PREPARATION AND PTCR PROPERTIES OF MnO_2 doped $BaTiO_3$-$(Bi_{1/2}Na_{1/2})TiO_3$ LEAD FREE PTCR CERAMICS WITH HIGH Tc (>160°C)

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Introduction

Non-conductive $BaTiO_3$ (BT) ceramics shows semiconducting characteristics when a small amount of donor is doped adequately.[1] The donor-doped $BaTiO_3$ based ceramics exhibits an abrupt increase in resistance at temperatures near to Curie point (T_C).[2] This behavior is generally referred to positive temperature coefficient of resistivity (PTCR) effect. $PbTiO_3$ with T_C of 490°C has been widely used to shift T_C to higher temperature than that of BT (~120°C).[3] However, since Lead will be probably prohibited to use in the electric devices for environment protection, it is necessary to develop new candidate materials for lead-free PTC thermistors. The $(Bi_{0.5}Na_{0.5})TiO_3$ (BiNT), which has a relatively high T_C of 320°C, is a promising candidate to replace $PbTiO_3$.[4] Recently, various investigations about fabrication and PTCR characteristics of the BT-BiNT system have been reported by Shiosaki et al.[5,6] According to the reports, the BT-BiNT ceramics prepared in air showed unsatisfactory resistivity at room temperature (ρ_{RT}), which is important factor for PTC thermistors. Even though control of various gas atmospheres such as N_2 or O_2 during sintering process resulted in the improvement of ρ_{RT} and PTCR properties of the ceramics, the sintering process is not simple and its characteristics are not still satisfactory.[6] Therefore, in this study, MnO_2 doped BT-BiNT lead free ceramics was fabricated using a simple solid state reaction in air and its PTCR characteristics were systemically investigated.

Experimental

Using conventional solid-state synthesis, 0.95BT-0.05BiNT-xmol% MnO_2 (BaBiNT-x) ceramics with $0 \leq x \leq 0.04$ were prepared from oxides of >99.5% purity. The BiNT, sintered at 850°C for 2 h, was synthesized in advance. Thereafter, BT, BiNT and MnO_2 were mixed for 24 h in a nylon jar with ZrO_2 balls and then dried. The dried powers were calcined at 1150°C for 4 h. After remilling for 24 h, the powers were pressed into disks under a pressure of 1 ton/cm^2 and sintered at 1300°C for 4 h. The structural properties of the specimens were examined by SEM (Topcon). The specimens were ground and the electrodes were made on the face of the disks using Ag-Zn paste. The resistance of the specimens was measured during heating from room temperature to 350°C and then its resistance was calculated.

Results and Discussion

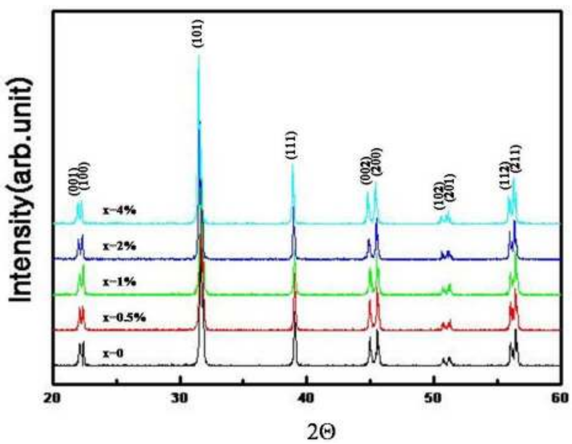

Figure 1. XRD patterns of the BaBiNT-x ceramics with $0 \leq x \leq 0.04$.

Fig. 1 shows the XRD patterns of the BaBiNT-x ceramics with $0 \leq x \leq 0.04$. All the specimen exhibited a typical perovskite structure with a tetragonal symmetry and no secondary phase was not observed. Therefore, it is considered that the BaBiNT-x ceramics are successfully developed.

Fig. 2 shows surface SEM images of BaBiNT-x ceramics with (a) x=0, (b) x=0.5%, (c) x=1% and (d) x=2%. No impurity phase was examined in all the ceramics. It was observed that the area of large grains was decreased with increasing MnO_2 contents.

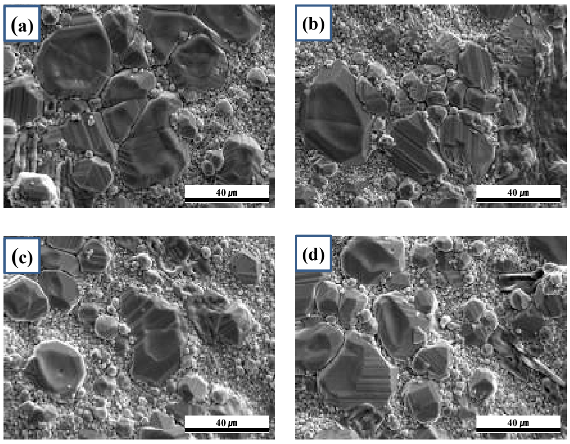

Figure 2. surface SEM images of BaBiNT-x ceramics sintered at 1300°C for 4 h with (a) x=0, (b) x=0.5%, (c) x=1% and (d) x=2%.

Fig. 3 shows the temperature dependence of resistivity (ρ) of BaBiNT-x ceramics with 0≤x≤0.04. The pure BaBiNT ceramics showed good PTCR behavior with low ρ_{RT}. The ρ_{RT} increased with increasing MnO_2 content and T_C was as high as >160°C for all the specimens. It is generally accepted that the decrease of resistivity is associated with the increase of grain size because decrease of grain boundary volume is beneficial to conductivity. Therefore, it could be found that the grain size was responsible for the ρ_{RT} for the BaBiNT-x ceramics as shown in Fig. 1. In particular, BaBiNT-0.04 ceramics showed good PTCR characteristics; ρ_{RT} of 1815 Ω·cm, PTC jump of 1.2×10^5, resistivity temperature factor (α) of 134%/°C along with high Tc of 168°C. The PTCR properties of BaBiNT-x ceramics was summarized in the Table I.

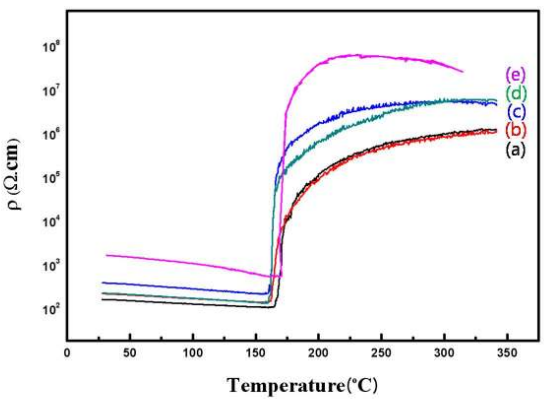

Figure 3. Temperature dependence of resistivity (ρ) of BaBiNT-x ceramics with 0≤x≤0.04.

Table I. PTCR characteristics of BaBiNT-x ceramics.

Contents of MnO_2 (x)	Room Resistivity (Ω*cm)	Magnitude of PTCR effect (ρ_{max}/ρ_{min})	Resistivity temperature factor (%℃)	T_c(℃)
0	177	1.05×10^4	42.9	167
0.5%	239	8.4×10^3	33.9	163
1%	424	2.5×10^4	70.7	161
2%	247	4.6×10^4	64.3	161
4%	1815	1.2×10^5	134	168

Conclusion

The BaBiNT-x lead free ceramics was successfully fabricated using a simple solid state reaction in air. All the specimens exhibited a tetragonal symmetry and good PTCR properties. Especially, the BaBiNT-0.04 ceramics showed good PTCR characteristics; ρ_{RT} of 1815 Ω·cm, PTC jump of 1.2×10^5, resistivity temperature factor (α) of 134%/°C along with high Tc of 168°C.

References

1. Saburi, O. Properties of semiconductive barium titanates. J. Phys. Soc. Jpn., 14 (1959) 1159-1174.
2. Harman, G. G. Electrical properties of $BaTiO_3$ containing samarium. Phys. Rev., 106 (1957) 1159-1358.
3. Lin, Y. Y., Hu, C. T., Chang, H. Y. and Lin, I. N. Electrical properties of the positive temperature coefficient of resistivity materials with 490°C critical temperature. J. Appl. Phys., 83 (1998) 1321-1326.
4. Viviani, M., Leoni, M., Bascaglia, M. T. and Buscaglia, V. Positive temperature coefficient of electrical resistivity below 150 K in barium strontium titanate. J. Am. Ceram. Soc., 87 (2004) 756-758.
5. Takeda H., Shimada, T., Katsuyama, Y. and Shiosaki, T. Fabrication and operation limit of lead-free PTCR ceramics using BaTiO3-(Bi1/2Na1/2)TiO3 system. J. Electroceram., 22 (2009) 263-269.
6. Shimada, T., Touji, K., Katsuyama, Y., Takeda. H. and Shiosaki, T. Lead free PTCR ceramics and its electrical properties. J. Eur. Ceram. Soc., 27 (2007) 3877-3882.