Sr)TiO_3$ for the temperatures lower than 120 °C and $(Ba,Pb)TiO_3$ for the temperatures higher than 120 °C. It has been a large interest in its fundamental behavior such as electronic transport properties, microstructure and lattice dynamics [3–7]. The stability of the electric properties is important for the practical application. But, in fact, the electrical properties of the PTCR elements would deteriorate during enduring under various conditions such as electric field, humidity and high temperature, etc. The PTCR effect becomes worse in H_2 atmosphere [8] and under N_2 atmosphere [9]. However, the PTCR characteristics improved when the element was held in oxidizing environment [10], and the resistivity was closely related to treatment temperature [11]. Ageing treatment in air is also one way to study the influence of temperature on the stability of the electrical properties of the ferroelectric ceramics [12]. Our recent results in aged $BaTiO_3$ ceramics revealed that the ageing characteristics depended on the type of dopant because of different electronegativity, besides the influence of the temperature [13]. The combination of interior oxidation and reduction reactions of the ceramics and the electronegativities of the doping elements could explain the abnormal ageing characteristics [12,13].

In this report, we will describe an abnormal ageing characteristics of $(Ba_{0.69}Pb_{0.31})TiO_3$ PTCR ceramic thermistors. The influence of ageing on the electrical properties will be discussed by considering interior oxidation and reduction reactions.

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2. Experimental

$(Ba_{0.69}Pb_{0.31})TiO_3$ ceramics was prepared by using $BaCO_3$ (99%, Merck Darmstadt, Germany), PbO and TiO_2 (99%, British Drug Houses Ltd., UK) by traditional solid sintering method. The Curie temperature of the sample is of about 235 °C. The powders were mixed by ball milling using distilled water for 18 h, followed by calcination at 900 °C for 1.5 h. Bi_2O_3 (99.8%, Merck Darmstadt, Germany) and Sb_2O_5 (99.8%, Kebo Lab, Sweden) were added by the concentration of 0.06 mol% Bi cation and 0.10 mol% Sb cation, respectively, in order to obtain the semiconducting behavior. The addition of 1 mol% Al_2O_3 and 1.4 mol% SiO_2 (95%, Fisher Scientific, USA) favors the formation of the liquid phase during sintering and can thus improve the properties of the ferroelectric ceramics. The mixture was mixed by ball milling for 18 h, and then dried at 120 °C. The dried powder was granulated by using polyvinyl alcohol and pressed into pellets of 15 mm diameter and thickness of about 4 mm. Sintering was performed at 1280 °C for 30 min in a box furnace (model VMK 1800, Linn High Therm GmbH, Germany) in air. All sintered samples were ground to a thickness of about 2.5 mm. Gold paste was painted on the sample surfaces, and then the samples were heated to 1020 °C for 1 h to make the good-contact electrode.

Ageing treatment was performed in air at temperatures of 170, 200, 250 and 300 °C, respectively. The room-temperature (20 °C) electrical resistivity (ρ_{room}) was measured by a standard ohmmeter before and after different treatments. The resistivity-temperature (ρ–T) curves were recorded at a heating rate of 1 °C/min before and after each treatment. Here the resistivity change (γ) is defined as

$$\gamma = \frac{\rho_{room} - \rho_0}{\rho_0} \times 100\%$$

where ρ_{room} is the room-temperature resistivity after various ageing treatment, ρ_0 is the room-temperature resistivity of the sample before ageing treatment.

3. Results

Fig. 1 shows the resistivity change versus ageing time of the samples aged at 170, 200, 250 and 300 °C, respectively. Two types of ageing characteristics can be summarized from these results. One, for the ageing temperatures of 250 and 300 °C, the room-temperature resistivity increased rapidly during the initial treatment stage, and then increased slightly and monotonously with ageing time in the later stage. Another, for the ageing temperatures of 170 and 200 °C, however abnormal ageing characteristics was obtained: the ρ_{room} decreased at the initial treatment stage; and then the ρ_{room} increased monotonously during the later ageing stage.

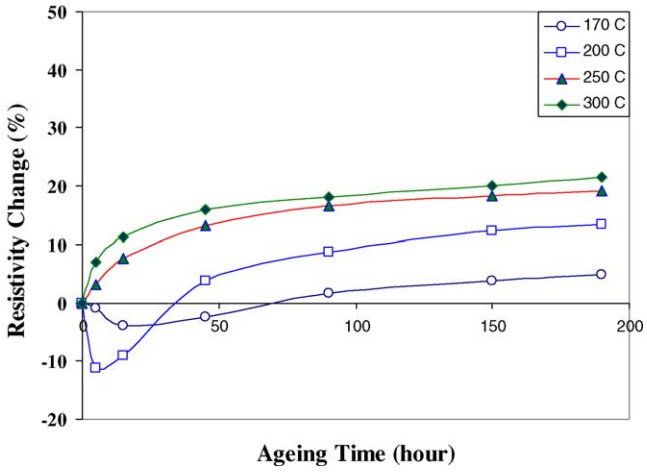

Fig. 1. Resistivity change versus the ageing time in $(Ba_{0.69}Pb_{0.31})TiO_3$ ceramic thermistors.

Fig. 2a shows ρ–T curves of a sample before ageing (open circles) and after ageing at 200 °C for 5 h (full squares). Both the low-temperature resistivity and the high-temperature resistivity of the aged samples are lower than before ageing. Similar results were also obtained in the sample aged at 170 °C.

Fig. 2b shows the temperature dependence of resistivity of a sample before (open circles) and after 250 °C ageing treatment for 170 h (full squares). It can be seen that both the low-temperature resistivity and the high-temperature resistivity of the aged samples are higher than before ageing treatment. Furthermore, a sample aged at 300 °C gave the same results.

4. Discussion

Generally, the room-temperature resistivity of a PTCR ceramic thermistor can be attributed to the resistivities of grain interiors, grain boundaries, electrode, and the interface between the electrode and the ceramic body. It is well known that, for the PTCR ceramic thermictors, the grain boundary is the major contributor to the high-temperature electrical resistivity [2,9]. As described above, two different results were obtained: (i) when the samples were aged at either 170 or 200 °C, the ρ_{room} decreased at the initial treatment stage, the high-temperature resistivities (specially, the maximum resistivity) were also lower than those before ageing (Figs. 1 and 2a); (ii) the ρ_{room} and high temperature resistivities of the samples aged at 250 and 300 °C were larger than those before ageing (Figs. 1 and 2b). This indicates that the room-temperature resistivity changes mainly must be related to the change of the status of grain boundaries instead of the electrode and the electrode/ceramic interface. The ageing characteristics may result from the thermal effect of the thermistors. The different ageing characteristics may be due to different ageing mechanisms. For example, desorption

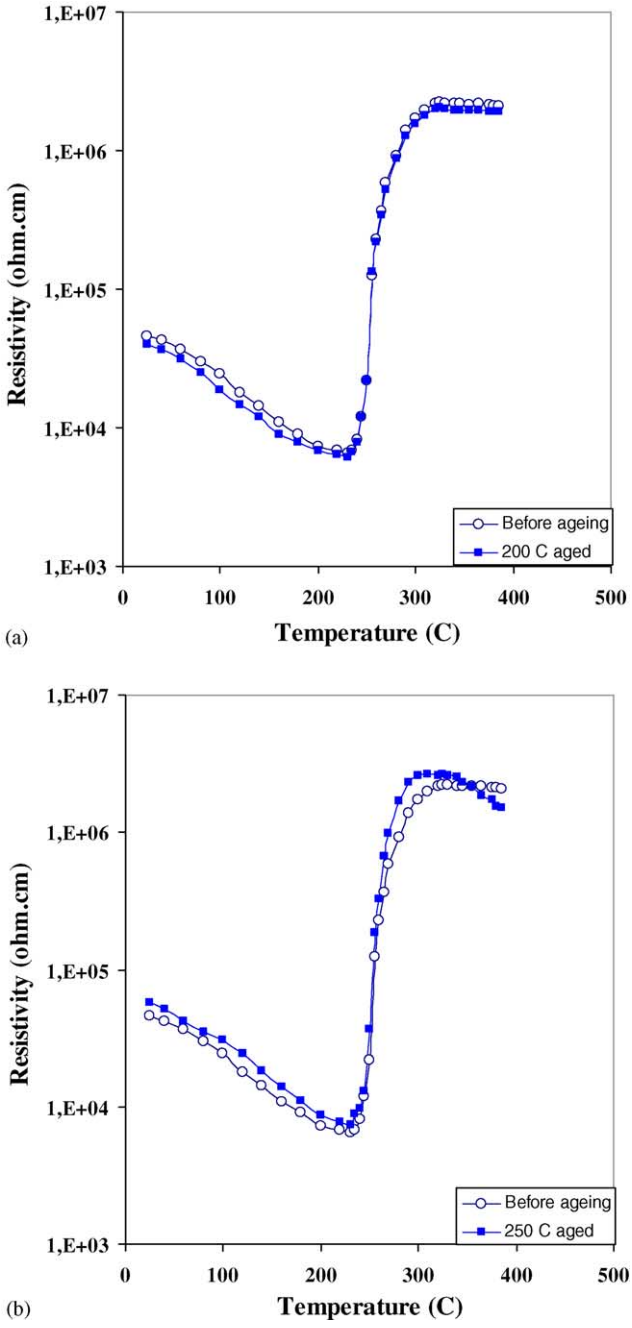

Fig. 2. Temperature dependence of resistivity of $(Ba_{0.69}Pb_{0.31})TiO_3$ ceramic thermistors: (a) before and after ageing for 5 h at 200 °C, (b) before and after ageing for 170 h at 250 °C.

and adsorption of oxygen probably lead to release and concentration of some captured electrons in grain boundaries, respectively, resulting in a resistivity change during ageing [1,7,12,13].

Following, we will first discuss the ageing characteristics of the samples aged at 250 and 300 °C by considering the oxidation mechanism. Then we will discuss an interior reduction mechanism for the abnormal ageing characteristics in the samples aged at 170 and 200 °C.

Tri-valent (Bi) and penta-valent (Sb) dopants act as donor dopants, and they replace A-site and B-site in ABO_3 perovskite structure, respectively, inside the grains of the samples [3,6,14]:

$$2Bi_2O_3 + 4BO_2 \rightarrow 4Bi_A^{\bullet} + 4B_B + 12O_o + O_2 + 4e' \quad (1a)$$

$$2Sb_2O_5 + 4AO \rightarrow 4Sb_B^{\bullet} + 4A_A + 12O_o + O_2 + 4e' \quad (1b)$$

where $Bi_A^{\bullet}$ and $Sb_B^{\bullet}$ are the positions the dopants occupy in the A-site (Ba- or Pb-site) and B-site (Ti-site), respectively, O_o is an oxygen ion at O-site, e' is an electron in the conduction band. At the same time, the oxygen absorption at the grain boundaries acts as an oxidizing reaction:

$$2BO_2 + O_2 \rightarrow 2B_B + 6O_O + 2V_A'' + 4h^{\bullet} \quad (2)$$

where V_A'' is a cation vacancy of A-site and $h^{\bullet}$ represents the holes contributing to conduction. This reaction is then gradually propagating into the interior of the grains. Combining this reaction with that in Eq. (1a), the following result is obtained:

$$2Bi_2O_3 + 6BO_2 + O_2 \rightarrow 4Bi_A^{\bullet} + 6B_B + 18O_o + O_2 + 4e' + 4h^{\bullet} \quad (3)$$

The electron compensation occurs as:

$$4e' + 4h' \rightarrow \text{nil} \quad (4)$$

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 (Sb), a similar reaction can occur by combining Eqs. (2) and (1b), and the same result as shown in Eq. (4) is obtained. On the other hand, the cation vacancy compensation reaction predominates at the grain boundaries:

$$2Bi_2O_3 + 6BO_2 \rightarrow 4Bi_A^{\bullet} + 6B_B + 18O_o + 2V_A'' \quad (5a)$$

$$2Sb_2O_5 + 2AO \rightarrow 4Sb_B^{\bullet} + 2A_A + 12O_o + 2V_A'' \quad (5b)$$

Reactions by Eqs. (4), (5a) and (5b) cause the concentration of the cation vacancies to increase and the electron concentration to decrease. Thus, the room-temperature resistivity of the aged samples increases. Because these reactions occur mainly at grain boundaries, it is reasonable to assume that the high temperature resistivity also increases after ageing as shown in Fig. 2b.

If the oxygen absorption at the grain boundaries only occurs during ageing, it is impossible to get the results after ageing at 170 and 200 °C shown in Fig. 2a. The resistivity decrease must result from the other reaction, which is suggested to be the reduction reaction occurring at grain boundaries:

$$2BO_2 - O_2 \rightarrow 2B_B + 2O_o + 2V_A'' - 4h^{\bullet} \quad (6)$$

Combining this reaction with that shown in Eqs. (1a) and (1b), the following result is obtained:

$$2Bi_2O_3 + 4BO_2 - O_2 \rightarrow 4Bi_A^{\bullet} + 4B_B + 12O_o + 4e' - 4h^{\bullet} \quad (7a)$$

$$2Sb_2O_5 + 4AO + 2BO_2 - O_2 \rightarrow 4Sb_B^{\bullet} + 4A_A + 2B_B + 16O_o + 4e' - 4h^{\bullet} \quad (7b)$$

Therefore, the concentration of hole electrons decreases at the grain boundaries during ageing and the concentration of conducting electrons increases, resulting in decreased room-temperature resistivity during the initial ageing stage. On the other hand, the free electrons will be captured by the barium vacancy at the grain boundary during the ferroelectric phase transformation when the samples are heated above the Curie temperature. This electron capturing process should respond the PTCR effect [8]. So the PTCR effect of the ceramics depends on the concentration of electrons and 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 ρ–T behavior shown in Fig. 2b.

5. Conclusion

1. For ageing temperatures of 170 and 200 °C, the room-temperature resistivity of $(Ba_{0.69}Pb_{0.31})TiO_3$ ceramic thermistors decreases at the initial ageing stage, and then increases with ageing time. The maximum resistivity and the resistivity rise in PTCR effect at the initial ageing stage became less than those before ageing;
2. For ageing temperatures of 250 and 300 °C, the room-temperature resistivity increases monotonously during the whole treatment stage. The maximum resistivity and the resistivity rise became larger than those before ageing.
3. The ageing characteristics are related to interior oxidation and reduction reactions. The oxidation leads to increased concentration of the cation vacancies and decreased electron concentration close to the grain boundaries, resulting in a simultaneously increased low-temperature and high-temperature resistivity; the reduction contributed to decreased concentration of hole electrons and increased concentration of conducting electrons at grain boundaries, resulting in decreased resistivities at low and high temperature.

References

[1] I.C. Ho, S.L. Fu, Effect of reoxidation on the grain-boundary acceptor-state density of reduced $BaTiO_3$ ceramics, J. Am. Ceram. Soc. 75 (1992) 728–730.
[2] J.K. Lee, J.S. Park, K.S. Hong, K.H. Ko, B.C. Lee, Role of liquid phase in PTCR characteristics of $(Ba_{0.7}Sr_{0.3})TiO_3$ ceramics, J. Am. Ceram. Soc. 85 (2002) 1173–1179.
[3] S. Urek, M. Drofenik, PTCR behavior of highly donor doped $BaTiO_3$, J. Eur. Ceram. Soc. 19 (1999) 913–916.
[4] N.H. Chan, D.M. Smyth, Defect chemistry of donor-doped $BaTiO_3$, J. Am. Ceram. Soc. 67 (1985) 285–288.
[5] C.H. Lai, Y.Y. Lu, T.Y. Tseng, Calculations and models of grain-boundary acceptor states for (Ba, Pb) TiO_3 positive temperature coefficient ceramics, J. Appl. Phys. 74 (1993) 3383–3388.
[6] E. Bzozowski, M.S. Castro, Conduction mechanism of barium titanate ceramics, Ceram. Int. 26 (2000) 265–269.
[7] D. Makovec, M. Drofenik, Microstructural changes during the reduction/reoxidation process in donor-doped $BaTiO_3$ ceramics, J. Am. Ceram. Soc. 83 (2000) 2593–2599.
[8] H. Igarishi, S. Hayakawa, K. Okazaki, PTCR behavior of semiconductive ceramics under reduced atmosphere, Jpn. J. Appl. Phys. Suppl. 20 (1981) 135–138.
[9] G.H. Konker, Determination of the potential barriers height in barium titanate ceramics, Solid State Electron. 27 (1984) 935.
[10] T.Y. Tian, W.F. Carlson, Influence of oxygen partial pressure on properties of semiconducting barium titanate, J. Am. Ceram. Soc. 46 (1963) 297–298.
[11] S.L. Jiang, D.X. Zhou, S.P. Gong, X.Y. Guan, Effect of heat-treatment under oxygen atmosphere on the electrical properties of $BaTiO_3$, Microelectron. Eng. 66 (2003) 896–903.
[12] B.Y. Li, D.X. Zhou, D.L. Zhang, S.L. Jiang, Analysis on the aging characteristics of PTCR of donor-doped barium titanate, Mater. Sci. Eng. B99 (2003) 394–398.
[13] Z.C. Li, B. Bergman, Electrical properties and ageing characteristics of $BaTiO_3$ ceramics doped by single dopants, J. Eur. Ceram. Soc. 25 (2005) 441–445.
[14] J.Q. Qi, Z.L. Gui, Y.L. Wang, Q. Zhu, Y.J. Wu, L.T. Li, The PTCR effect in $BaTiO_3$ ceramics modified by donor dopant, Ceram. Int. 28 (2002) 141–143.