

Lead free PTCR ceramics and its electrical properties

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Abstract

Lead free positive temperature coefficient of resistivity (PTCR) ceramics based on $\text{BaTiO}_3-(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BT–BNT) solid solution were prepared by a conventional solid state reaction method using high purity reagents. Temperature dependence of the electrical resistivity was measured and a typical PTCR effect was confirmed in the solid solutions up to 30 mol% addition of BNT. Especially 8.8 mol% BNT added sample indicated superior PTCR properties by optimizing the preparation conditions. Thermal electrical properties and crystal structure were investigated in order to elucidate the origin of the PTCR effect in this system. The DSC spectra of this system indicated the transition to cubic from tetragonal crystal structure and the transition temperature increased with BNT addition up to about 175 °C. Also the boundary layer on the grains was observed by Scanning Spreading Resistance Microscope (SSRM) technique. And then the broad signal of electron emission concerning the interface states was observed using Isothermal Capacitance Transient Spectroscopy (ICTS) technique. In our study, it was found that the PTCR ceramics in BT–BNT system has extremely similar properties to the conventional lead contained one.

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1. Introduction

A semiconductive ceramics based on donor doped BaTiO_3 with positive temperature coefficient of resistivity (PTCR) effect is well known. This semiconductive ceramics called PTCR ceramics was discovered in the middle of 1950s and developed in 1960s.^{1–4} The significant feature of the PTCR ceramics is to show an anomalous increase in electrical resistance above Curie temperature (T_c) and this property is applied for several electric devices, for example, temperature sensor, self-controlled heater and device for overcurrent protection. As well known, since the T_c of the BaTiO_3 is about 120 °C, the BaTiO_3 PTCR ceramics is used for the electric devices performed at temperatures less than 120 °C. When the PTCR ceramics is used at a temperature above 120 °C, PbTiO_3 (PT) is added to the BaTiO_3 , in order to shift the T_c to a temperature above 120 °C.

However, recently, it has been begun to discuss many environmental problems concerning use of the injurious chemicals diffusing in the electroceramics field.⁵ Lead is one of the objects of this discussion and several products, besides solder, will be

perfectly prohibited to use in the electric devices. As mentioned above, the PTCR ceramics having higher T_c than 120 °C contains the PbTiO_3 to shift the T_c . Therefore, it is required to develop the lead free PTCR ceramics in order to improve such an environmental problem for the lead compound use. In 2003, we have successfully developed the lead free PTCR ceramics based on $\text{BaTiO}_3-(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BT–BNT) system and measured its electrical properties and studied microstructure structure of this material.

In the present study, we would like to introduce lead free PTCR ceramics, which possesses higher T_c , from 120 to 180 °C, and show their resistivity variations with temperature. In addition using Scanning Spread Resistance Microscopy (SSRM) and High Resolution Transmission Electron Microscopy (HRTEM), the high resistance regions formed around the grains and the microstructure of the lead free PTCR ceramics were investigated in this paper.

2. Experimental procedure

Since the lead free PTCR ceramics consisted of solid solutions of BaTiO_3 (BT) and $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT), their compositions are abbreviated $(1-x)\text{BT}-x\text{BNT}$ in this paper.

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The $(1-x)\text{BT}-x\text{BNT}$ solid solutions were prepared by the conventional mixed-oxide technique using high purity oxides of titanium and bismuth oxide (more than 99.9 mol%) and barium and sodium carbonates (dried powder has purity of 99.9 mol%). Stoichiometric amounts of the oxides and carbonates were weighed and thoroughly mixed in ethanol using a ball mill pot for 5 h. The mixed powder was calcined for 4 h at 1000 °C. After granulation with PVA, the powder was pressed into a board shaped pellets at a pressure of 150 MPa and sintered in an electric furnace with controlled oxygen concentration (less than 10 ppm oxygen) at 1290 and 1320 °C. The sintered samples were cut to 10 mm² in square and grinded up to 1 mm in thickness. And then 10 μm thickness of the ohmic electrodes were constructed on the two grinded surfaces using the screen printing method.

The crystalline phases of the sintered ceramics were identified by X-ray powder diffraction method (JEOL JDX8200) and the change of phase transition temperature of each composition was observed by Differential Scanning Calorimetry (DSC). The shifts of the diffraction lines were observed. Resistivities of the ceramics were measured by the two probes electrodes method under extremely low current (DC and AC currents were under 0.01 nA and 0.1 μA, respectively) between the probes using HP3458A multimeter. The samples were heated until 260 °C from room temperature by 1.5 °C min⁻¹ in thermo chamber with the temperature control unit. The samples adjusted as the T_c is approximately equal to 160 °C were prepared and sintered in the atmosphere controlled in the oxygen concentration range of 6–9 ppm at 1320 °C so that the resistivity at room temperature decreased and was than 100 Ωcm. Then the samples were pol-

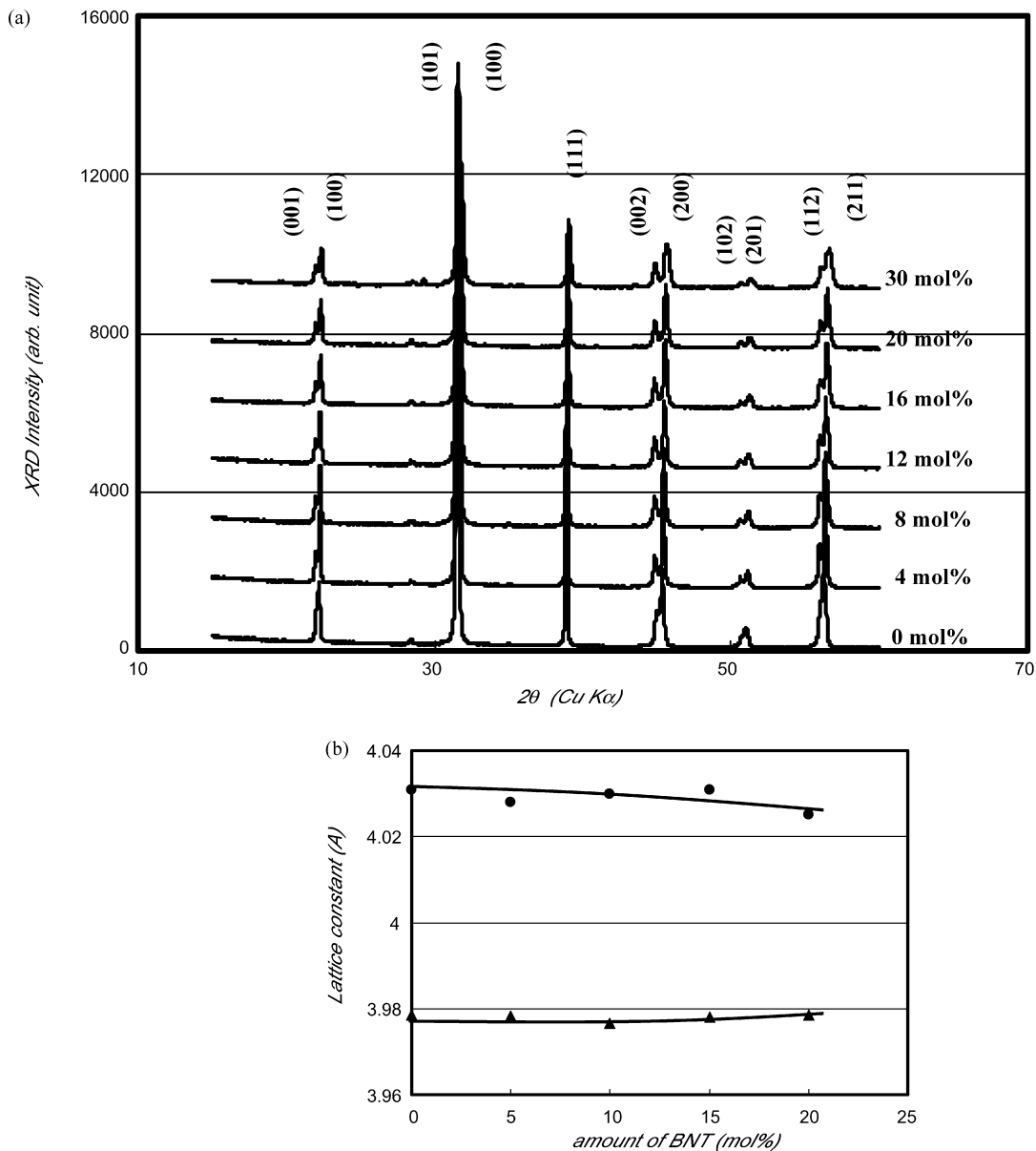


Fig. 1. XRD patterns of $(1-x)\text{BT}-x\text{BNT}$ system, BNT additions were in 0–30 mol% ($x=0-0.3$).

ished until average roughness (Ra) was less than 1 μm in order to observe the Schottky barrier formed around the grain boundary using the Scanning Spreading Resistance Microscope (SSMR), which is a kind of special technique to measure the resistance distribution applying Atomic Force Microscopy (AFM) to the resistance measurement.⁶ Also the High Resolution Transmission Electron Microscopy was used for observation if the layered phases were formed at the grain boundaries or not. In addition a part of the sample was processed to the chips having 2 mm in thickness, 3 mm in wide and 5 mm in height to measure Isothermal Capacitance Transient Spectroscopy (ICTS). Also the samples, which were prepared in the composition having $T_c = 160$, were sintered under the optimized conditions mentioned above and were cut to a rectangular disc (6 mm \times 30 mm and 1 mm in thickness), and then these elements were mounted into PTCR heater unit and the properties as a heater, for example, surface temperature, voltage–current curves and so on, were measured.

3. Results and discussion

Fig. 1 (a) shows the XRD patterns of the $(1-x)\text{BT}-x\text{BNT}$ samples with x up to 0.30. The secondary phases were not confirmed for each solid solution system in the XRD patterns. The $(00n)$ and (201) lines kept 2θ to constant values and only (102) line decrease slightly to 49.74° from 50.24° . The other diffraction lines shifted to higher angles with BNT addition. As shown in Fig. 1 (b), this variation means that the a - and c -axes of the tetragonal structure decreased and increased, respectively, with the substitution of Bi and Na ions to A site in the BT and it brought the volume decreasing of the unit cell in the BT–BNT. It was considered that the shrinkage of the lattice volume was due to relatively small ion size⁷ of Bi (0.96 Å) and Na (0.97 Å) in comparison with Ba ion (1.34 Å). Fig. 2 shows the variation of DSC spectra in the temperature range of 100–200 $^\circ\text{C}$ with BNT addition. The spectra were measured with decreasing temperature from 400 to 90 $^\circ\text{C}$, therefore the all spectra showed

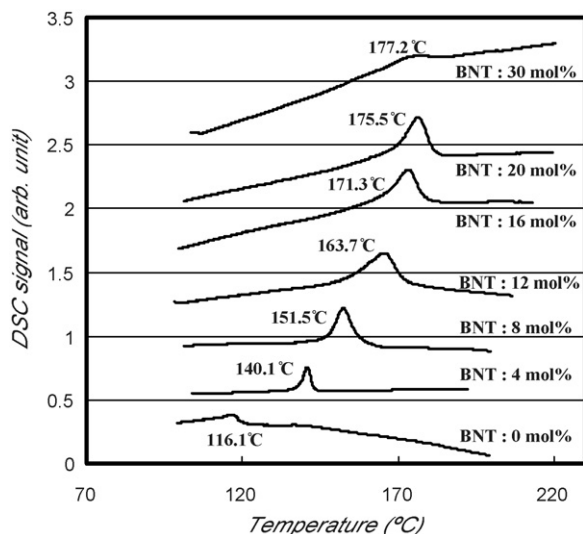


Fig. 2. Variation of DSC signals with increase in amount of BNT.

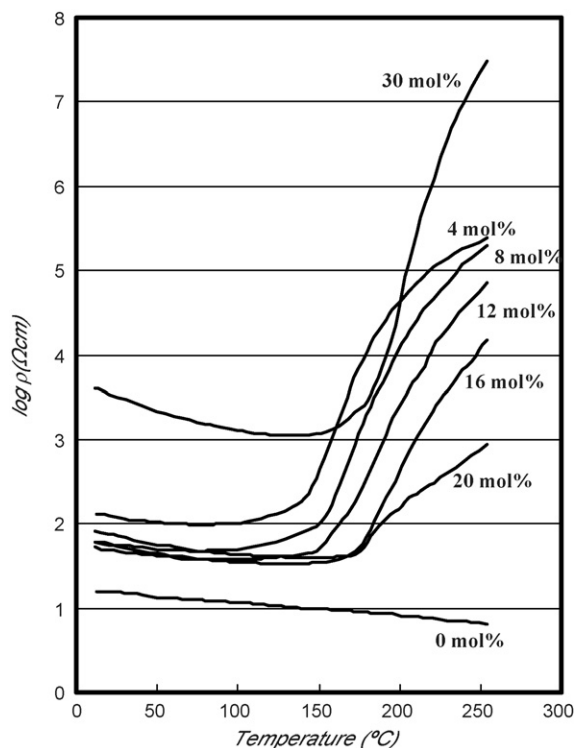


Fig. 3. Temperature dependence of resistivity, this measurement was carried out for BT–BNT samples sintered at 1290 $^\circ\text{C}$.

exothermic transition. The temperatures indicated by peaks in the spectra are the phase transition temperature for each addition ratio of the $(1-x)\text{BT}-x\text{BNT}$. As shown in Fig. 2, the phase transition temperature increased maximum to 175 $^\circ\text{C}$ with the BNT addition up to 20 mol%. For 30 mol% there is a deviation from this behavior.

Figs. 3 and 4 show the temperature dependence of the resistivity of the $(1-x)\text{BT}-x\text{BNT}$ samples sintered at 1290 and 1320 $^\circ\text{C}$, respectively. The anomalous increase in resistivity of BT sintered at 1290 $^\circ\text{C}$ was not observed at all for the pure BT. It is well known that oxygen treatment is necessary to give a jump property for the BT. Since the sintering was carried out in low oxygen concentration in this experiment, the BT did not show PTCR effect. In Fig. 4, however, the slight PTCR effect of the BT appeared in the temperature–resistivity curve. We inferred that the difference between Figs. 3 and 4 came from the slight difference of sintering atmosphere. This means that the condition in sintering system is important for the preparation of PTCR ceramics based on BT, and this atmosphere dependence of the PTCR effect is a big difference from BT–BNT system.⁸ The temperature coefficient of the resistivity (α) above the Curie point of BT–BNT systems indicated the abruptly anomalous resistivity increasing. The order of the anomalous resistivity changes were decreased with increase in BNT additions. The tendency that the T_c is saturated at more than 30 mol% BNT addition is in agreement with the results of the DSC measurements. As shown in Figs. 3 and 4, the T_c was hardly changing by the sintering temperature, but the scattering of the resistivity at room temperature and the resistivity jump property was slightly decreased in the samples sintered at 1320 $^\circ\text{C}$. It was considered that this change

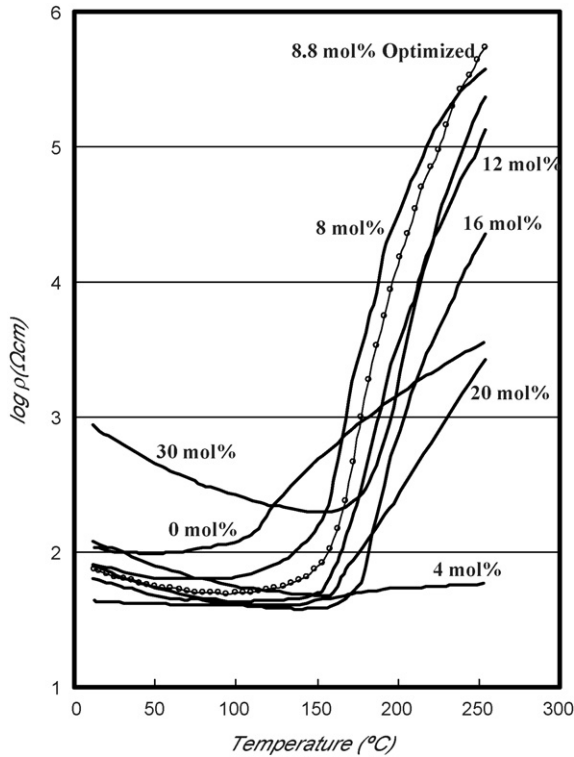


Fig. 4. Temperature dependence of resistivity, BT–BNT samples sintered at 1320 °C and the sample was prepared at atmosphere controlled in the range of 6–9 ppm of oxygen concentration.

was due to imperfection of the solid solution in the BT–BNT system. And the resistivity variation of the sample with optimized sintering conditions is also shown in Fig. 4, this sample contained 8.8 mol% BNT in BT. The jump property was higher

compared with other samples and it was evaluated that the α was about 21.4% K^{-1} .

Fig. 5(a and b) shows the AFM images and the distribution of the resistance in the sample sintered under the optimum conditions, respectively. From Fig. 5(a), it can be seen that the scanned surface was approximately flat over the observation region. Therefore, the variation of the resistivity in Fig. 5(b) was not caused by roughness of the observed surface. Obviously the region at which the resistance was higher than the center of the grains was formed along with the grain boundary. This means that the PTCR effect in the BT–BNT systems probably takes place according to the same mechanism as the BT and lead containing BT or other semiconducting materials. In addition, especially, the triple points around the grains had higher resistance compared with the grain boundaries. It is well known that these high resistivity regions around the grain boundaries formed the electron state at the interface of the multi grains.⁹ These grain boundaries are known as double Schottky barrier which is unique for the semiconductive ceramics. Fig. 6 shows HRTEM image and electron diffraction near the grain boundary of the sample sintered at 1320 °C. It was reported that the interface layers were formed between grains in BT or BT–PT solid solution PTCR ceramics.¹⁰ In the BT–BNT system, however, there are no layers as shown in Fig. 6. Also the electron diffraction shows tetragonal crystal structure for this solid solution, this means that the special component structure like a layered boundary does not make the Schottky barrier between the grains. Namely, also in the BT–BNT system, the electron trap formed only from the boundary junction contributes to form the Schottky barrier. The electron states at the boundary can be measured by variation of the capacitance of the grain boundary as a typical method like the ICTS or deep level transient spectroscopy

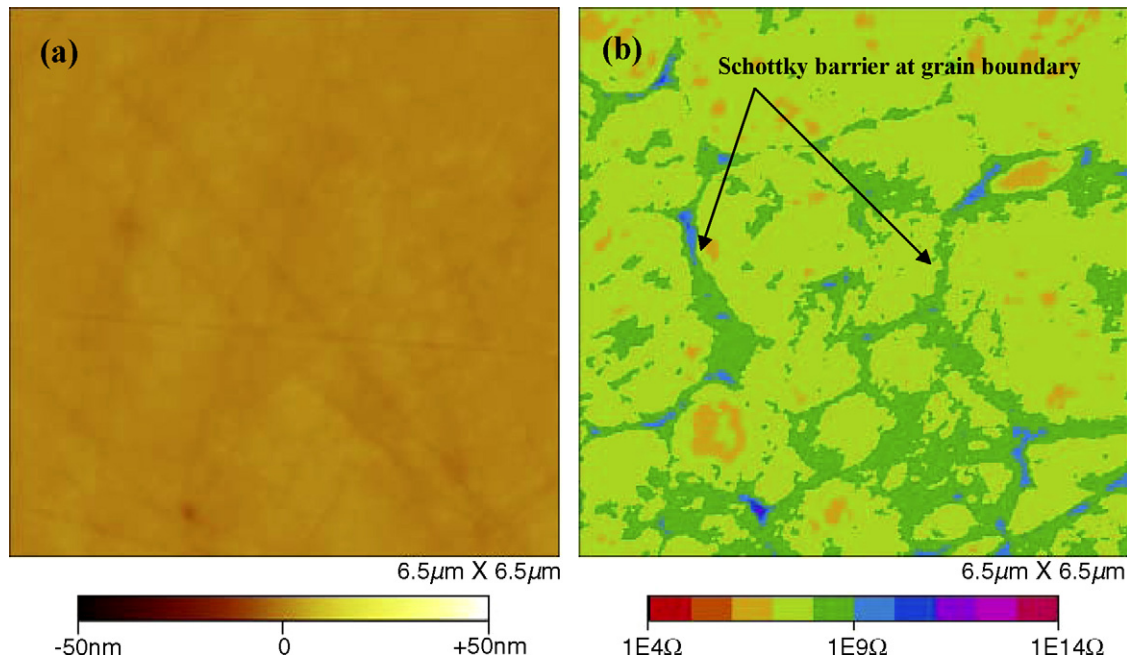


Fig. 5. SSRM images of grain boundary for 0.912BT–0.088BNT sample sintered at 1320 °C under optimized condition (a) AFM image (b) SSRM image, SSRM is a special technology developed as an application of AFM surface measurement.

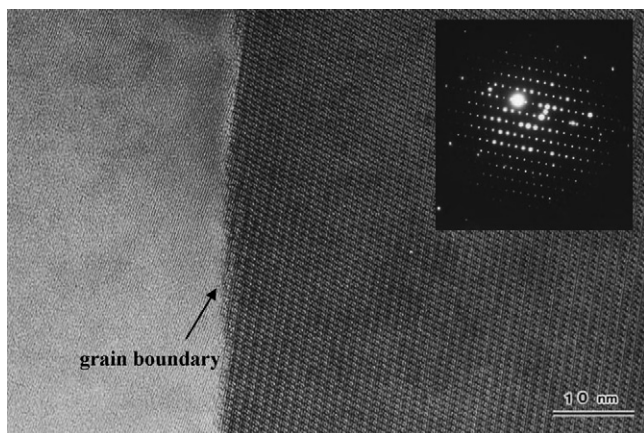


Fig. 6. HRTEM image and electron diffraction near the grain boundary for 0.912BT–0.088BNT sample sintered at 1320 °C.

(DLTS). Fig. 7 shows the ICTS signal at 380 K for the BT–BNT sample sintered at 1320 °C. The pulse intensity of electric voltage was 5 V for the sample. As shown in the spectrum, the signals are complicated, especially for the fast response. In the measurement of the semiconductive ceramics, generally, the simple signals as obtained in single crystal are hardly observed,¹¹ but the temperature dependence of the signals permits to identify the interface states of the electron. Only the slowest signal in Fig. 7 indicated typical temperature dependence, which means that the peak response time shifts to the high value with increasing temperature, and it can be also confirmed that this signal was an extremely broad one.

Many electrical and crystal data obtained from the above mentioned investigations indicated the typical PTCR effect of the BT–BNT system. We wanted to demonstrate the performance of this material as a PTCR heating element. The PTCR elements were manufactured in pre-mass production scale. Fig. 8 shows the electrical and thermal properties of the BT–BNT samples compared with data of the existing lead containing PTCR element. It was confirmed that the lead free PTCR ceramics showed the comparable properties with the lead containing one, therefore it should be possible to replace the PTCR ceramics to the new lead free PTCR ceramics. These results mentioned

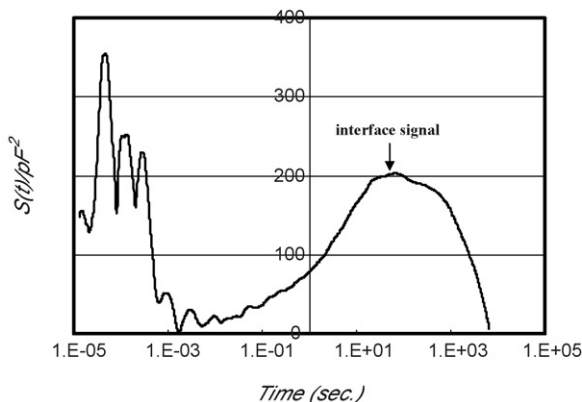


Fig. 7. ICTS of BT–BNT ceramics measured at 380 K for 0.912BT–0.088BNT sample sintered at 1320 °C.

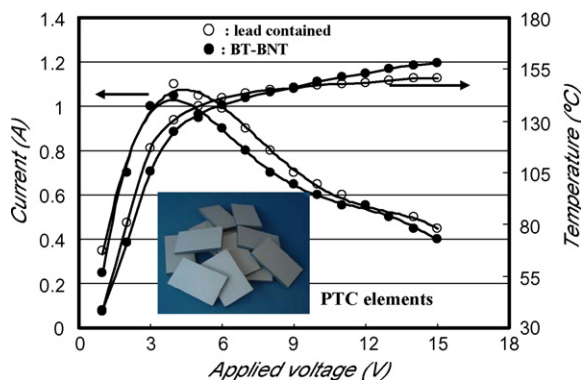


Fig. 8. Applied voltage dependence of surface temperature and current in lead free PTCR thermistors prepared by pre-mass production, these samples contained 8.8 mol% BNT and had resistance of 3 Ω at 25 °C and α more than 20% K⁻¹.

above suggest the possibility for the environmental friendly use of the new lead free PTCR ceramics, however further investigations concerning the quality and reliability of the lead free PTCR ceramics are required for the industrial utilization in near future.

4. Conclusions

Production of the lead containing materials is linked to the grave social problem brought by the waste of heavy element. Therefore, it is expected to develop the lead free materials and electric devices. In the present study, the variation of the electrical properties and the crystallographic investigations of BT–BNT system were carried out in order to confirm the possibility for its industrial utilization as a lead free PTCR element. Then we obtained the following results for the lead free PTCR ceramics in the BT–BNT system. (a) The electrical properties of the PTCR ceramics in BT–BNT system are similar to that of the existing lead containing PTCR ceramics. (b) The formation of Schottky barrier at the grain boundary was confirmed by the observation of the SSRM image of the grains. (c) No secondary layer giving an influence to PTCR effect was observed. (d) The interface electron states were confirmed using ICTS technique and the electrons in their states emission were extremely slow.

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