Studies on semiconductive $(Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1})O_3$ ceramics

SHEN-LI FU, IN-CHYUAN HO, LIH-SHAN CHEN
Department of Electrical Engineering, National Cheng Kung University, Tainan, Taiwan

In order to produce semiconductive $(Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1})O_3$ ceramics (BSZT), providing low resistivity for boundary-layer capacitor applications, a controlled valency method and a controlled-atmosphere method were applied and studied. In the controlled-valency method, trivalent ions (La^{3+}, Sb^{3+}) and pentavalent ions (Nb^{5+}, Sb^{5+}, Ta^{5+}) were doped into BSZT ceramics, while in the controlled-atmosphere method, samples were sintered in air and a reducing atmosphere. The doped BSZT ceramics sintered in the reducing atmosphere showed much lower resistivities and smaller temperature coefficient of resistivity (TCR) than those sintered in air, indicating that low partial pressure of oxygen will increase the solubility of the donor dopant and enhance the grain growth. In addition, a small negative TCR at low temperature, as well as a small positive TCR at higher temperature, are also observed for specimens fired in a reducing atmosphere. The former is attributed to the semiconductive grain and the latter to the small barrier layer formed at the grain boundary.

1. Introduction

It is well known that a grain-boundary barrier layer (GBBL) capacitor may be fabricated by diffusing painted oxide into the grain boundary of semiconductive ceramics. The $BaTiO_3$-based GBBL capacitor was designed by Glaister [1]. In order to lower the grain interior resistivity, which will shift the capacitance dispersion to higher frequency, and to promote the stability of bias dependence, $SrTiO_3$ is widely used as the basic composition [2, 3]. However, the high sintering temperature is still a disadvantage and the non-ferroelectric composition from the solid solution of (Ba, Sr)TiO_3 [4] is thus adopted. To improve further the temperature and bias stability, ZrO_2 was added to diffuse the phase transition [5] and the (Ba_xSr_{1-x}) – $(Ti_yZr_{1-y})O_3$ ceramics were thus fabricated [6]. In this study, a composition of $(Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1})O_3$, which is near the morphotropic phase boundary (MPB) [7], is adopted as the basic composition to improve its electrical characteristics.

Numerous studies on the effect of various rare-earth ions on the semiconducting barium titanate have been reported [8–10]. In order to account for the conductivity of the donor-doped ceramics, two conduction models have been proposed: the hopping conduction and the band conduction [11]. However, when sintering is conducted in a low partial pressure of oxygen atmosphere, the reduction behaviour results in an imbalance in the ideal cation-to-anion ratio and thus leads to nonstoichiometry, in which oxygen vacancies are found to dominate the semiconductive properties [12].

The purpose of this study was to determine the predominant factors and their effects in fabricating the semiconducting BSZT ceramics. Both the controlled valency method, by doping trivalent or penta- valent ions, and the controlled atmosphere method, by firing the samples in air or a reducing atmosphere, were undertaken in this study.

2. Experimental procedure

The raw materials – $BaCO_3$, $SrCO_3$, TiO_2, and ZrO_2 (Reagent grade, Merck) – were weighed in appropriate proportions to prepare BSZT ceramics. Into this basic composition, suitable amounts of trivalent dopants (La_2O_3 and Sb_2O_3) and pentavalent dopants (Sb_2O_5, Nb_2O_5, and Ta_2O_5) were blended as donor dopants. Small amounts of TiO_2 and SiO_2 were also added to promote sintering.

After blending thoroughly in a ball mill with distilled water for about 4 h, the mixture was dried and then calcined at 1100° C for 2 h. Before grinding the calcined powder for pressing and then sintering, it was subjected to CuK_α X-ray diffraction (XRD) analysis to ensure the formation of perovskite structure.

The calcined powder was then pressed into disc-shaped samples under a pressure of $250\,kg\,cm^{-2}$. The sintering process was conducted at 1380° C for 4 h. Samples containing different dopants (La_2O_3, Sb_2O_3, Nb_2O_5, Sb_2O_5, Ta_2O_5) and with different amounts of dopant were sintered either in air or in a reducing atmosphere (98% N_2 + 2% H_2) to examine the effect of sintering atmospheres.

The resistivities of the sintered samples were measured with a digital multimeter. Both the relationships between the resistivity and ambient temperature, and its relationships with doping amounts and sintering atmospheres were examined. A temperature-programmable testing apparatus (KATO SE43CRA) was used to control the testing temperature. In order to examine the microstructures, which are known to affect the electrical properties obtained, scanning
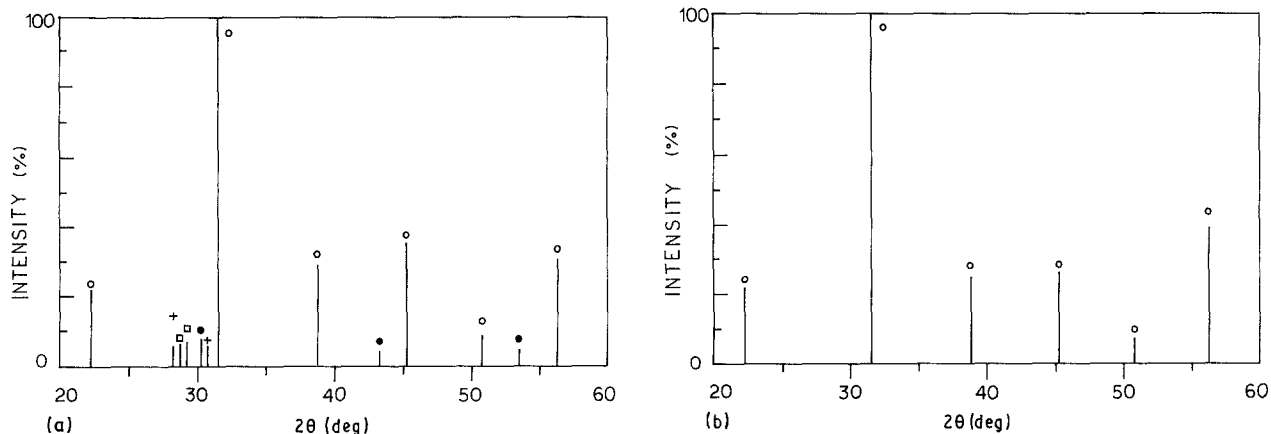
Figure 1 X-ray diffraction pattern of BSZT (a) calcined at $1100°$C for 2 h, (b) lanthanum-doped sintered at $1380°$C for 4 h in 98% N_2 + 2% H_2. (O) Perovskite, (●) $BaZrO_3$, (+) $BaTi_3O_7$, (□) $Ba_6Ti_{17}O_{40}$.

electron microscopic (SEM) observations were also made.

3. Results and discussion

In the $(Ba_{0.8}Sr_{0.2})(Ti_{0.9}Zr_{0.1})$ ceramic, reactants of $BaCO_3$, $SrCO_3$, TiO_2, and ZrO_2 are included. Many reactions may occur between carbonates and oxides. The most possible reaction is the formation of $BaTiO_3$ structure, which can be obtained at $1000°$C [13]. The temperature required for the formation of $SrTiO_3$, $BaZrO_3$ and $SrZrO_3$ is higher than that of barium titanate [14].

The XRD pattern of the powder calcined at $1100°$C for 2 h is depicted in Fig. 1a, which confirms the formation of perovskite structure. Nevertheless, second phases, including $BaZrO_3$, $BaTi_3O_7$ and $Ba_6Ti_{17}O_{40}$, are formed. Fig. 1b illustrates the perovskite structure pattern of specimens which were sintered in a reducing atmosphere at $1380°$C for 4 h with 0.2 mol % La_2O_3 dopant. From Fig. 1b, it can be seen that the diffraction peaks of the second phases have all disappeared, showing a complete reaction. For specimens with the same dopants but sintered in air at $1380°$C, no difference was found in the XRD patterns, compared to those shown in Fig. 1b. Thus complete solid solutions were formed under both conditions, i.e. sintering in a reducing atmosphere and in air, at $1380°$C, respectively.

The relationships between the logarithmic values of resistivities and the amounts of dopants are shown in Fig. 2a, where the samples are sintered in air at

$1380°$C for 4 h. Fig. 2a shows a minimum value of resistivity for each kind of dopant at the concentration of about 0.2 mol %. The niobium- and lanthanum-doped samples show the lowest resistivity of the five dopants at 0.2 mol % dopant concentration. The minimum resistivity obtained at 0.2 to 0.3 mol % dopant is thought to be due to the solubility limit, similar to that found in $BaTiO_3$ by other authors [15–17], which shows an increasing resistivity when the controlled valency substitution mechanism is saturated. Because the enthalpy required for substitution depends on the vicinity of the ionic radii and the valencies of the dopant and the substituted atom [18], Nb^{5+} and La^{3+} are thus expected to achieve the most effective substitution, and show the lowest resistivity among the pentavalent and trivalent dopants, respectively. In addition, because the donor levels of $La_{Ba}^{.}$ and $Nb_{Ti}^{.}$ in $BaTiO_3$, which are 0.1 and 0.12 eV, respectively, calculated by Seuter [19], the lower resistivity of the lanthanum-doped sample compared to that of the niobium-doped sample as found in Fig. 2a, is expected.

However, when the samples are sintered in a reducing atmosphere, as shown in Fig. 2b, a much lower resistivity value is found even with a dopant level of only 0.1 mol %, and a nearly stable resistivity is observed for doping levels of 0.2 mol % or higher. This shows that the formation of oxygen vacancies predominates the electrical properties when compared to the substitution mechanism. The solubility limit of the dopant is believed to be broadened when the
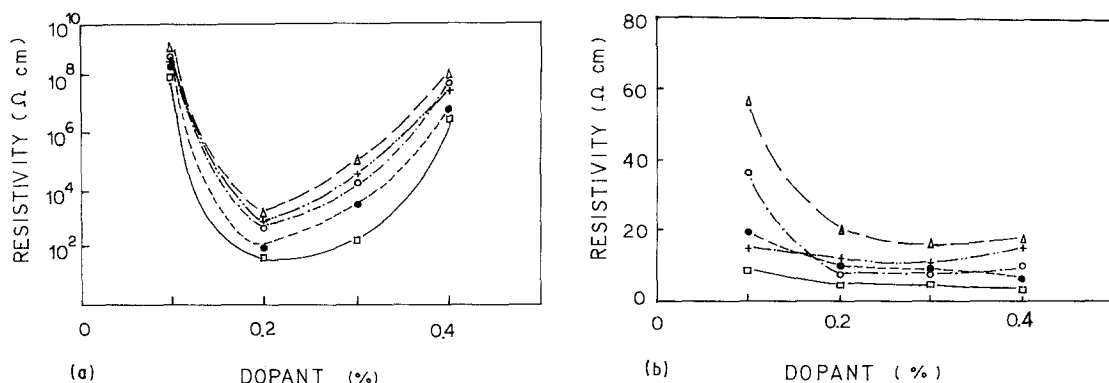

Figure 2 Resistivity of semiconductive BSZT with various additional oxides as a function of doping level after (a) sintering at $1380°$C for 4 h in air, (b) sintering at $1380°$C for 4 h in 98% N_2 + 2% H_2. (□) La, (O) Nb, (+) Sb [3], (●) Ta, (△) Sb [5].
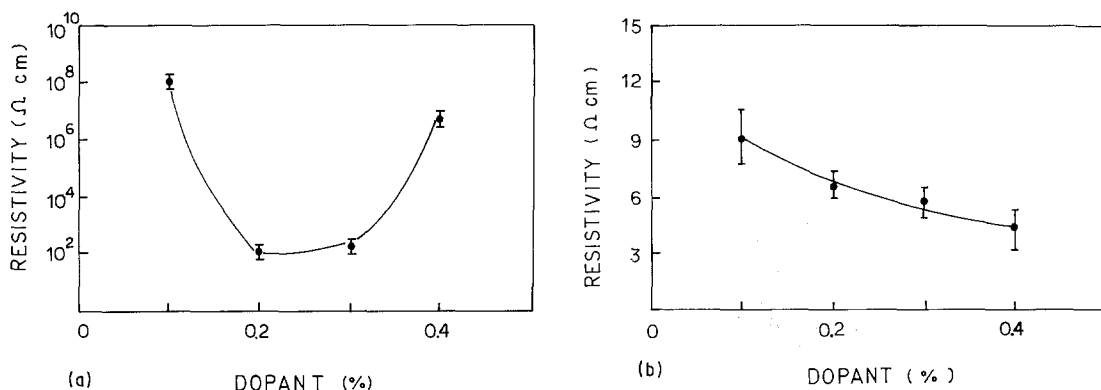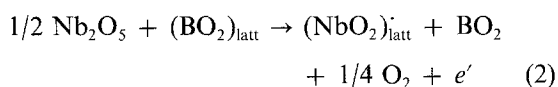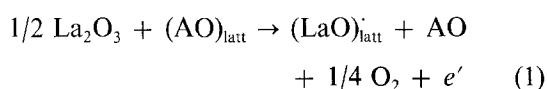
Figure 3 Resistivity of semiconductive lanthanum-doped BSZT as a function of doping level: (a) sintered at 1380° C for 4 h in air; (b) sintered at 1380°C for 4 h in 98% N_2 + 2% H_2.

partial pressure of oxygen is lowered. At low partial pressure of oxygen, grain growth and donor incorporation are not hindered in $BaTiO_3$ [20, 21], thus, similarly, in this case it is expected that a higher amount of dopant can be incorporated. The substitutional reaction during grain growth can be expressed as

$$1/2\ La_2O_3 + (AO)_{latt} \rightarrow (LaO)_{latt}^{\cdot} + AO$$
$$+ 1/4\ O_2 + e' \quad (1)$$
$$1/2\ Nb_2O_5 + (BO_2)_{latt} \rightarrow (NbO_2)_{latt}^{\cdot} + BO_2$$
$$+ 1/4\ O_2 + e' \quad (2)$$

where A and B represent the metallic atom at the A site (barium or strontium) and the B site (titanium or zircon) in the perovskite structure, respectively. When sintering in a reducing atmosphere, the Equations 1 and 2 will tend towards the right due to the low partial pressure of oxygen. This leads to an increasing incorporation of dopant and faster grain growth.

The relationship of resistivity to donor dopant is shown in Figs 3 and 4 for the La_2O_3- and Nb_2O_5-doped BSZT ceramics, respectively. Both show a much lower resistivity for samples sintered in a reducing atmosphere. While the microstructures of the 0.1 and 0.3 mol % lanthanum-doped samples shown in Fig. 5 reveal enhanced grain growth in a reducing atmosphere compared with those sintered in air. The broadened solubility limit of the dopant and the increased concentration of electrons are thus confirmed.

Although the solubility limit is raised by sintering in a low partial pressure of oxygen atmosphere, the grain growth of the donor-doped BSZT ceramics depends on the amount of dopant even in a reducing atmosphere. It seems that the role of grain-growth inhibitor of donor-dopant in $BaTiO_3$ [22] is still effective in the BSZT ceramics, for both sintering in air and in a reducing atmosphere. As seen in Fig. 5, the grain size of the 0.3 mol % La_2O_3-doped BSZT ceramics is smaller than in the 0.1 mol % La_2O_3-doped one, either sintered in air (Fig. 5a, b) or in a reducing atmosphere (Figs 5c, 5d). It is thought that the excess dopant will segregate at the grain boundary, which inhibit the grain growth due to the decrease in boundary mobility during sintering [23, 24].

In order to ascertain the effect of sintering atmosphere on resistivity of BSZT ceramics, and to understand its temperature stability, the resistivity values of lanthanum- and niobium-doped BSZT ceramics, sintered either in air or in a reducing atmosphere, were examined by measuring the resistivities in the temperature range -20 to $+100°C$. Fig. 6 shows the results of the lanthanum-doped BSZT, with doping levels of 0.2 and 0.3 mol %, fired in air and in a reducing atmosphere, respectively. Figs 7a and b show the temperature dependence of resistivities for lanthanum- and niobium-doped BSZT ceramics sintered in a reducing atmosphere.

A positive temperature coefficient of resistivity is observed for samples sintered in air. In general, a negative TCR is first found and then a positive TCR is observed, for samples sintered in a reducing
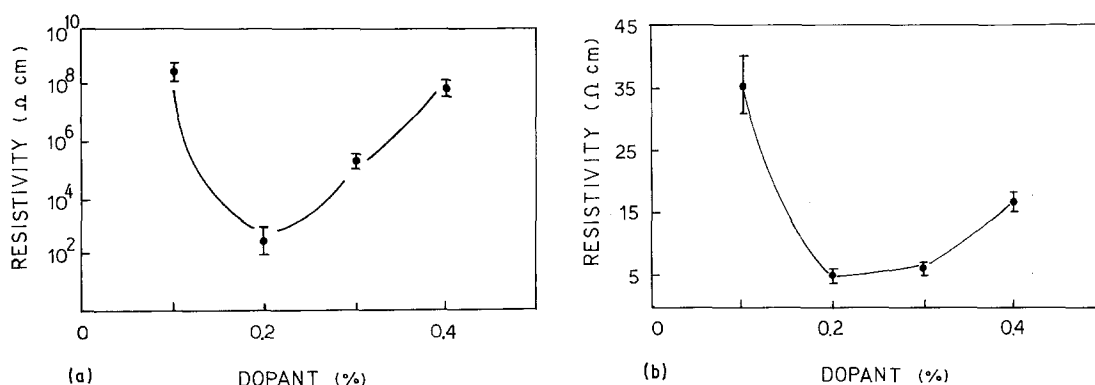

Figure 4 Resistivity of semiconductive niobium-doped BSZT as a function of doping level: (a) sintered at 1380° C for 4 h in air; (b) sintered at 1380°C for 4 h in 98% N_2 + 2% H_2.
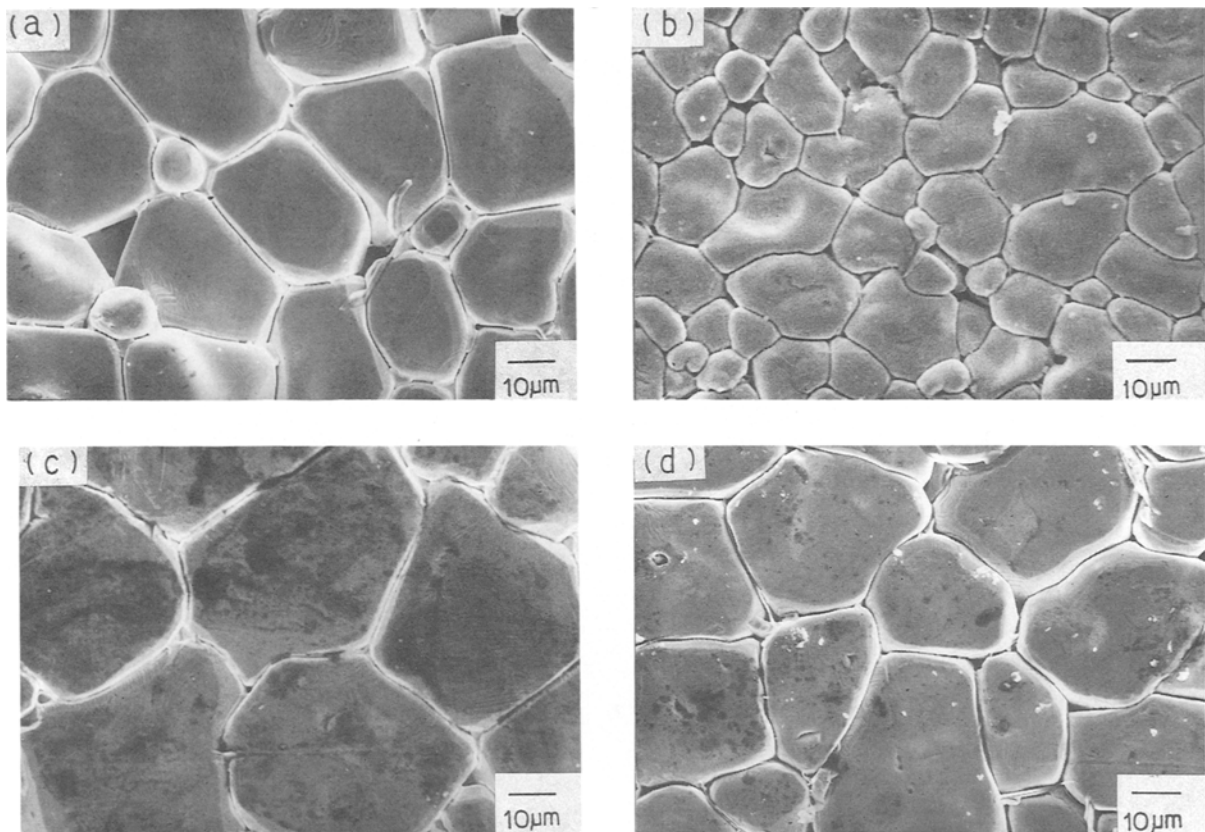
Figure 5 Scanning electron micrographs of the surface of semiconductive lanthanum-doped BSZT sintered at 1380°C for 4 h with (a) 0.1 mol % La_2O_3, in air, (b) 0.3 mol % La_2O_3, in air (c) 0.1 mol % La_2O_3 in 98% N_2 + 2% H_2, (d) 0.3 mol % La_2O_3, in 98% N_2 + 2% H_2.

atmosphere, when the temperature is raised from -20 to 100°C. It is well known that a naturally occurring semiconductor has a negative temperature coefficient of resistivity [25]. Thus the positive TCR effect can only be realized and attributed to the boundary effect. A potential barrier, which is similar to that observed in PTC barium titanate [26], is believed to be the reason, except that the slope is not as steep because the phase transition of the BSZT ceramics is diffused. However, for the specimens sintered in a reducing atmosphere, the barrier effect is diminished, which is only effective at elevated temperature and is negligible at low temperature. Thus, a negative TCR is observed at low temperature owing to its inherent semiconducting property. As the temperature rises, the barrier effect gradually becomes apparent due to the disappearance of spontaneous polarization as phase transition occurs. Such a superposition of small PTCR and NTCR effect produces a good temperature stability in BSZT ceramics sintered in a reducing atmosphere, which together with the low electrical resistivity, makes it a good candidate for a semiconductive substrate in boundary-layer capacitor application.

4. Conclusions

From the experimental results discussed above, conclusions are deduced for the BSZT ceramics as follows:

1. To produce semiconductive BSZT ceramics, controlled valency and controlled atmosphere methods can be used. Both methods may be used to lower its resistivity further.

2. With the controlled valency method, La^{3+} is the most effective dopant for the BSZT ceramics, while Nb^{5+} is next to it. In general, 0.2 mol % is adequate for this method.

3. With the controlled atmosphere method, a low partial pressure of oxygen will increase the solubility of the donor dopant and enhance the grain growth during sintering.

4. The grain growth will be inhibited by excess donor dopant, either sintered in air or in a reducing atmosphere. The grain size, with the same amount of dopant, is larger for sintering in a reducing atmosphere than that in air.

5. The released oxygen might contribute to the trapping states at grain boundaries and form a small
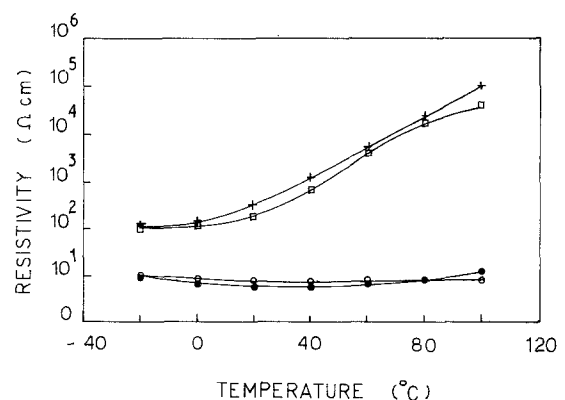

Figure 6 Temperature dependence of resistivity of lanthanum-doped BSZT sintered at 1380°C for 4 h in air or in 98% N_2 + 2% H_2. ($\square$) 0.2 mol % in air, ($+$) 0.3 mol % in air, ($\bigcirc$) 0.2 mol % in 98% N_2 + 2% H_2, ($\bullet$) 0.3 mol % in 98% N_2 + 2% H_2.
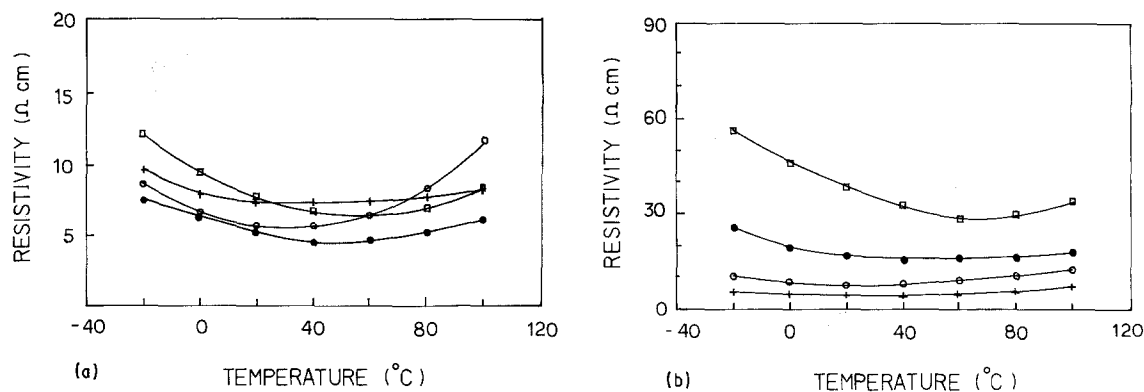
4045

Figure 7 Temperature dependence of resistivity of donor-doped BSZT sintered at 1380° C for 4 h in 98% N_2 + 2% H_2 for (a) lanthanum, (b) niobium dopant. (□) 0.1 mol %, (+) 0.2 mol %, (O) 0.3 mol %, (●) 0.4 mol %.

barrier layer in the Heywang model, which results in a small positive TCR effect.

6. Owing to the diffused-phase transition, the reduced BSZT ceramics shows a good temperature stability of resistivity. However, small NTCR and PTCR effects are both observed in a different temperature range. The former is attributed to the semiconductive grains and the latter to the small barrier at the grain boundaries.

Acknowledgement

References

1. R. M. GLAISTER, Brit. Pat. 849 938, 28 September 1960.
2. S. WAKU, *Rev. Electr. Commun. Lab.* **15** (1967) 689.
3. N. YAMAOKA, *Ceram. Bull.* **65** (1986) 1149.
4. N. YAMAOKA and T. MATSUI, in "Advances in Ceramics", Vol. 1, edited by L. M. Levinson (American Ceramic Society, Columbus, Ohio, 1981) p. 232.
5. D. HENNINGS and A. SCHNELL, *J. Amer. Ceram. Soc.* **65** (1982) 539.
6. S. L. FU, C. F. YANG and S. Y. CHENG, in Proceedings of the 5th International Microelectronics Conference, (ISHM Japan Chapter) Tokyo, May 1988, p. 201.
7. D. BARB, E. BĂRBULESCU and A. BĂRBULESCU, *Phys. Status Solidi* (a) **74** (1982) 79.
8. O. SABURI, *J. Phys. Soc. Jpn* **14** (1959) 1159.
9. J. B. MacCHESNEY, P. K. GALLAGHER and F. V. DIMARCELLO, *J. Amer. Ceram. Soc.* **46** (1963) 197.
10. V. J. TENNERY and R. L. COOK, *ibid.* **44** (1961) 187.
11. S. SHIRASAKI, M. TSUKIOKA, H. YAMAMURA and H. OSHIMA, *Solid State Commun.* **19** (1976) 721.
12. N. H. CHAN and D. M. SMYTH, *J. Electrochem. Soc.* **128** (1981) 1762.
13. A. AMIN, M. A. SPEARS and B. M. KULWICKI, *J. Amer. Ceram. Soc.* **66** (1983) 733.
14. G. H. JONKER, *ibid.* **41** (1958) 390.
15. R. WERNICKE, *Phys. Status Solidi* (a) **47** (1978) 139.
16. T. FUKAMI and H. TSUCHIYA, *Jpn. J. Appl. Phys.* **18** (1979) 735.
17. N. H. CHAN, M. P. HARMER and D. M. SMYTH, *J. Amer. Ceram. Soc.* **69** (1986) 507.
18. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, "Introduction to Ceramics", 2nd Edn. (Wiley, New York, 1976) p. 900.
19. A. M. J. H. SEUTER, *Philips Res. Rep. Suppl.* **3** (1974) 45.
20. M. DROFENIK, *J. Amer. Ceram. Soc.* **70** (1987) 311.
21. M. DROFENIK, A. POPVIC and D. KOLAR, *Amer. Ceram. Soc. Bull.* **63** (1984) 702.
22. K. S. MAZDIYASNI and L. M. BROWN, *J. Amer. Ceram. Soc.* **54** (1971) 539.
23. K. H. YOON, H. W. CHEONG, S. O. YOON and N. Y. LEE, *Mater. Res. Bull.* **23** (1988) 1527.
24. W. D. KINGERY, H. K. BOWEN and D. R. UHLMANN, "Introduction to Ceramics", 2nd Edn (Wiley, New York, 1976) p. 456.
25. M. TSUKIOKA, J. TANAKA, Y. MIYAZAWA and Y. MORI, *Solid State Commun.* **32** (1979) 223.
26. W. HEYWANG, *J. Mater. Sci.* **6** (1971) 1214.