Available online at www.sciencedirect.com

Journal of the European Ceramic Society 30 (2010) 555–559

www.elsevier.com/locate/jeurceramsoc

# Fabrication and positive temperature coefficient of resistivity properties of semiconducting ceramics based on the $BaTiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ system

H. Takeda[a,*], H. Harinaka[b], T. Shiosaki[b], M.A. Zubair[c], C. Leach[c],
R. Freer[c], T. Hoshina[a], T. Tsurumi[a]

[a] *Graduate School of Science and Engineering, Tokyo Institute of Technology, 2-12-1 Ookayama, Meguro, Tokyo 152-8552, Japan*
[b] *Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama-cho 8916-5, Ikoma, Nara 630-0192, Japan*
[c] *Materials Science Centre, School of Materials, University of Manchester, Manchester M1 7HS, UK*

**Abstract**

$BaTiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ (BT–BKT) ceramics have a low $\rho_{RT}$ of $10^1$–$10^2\ \Omega\,cm$ like that of semiconducting materials prepared by sintering in a $N_2$ flow with low $O_2$ concentration. By annealing in air, the BT–BKT ceramics show an abrupt increase in their resistivity near the $T_c$, namely, a positive temperature coefficient of resistivity (PTC) characteristic. With 5 mol% and 10 mol% BKT added to BT, the ceramics display the PTC characteristic at 155 °C and 165 °C, respectively. Furthermore, the ratio, $\rho_{max}/\rho_{RT}$, of the highest resistivity ($\rho_{max}$) and the resistivity at room temperature ($\rho_{RT}$) of the ceramics increased on adding a small amount of Mn and a sintering aid.

*Keywords:* $BaTiO_3$ and titanates; PTC devices

## 1. Introduction

Barium titanate ($BaTiO_3$: BT)-based semiconducting ceramics are widely utilized as materials with a positive temperature coefficient of resistivity (PTC).[1] Numerous applications, such as current limiters, constant temperature heaters and thermal sensors, make use of this PTC effect.[2] It is well known that the PTC property is exhibited near the ferroelectric Curie temperature, $T_c$. The control of the $T_c$ is easily achieved by substituting $Sr^{2+}$ or $Pb^{2+}$ for $Ba^{2+}$.[3] For commercial PTC heater devices, $Pb^{2+}$ has been considered as the only element to achieve $T_c > 130$ °C. Actually, the $BaTiO_3$–$PbTiO_3$ system shows excellent PTC characteristics.[4] Lead-free materials recently have been demanded from the viewpoint of environmental protection. For this reason, PTC thermistor materials without the lead element have been developed recently. Takeda et al.[5] has proposed a semiconducting $BaTiO_3$–$(Bi_{1/2}Na_{1/2})TiO_3$ (BT–BNT) system as a new lead-free PTC thermistor material with a $T_c > 130$ °C. An excellent PTC property at about 170 °C has been demonstrated in lanthanum (La) doped BT–BNT ceramics. Subsequently, Shimada et al.[6] reported that 8.8 mol% BNT added to a sample sintered in a $N_2$ flow displayed an especially superior PTC characteristics, comparable to those of lead-containing PTC materials by optimizing the preparation conditions. Furthermore, Xiang et al.[7,8] reported the ceramics prepared with 20 mol% BNT additions, and the obtained BT–BNT ceramics sintered in a $N_2$ flow showed a resistivity anomaly starting at about 210 °C. These reports indicate that the BT–BNT system shows an excellent PTC characteristics. Therefore, incorporation of the BNT phase into the semiconducting BT-based ceramics is considered an effective way to increase the temperature of resistivity anomaly. In order to raise the temperature of resistivity anomaly to a high temperature, we have investigated another candidate for a lead-free end member compound, namely bismuth potassium titanate, $(Bi_{1/2}K_{1/2})TiO_3$ (BKT) with a $T_c = 380$ °C,[9] which is higher than the $T_c$ of BNT ($T_c = 320$ °C).

In this study, we report the synthesis and electrical properties of BT–BKT ceramics with a BT-rich composition. We show the PTC characteristics of the ceramics after sintering in a $N_2$ atmosphere with low $O_2$ concentration and subsequent annealing in air and propose a new PTC material without lead as well as one having a higher $T_c$. We also describe a process of improving the PTC properties by adding a small amount of Mn and a sintering aid and also the characterization of the BT–BKT ceramics.

---

* Corresponding author. Fax: +81 3 5734 2514.
*E-mail address:* htakeda@ceram.titech.ac.jp (H. Takeda).

0955-2219/$ – see front matter © 2009 Elsevier Ltd. All rights reserved.
doi:10.1016/j.jeurceramsoc.2009.08.009

## 2. Experimental procedure

The conventional ceramic fabrication technique was used to prepare $Ba_{1-x}(Bi_{1/2}K_{1/2})_xTiO_3$ (abbreviated BBKT100$x$) solid solution ceramics. Powders of $BaCO_3$, $TiO_2$, and $K_2CO_3$ with 99.99% purity and $Bi_2O_3$ with 99.999% purity were used as the starting raw materials. These oxide or carbonate powders were mixed in ethanol with yttrium-stabilized zirconia balls by ball milling for 10 h followed by calcining at 800 °C for 2 h and 1000 °C for 2 h in an alumina crucible. After granulation with a binder (2 wt% polyvinyl alcohol), these powders were uniaxially pressed into disks of 13 mm diameter and about 1 mm thickness at a pressure of 190 MPa. These disk samples were sintered at 1290–1320 °C for 2 h in air and 1300–1350 °C for 2 h in a $N_2$ flow with low $O_2$ concentration. The resulting samples did not show PTC properties, as will be explained later. Hence, we annealed the as-sintered ceramics in air to obtain the PTC property, which means an abrupt increase in resistivity over the Curie temperature. As-sintered samples were heated to the desired temperature at 20 °C min$^{-1}$, held at that temperature for the required time and then cooled down to room temperature at the natural cooling rate of the furnace. Furthermore, in order to improve the PTC property, the ceramics were sintered after adding 5 mol% of a mixed powder of $Al_2O_3$:$SiO_2$:$TiO_2$ = 4:9:3 mole ratio (abbreviated AST) and/or 0.1 wt% $MnCO_3$.[10,11] In this paper, the ceramics with added AST and Mn are defined as BBKT100$x$-ASTMn. For comparison, the BT and Nb-doped BT ceramics with a chemical composition of $BaTi_{0.999}Nb_{0.001}O_3$ were fabricated by sintering in a $N_2$ flow and in air at 1400 °C for 2 h, respectively.

The phase identification of the sintered ceramics was determined using a powder X-ray diffractometer (XRD, MAC Science M18XHFVA). The densities of the ceramics were measured by the Archimedes method using distilled water. The sintered surfaces of the samples were observed using a scanning electron microscope (SEM, TOPCON SM-300) in order to investigate the microstructure. For the measurement of electrical properties, Ag–Zn paste was applied to both surfaces of the samples as an electrode and fired at 500 °C for 10 min. The temperature dependence of the dielectric properties was measured using an impedance/gain phase analyzer (Agilent HP4194A) from room temperature to 500 °C at a heating rate of 2 °C min$^{-1}$. The temperature dependence of resistivity was measured using a digital resistance meter (ADVANTEST R8340). Quantitative chemical analysis of the samples was carried out using an electron probe microanalyzer (EPMA, SHIMADZU EPMA-1610) equipped with a wavelength dispersive X-ray spectrometer (WDS).

## 3. Results and discussion

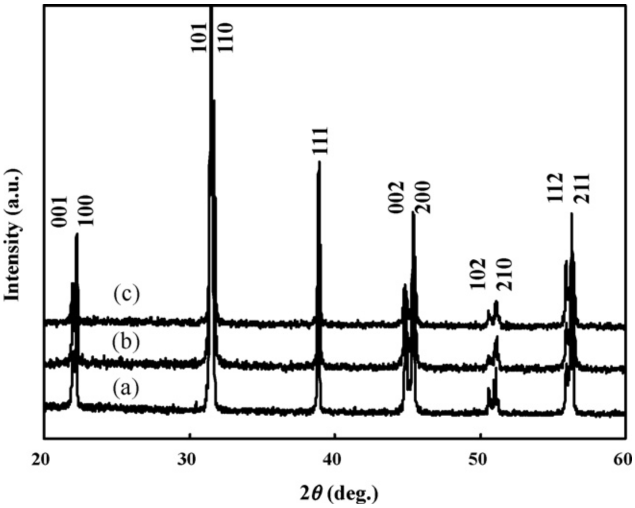

Fig. 1. Powder X-ray diffraction patterns of (a) pure BT (b) BBKT5 and (c) BBKT10 sintered in a $N_2$ flow.

Fig. 1 shows the X-ray powder diffraction patterns of the pure BT, BBKT5 and BBKT10 ceramics fabricated by sintering in a $N_2$ flow with low $O_2$ concentration. At room temperature, the diffraction patterns of the BBKT ceramics show a tetragonal structure similar to that of the pure BT ceramics. All diffraction peaks of the BBKT samples were indexed according to the BT standard sample (ICCD No. 05-0626), indicating no formation of by-products. On the basis of the XRD results, the calculated lattice constants of the BBKT5 and BBKT10 are $a = 0.3991(4)$ nm, $c = 0.4038(8)$ nm and $a = 0.3989(5)$ nm, $c = 0.4039(4)$ nm, respectively. In comparison with the lattice constants of the pure BT ($a = 0.3994(6)$ nm, $c = 0.4038(0)$ nm), the values of the $c$-axis of the BBKT ceramics are almost the same as those of the pure BT; however, a slight decrease is found in the value of the $a$-axis. The fact that the lattice constants of the BBKT ceramics change with the BKT content demonstrates that the BT and BKT phases have formed a solid solution.

Fig. 2 shows the temperature dependence of the dielectric constant, $\varepsilon_s$, and dielectric loss, $\tan\delta$, of the BBKT100$x$ ($x = 0$, 0.05 and 0.1) ceramics sintered in air measured at a frequency of 10 kHz. The peak of the pure BT is sharp; however, the shape of the peaks gradually became broad and the $\varepsilon_s$ at room temperature decreased with the increasing amount of the BKT. The $T_c$ shifted to a higher temperature with increasing amount of BKT. The $T_c$ values of the BBKT5 and BBKT10 were 170 °C and 180 °C, respectively.

According to the work of Takeda et al.,[5] Shimada et al.,[6] and Xiang et al.,[7,8] the BBKT5 ceramics were sintered in a $N_2$ flow with low $O_2$ concentration, and their temperature dependences of resistivity were investigated. The BBKT5 ceramics sintered at 1350 °C showed a low $\rho_{RT}$ of $10^1$–$10^2$ Ω cm but displayed a very small resistivity anomaly at about 155 °C. This feature is the same as that of pure BT ceramics but is different from that in BT–BNT system. The origin of the difference between the BT–BNT and BT–BKT systems requires further investigation. It has been reported that the BT-based semicondouting, not semicondouting ceramics sintered in a reducing atmosphere show a clear PTC property after annealing in air.[12–14] Hence the as-sintered semiconducting samples, BBKT5 ceramics sintered at 1350 °C in a $N_2$ flow with low $O_2$ concentration were annealed in air at various soaking temperatures and times. Fig. 3 shows the ratio, $\rho_{max}/\rho_{RT}$, of the highest resistivity ($\rho_{max}$) and the resistivity at room temperature ($\rho_{RT}$) of the ceramics annealed at

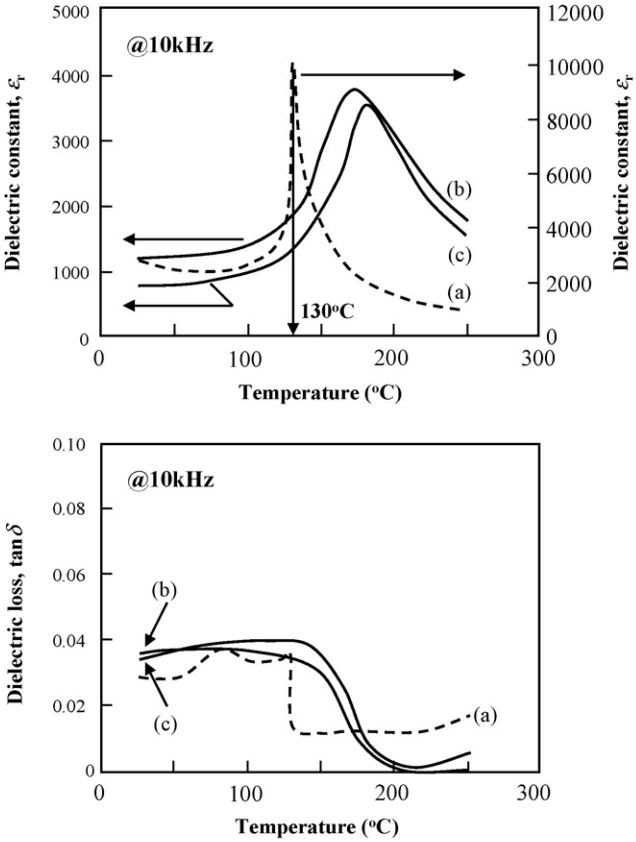

Fig. 2. Temperature dependence of dielectric constants, $\varepsilon_s$, (upper) and loss, $\tan\delta$, (lower) of (a) pure BT, (b) BBKT5 and (c) BBKT10 ceramics sintered in air.

1000–1300 °C for 0–10 h. The $\rho_{max}/\rho_{RT}$ ratio increased with the increased soaking temperature below 1250 °C and dropped at 1300 °C. The ratio generally increased with the soaking time up to 5 h. However, the resistivity ratio of the sample annealed at 1200 °C for 5 h was almost the same as that for 10 h. Based on these results, we judged that the appropriate annealing conditions for the BBKT5 ceramics are a soaking temperature 1250 °C and a time of 5 h.

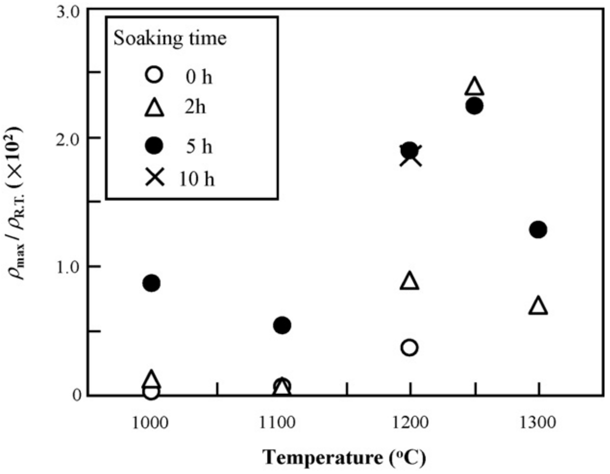

Fig. 3. Comparison of resistivity ratio ($\rho_{max}/\rho_{RT}$) after annealing at 1000–1300 °C for 0–10 h.

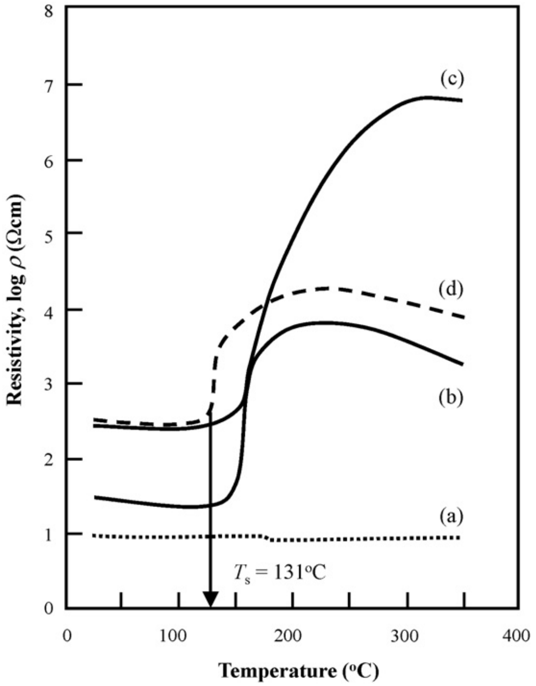

Fig. 4. Temperature dependence of resistivity of (a) as-sintered BBKT5, (b) BBKT5 after annealing, (c) BBKT5-ASTMn after annealing and (d) Nb-doped BT ceramics.

Fig. 4 shows the temperature dependence of the resistivity of BBKT5 ceramics. As mentioned above, the as-sintered BBKT5 ceramics in a $N_2$ flow showed a lower $\rho_{RT}$ of 10 Ω cm but a smaller increase in resistivity over the measured temperature range (Fig. 4a). Fig. 4(b) and (c) shows the temperature dependences of resisitivity of the BBKT5 and BBKT5-ASTMn ceramics annealed at 1250 °C and 1200 °C for 5 h, respectively. The BBKT5 and BBKT5-ASTMn ceramics in these figures were sintered at 1350 °C and 1300 °C, respectively. The annealing conditions for the BBKT5-ASTMn samples were determined in the same manner as those for the BBKT5 described earlier. After the annealing treatment, the PTC characteristic of the BBKT5 ceramics was significantly improved. The $\rho_{max}/\rho_{RT}$ ratio of the BBKT5-ASTMn is over $10^2$ times that of the BBKT5 as shown in Fig. 4(b) and (c). For comparison of the PTC properties, the Nb-doped BT sintered in air at 1400 °C is also shown in Fig. 4(d). The switching temperature $T_s$, which is almost equal to the $T_c$ for PTC materials, was determined from the temperature showing $\rho = 2\rho_{RT}$.[15] The Nb-doped BT shows an abrupt change in the resistivity at 131 °C. The BBKT5 and BBKT5-ASTMn after annealing show a resistivity anomaly at about 155 °C. These observations indicate that the $T_c$ of the BBNT5 ceramics is apparently higher than that of pure BT. We also fabricated both AST-added (BBKT5-AST) and Mn-added BBKT5 ceramics (BBKT5-Mn) by sintering at 1300 °C and 1350 °C for 2 h in a $N_2$ flow and by annealing at 1200 °C and 1250 °C for 5 h, respectively. The temperature dependence of the resistivity of the BBKT-AST ceramics was the same as that of the BBKT5 ceramics. However, the BBKT5-Mn sample showed a high $\rho_{RT}$ over $10^{12}$ Ω cm, namely, an insulating characteristic. As mentioned above, in the AST and Mn co-added ceramics, the $\rho_{RT}$

significantly decreased by the order of about $10^{10}$ at RT and showed a high resistivity change. According to Nikahara and Murakami[16] and the work reported in reference,[17] we assume the following mechanisms. In the BBKT5-Mn ceramics, Mn diffuses into the grain and increases the resistivity. On the other hand, in the BBKT5-ASTMn ceramics, Mn preferentially segregates to the grain boundaries and results in an increase of the surface-state acceptor density and the consequent enhancement of the PTC effect.

The BBKT10 ceramics were fabricated under the same conditions as the BBKT5 samples and annealed in air. Fig. 5 shows the temperature dependence of resistivity of the (a) as-sintered BBKT10, (b) BBKT10 after annealing and (c) BBKT10-ASTMn after annealing the samples. The fabrication conditions and the obtained PTC properties of the BBKT5 and BBKT10 ceramics are summarized in Table 1. The temperature coefficient of resistivity ($\alpha$)[15] of the BBKT10 samples is also higher than that of the BBKT5 materials. The $T_s$ of the BBKT10 samples after annealing is almost the same as that of BBKT5. The $Bi^{3+}$-doped BT ceramics show a PTC characteristic, but the $T_c$ of these ceramics is almost same as that of the pure BT.[18] Because it is known that the BT and BKT phases have formed a solid solution,[19] the BBKT ceramics should show a higher $T_s$ and $T_c$ than 130 °C (= $T_c$ of BT). As shown in Figs. 4 and 5, incorporation of the BKT phase as well as BNT into the BT sample is also considered an effective way to increase $T_s$.

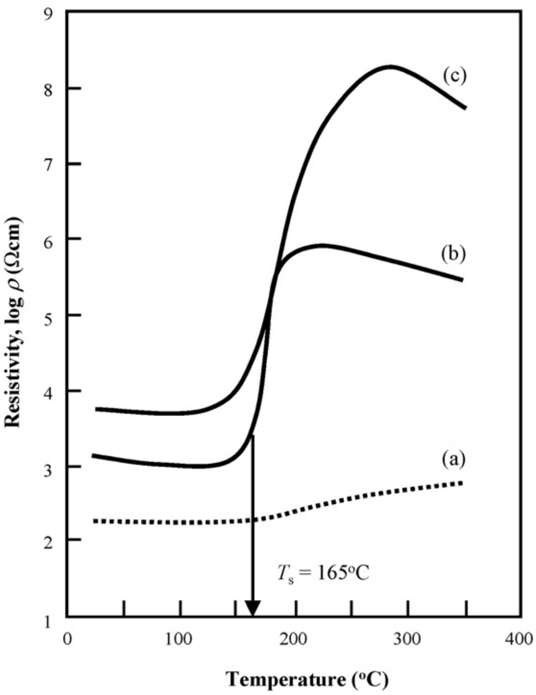

Fig. 5. Temperature dependence of resistivity of (a) as-sintered BBKT10, (b) BBKT10 after annealing and (c) BBKT10-ASTMn after annealing ceramics.

Fig. 6 shows typical SEM images of the BBKT5-ASTMn and BBKT10-ASTMn samples after annealing treatment. Although the relative density of BBKT10-ASTMn ceramics is lower than that of the BBKT5-ASTMn materials as shown in Table 1, the microstructure of both ceramics was the same. The grain size of both ceramics is about 10 μm. A chemical analysis using EPMA-WDS showed that no impurity phases were

Table 1
Summary of the sintering conditions and results for BBKT100*x* ceramics.

| Sample | Sintering conditions | | | Results | | | |
|---|---|---|---|---|---|---|---|
| | Sintering temperature (°C) | Soaking time (h) | $O_2$ concentration (%) | Relative density (%) | $\rho_{RT}$ (Ω cm) | $T_s$ (°C) | $\alpha$ (%/°C) |
| BBKT5 | 1350 | 2 | 0.15 | 93.0 | $3.1 \times 10^1$ | 153 | 9.1 |
| BBKT5-ASTMn | 1300 | 2 | 0.15 | 83.2 | $3.1 \times 10^2$ | 156 | 10.8 |
| BBKT10 | 1350 | 2 | 0.4 | 89.9 | $1.3 \times 10^3$ | 165 | 11.4 |
| BBKT10-ASTMn | 1300 | 2 | 0.4 | 69.9 | $5.6 \times 10^3$ | 151 | 11.6 |

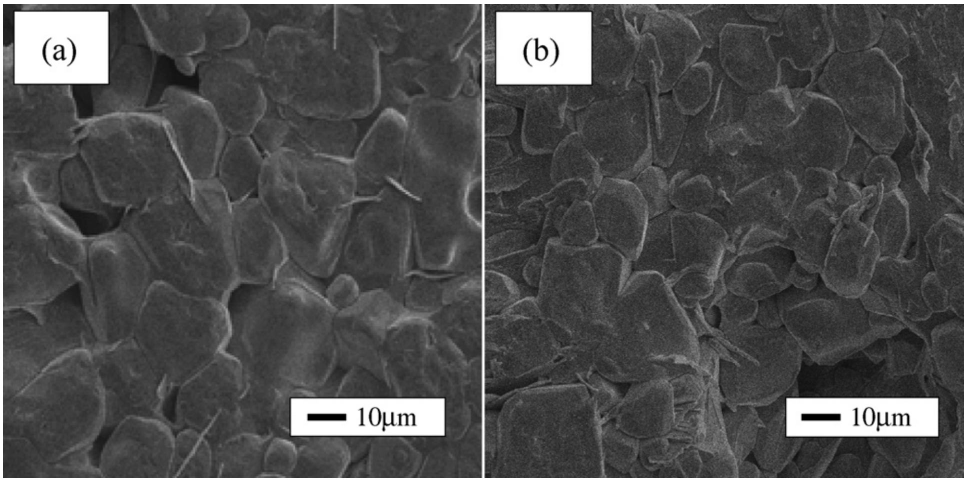

Fig. 6. SEM images of (a) BBKT5-ASTMn and (b) BBKT10-ASTMn after annealing treatment.

detected in the grain interiors and grain boundaries of either ceramics. Furthermore from the chemical analysis, it was found that the molar ratios of the BBKT5 ceramics sintered in air and in $N_2$ flow are Ba:Bi:K:Ti = 0.95:0.020:0.017:1 and = 0.95:0.017:0.015:1, respectively. In addition, the molar ratios of the BBKT10 ceramics sintered in air and in $N_2$ flow are Ba:Bi:K:Ti = 0.90:0.038:0.030:1 and = 0.90: 0.023:0.016:1, respectively. In these determined chemical compositions, the content of Ti was fixed at unity, because it was reported that defect formation at the B site in perovskite-type ($ABO_3$) structures is very difficult.[20,21] These results indicate that the extent of evaporation of Bi and K in the semiconducting ceramics sintered in a $N_2$ flow is greater than that of the dielectric ceramics sintered in air. In fact, by comparing Figs. 2a and 4d, it can be seen that the $T_s$ of the BT semiconducting ceramics agrees with the $T_c$. On the other hand, the $T_s$ values of the BBKT ceramics were 15–30 °C lower than the $T_c$. Hence, it is clear that the $T_s$ values in the BBKT5 and BBKT10 semiconducting ceramics obtained by sintering in an $N_2$ flow are lower than the $T_c$ determined using the dielectric samples, because the $T_c$ of BBKT ceramics depends on the BKT content. We believe that the hot pressing method suppress as the evaporation of Bi and K.[22]

## 4. Conclusions

We have fabricated lead-free BT–BKT semiconducting ceramics with low $\rho_{RT}$ by sintering in a $N_2$ flow with low $O_2$ concentration. The PTC characteristics of the BT–BKT can be improved by annealing in air and adding a small amount of Mn and a sintering aid. By incorporating the BKT phase into BT, we were able to increase the $T_s$ of the PTC ceramics and achieve a value over 130 °C, which is the $T_s$ value of BT. Although the PTC characteristics of the BT–BKT are currently inferior to those of the existing lead-containing PTC ceramics, this BT–BKT system may be a promising lead-free material in addition to the BT–BNT system.

## Acknowledgment

The authors would like to thank to Ph.D. K. Uchiyama, Ph.D. T. Nishida, Ph.D. P.-H. Xiang of Nara Institute of Science and Technology for fruitful discussions about electrical measurements. This work was partially supported by JSPS which the author (HT) gratefully acknowledges.

## References

1. Saburi, O., Wakino, K. and Fujikawa, N., $BaTiO_3$ and it's applications (I)–(III). *"Titabari-kei Handotai" (Semiconducting Barium Titanates)*. Elecera Shuppan Iinkai, Giken, Tokyo, 1980, pp. 11–45 [in Japanese].
2. Huybrechts, B., Ishizaka, K. and Takata, M., The positive temperature coefficient of resistivity in barium titanate. *J. Mater. Sci.*, 1995, **30**, 2463–2474.
3. Andrich, E., PTC thermistors as self-regulating heating elements. *Philips Tech. Rev.*, 1969, **30**, 170–177.
4. Lai, C. H. and Tseng, T. Y., Investigation of resistivity and permittivity for $(Ba,Pb)TiO_3$ PTCR ceramics. *J. Am. Ceram. Soc.*, 1994, **77**, 2419–2424.
5. Takeda, H., Aoto, W. and Shiosaki, T., $BaTiO_3$–$(Bi_{1/2}Na_{1/2})TiO_3$ solid solution semiconducting ceramics for lead-free PTCR materials with $T_c > 130$ °C. *Appl. Phys. Lett.*, 2005, **87**, 102104.
6. Shimada, T., Touji, K., Katsuyama, Y., Takeda, H. and Shiosaki, T., Lead free PTCR ceramics and its electrical properties. *J. Eur. Ceram. Soc.*, 2007, **27**, 3877–3882.
7. Xiang, P.-H., Takeda, H. and Shiosaki, T., Positive temperature coefficient of resistivity effect of semiconducting $BaTiO_3$–$(Bi_{1/2}Na_{1/2})TiO_3$ ceramics prepared by a wet-chemistry route. *Jpn. J. Appl. Phys.*, 2007, **46**, 6995–6998.
8. Xiang, P.-H., Takeda, H. and Shiosaki, T., High $T_c$ lead-free $BaTiO_3$–$(Bi_{1/2}Na_{1/2})TiO_3$ positive temperature coefficient of resistivity ceramics with electrically heterogeneous structure. *Appl. Phys. Lett.*, 2007, **91**, 162904.
9. Buhrer, C. F., Some properties of bismuth perovskites. *J. Chem. Phys.*, 1962, **36**, 798–803.
10. Matsuo, Y., Fujimura, M., Sasaki, H., Nagase, K. and Hayakawa, S., Semiconducting $BaTiO_3$ with Additions of $Al_2O_3$, $SiO_2$ and $TiO_2$. *Am. Ceram. Soc. Bull.*, 1968, **47**, 292–297.
11. Ueoka, H. and Yodogawa, M., Ceramic manufacturing technology for the high performance PTC thermistor. *IEEE Trans. Manuf. Technol., MFT-3*, 1974, 77–82.
12. Ueda, I. and Ikegami, S., Oxidation phenomena in semiconducting $BaTiO_3$. *J. Phys. Soc. Jpn.*, 1965, **20**, 546–552.
13. Al-Allak, H. M., Brinkman, A. W., Russell, G. J. and Woods, J., The effect of Mn on the positive temperature coefficient of resistance characteristics of donor doped $BaTiO_3$ ceramics. *J. Appl. Phys.*, 1988, **63**, 4530–4535.
14. Gallego, M. M. and West, A. R., Effect of annealing treatments on positive temperature coefficient of resistance properties of barium titanate ceramics and a new model for the positive temperature coefficient of resistance effect. *J. Appl. Phys.*, 2001, **90**, 394–403.
15. Japan Electronic Materials Manufactures Association Standard EMAS-8202; 1988 [in Japanese].
16. Nakahara, M. and Murakami, T., Electronic states of Mn ions in $Ba_{0.97}Sr_{0.03}TiO_3$ single crystals. *J. Appl. Phys.*, 1974, **45**, 3795–3800.
17. Murakami, T., Boundary layers of $BaTiO_3$. *"Titabari-kei Handotai" (Semiconducting Barium Titanates)*. Elecera Shuppan Iinkai, Giken, Tokyo, 1980, pp. 71–76 [in Japanese].
18. Saburi, O., Properties of semiconductive barium titanates. *J. Phys. Soc. Jpn.*, 1959, **14**, 1159–1174.
19. Hiruma, Y., Aoyagi, R., Nagata, H. and Takenaka, T., Piezoelectric properties of $BaTiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ ferroelectric ceramics. *Jpn. J. Appl. Phys.*, 2004, **43**, 7556–7559.
20. Moriwake, H., First-principles calculation of formation energy of neutral point defects in perovskite-type $BaTiO_3$. *Int. J. Quantum Chem.*, 2004, **99**, 824–827.
21. Shigemi, A. and Wada, T., Enthalpy of formation of various phases and formation energy of point defects in perovskite-type $NaNbO_3$ by first-principles calculation. *Jpn. J. Appl. Phys.*, 2004, **43**, 6793–6798.
22. Hiruma, Y., Aoyagi, R., Nagata, H. and Takenaka, T., Ferroelectric and piezoelectric properties of $(Bi_{1/2}K_{1/2})TiO_3$ ceramics. *Jpn. J. Appl. Phys.*, 2005, **44**, 5040–5044.