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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

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Abstract

$BaTiO_3$–$(Bi_{1/2}K_{1/2})TiO_3$ (BT–BKT) ceramics have a low ρ_{RT} of 10^1–10^2 Ω 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, ρ_{max}/ρ_{RT}, of the highest resistivity (ρ_{max}) and the resistivity at room temperature (ρ_{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.

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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 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.

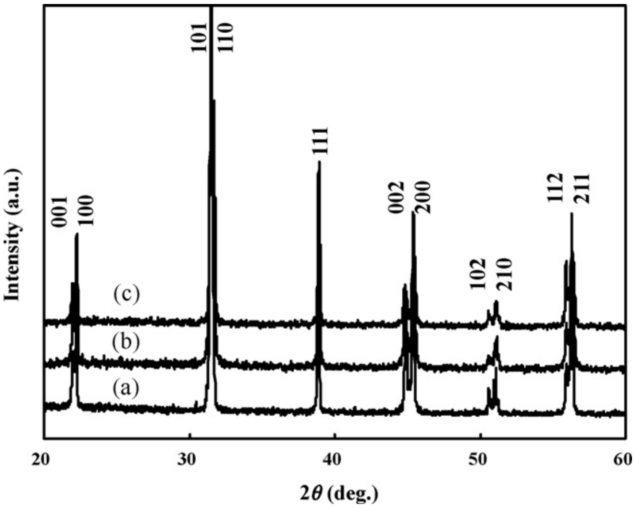

Fig. 1. Powder X-ray diffraction patterns of (a) pure BT (b) BBKT5 and (c) BBKT10 sintered in a N_2 flow.

Fig. 2 shows the temperature dependence of the dielectric constant, ε_s, and dielectric loss, tan δ, 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 ε_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 ρ_{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, ρ_{max}/ρ_{RT}, of the highest resistivity (ρ_{max}) and the resistivity at room temperature (ρ_{RT}) of the ceramics annealed at