BaTiO 3 – (Bi 1⁄2 Na 1⁄2) TiO 3 solid-solution semiconducting ceramics with T c > 130 ° C

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Citation: Applied Physics Letters **87**, 102104 (2005); doi: 10.1063/1.2042551
View online: http://dx.doi.org/10.1063/1.2042551
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/87/10?ver=pdfcov
Published by the AIP Publishing

$BaTiO_3-(Bi_{1/2}Na_{1/2})TiO_3$ solid-solution semiconducting ceramics with $T_c>130$ °C

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(Received 11 April 2005; accepted 16 July 2005; published online 2 September 2005)

As a candidate of a lead-free positive temperature coefficient of resistivity (PTCR) material, barium titanate ($BaTiO_3$)-based solid-solution ceramics, $Ba_{1-x}(Bi_{1/2}Na_{1/2})_xTiO_3$ with $x=0.05$ (BBNT5), have been synthesized by an ordinary sintering technique. Temperature dependences of the dielectric and ferroelectric properties show ferroelectric and paraelectric phase transition of the ceramics with the Curie temperature of $T_c=170$ °C, which is higher than that of $BaTiO_3$ (130°C). The La-doped BBNT5 ceramics display low ρ values of 10^2-10^3 Ω cm at room temperature and their abrupt changes of 10^2-10^4 at about 220 °C. The reduced BBNT5 ceramics show small PTCR characteristics compared to the La-doped ones. © *2005 American Institute of Physics*.
[DOI: 10.1063/1.2042551]

Barium titanate ($BaTiO_3$; BT)-based semiconductor ceramics are widely utilized as positive temperature coefficient of resistivity (PTCR) materials.[1] The PTCR characteristic is associated with the ferroelectric Curie point, T_c. Blending BT with lead titanate ($PbTiO_3$, $T_c=490$ °C)[2] is necessary if the device is to have a higher switching temperature than the T_c of BT (=130 °C).[3] Moreover, it is currently believed that one can fabricate PTCR materials with $T_c>130$ °C only using $PbTiO_3$. Recently, there has been a strong demand to develop environmentally friendly, that is, lead-free ceramics whose electric properties are comparable to those of the lead-containing ones. The aim of this study is to develop lead-free PTCR materials. For this goal, we selected a ferroelectric lead-free perovskite-type compound $(Bi_{1/2}Na_{1/2})TiO_3$ (BNT, $T_c=320$ °C)[4] as another end member of BT-based solid solutions. The BNT ceramics are very attractive lead-free piezoelectric materials. The ceramics with the BT:BNT=6-7:94-93 molar ratio compositions, corresponding to the morphotropic phase boundary one, show superior piezoelectric properties.[5] Since many studies have focused their interests on BNT-based solid solutions,[6–8] there is little information about the BT-BNT solid solution ceramics with a BT-rich composition. Furthermore, there are few reports about the PTCR characteristic of the ceramics.

In this study, we report the synthesis and electric properties of BT-BNT ceramics with a BT-rich composition compared with the pure BT one. We also show the PTCR characteristics of the ceramics by doping La^{3+} or reducing, and propose a new PTCR material without lead as well as having a higher T_c.

Powders with the nominal composition $Ba_{1-x}(Bi_{1/2}Na_{1/2})_xTiO_3$ with $x=0$ and 0.05 (BT and BBNT5) were prepared using $BaCO_3$ (Rare Metallic Co., Ltd.), Na_2CO_3, TiO_2 (Kojyundo Chemical Laboratory Co., Ltd.), of 99.99% and Bi_2O_3 (Rare Metallic Co., Ltd.) of 99.9% purity as the starting materials. The powders were mixed in acetone, dried, and then calcined at 800–1000 °C for 2 h. The BT and BBNT5 powders with a binder (2 wt % polyvinyl alcohol) were uniaxially pressed into a disk with a 15 mm diameter and 1 mm thickness at 190 MPa. The disk samples, directly placed on a platinum sheet, were put in furnace and heated at 1300–1350 °C for 2 h in air. For the phase identification using the powder x-ray diffraction (XRD) technique, the ceramic samples were ground and pulverized. The densities of the BT and BBNT5 ceramics were measured by the Archimedes method using distilled water. Using a fired-on Ag–Zn paste or sputtered Au films, the electrodes were formed on polished ceramic surfaces for the electrical measurements. The frequency dependence of the dielectric constant, ϵ_s and the dielectric loss factor, tan δ, at room temperature (RT) were measured at 100 Hz–10 MHz using an impedance analyzer (HP4194A). The change of ϵ_s and tan δ in the temperature range from RT to 500 °C were also investigated. The polarization-electric field (*P-E*) hysteresis loops were measured using a standard RT6000 (Radiant Technologies, Inc.) from RT to 200 °C.

The BBNT5 ceramics showing the PTCR behavior were prepared by La^{3+} doping or a reducing process. In the La^{3+} doping process, we prepared the starting materials with chemical compositions $[Ba_{1-x}(Na_{1/2}Bi_{1/2})_x]_{1-y}La_yTiO_3$ ($x=0.05$, $y=0.002-0.005$:100yLa−BBNT5) using La_2O_3 (Rare Metallic Co., Ltd.) and the raw material powders described in the previous paragraph. We selected the content of the dopant (La) by referring to the paper of Saburi.[9] The calcination and pressing processes were the same as in the previous paragraph. The green bodies of 100*y*-BBNT5 were placed on a platinum sheet covered with zirconium oxide powder (Kojyundo Chemical Laboratory Co., Ltd.; Lot. No.28610K) and sintered at 1350 °C for 2 h in air. The sintered samples were cooled in the furnace down to room temperature. We also prepared La-doped BT ceramics, $Ba_{0.998}La_{0.002}TiO_3$, sintered at 1390 °C for 2 h in air for comparison of PTCR properties. For the reduced BBNT5 ceramic samples, we used the BBNT5 calcined powders as the starting materials and sintered the green bodies of BBNT5 at 1350 °C for 2 h in an N_2 gas flow. The resistivity was determined by direct measurement of the current flowing through the samples under the impressed field of 0.1–10 V/mm us-

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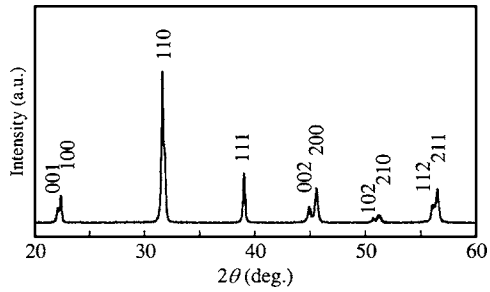

FIG. 1. XRD profiles of BBNT5 powders obtained by pulverizing the ceramics sintered at 1200 °C for 2 h in air.

ing a digital resistance meter (ADVANTEST R8340) from room temperature to 250 °C.

Figure 1 shows the XRD profiles of the BBNT5 powders obtained by pulverizing the ceramic samples. The diffraction pattern is the same as that of the BT. All the peaks of the BBNT5 samples were indexed on the basis of the published data of the host $BaTiO_3$ (ICCD No. 05-0626), indicating no formation of byproducts. These results indicate that the specimens consisted of the single phase of BBNT5 with a tetragonal symmetry [lattice parameters of $a=3.977$ (2) and $c=4.014(3)$Å]. The theoretical density, D_x, is 6.069 g/cm^3. The lattice parameters of BBNT5 were slightly smaller than those of BT ($a=3.994$ and $c=4.038$ Å), in which the A site in an ABO_3 perovskite structure was composed of only barium. This result is reasonable from the viewpoint of the ionic size [Ba^{2+} ($r^{VIII}=1.42$ Å), Na^+(1.18 Å), and Bi^{3+}(1.17 Å)][10] and suggested that the Na^+ and Bi^{3+} cations were introduced into the Ba site.

Figure 2 shows the temperature dependence of the dielectric constant, ϵ_s, and dielectric loss tangent, tan δ, measured at frequencies of 1 MHz for the BBNT5 ceramics. The values of ϵ_s and tan δ for the BBNT5 ceramics at room temperature and at 1MHz were 820 and 0.06, respectively. The plots of the dielectric constant, ϵ_s [Fig. 2(a)] show a peak at 170 °C, which corresponds to the Curie temperature, T_c. The peak position of T_c did not depend on the measurement frequency. This indicates that no relaxation effect has been observed for the BBNT5 ceramics. As shown in Fig. 2(b), the tan δ value drops near the temperature as a peak position of ϵ_s. The T_c value of the BBNT5 ceramics is apparently higher than that (130 °C) of BT. The T_c of the BT ceramics synthesized in this study was identical to that reported in the paper of Jhonson.[3]

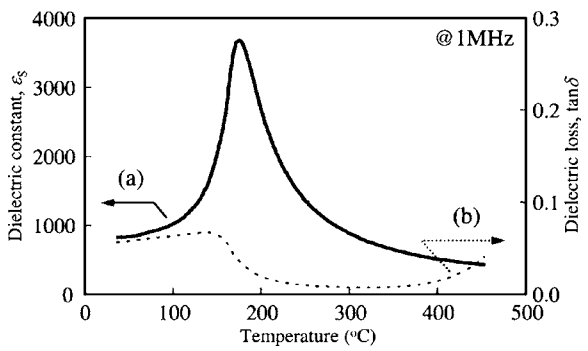

FIG. 2. Temperature dependence of (a) dielectric constant, ϵ_s, and (b) dielectric loss factor, tan δ, as a function of temperature for the BBNT5 ceramics, measured at 1 MHz. Curie temperature (T_c)=170 °C.

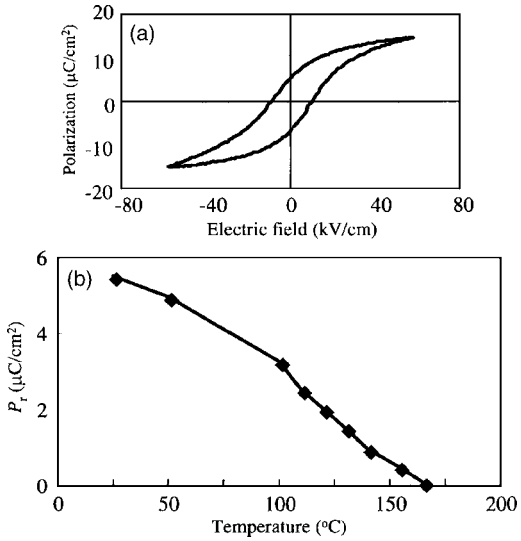

FIG. 3. (a) Typical P-E hysteresis loop measured at room temperature and (b) temperature dependence of calibrated remanent polarization P_r for the BBNT5 ceramics.

Figure 3(a) shows a typical polarization hysteresis loop for the BBNT5 ceramics measured at room temperature. A well-developed hysteresis loop is observed. The remanent polarization, P_r and coercive fields, E_c, were 5.5 μC/cm^2 and 45 kV/cm, respectively. Temperature dependence of P_r is shown in Fig. 3(b). The P_r values in Fig. 3(b) were determined using switching and nonswitching polarizations, which were measured using the pulse sequence reported in literature.[11,12] Hence, the P_r values in Fig. 3(b) represent the calibrated spontaneous polarization, and the P_r at RT is smaller than that derived from the hysteresis loop in Fig. 3(a). The P_r value gradually decreases with an change in temperature and vanishes near 170 °C. This means that the spontaneous polarization of the BBNT5 ceramics disappeared at this temperature. Therefore, we found that the T_c of 170 °C corresponds to ferroelectric and paraelectric phase transition temperature of the BBNT5 ceramics.

Using the BBNT5 ceramics, the temperature dependence of the resistivity was investigated. The BBNT5 ceramics showed an insulative characteristic in the temperature range of this study, as shown in Fig. 4(a). However, for the La-doped BBNT5 ceramic samples, the resistivity significantly decreased on the order of 10^8-10^9 at RT. All of the 100y-BBNT5 ($y=0.02-0.05$) samples had a low resistivity ρ_{RT} of 10^2-10^3 Ω cm at RT, such as semiconducting materials. In Fig. 4(b), we demonstrate a PTCR characteristic of the 0.4La-BBNT5 ceramics with the lowest ρ_{RT} of 1.6×10^2 Ω cm. The resistivity abruptly increased near 160 °C and reached the maximum ρ_{max} of 7×10^5 Ω cm at 220 °C. In Fig. 4(c), the PTCR characteristic of the La-doped BT ceramics is described. An increase of their resistivity occurs at 130 °C, and the extent of the change is comparable to that reported in Ref. 9. These observations corroborate that the T_c of the BBNT5 ceramics is apparently higher than that of pure BT. The ρ_{max}/ρ_{RT} ratio for the 100y-BBNT5 ($y=0.02-0.05$) ceramic samples was on the order of 10^2-10^4. The temperature coefficient of resistivity denoted as "α", which is defined in the paper of Saburi and Wakino,[13] was 9–15%/°C. As shown in Fig. 4(d), the reduced BBNT5 ceramics show lower ρ_{RT} of 1.0×10^2 Ω cm but smaller increase of resistivity compared with the La-doped ones. This

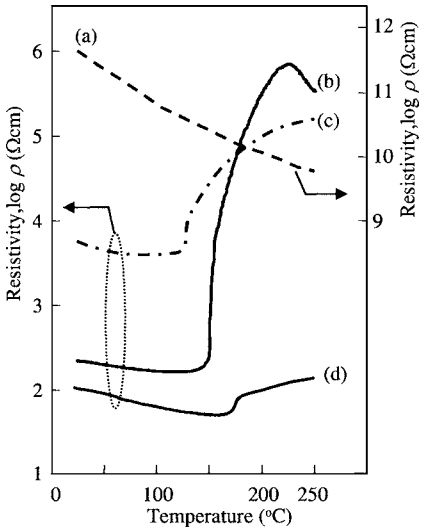

FIG. 4. Temperature dependences of resistivity of (a) nondoped BBNT5, (b) La-doped BBNT5 (0.4La-BBNT5), (c) La-doped BT ($Ba_{0.998}La_{0.02}TiO_3$), and (d) reduced BBNT5 ceramics.

tendency is consistent with the data obtained for the Gd(Dy)-doped BT ceramics sintered in N_2 and/or O_2 atmosphere.[14,15] The ρ_{max}/ρ_{RT} ratio and α values for the La-doped BBNT5 ceramic samples are comparable to those of the conventional PTCR materials, such as a lead-contained BT semiconducting ceramics.[1] The Bi^{3+}-doped BT ceramics exhibit a PTCR characteristic but the T_c of their ceramics is almost the same as the pure BT ceramics.[9] In this study, we have shown the smaller lattice constants and higher T_c of the BBNT5 ceramics compared to the BT ceramics. We consider that the Bi^{3+} cations with the Na^+ ones are incorporated into a $BaTiO_3$ crystal lattice and play an important part in the formation of the BT-BNT solid solution. When the ρ_{RT} of the BBNT5 ceramics can be reduced to one-half or one-third its current value, practical applications will be developed. Of course, the BBNT ceramics displaying PTCR characteristics are also of interest from the viewpoint of solid-state physics.

In conclusion, we have successfully synthesized BT-rich BT-BNT solid solution ceramics with a PTCR above 130 °C, using an ordinary sintering technique. The PTCR characteristics comparable to those of the existing lead-contained PTCR ceramics indicate that this BT-BNT system may be a promising lead-free material for a wide range of PTC thermistor applications.

The authors would like to thank to Dr. S. Okamura and R. Goto of NAIST for advice regarding measurement of the electrical properties. This work was partially supported by Nissan Science Foundation.

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