

Fabrication and operation limit of lead-free PTCR ceramics using $\text{BaTiO}_3\text{-(Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ system

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Received: 10 April 2007 / Accepted: 11 December 2007 / Published online: 4 January 2008
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Abstract The electric properties of $\text{BaTiO}_3\text{-(Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BT–BNT) solid solution ceramics were studied as a lead-free PTCR (positive temperature coefficient of resistivity) thermistor material usable over 130°C. For determining the maximum switching temperature T_s , the phase diagram of BT–BNT binary system was clarified. Two semiconductorization processes and their electric properties are described. The lanthanum(La)-doped BBNT ceramics sintered in air still showed dielectric behaviors, but the niobium(Nb)-doped ones had a low resistivity at room temperature, ρ_{RT} , on the order of $10^3 \Omega\text{cm}$ and showed a PTC behavior. Sintering under a low O_2 atmosphere produces BT–BNT ceramics with less than $10^2 \Omega\text{cm}$ compared to those prepared in air. Our current research produced the BBNT ceramics with T_s values around 210°C by increasing the $(\text{Bi}_{1/2}\text{Na}_{1/2})$ content in the ceramics.

Keywords PTCR · Thermistors · Electrical properties · Perovskites · Lead-free

1 Introduction

Donor-doped barium titanate (BaTiO_3 ; BT)-based semiconductor ceramics are well-known to have a positive

temperature coefficient of resistivity (PTCR) [1–4]. The significant feature of the PTCR ceramics is an anomalous increase in their electrical resistance above the Curie temperature (T_c), and this property, used for PTCR thermistors, is widely used for current control elements, self-controlled heaters and sensors for overcurrent protection, etc. As is well known, the T_c of the BT is about 130°C [5], and the BT PTCR ceramics are used in electric devices at temperatures less than 130°C. Hence, the BT ceramics including lead titanate (PbTiO_3 , $T_c=490^\circ\text{C}$ [6]) are usually adopted for high temperature heater elements over 130°C.

Recently, it has been required to reduce the amount of lead in electronic devices. As mentioned above, the PTCR ceramics having a T_c higher than 130°C contains PbTiO_3 in order to shift the T_c . For a lead-free PTCR ceramic candidate, we selected four kinds of perovskite-type compounds, $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT, $T_c=320^\circ\text{C}$)[7], $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BKT, 380°C)[7], NaNbO_3 (643°C)[8] and BiFeO_3 (850°C)[9] instead of PbTiO_3 . The BT-based ceramics including these compounds were synthesized and their electric properties were also investigated. The ceramics using the BT–BNT and BT–BKT systems possessed a higher Curie temperature than BT and showed PTCR behaviors by sintering at a low oxygen partial pressure and including additives [10]. Among these two systems, the BT–BNT ceramics demonstrated low resistivity values on the order of $10 \Omega\text{cm}$ at room temperature and an abrupt resistivity change near T_c [11]. Using such BT–BNT ceramics, the PTCR elements were fabricated for constant temperature heating [12]. These elements demonstrated a performance comparable to those made of the Pb-contained PTCR ones. Therefore, we have proposed the semiconducting ceramics of the BT–BNT system as new lead-free PTCR thermistor materials with $T_c > 130^\circ\text{C}$.

In this study, we demonstrated the detailed studies of the synthesis and electric properties of the semiconducting

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ceramics using the BT–BNT system. We showed an increase in the switching temperature of resistivity by increasing the $(\text{Bi}_{1/2}\text{Na}_{1/2})$ content as well as its operation limit at high temperature. This operation limit relates to the depolarization temperature of the BT–BNT ceramics based on the di-, pyro-, and ferro-electric measurements.

2 Experimental procedure

A conventional ceramics fabrication technique was used to prepare the $(1-x)\text{BT}-x\text{BNT}$ solid-solutions. As the starting powders, we used BaCO_3 , Na_2CO_3 , TiO_2 , of 99.99% and Bi_2O_3 of 99.9% purity. The composition (x) was set at $x=0.00$ – 1.00 . The powders were mixed in acetone, dried, and then calcined at 800 – 1000°C for 2 h. The calcined powders with a binder (2 wt% poly vinyl alcohol) were uniaxially pressed into a disk with a 15-mm diameter and 1-mm thickness at 190 MPa. The disc samples, directly placed on a platinum sheet, were placed in a furnace and heated at 1300 – 1350°C for 2 h. The sintered disk ceramics with an 11.0 mm diameter were polished for characterization of their electric properties. For the phase identification using the powder X-ray diffraction (XRD) technique, the ceramic samples were ground and pulverized. The densities of the ceramics were measured by Archimedes method using distilled water. The electrodes were made on the face of the disks using fire-on Ag paste or sputtered Au films. The frequency dependence of the dielectric constant ϵ_s and dielectric loss factor $\tan\delta$ of the ceramic samples were measured in the frequency range of 10 kHz to 1 MHz using an impedance analyzer (HP4194A). We performed the poling treatment on the samples before the pyroelectric measurements. The samples were poled at 100°C in a silicone oil bath with an electric field of over 20 kV/cm for 30 min. Referring to the Japan Industrial Standard R1651 [13], the depolarization current was measured using a digital resistance meter (ADVANTEST R8340) during heating from room temperature (RT) to 500°C , and then a pyroelectric coefficient, γ , was calculated.

We attempted to obtain ceramics showing PTCR characteristics by doping with La^{3+} or Nb^{5+} and sintering in air. We selected the dopant (La and Nb) content by referring to the paper of Saburi [3]. For the La^{3+} and Nb^{5+} doping process, we prepared the starting materials with the following chemical compositions $[\text{Ba}_{0.94}(\text{Bi}_{1/2}\text{Na}_{1/2})_{0.06}]_{1-y}\text{La}_y\text{TiO}_3$ (100yLa-doped BNT 6 mol%) and $[\text{Ba}_{0.95}(\text{Bi}_{1/2}\text{Na}_{1/2})_{0.05}]\text{Ti}_{1-\delta}\text{Nb}_\delta\text{O}_3$ (Nb-doped BNT 5 mol%) using La_2O_3 and Nb_2O_5 and the raw material powders described in the previous paragraph. The calcination and pressing processes were the same as already described. The green bodies were placed on a platinum sheet covered with zirconium oxide powder and sintered for 2 h in air. In this

study, we also did the sintering in flowing N_2 as another semiconductorization process. The electrodes were formed on polished ceramic surfaces for the electrical measurements using a fired-on Ag–Zn paste. The baking was performed at 500°C for 10 min in air. The sintered samples were then cooled in the furnace to room temperature. The resistivity, ρ , was determined by direct measurement of the current flowing through the samples under the impressed field of 0.1–10 V/mm using a digital resistance meter (ADVANTEST R8340) from RT to 500°C .

3 Results and discussion

3.1 Dielectric property and its temperature behavior of BT–BNT ceramics

Figure 1 shows the XRD profiles of the BT–BNT powders obtained by pulverizing the ceramics. The data were collected at room temperature (RT). All the diffraction peaks were successfully indexed on the basis of the published data of the host BaTiO_3 (ICCD #05-0626) and then demonstrated that all the BT–BNT ceramics consisted of a single phase with a tetragonal symmetry. In the BT–BNT systems, the tetragonal phase with the BT structure remains up to $x=0.9$. These data were supported by the phase diagram reported in [14]. The lattice parameters, the a - and c -axis lengths, of the BT–BNT ceramics decreased with the increasing BNT content. Both of them monotonously decreased from 3.997(2) to 3.895(4) Å for the a -axis

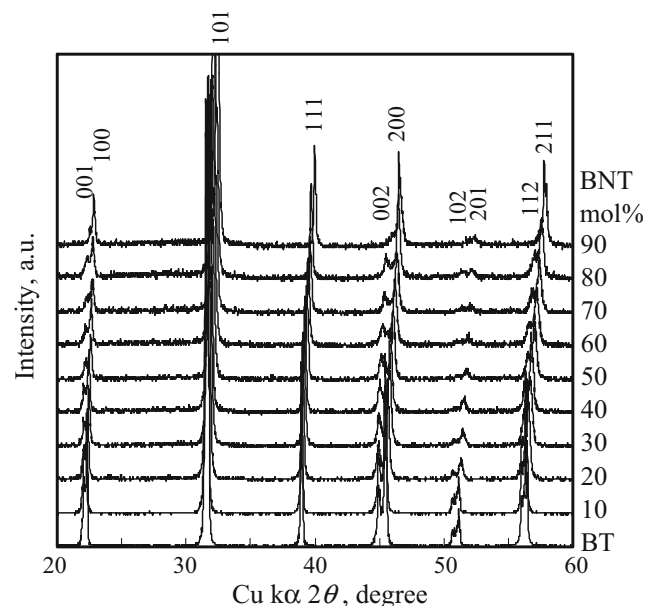


Fig. 1 Powder X-ray diffraction profiles of pulverized specimens of BT–BNT ceramics

and 4.024(2) to 3.953(5) Å for the *c*-axis, in which the parentheses represent the standard deviation. These results are reasonable from the viewpoint of the ionic size (Ba^{2+} ($r^{\text{VIII}}=1.42$ Å), Na^+ (1.18 Å) and Bi^{3+} (1.17 Å) [15]) and suggested that the Na^+ and Bi^{3+} cations were introduced into the Ba site.

Figure 2 shows the sintering temperature of the BT–BNT ceramics with the relative density $D_r > 90\%$, where D_r is defined as the ratio of the specimen density to the theoretical density. The density of the ceramics significantly affects the electric properties. For a fair comparison of the electric properties, therefore, we tried to obtain a density $>90\%$ for all the solid-solution ceramic specimens by changing the sintering temperature. As shown in Fig. 2, the sintering temperature decreased with the increasing BNT content. This was because the Bi_2O_3 content with a low melting temperature in the starting material powders increased with the BNT content.

We investigated the T_c change of the BT–BNT ceramics with the BNT content for disclosing the maximum switching temperature T_s of the BT–BNT PTCR ceramics, which is defined as the temperature showing $\rho=2*\rho_{\text{RT}}$ in [3] and is almost equal to T_c . Figure 3 shows the temperature dependence of the dielectric constant, ϵ_s , and dielectric loss tangent, $\tan\delta$, measured at frequencies of 1 MHz for the BNT 50 mol% ceramics. In this figure, the pyroelectric coefficient, γ , that changed during the heating process is also listed. The values of ϵ_s and $\tan\delta$ for the ceramics at room temperature and at 1 MHz were 390 and 0.04, respectively. The plots of ϵ_s and $\tan\delta$ show a peak at 240 and 220°C, respectively. The plot of γ shows a peak at 230°C (T_p). In this paper, we defined the peak temperatures of ϵ_s , $\tan\delta$, and γ as T_m , T_d and T_p , respectively. Up to a 40 mol% BNT content, T_m agreed with T_d and T_p , and did not depend on the measurement frequency. However, as shown in Fig. 3, in the 50 mol% BNT ceramics, T_m

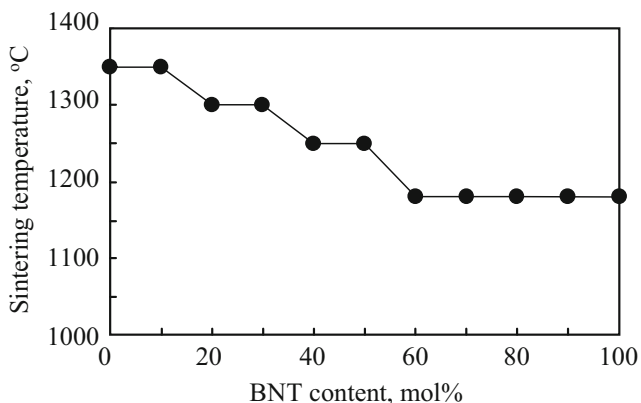


Fig. 2 Sintering temperature change in BT–BNT ceramics with the relative density $D_r > 90\%$

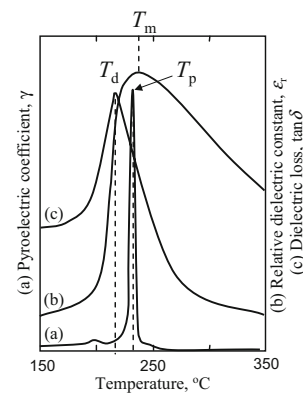
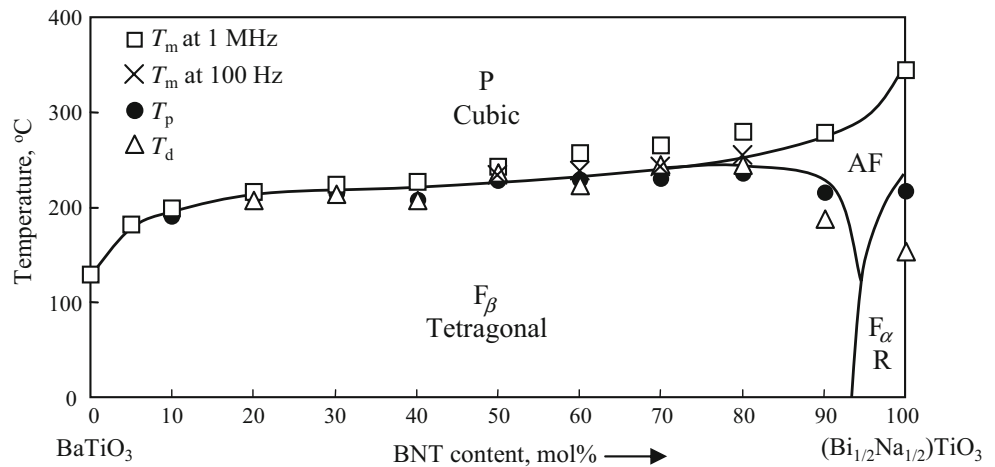


Fig. 3 Temperature dependence of (a) pyroelectric current, (b) dielectricity, and (c) dielectric loss of the BNT 50 mol% ceramics. This figure is used in this study for providing a definition of T_m , T_d , and T_p , which indicate the temperatures with the maximum values

disagreed with T_d and T_p . Moreover, from the 50 to 90 mol% BNT content, the T_m shifted to a higher temperature with a change in the measurement frequencies, that is, relaxor characteristics were observed in that composition range. These observations agreed with those reported in [16–18]. A depolarization current was observed when any phase transition, including the ferroelectric–ferroelectric one, occurs in ferroelectric materials. In [16, 19], there is no phase transition below T_d and T_p in the BT–BNT ceramics. Hence, the T_p obtained in the BT–BNT ceramics indicates a temperature that the ferroelectricity vanished, thus we can say that T_p is the T_c below the 40 mol% BNT content. The T_c value of the BT–BNT ceramics is apparently higher than that of BT.

We obtained the T_m , T_d and T_p values in the composition range from the 5 to 100 mol% BNT content, and constructed a BT–BNT binary phase diagram. We investigated the relationship between the phase transition temperature and chemical composition. Figure 4 shows the constructed phase diagram for the BT–BNT binary system. For drawing the phase boundary lines over 80 mol% BNT, we referred to the report by Takenaka et al. [14]. As shown in Fig. 4, up to a 10 mol% BNT content, the T_c drastically increases from 130 to 200°C. At the 20 mol% BNT content, the T_c reaches 220°C. From 20 to 40 mol%, the slope is gentle, and T_c gradually increases to 230°C. From the 50 to 80 mol% BNT content, T_m depends on the measurement frequency (see closely, T_m 's at 100 Hz and 1 MHz), whereas T_p does not change around 230°C. In the Heywang [20] and Jonker [21] models, it is well explained that the resistivity anomaly observed in the PTCR ceramics was due to the disappearance of the spontaneous polarization. On the basis of this phase diagram, we can control the T_c between 130 and 230°C by changing the BNT content. It is expected that the BT–BNT PTCR ceramics can be applied for heater elements working at about 230°C.

Fig. 4 Phase diagram of a BT–BNT binary system constructed from the results of the di-, pyro-, and ferro-electric measurements of the BT–BNT ceramics



3.2 PTCR properties of BT–BNT ceramics

We prepared the BT–BNT semiconducting ceramics by sintering at the temperature described in Fig. 2. The BT–BNT ceramics were rendered semiconductive by La- or Nb-doping and sintering in air. Figure 5 shows the temperature responses of the resistivity of the 0.1 La-doped 6 mol% BNT and Nb-doped 5 mol% BNT ceramic samples. For the La-doped ceramic samples, the ρ values are almost on the order of 10^{12} Ωcm at RT. The ρ monotonously decreased with the increasing temperature and the high value of $>10^8$ Ωcm remained up to 200°C as shown in Fig. 5(a). We changed the La content y of the ceramics from 0.001 to 0.005, but no PTC behavior was obtained for all the

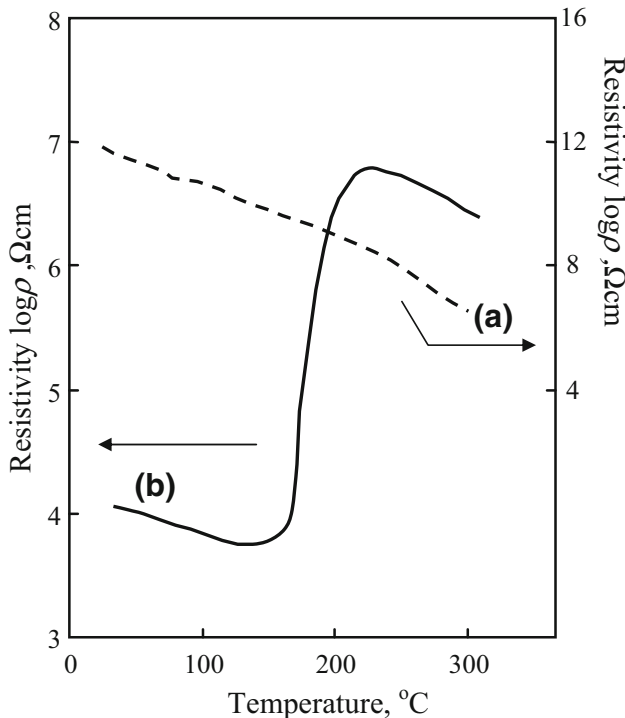


Fig. 5 Temperature dependence of resistivity ρ of (a) La- and (b) Nb-doped BNT 6mol% ceramics sintered in air

samples. The T_c decreased with an increase in y from 180°C ($y=0.001$) to 160°C ($y=0.0005$). Moreover, no change in the lattice constants was obtained because the La content in the sample is very low and the size of the La^{3+} ion is almost the same as that of the Bi^{3+} ion. Although La-doping has commonly been utilized for the semiconductorization of BT-based ceramics [1], this method was not in use for the BT–BNT ceramics. In contrast, for the Nb-doped 5 mol% BNT ceramic samples, the resistivity significantly decreased to on the order of 10^8 at RT. The sample had the low resistivity ρ_{RT} at room temperature of 10^3 Ωcm like the semiconducting materials shown in Fig. 5(b). The ρ values increased near 160°C. In this study, only the Nb-doped samples displayed the PTC behavior. For the Nb doping of BT–BNT, Nb^{5+} directly substitutes of the Ti^{4+} site. In general, since some Ti^{4+} ions are changed to Ti^{3+} by the electric charge compensation due to doping [1], the BT-based semiconducting ceramics showed an n -type conductivity and PTC behavior. Since bismuth is volatile at the sintering temperature, we suggested that the La^{3+} ions were incorporated into the BT–BNT crystal lattices instead of

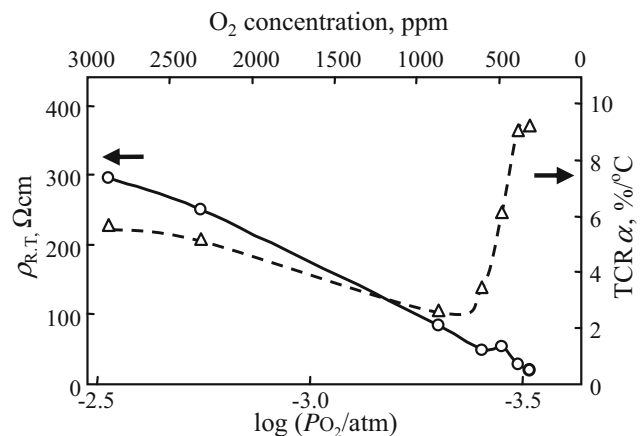
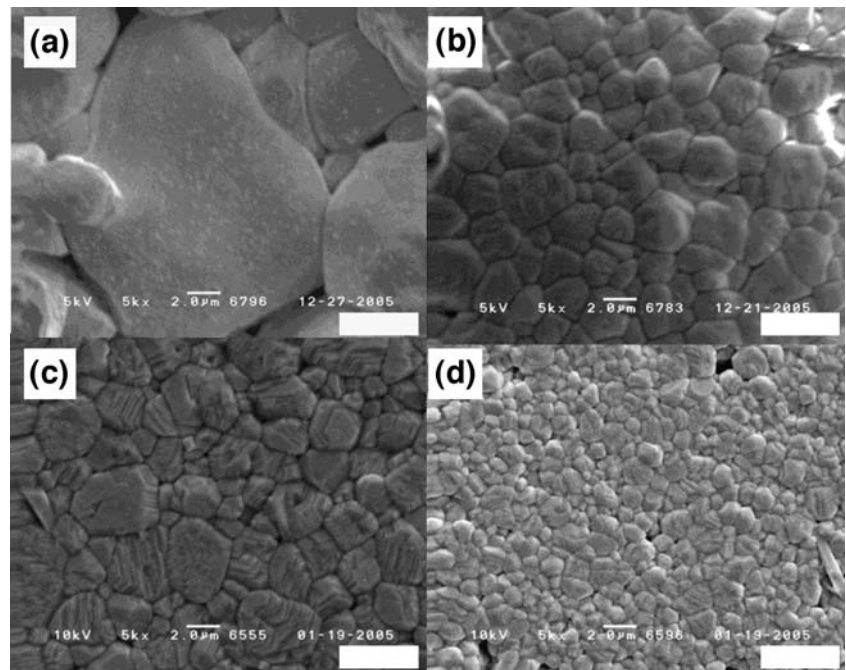


Fig. 6 Dependences of resistivity at room temperature (25°C) ρ_{RT} and temperature coefficient of resistivity (TCR) α of the BNT 6 mol% ceramics on oxygen partial pressure during sintering process

Fig. 7 Scanning electron micro-photographs of the (a) 6 mol%, (b) 40 mol%, (c) 60 mol% and (d) 80 mol% BNT ceramic surfaces sintered at 1340°C for 2 h in N₂ atmosphere with 300 ppm oxygen concentration

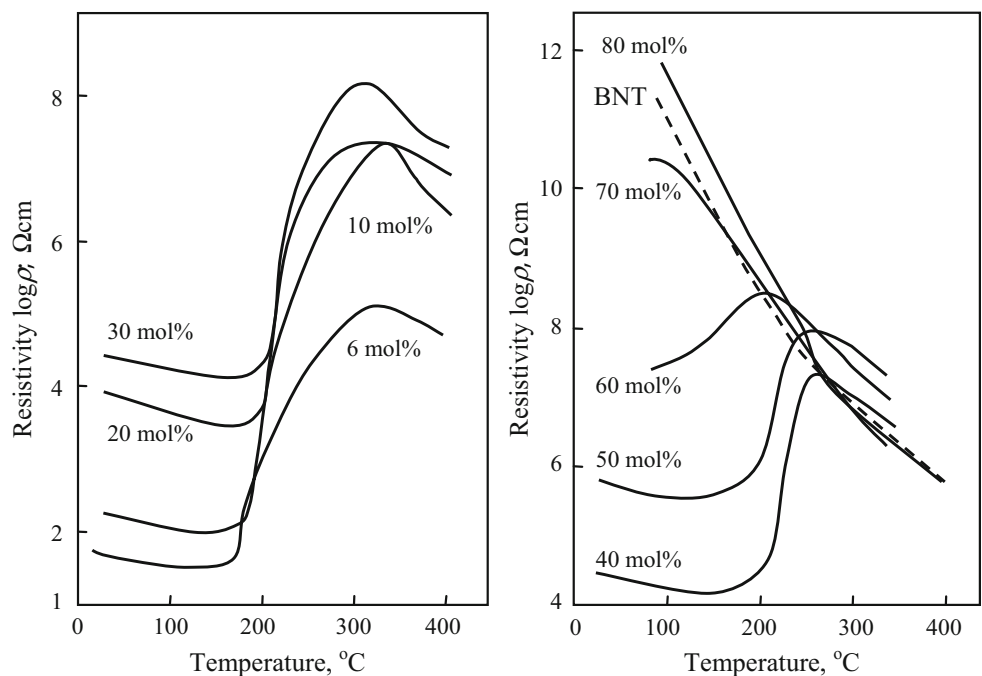


Bi³⁺, therefore, the chemical formula is represented by Ba_{1-z}[(Bi,La)_{1/2}Na_{1/2}]_zTiO₃.

In our previous studies [10, 12], we reported that a sintering in flowing N₂ with a low O₂ atmosphere is effective for semiconductization of the BT–BNT ceramics. When this technique is applied to the BT ceramics, oxygen vacancies occur in the BT, and then the Ti⁴⁺ ions are changed to Ti³⁺ by the electric charge compensation [3]. In this study, we investigated the effect of the atmospheric oxygen concentration on the PTCR property of the BT–

BNT ceramics. Figure 6 shows the O₂ concentration dependence of ρ_{RT} and the temperature coefficient of the resistivity α, which is defined in the paper of Saburi and Wakino [3], of the BNT 6 mol% ceramics. The ρ_{RT} monotonously decreased with the decreasing O₂ concentration. On the other hand, the α decreased at >1000 ppm, but increased below the O₂ concentration of 1,000 ppm. Both ρ_{RT} and α have lower values in the BT semiconducting ceramics at a low oxygen concentration [22]. Hence, this observation needs clarifying by a detailed investigation of

Fig. 8 Temperature dependence of resistivity ρ of BT–BNT ceramics sintered at 1340°C for 2 h in N₂ atmosphere with 300–400 ppm oxygen concentration



the local property of grain boundaries as introduced in ref. [23]. In this study, the O₂ concentration of 300 ppm produced ceramics with the lowest ρ_{RT} and the sharpest increase in ρ . The PTCR characteristics included a ρ_{RT} of 20 Ωcm , $\rho_{\text{max}}/\rho_{RT}$ ratio of 10³, and α of 9%/°C. The ρ_{RT} values and $\rho_{\text{max}}/\rho_{RT}$ ratio for these ceramic samples are comparable to those of the conventional lead-containing PTCR materials.

We attempted to raise the switching temperature T_s by increasing the BNT content of BT–BNT. Figure 7 shows SEM micrographs of the surface microstructures of the (a) 6 mol%, (b) 40 mol%, (c) 60 mol% and (d) 80 mol% BNTs. The microstructure of all the ceramics shows randomly oriented round grains with irregular shapes. The grains of the ceramics shrunk with the increasing BNT content. It was assumed that the grain growth during the sintering process was inhibited by the BNT incorporation. However, the XRD profiles of the all ceramic surfaces were not different and showed no preferred orientation. Also, no impurity phases were detected in all the ceramics. Therefore, their PTCR properties could be compared to each other.

Figure 8 shows the composition dependence of the PTCR behaviors on the BT–BNT ceramics. All samples were without any dopants and prepared by sintering at the O₂ concentration of 300 ppm. Up to the BNT 50 mol% ceramics, by increasing the (Bi_{1/2}Na_{1/2}) content, the ρ_{RT} increased from 20 to 10⁴ Ωcm , the T_s was raised from 180 to 210°C, and the α was between 9 and 13%/°C. The BNT 60 mol% ceramics showed a very small resistivity jump, and the samples over 70 mol % BNT were still insulating. Knowing that Na and Bi easily vaporize, our opinion is as follows: Na and/or Bi vacancies are introduced into the BT–BNT crystal lattice during sintering, and then the electric charge become negative. These vacancies cancel out the change of Ti⁴⁺ to Ti³⁺ introduced by oxygen vacancies [1], which could be generated by sintering in a reduced atmosphere. Therefore, we guess that the ceramics with $x > 0.4$ need a lower O₂ concentration or active reducing atmosphere such as a low H₂ gas flow during the sintering process to produce a low resistivity and PTCR property.

In Fig. 8, the T_s of the BT–BNT ceramics do not seem to increase by changing the BNT content. Therefore, for each ceramic sample, the resistivity was normalized by the value at room temperature. Figure 9 shows the temperature dependence of relative resistivity ρ^* of the BT–BNT ceramics, which equals the ρ value at a measurement temperature divided by ρ_{RT} . In this figure, for up to 20 mol% BNT, the T_s clearly increased from 120 (La-doped BT) to 210°C with the increasing BNT content. The T_s stagnated from 20 to 50 mol% BNT. These observations are consistent with those obtained from the phase diagram

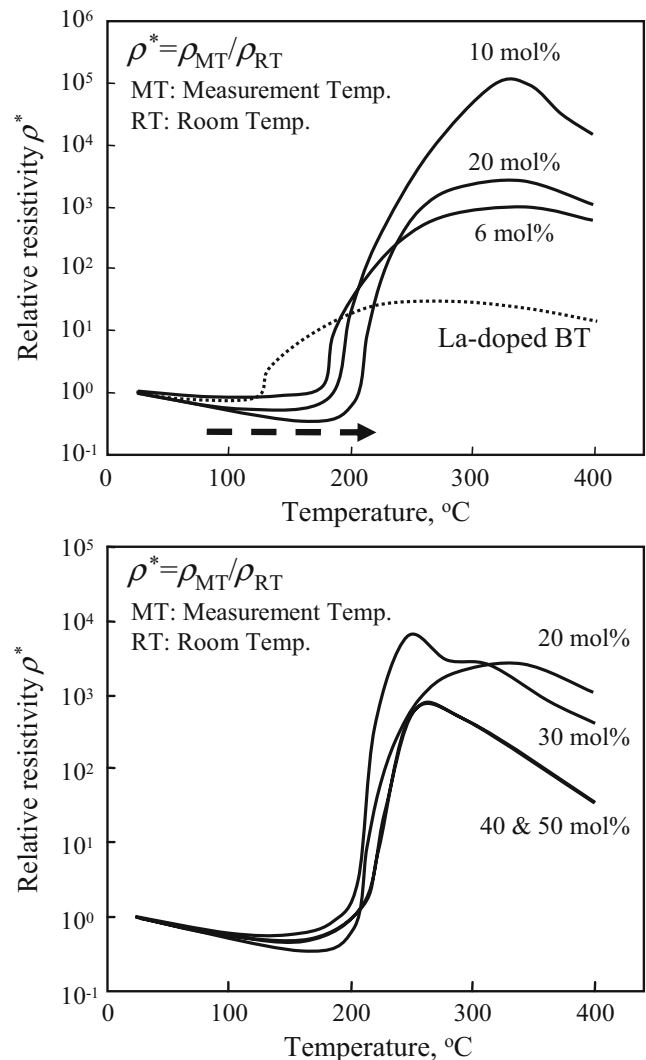


Fig. 9 Temperature dependence of relative resistivity ρ^* of BT–BNT ceramics

shown in Fig. 4, namely, the increase in T_s agrees with that of the T_c in the BT–BNT system. Therefore, in the PTCR ceramics using the BT–BNT system, the T_s can be controlled from 130 to approximately 220°C.

4 Conclusions

In this study, we constructed the phase diagram of the BT–BNT binary system and estimated the operation limit of T_s using the ceramics of this system. We also successfully synthesized BT–BNT ceramics with a PTC behavior above 130°C using an ordinary sintering technique. For the ceramics in the BT–BNT system, excellent PTC properties (low ρ_{RT} and high α) were obtained in the ceramics fabricated by sintering in an N₂ flow with a low O₂ concentration. In the PTCR ceramics using the BT–BNT system, we disclosed that the T_s can be controlled from 130

to approximately 220°C. It is expected that the BT–BNT ceramics can replace part of the current Pb-containing BT ones as PTCR thermistors for use over 130°C.

Acknowledgement The authors would like to thank to Mr. W. Aoto, Mr. T. Sato, Mr. R. Goto, Mr. T. Kinoshita, Mr. H. Harinaka and Mr. Y. Hoshi of NAIST for their help with the fabrication and measurements of the ceramic specimens. This work was partially supported by the Nissan Science Foundation which the author (HT) gratefully acknowledges.

References

- O. Saburi, *J. Phys. Soc. Jpn.* **14**, 1159 (1959)
- G.G. Harman, *Physical Review*. **106**, 1159 (1957)
- O. Saburi, K. Wakino, *IEEE Tran. Comp.* **10**, 53 (1963)
- M. Nakahara, T. Murakami, *J. Appl. Phys.* **45**, 3795 (1974)
- C.J. Jhonson, *Appl. Phys. Lett.* **7**, 221 (1965)
- G. Shirane, S. Hoshino, *J. Phys. Soc. Jpn.* **6**, 265 (1951)
- G.A. Smolensky, V.A. Isupov, A.I. Agranovskaya, N.N. Krainik, *Sov. Phys. Solid. State*. **2**, 2651 (1961)
- K. Ishida, G. Honjo, *J. Phys. Soc. Jpn.* **34**, 1279 (1973)
- S.A. Fedulov, *Sov. Phys. "Doklady"*. **6**, 729 (1962)
- T. Shiosaki, H. Takeda, T. Sato, R. Goto, T. Nishida, *Extend. Abst. 12th US–Japan Sem. Dielectric and Piezoelectric Ceram.* 365 (2005)
- H. Takeda, W. Aoto, T. Shiosaki, *Appl. Phys. Lett.* **87**, 102104 (2005)
- T. Shimada, K. Touji, Y. Katsuyama, H. Takeda, T. Shiosaki, *J. Euro. Ceram. Soc.* **27**, 3877 (2007)
- JIS R1651 "Method for measurement of pyroelectric coefficient of fine ceramics", the Japan Industrial Standard (2002) [in Japanese]
- T. Takenaka, K. Maruyama, K. Sakata, *Jpn. J. Appl. Phys.* **30**, 2236 (1991)
- R.D. Shannon, *Acta Crystallogr.* **A47**, 751 (1976)
- J. Suchanicz, J. Kusz, H. Böhm, *Mate. Sci. Eng. B.* **97**, 154 (2003)
- T. Oh, M.-H. Kim, *Mate. Sci. Eng. B.* **132**, 239 (2006)
- J. Suchanicz, J. Kusz, H. Böhm, G. Stopa, *J. Mater. Sci.* **42**, 7827 (2007)
- I.G. Siny, C.S. Tu, T.V. Schmidt, *Physical Review B.* **51**, 5659 (1995)
- W. Heywang, *J. Am. Ceram. Soc.* **47**, 484 (1964)
- G.H. Jonker, *Solid-State Electron.* **7**, 895 (1964)
- H. Ikushima, S. Hayakawa, *National Tech. Rept.* **13**, 209 (1967) [in Japanese]
- R. Freer, C. Leach, *Solid State Ionics.* **173**, 41 (2004)