

ภาคผนวก

ภาคผนวก ก



เมื่อดเซรามิก $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3\text{-LiSbO}_3$ มีลักษณะหัก และบดเปรี๊ว ทำให้ไม่สามารถวัดคุณสมบัติทางไฟฟ้าได้
ทางคณะผู้วิจัยได้แก้ไขเปลี่ยนแปลงสารเจือจาก LiSbO_3 มาเป็นสารเจือ SrTiO_3

Electrical properties of Bismuth Potassium Titanate-Strontium Titanate Ferroelectric Ceramics

Prapapim Phetmoi¹, Surasak Niemcharoen^{1*}, Rangson Muanghlua¹, Manoon Sutapun² and Naratip Vittayakorn^{3,3}

¹ Electronics Research Center, Department of Electronics, Faculty of Engineering, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand

² College of KMITL Nanotechnology, King Mongkut's Institute of Technology, Bangkok, Thailand

³ Materials Science Research Unit, Department of Chemistry, Faculty of Science, King Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand

*Corresponding author, e-mail: knsurasa@kmitl.ac.th

Abstract. In this paper, lead-free $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ ceramics doped with SrTiO_3 was prepared by the conventional solid state reaction method with sintering temperature at 1040°C . The samples were characterized by X-ray diffraction analysis and Scanning Electron Microscopy. The dielectric, ferroelectric properties were also investigated. The results of X-ray diffraction reveal that SrTiO_3 diffuse into the $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ lattices to form a solid solution with a pure perovskite structure. After the introduction of SrTiO_3 into $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$, the dielectric constant at room temperature (ϵ_r) was found to decrease with increasing SrTiO_3 . The broadness of the dielectric constant peak was observed with increasing SrTiO_3 content, especially that of the $0.94\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 - 0.06 \text{SrTiO}_3$ ceramic which exhibited a very broad curve over a wide temperature range. The $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 - \text{SrTiO}_3$ system was expected to be a new and promising candidate for lead-free capacitors.

I. INTRODUCTION

Lead zirconate titanate [$\text{Pb}(\text{Zr,Ti})\text{O}_3$; PZT] are widely used for piezoelectric actuators, sensors and transducers due to their excellent piezoelectric properties [1,2]. However, the toxicity of lead oxide and its high vapor pressure during processing demand alternative environmentally friendly materials. In Europe, the legislation on waste electrical electronic equipment has been issued; the use of hazardous substances such as lead in electrical parts is prohibited from 2006. From the viewpoint of sustainable development of world

society, the use of toxic substances should be prohibited in many other countries in the field of piezoelectric ceramics. Therefore, it is necessary to develop lead-free ceramics with excellent piezoelectric properties [3].

Bismuth potassium titanate ($\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$; BKT) is considered as the one of the candidates for lead-free piezoelectric ceramics. BKT was discovered by Smolenskii [4]. And it has a perovskite structure belonging to tetragonal crystal system at room temperature. It undergoes a phase transition around 380°C , the ferroelectric Curie point (T_C). Li et al. [5] reported the dielectric relaxor properties of ferroelectric $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ prepared by sol-gel method. Their structural studies indicate the tetragonal lattice type for BKT with point group $4mm$ and lattice parameters $a = 3.941 \text{ \AA}$ $c = 4.000 \text{ \AA}$. Gadzhiziyev et al. [6] and Elkechai et al. [7] suggested that BKT, at high temperature has cubic symmetry on cooling to a temperature $T_C = 380^\circ\text{C}$, a transition from cubic to tetragonal symmetry take place. According to Ivanova et al. [8], there is a second phase transition at above $T_I = 270^\circ\text{C}$, while Gadzhiziyev et al. observed this second order phase transition at 300°C and they ascribe this phase transition as the one associated with anti-ferroelectric character of the phase. Hou et al. [9] synthesized BKT by sol-gel technique and prepared high-density ceramic samples sintered at 1050°C . Their studies indicate relaxor behavior with dielectric maximum around $380-400^\circ\text{C}$.

Pyroelectric properties, Vijaya Bhaskar Rao et al. [10] reported the pyroelectric maximum at 380°C and observed remnant polarization is about 2 $\mu\text{C}/\text{cm}^2$

With the increasing demand of oxide ferroelectrics, paraelectric Strontium Titanate (SrTiO_3 ; ST) are most promising capacitor materials, because of their high dielectric constant and thermal stability. ST is a quantum paraelectric, where the ferroelectric fluctuations are suppressed by the quantum fluctuations of the atomic positions [11]. It is known that the polar state in ST can be induced via: electric field [12] uniaxial stress [13] cation [14] or oxygen isotope substitutions in the lattice [15]. However the role of Sr/Ti ratio on the dielectric response as well as on the grain growth of undoped ST is not definite. Moreover, the dependence of the quantum behavior on the grain size of undoped ST materials is not clearly established. The optimization of the dielectric response is closely related to the precise control of the composition [16]. In this paper, it has been indicated that ST doping of BKT ceramics show improvement of electrical properties.

II. EXPERIMENTAL

The $(1-x)\text{BKT}-x\text{ST}$; $x = 0.00-0.10$ lead-free ceramics were synthesized by the conventionally solid state reaction methods. This method used high purity AR grade K_2CO_3 (99.0%), Bi_2O_3 (99.5%), SrCO_3 (99.9%) and TiO_2 (99.0%). Alkali carbonates were used as a starting material, which had been treated carefully by a special drying process before use. These powders were placed in an oven at 230°C for 2 days and then stored in a moisture-free vessel [17]. Reagent grade oxide powders were weighed according to stoichiometric formula, and ball-milled with ethanol and yttrium-stabilized zirconia media for 18 h. After drying, the mixture was calcined at 850°C for 4 h. The calcined powders, with polyvinyl alcohol (PVA) added as binder, were pressed into pellets of 15 mm diameter and 2 mm thickness, and sintered at 1,040°C in BKT-atmosphere for 2 h in a closed alumina crucible. X-ray diffraction (XRD; Bruker-AXS D8) using $\text{CuK}\alpha$ radiation was used to determine the phases formed and optimum firing

temperatures for formation of the desired phase. The microstructure analyses were undertaken by scanning electron microscopy (SEM, Leo 1455VP). The dielectric constant was then calculated from $\epsilon_r = Cd/\epsilon_0 A$, where C was the capacitance of the sample, d and A were the thickness and area of the electrode, respectively, and ϵ_0 was the dielectric permittivity of vacuum (8.854×10^{-12} F/m). Polarizations, as a function of electric field (P-E loop) at 4 Hz of the samples, were observed using a ferroelectrics test system (RT66B; Radiant Technologies, Inc.). The peak field was maintained at 50 kV/cm during measurement.

III. RESULTS AND DISCUSSION

Fig. 1 shows the x-ray diffraction patterns of the $(1-x)\text{BKT}-x\text{ST}$; $x = 0.00-0.10$ ceramics. It can be seen that all the ceramics were detected as single perovskite structure.

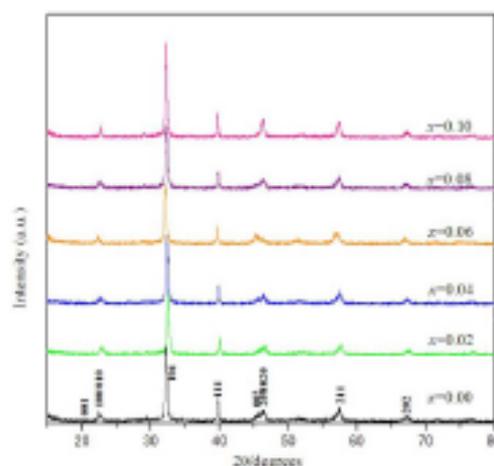


Figure 1. XRD patterns of $(1-x)\text{BKT}-x\text{ST}$ ceramics sintering at 1040°C for 2 h

The result indicated that the dopants were completely diffused into the $(\text{Bi}_{0.5}\text{K}_{0.5})\text{TiO}_3$ lattices, with Sr^{2+} entering the $(\text{Bi}_{0.5}\text{K}_{0.5})^{3+}$ sites to form a homogeneous solid solution. Furthermore, it can be clearly seen that crystal structure of samples with $x \leq 0.08$ exhibited a tetragonal structure. At the composition $x = 0.1$, the ceramic has a cubic structure. As increasing the ST content, the peaks shift toward a higher angle

slightly because the host Bi^{3+} (ionic radius 1.14 Å) and K^+ (1.64 Å) are replaced by doped Sr^{2+} (1.44 Å). Figure 2 shows the SEM images of the fractured surfaces of the $(1-x)\text{BKT}-x\text{ST}$; $x = 0.00-0.10$ ceramics. It is well known that the pure BKT could not be sintered to obtain sufficient density.

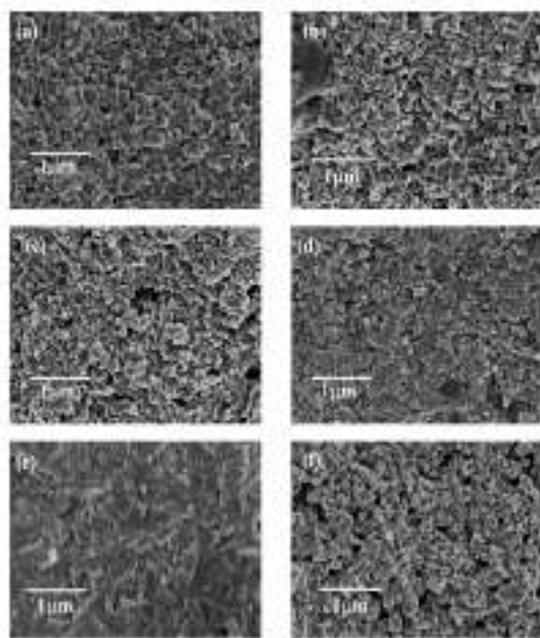


Figure 2. SEM micrograph of fracture surfaces of the $(1-x)\text{BKT}-x\text{ST}$ ceramics sintered at 1040°C for 2 h with (a) $x = 0.00$, (b) $x = 0.02$, (c) $x = 0.04$, (d) $x = 0.06$, (e) $x = 0.08$ and (f) $x = 0.10$

After the doping of ST, the ceramics become denser, porosity degrades and the grain size increases. Figure 3 shows the temperature dependence of dielectric constant of the $(1-x)\text{BKT}-x\text{ST}$; $x = 0.00-0.10$ ceramics. The broadness of the dielectric constant peak was observed with increasing SrTiO_3 content, especially that of the $0.94\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3 - 0.06\text{SrTiO}_3$ ceramic which exhibited a very broad curve over a wide temperature range.

It is also apparent in figure 3 that there is a systematic broadening of peak in dielectric constant at T_c with increasing ST content. The broadening of the peak may be an indication that the grain size of the ceramics slightly increases with increasing ST content. Phenomenon suggests a transition from a normal ferroelectric to 'relaxorlike' ferroelectric [18] due to

the cation disorder in perovskite unit cell and the formation of microdomain since non-ferroelectric ST was added. However a more detailed study is required in order to establish the cause. Figure 4 shows the $P-E$ hysteresis loops of polarization versus electric field for the ST-substituted BKT ceramics measured at room temperature and 4 Hz.

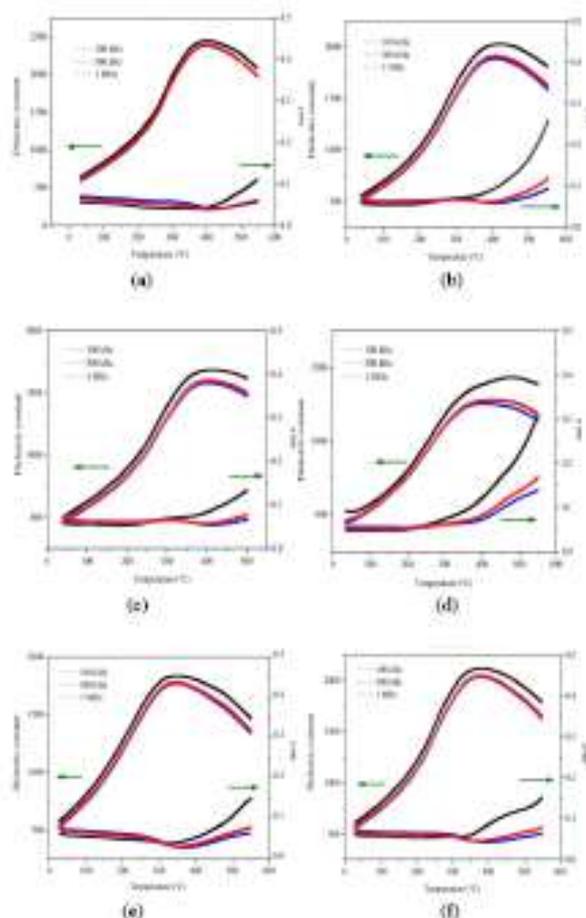


Figure 3. Temperature dependence of dielectric constant (a) and dielectric loss (tan δ) (b) of the $(1-x)\text{BKT}-x\text{ST}$ ceramics sintered at 1040°C for 2 h with (a) $x = 0.00$, (b) $x = 0.02$, (c) $x = 0.04$, (d) $x = 0.06$, (e) $x = 0.08$ and (f) $x = 0.10$

It is seen that typical ferroelectric polarization hysteresis loops were obtained for all the ceramics. The decrease of the remnant polarization (P_r) indicates that the addition of ST could transform the base composition into a soft ferroelectric material. The slightly distorted $P-E$ loop for the BKT ceramic with $x = 0.1$ indicates the weakening of ferroelectricity when the ST content is higher.

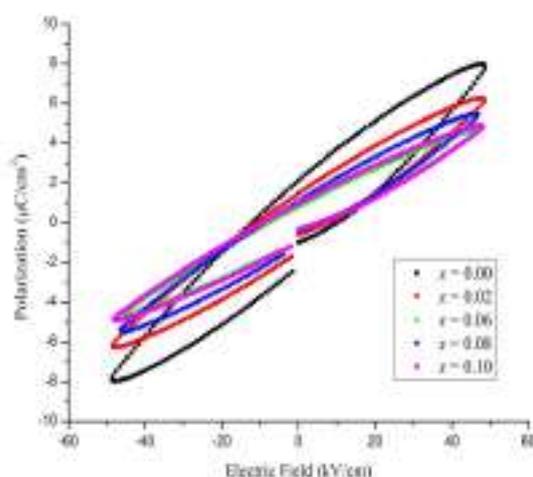


Figure 6. The P-E hysteresis loops of the (1-x)BKT-xST ceramics

The ceramics with higher ST content exhibit a lower area of the hysteresis loop and as a result hysteretic losses are lower too.

IV. CONCLUSIONS

Lead free piezoelectric ceramics BKT-ST have been prepared the conventional mixed oxide route with normal sintering. At room temperature, the ceramics with a perovskite structure are in the tetragonal phase at $x \leq 0.08$. At $0.1 \leq x$, they become a cubic perovskite structure. The results of X-ray diffraction reveal that SrTiO₃ diffuse into the Bi_{0.5}K_{0.5}TiO₃ lattices to form a solid solution with a pure perovskite structure. After the introduction of SrTiO₃ into Bi_{0.5}K_{0.5}TiO₃, the dielectric constant at room temperature (ϵ_r) was found to decrease with increasing SrTiO₃. The broadness of the dielectric constant peak was observed with increasing SrTiO₃ content, especially that of the 0.94Bi_{0.5}K_{0.5}TiO₃ - 0.06 SrTiO₃ ceramic which exhibited a very broad curve over a wide temperature range. The Bi_{0.5}K_{0.5}TiO₃ - SrTiO₃ system was expected to be a new and promising candidate for lead-free capacitors.

ACKNOWLEDGMENT

This work was supported by the National Research Council of Thailand (NRCT), Electronics Research Center (ERC) and King Mongkut's Institute of Technology Ladkrabang (KMITL).

REFERENCES

- [1] J.W. Waser, *Piezoelectric Ceramics-properties and Applications*, Philips Components, Eindhoven, 1991
- [2] B.JAFFE, W.R.COOK, H.JAFFE, *PIEZOELECTRIC CERAMICS*, ACADEMIC, NEWYORK, 1971
- [3] Yiping Guo, Ken-ichi Kakimoto, Hiroshi Ohnata, *Solid State Ionics* 129(2004) 279-284
- [4] G.A.Smolenskii, *Sov Phys Solid state* 1 (1959)1562
- [5] Z.F.Li, C.L.Wang, W.L.Zhong, J.C.Li,M.L.Zhao, *J.Appl Phys* 94 (2003) 2548
- [6] M.S. Gudzhiyev, A.K. Abiyev, V.A. Isupov, I.H. Ismailzade, *Fiz. Tverd. Tela* 27 (8) (1985) 2507.
- [7] O. Erkoçlu, M. Mazer, I.P. Mercari, *Phys. Stat. Sol.* 157 (1996) 499.
- [8] V.V. Ivanova, A.G. Kapayev, Y.N. Vozstava, V.S. Zhdanov, *Izv. Akad. Nauk SSSR, Ser. Fiz.* 24(1982)354
- [9] S.Y. Hou, M. Zhu, L. Han, J. Liu, J. Tang, H.Wang, H. Yan, *J. Cryst. Growth* 272 (2005) 506.
- [10] P.Vijaya Shankar Rao, E.V. Ramana, T. Bhima Shankam, *Alloys and compounds* (2006)
- [11] Müller, K. A. and Burdard, H., SrTiO₃ an intrinsic quantum piezoelectric below 4 K. *Phys. Rev. B*, 1979, **19**, 3599-3602.
- [12] Fleury, P. A., Scott, J. F. and Worlock, J. M., Soft phonon modes and the 110 K phase transition in SrTiO₃, *Phys. Rev. Lett.*, 1968, **21**,16-19.
- [13] Uwe, H. and Sakudo, T., Strain-induced ferroelectricity and soft phonon modes in SrTiO₃, *Phys. Rev. B*, 1976, **13**, 271-286.
- [14] Lemanov, V. V., Phase transitions in SrTiO₃ quantum piezoelectric with impurities. *Ferroelectrics*, 1999, **226**, 133-146.
- [15] Ishi, M., Wang, R., Inagawa, Y., Yamaguchi, T., Shan, Y.-J. and Nakamura, T., Ferroelectricity induced by oxygen isotopes exchange in strontium titanate perovskite. *Phys.Rev.Lett.*, 1999, **82**, 3540-3543
- [16] A. Tsuchi, P.M.Vilarinho, A.M.R.Senoz, A.L. Khalkin, M. J. Eur. Ceram. Soc. 25 (2005) 2769-2772.
- [17] M. Satapan, R. Mueangthai, C-C Heang, D. P. Cann, W. C. Vittayakorn And N. Vittayakorn, *Advanced Materials Research Vols. 55-57 (2008) pp 112-116*
- [18] Y. Guo, K. Kakimoto, H. Ohnata, Dielectric and piezoelectric properties of lead-free (Na_{0.5}K_{0.5})NbO₃-SrTiO₃ ceramics, *Solid State Commun.* 129 (2004) 279-284.

