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Fabrication of lead-free and high T_c $BaTiO_3$-based thermistor ceramics using deoxidizing effect of oxygen-containing α-zirconium

Hiroaki Takeda [a,*], Yoichiro Hoshi [a], Tsukuru Kinoshita [a], Toetsu Shishido [b], Takashi Nishida [a], Tadashi Shiosaki [a]

[a] *Graduate School of Materials Science, Nara Institute of Science and Technology, Takayama-cho 8916-5, Ikoma, Nara 630-0192, Japan*
[b] *Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan*

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Abstract

Oxygen-containing α-zirconium (α-ZrO_x) has been synthesized by an arc melting method. The oxidation of the α-ZrO_x powders occurs at 480 °C in air. After this oxidation, the reaction product is normal zirconia ZrO_2 powders. We demonstrate an application of this oxidation process. By firing green bodies of $BaTiO_3$–$(Bi_{1/2}Na_{1/2})TiO_3$ solid-solution ceramics in contact with the α-ZrO_x powders, the ceramics acquire a semiconductivity with a positive temperature coefficient of resistivity (PTC) behavior. We propose a method to prepare lead-free PTC thermistor ceramics with a Curie temperature T_c over 130 °C, which is that of $BaTiO_3$, in air.

Keywords: Arc melting; Oxidation; Reductant; PTC; Lead-free

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1. Introduction

Barium titanate ($BaTiO_3$; BT)-based semiconductor ceramics are well-known to have a positive temperature coefficient of resistivity (PTC) [1]. Such ceramics are widely used as PTC thermistors for current control element, heater and sensor uses. The BT ceramics including the element lead are usually adopted for higher temperature heater elements, which are operated at temperatures higher than the Curie temperature T_c of BT (=130 °C). Recently, there has been a requirement to reduce the amount of lead in electronic devices. In Refs. [2,3], as new lead-free PTC thermistor materials with a $T_c > 130$ °C, the semiconducting ceramics of the BT–$(Bi_{1/2}Na_{1/2})TiO_3$ (BNT, $T_c = 320$ °C [4]) system were proposed. Shimada et al. [5] obtained lead-free PTC materials with a low resistivity at room temperature ρ_{RT} and high temperature coefficient by sintering the La-doped $Ba_{1-x}(Bi_{1/2}Na_{1/2})_xTiO_3$ (BBNT) ceramics with small amounts of other additives (Al_2O_3, SiO_2, etc.) in a low O_2-containing atmosphere. The properties of a heater constructed using such BBNT ceramic elements were comparable to those of a heater using the conventional lead-containing ones.

In Refs. [1,6,7], BT semiconducting ceramics were obtained by doping trivalent (La^{3+}, Sm^{3+}, etc.) cations into the Ba^{2+} site or pentavalent (Nb^{5+}, Ta^{5+}, etc.) ones into the Ti^{4+} site. Moreover, the doped BT ceramics showed a semiconductivity even by sintering in air. On the other hand, a very low O_2 partial pressure of ppm order was quite effective for synthesizing BBNT semiconducting ceramics with low ρ_{RT} values [5,8]. The authors have developed a method for producing BBNT semiconducting ceramics in air in order to simplify the mass production process. One idea is the co-firing of BBNT ceramics with a reducing agent which has a deoxidizing effect. The authors paid attention to zirconia (ZrO_2) powders which are commonly used as a separator that prevents ceramics from reacting with the container materials during the sintering process. Oxygen deficient zirconia $ZrO_{2-\delta}$ or oxygen-containing α-zirconium (α-ZrO_x)[1] [9] is expected to be used as reducing agent candidates. Although a few researchers have

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[1] In Ref. [9], both pure and oxygen-containing α-zirconium are represented by α-Zr. The authors used the chemical formula α-ZrO_x in this paper for discrimination among them.

* Corresponding author.
E-mail address: hiro-t@ms.naist.jp (H. Takeda).

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reported the synthesis of α-ZrO$_x$ [10,11], there is no report about the oxidation process of such metals and their application.

In this paper, the authors report the synthesis of α-ZrO$_x$ by the arc melting method and investigation of its oxidation process. By oxidizing α-ZrO$_x$, the authors demonstrated the fabrication processes of BBNT semiconducting ceramics in air.

2. Experimental procedure

2.1. Synthesis and characterization of α-ZrO$_x$

The samples were prepared by the arc-melting method in a titanium-gettered argon atmosphere using 99.8% pure Zr metal pellets and 99.99% pure ZrO_2 powder as the raw materials. Approximately 4 g mixtures of the starting materials were melted for 2 min in an argon arc plasma flame using a dc power source at 20 V and 150 A. The samples were turned over and then remelted three times under the same conditions. The products were ground and pulverized for the phase identification using the powder X-ray diffraction (XRD) technique. The thermal behavior of the powder was investigated using a thermal gravity–differential thermal analysis (TG–DTA) instrument (Mac Science TG-DTA2020S). The TG–DTA was carried out up to 1100 °C at the heating rate of 10 °C min^{-1} in air. The powders heated at 1350 °C for 2 h were also checked by the powder XRD analysis. The powders used as the separator material during the sintering process of BBNT ceramics are described later.

2.2. Fabrication and characterization of lead-free PTC ceramics

Powders with the nominal composition $Ba_{1-x}(Bi_{1/2}Na_{1/2})_xTiO_3$ with $x = 0$, 0.05, 0.06, 0.1 (BT, BBNT5, BBNT6, BBNT10) were prepared using $BaCO_3$ (Rare Metallic Co. Ltd.), Na_2CO_3, TiO_2 (Kojyundo Chemical Laboratory Co. Ltd.), and Bi_2O_3 (Rare Metallic Co. Ltd.) of 99.99% purity as the starting materials. The powders were mixed in acetone, dried, and then calcined at 900–1000 °C for 2 h. All 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 in air. The densities of the ceramics samples were measured by 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 to 10 MHz using an impedance analyzer (HP4194A). The changes of ε_s and tan δ in the temperature range from RT to 500 °C were also investigated.

By La^{3+} doping [1,5], BBNT ceramics were sintered in order to produce the PTC behavior. The starting materials with the nominal chemical compositions $[Ba_{0.95}(Bi_{1/2}Na_{1/2})_{0.05}]_{0.996}La_{0.004}TiO_3$ (La–BBNT5) were prepared. The raw material powders were the same as described in the previous paragraph and 99.99% purity La_2O_3 (Rare Metallic Co. Ltd.). The calcination and pressing processes were the same as described in the previous paragraph. The green bodies of La–BBNT5 were placed on a platinum sheet covered with the separator material powders and sintered at 1340 °C for 2 h in air. Two types of separator material powders were used for the sintering. One of them was the normal ZrO_2 powders and the other was a mixture of the normal ZrO_2 powder and the α-ZrO$_x$ powder synthesized in this study. The sintered samples were cooled while in the furnace down to room temperature. The resistivity 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 room temperature to 250 °C.

3. Results and discussion

The authors synthesized the α-ZrO$_x$ phase by the arc melting technique using the mixture of Zr and ZrO_2 with various ratios as shown in Table 1. Table 1 includes the results of the phase identification by the powder XRD technique. Samples nos. 1 and 2 were composed of only the α-ZrO$_x$ phase. On the other hand, samples nos. 3–5 contained ZrO_2 as the secondary phase. In Ref. [10], the solubility of oxygen in *a*-zirconium is 28.6 at.% ($ZrO_{0.40}$). The result of the synthesis performed in this study agreed well with that reported in Ref. [10]. Since the Zr metal powder is flammable solid, it is difficult to handle in air and at high temperature. Therefore, sample no. 2, which consisted of the pure α-ZrO$_x$ phase with a high oxygen content,

Table 1
Composition and oxygen content of starting raw materials, and reaction products by arc melting

Sample no.	Starting raw materials			Arc melting results (XRD intensity ratio)[a]	
	Composition ratio		Oxygen (at.%)	α-ZrO$_x$	ZrO_2
	Zr	ZrO_2			
1	1	0.1	15	100	–
2	1	0.2	25	100	–
3	1	0.4	36	94	6
4	1	0.8	47	84	16
5	1	2	67	43	57

[a] Maximum intensity peak ratio: $I_{1\,0\,1}$(α-ZrO$_x$):$I_{-1,1,1}$(ZrO_2).

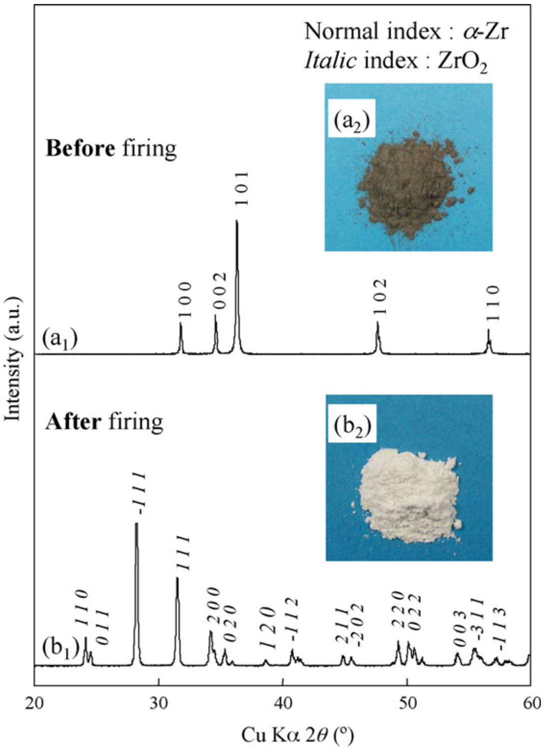

Fig. 1. Thermogravity and DTA curves of α-ZrO_x powders (sample no. 2).

was used for further investigation. The aggregate of sample no. 2 were pulverized and the α-ZrO_x powders were obtained.

Fig. 1(a_1) and (b_1) shows the XRD profiles of the α-ZrO_x powders (sample no. 2) before and after firing at 1340 °C for 2 h, respectively. The firing temperature was the same as the sintered one for the BBNT ceramics. The corresponding photographs are also shown in Fig. 1(a_2) and (b_2). As mentioned above, all the peaks of sample no. 2 before firing were assigned to those of the Zr metal. The diffraction pattern was indexed on the basis of the published data of zirconium (ICCD #05-0665), indicating no formation of byproducts. As shown in Fig. 1(b_1), the sample after firing was composed of only the zirconia (zirconium dioxide, ICCD #37-1484) phase. These results indicated that the α-ZrO_x powders reacted with oxygen in air and changed into ZrO_2.

The oxidation process of the α-ZrO_x phase was investigated by TG–DTA analysis. Fig. 2 shows the TG–DTA curves of sample no. 2 measured from room temperature to 1100 °C in air. The DTA curve has a slow exothermic peak from 400 to 800 °C. In the TG curve, an increase in the mass of the sample is observed from about 350 °C and finishes around 800 °C. It was determined that the mass increase in sample no. 2 occurs at 480 °C in air. Based on these results, the following equation is applicable:

$$\alpha - \mathrm{ZrO}_x + (1 - (x/2))\mathrm{O}_2 \rightarrow \mathrm{ZrO}_2 \quad \text{in air at } 480\,^{\circ}\mathrm{C} \tag{1}$$

For this TG–DTA measurement, 6.0 mg of sample no. 2 was used. As shown in Fig. 2, the sample gained 1.55 mg after the measurement. Because it was clear that the α-ZrO_x phase changed into the ZrO_2 one after heating in air, the oxygen content x of the initial α-ZrO_x phase was estimated using Eq. (1). The estimated value of $x = 0.41$ was very similar to the solubility limit $x = 0.40$ shown in the Zr–O binary phase diagram [10]. The α-ZrO_x powder was used as a reducing agent during the sintering process.

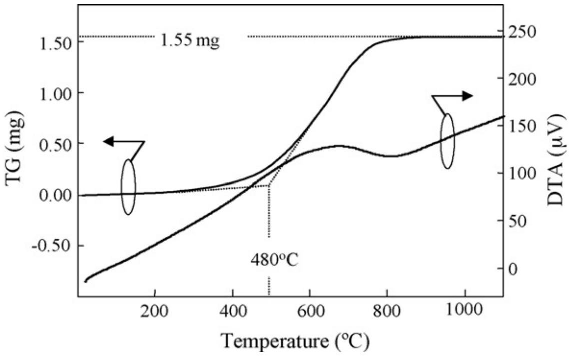

Fig. 2. X-ray diffraction profiles (a_1 and b_1) and photograph (a_2 and b_2) of α-ZrO_x powders of sample no. 2 before and after the sintering process.

Fig. 3 shows the temperature dependence of the dielectric constant, ε_s, and electric resistivity, ρ, for the BBNT5 and BBNT10 ceramics. The ε_s values were measured at the frequency of 1 MHz. The values of ε_s for both ceramics at room temperature at 1 MHz were about 1000. The plots of ε_s show peaks at 170 and 200 °C for the BBNT5 and BBNT10 ceramic specimens, respectively. The peak positions of T_c did not depend on the measurement frequency. This indicates that no relaxation effect has been observed for the BT-BNT solid-solution ceramics. The maximum ε_s values near the T_c were approximately 4000 for both ceramics. As shown in Fig. 3, the ρ values for both BBNT ceramics are almost on the 10^{12} Ω cm order at room temperature. The high ρ values of $>10^9$ Ω cm remained up to 200 °C. These results disclosed that the BBNT ceramics sintered in air have an insulative behavior and their T_c values are higher than that of BT.

The BBNT5 ceramics were rendered semiconductive by La-doping and sintering in air. Fig. 4 shows the temperature response of the resistivity of the non-doped BBNT5 and La–BBNT5 ceramics. As mentioned in the previous paragraph, the non-doped BBNT5 ceramics showed an insulative behavior as

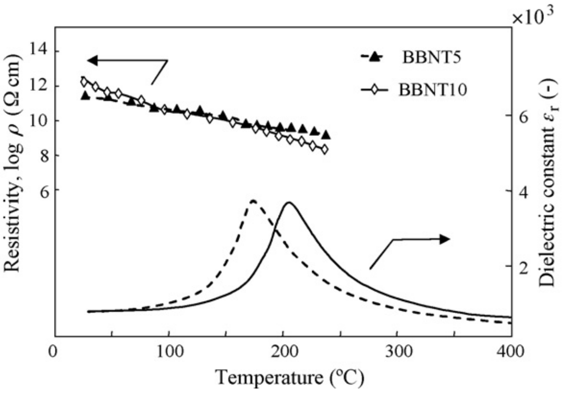

Fig. 3. Temperature dependence of dielectric constant, ε_s, measured at 1 MHz and resistivity, ρ, as a function of temperature for the BBNT5 and BBNT10 ceramics.

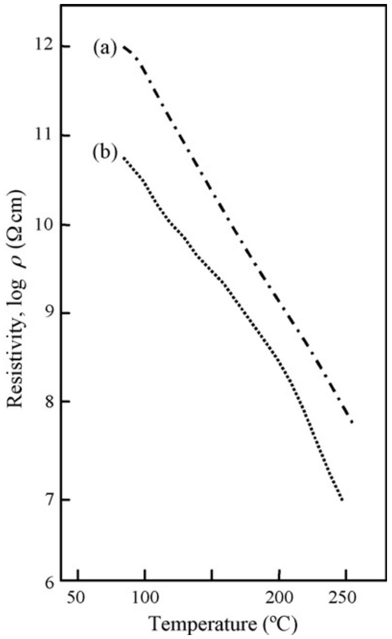

Fig. 4. Temperature dependences of resistivity of (a) non-doped BBNT5 and (b) La-doped BBNT5 (0.4La–BBNT5) ceramics. For fabrication of these ceramics, the green bodies were placed on normal ZrO_2 powder and sintered at 1340 °C for 2 h in air.

shown in Fig. 4(a). For the La–BBNT5 ceramic samples, one order of the ρ values decreased compared to that of non-doped BBNT5 ceramics. However, the temperature dependence of ρ was the same as that of the non-doped ceramics. The La–BBNT5 ceramics had the high value of $>10^7$ Ω cm even at 250 °C as shown in Fig. 4(b). Although the La–BBNT5 ceramics with various La contents were synthesized, no PTC behavior was obtained for all the samples. La-doping has commonly been utilized for the semiconductorization of BT-based ceramics [1], but is insufficient to give PTC properties to the BBNT ceramics. Since, bismuth oxide is volatile at high temperature, it seems that some of the Bi^{3+} ions were evaporated during the sintering process. As a result, because the La^{3+} ions in the La–BBNT5 ceramics did not act as a dopant, the ceramics still showed an insulative behavior.

Using the BBNT5 ceramics obtained by co-firing with the α-ZrO_x powder, the temperature dependence of the resistivity was investigated. At first, only α-ZrO_x powders were used as the separator during the sintering process. The products crumbled and the color was black. This result suggested that the reducing action of the α-ZrO_x powder was too strong. Therefore, for further sintering, the mixed powders of α-ZrO_x and ZrO_2 with a 1:9 weight ratio were used. Fig. 5 shows the temperature dependences of ρ of the BBNT ceramics fabricated by an oxidation process of α-ZrO_x during the sintering process. For checking the reducing effect of the α-ZrO_x powder, non-doped BBNT6 ceramics were prepared by sintering them around (not-contacted) or in contact with the mixture powders. The corresponding temperature dependences of ρ are shown in Fig. 5(a) and (b). On the basis of the reduction process proposed in Ref. [1], it was expected that the BBNT ceramics without any additives acquired their semiconducitivity through the following process:

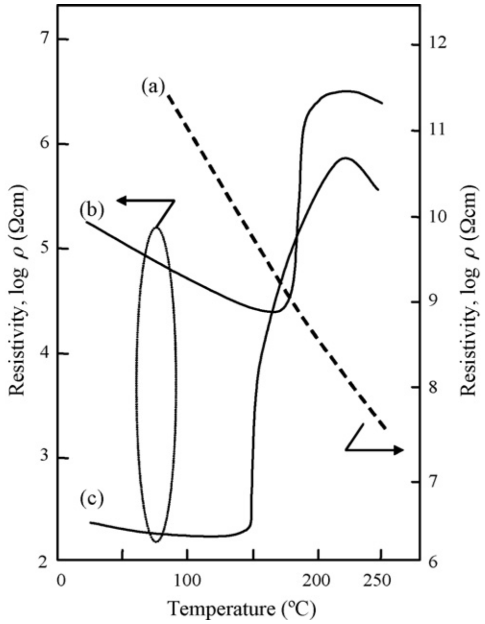

Fig. 5. Effect of oxidation of α-ZrO_x during sintering process on temperature dependences of resistivity of BBNT ceramics. The resistivity data of (a and b) non-doped BBNT6 and (c) 0.4La–BBNT5 ceramics are plotted. During the sintering process, the green bodies were placed (a) away from and (b and c) in contact with mixture powders of α-ZrO_x and normal ZrO_2 with 1:9 weight ratio. All the ceramic samples were sintered at 1340 °C for 2 h in air.

$$\begin{aligned}&\mathrm{Ba_{1-x}}^{2+}(\mathrm{Bi_{1/2}Na_{1/2}})_x{}^{2+}\mathrm{Ti}^{4+}\mathrm{O_3}^{2-} - \delta\mathrm{O}\\&\quad\rightarrow \mathrm{Ba_{1-x}}^{2+}(\mathrm{Bi_{1/2}Na_{1/2}})_x{}^{2+}\mathrm{Ti_{1-2\delta}}^{4+}\mathrm{Ti_{2\delta}}^{3+}\mathrm{O_{3-\delta}}^{2-}\end{aligned} \tag{2}$$

In this study, only the BBNT6 ceramics sintered in contact with the α-ZrO_x-containing powders showed small PTC properties as shown in Fig. 5(b). This means that the α-ZrO_x powder acted as a reducing agent and directly deoxidized the BBNT ceramics during the sintering process. In Fig. 5(b), the resistivity abruptly increased near 180 °C. This observation corroborated that the T_c of the BBNT6 ceramics is apparently higher than that of pure BT. Based on these observations, the La–BBNT5 ceramic samples were also prepared by sintering in contact with the α-ZrO_x-contained powders. In Fig. 5(c), the PTC properties of the La–BBNT5 ceramics are shown. The resistivity significantly decreased on the order of 10^8 to 10^9 at room temperature compared to that sintered on the normal ZrO_2 powders. The samples had a low resistivity ρ_{RT} on the order of 10^2 Ω cm at room temperature. The resistivity abruptly increased near 160 °C and reached the maximum ρ_{max} of 7×10^5 Ω cm at 220 °C. The ρ_{RT} value and ρ_{max}/ρ_{RT} ratio for the La–BBNT5 ceramic samples are comparable to those of the conventional PTC thermistor materials such as the lead-contained BT semiconducting ceramics [12]. The use of the α-ZrO_x powder enables air sintering, namely, the conventional sintering process of the BBNT semiconducting ceramics.

4. Summary

In this study, the pure α-ZrO_x phase was synthesized by the arc melting method. The oxidation process of the α-ZrO_x

powder during heating in air was clarified and an application of its reducing action was proposed. Using α-ZrO_x-containing ZrO_2 powders as a separator, BBNT semiconducting ceramics with a PTC property were successfully synthesized in air. Therefore, the α-ZrO_x powder is expected to be a reducing agent which works at high temperature.

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