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Formation of MPB in $(Na_{0.5}K_{0.5})NbO_3$-$BaZrO_3$-$(Bi_{0.5}Li_{0.5})TiO_3$ lead-free piezoelectric ceramics

無鉛圧電セラミックス $(Na_{0.5}K_{0.5})NbO_3$-$BaZrO_3$-$(Bi_{0.5}Li_{0.5})TiO_3$ における MPB の形成

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1. Introduction

The market of piezoceramics compounds is presently dominated by lead-based $Pb(Zr_{1-x}Ti_x)O_3$ (PZT) ceramics. PZT has the perovskite ABO_3 structure, and it shows high dielectric and piezoelectric properties near a tetragonal-rhombohedral morphotoropic phase boundary (MPB) at room temperature. But, it contains a large quantity of harmhul lead. From the environmental point of view, it is desireble to develop lead-free piezoelectric ceramics to replace PZT. It is highly expectable that dielectric and piezoelectric properties of perovskite lead free piezoelectric ceramics could be greatly improved via forming the same tetragonal-rhombohedral MPB as in PZT.

Recently, much attention has been paid to $(Na_{0.5}K_{0.5})NbO_3$(NKN)-based piezoelectrics since they show higher dielectric and piezoelectric properties than other lead-free ceramics[1-3]. However, NKN-based piezoelectrics show poor temperature stability, because of the presence of several phase transitions. Therefore, many studies for adjusting the phase transition temperatures of NKN-based ceramics to an appropriate temperature to fit the requirements of applications have been carried out[4-6].

For forming MPB, two end members, one with tetragonal symmetry and the other with rhombohedral symmetry at room temperature, are necessary. According to Wang *et. al*., $(1-x)(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$ has a rhombohedral phase ($0.08 \leq x \leq 0.15$) and $(1-x)(Na_{0.5}K_{0.5})NbO_3$-$x(Bi_{0.5}Li_{0.5})TiO_3$ has a tetragonal phase ($0.06 \leq x \leq 0.15$), at room temperature. Therefore, by co-incorparating $BaZrO_3$ and $(Bi_{0.5}Li_{0.5})TiO_3$ into $(Na_{0.5}K_{0.5})NbO_3$, the formation of MPB is possible. In this study, for the purpose of developing high performance lead-free NKN-based piezoelectric ceramics which has MPB, $(Bi_{0.5}Li_{0.5})TiO_3$- and $BaZrO_3$-codoped ceramics: $0.90(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-$(0.10-x)(Bi_{0.5}Li_{0.5})TiO_3$ ceramics are fabricated. Their dielectric and piezoelectric properties are evaluated, and vibrational properties are also investigated.

2. Experimental procedure

The powder of $0.90(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-$(0.10-x)(Bi_{0.5}Li_{0.5})TiO_3$ ceramics were made by the conventional solid state reaction method and then sintered under ambient pressure. The crystal structures and the microstructure of the samples were investigated by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), respectively. The dielectric constant was measured by an impedance analyzer (Agilent, 4263B) from room temperature to 400 ^oC. The piezoelectric d_{33} constant was measured by a piezo-d_{33} meter (APC International, Ltd.). The electromechanical coupling coefficient k_p were determined by the resonance-anti-resonance method with an impedance analyzer (Agilent, 4294A). Raman scattering spectra were measured by a double-grating spectrometer (Horiba-JY, U1000).

3. Results and discussion

From the SEM images, few pores are observed and the density of the samples is high. The X-ray diffraction (XRD) patterns are shown in Fig. 1. All the samples show a single perovskite phase from Fig. 1(a), indicating that $BaZrO_3$ and $(Bi_{0.5}Li_{0.5})TiO_3$ have completely dissolved in $(Na_{0.5}K_{0.5})NbO_3$ and a uniform solid solution has been formed. Fig. 1(b) shows the diffraction peak located at 44-46^o, which corresponds to the pseudocubic (200) reflection. When $x = 0.01$, two distinct peaks are observed, which reveal that the structure is tetragonal. With increasing x, the split of these peaks decreases and two peaks merge into a peak at last for $x \geqq 0.08$. This one peak shows that the crystal structure for $x \geqq 0.08$ is a rhombohedral or a cubic.

To determine the crystal structure, the XRD data shown in Fig. 1 were refined by the Rietveld method using RIETAN-FP[7]. It is found that the structure of $0.90(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-$(0.10-x)(Bi_{0.5}Li_{0.5})TiO_3$ could be well refined using a tetragonal P4mm structural model for $x \leqq 0.07$ samples and a rhombohedral R3m structural model

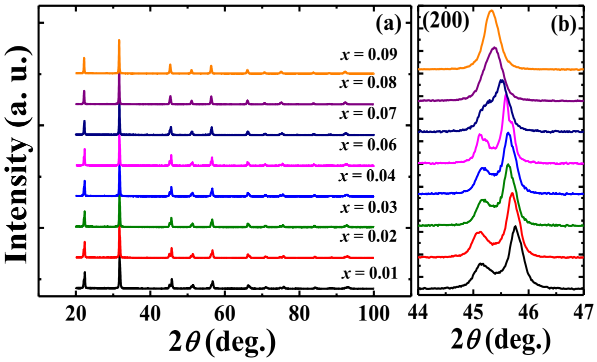

Fig. 1, (a) XRD patterns at room temperature; (b) Pseudo (200) refrection peaks for $0.90(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-(0.10-$x$)($Bi_{0.5}Li_{0.5}$)$TiO_3$ ceramics.

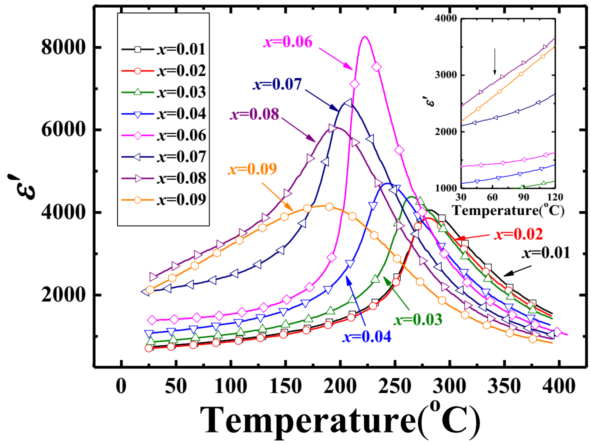

Fig. 2, The temperature dependence of the dielectric constant for $0.90(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-(0.10-$x$)($Bi_{0.5}Li_{0.5}$)$TiO_3$ ceramics.

for x ≧ 0.08 samples. The goodness-of-fit indicator S (= R_{wp}/R_e) value is between 1.20 and 1.45, which is low enough to suggest that the structural models assigned to each composition are reasonable. This result indicates that the MPB is formed and located between x = 0.07 and x = 0.08.

Fig. 2 shows the temperature dependence of the dielectric constant at 100 kHz. With increasing x, the cubic-tetragonal phase transition temperature T_C shifts to lower temperatures. With x ≧ 0.08, a broad peak is observed near room temperature (Fig. 2, insert), which corresponds to a tetragonal-rhombohedral phase transition. However, the similar peak can't be observed for $x \leq 0.07$. The result further confirms that $0.90(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-(0.10-$x$)($Bi_{0.5}Li_{0.5}$)$TiO_3$ ceramics has a MPB between x = 0.07 and x = 0.08. Phase diagram constructed from dielectric constant measurements are summarized in Fig. 3(a).

Figs. 3(b), (c), and (d) show the composition dependence of the electromechanical coupling coefficient k_p, the piezoelectric d_{33}, and the value of dielectric constant ε_{RT} at room temperature, respectively. Around a MPB composition determined by structural analysis and the dielectric measurement, the dielectric and piezoelectric properties become maximum. Such behavior is the same as that of PZT. Raman scattering spectra were also measured to clarify the existence of MPB.

4. Conclusion

In this study, $0.90(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-(0.10-$x$)($Bi_{0.5}Li_{0.5}$)$TiO_3$ ceramics have been prepared by the conventional solid state reaction method. XRD measurements have been carried out to reveal the composition dependence of crystal structure at room temperature. The result shows that $0.90(Na_{0.5}K_{0.5})NbO_3$-$x$$BaZrO_3$-(0.10-$x$)($Bi_{0.5}Li_{0.5}$)$TiO_3$ solid solutions form the

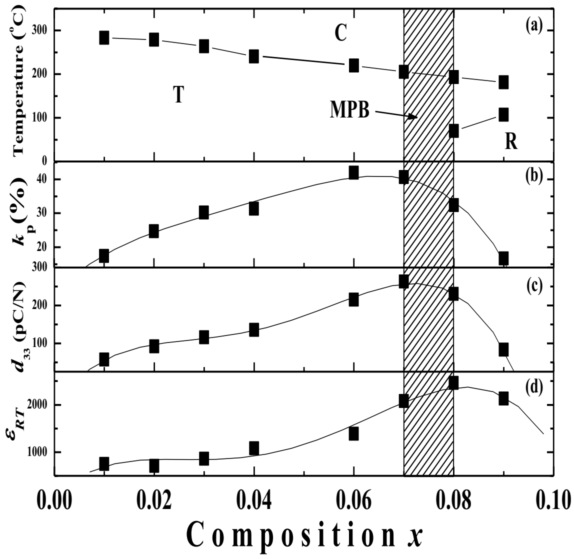

Fig. 3, (a) Phase diagram, and (b),(c),(d) composition dependence of dielectric and piezoelectric properties.

rhombohedral-tetragonal MPB between x = 0.07 and x = 0.08. It is found that the dielectric and piezoelectric properties were enhanced near MPB.

References

1. T. Takenaka, H. Nagata, and Y. Hiruma: Jpn. J. Appl. Phys. **47** (2008) 3787.
2. T. Ariizumi, J. Zushi, S. Kojima, R. Wang, and H. Bando: Jpn. J. Appl. Phys. **51** (2012) 07GC01.
3. Y. Guo, K. Kakimoto, and H. Ohsato: Appl. Phys. Lett. **85** (2004) 4121.
4. R. Wang, H. Bando, and M. Itoh: Appl. Phys. Letts. **95** (2009) 092905.
5. R. Wang, H. Bando, T. Katsumata, Y. Inaguma, H. Taniguchi, and M. Itoh: Phys. Status Solidi RRL **3** (2009) 142.
6. R. Wang, H. Bando, M. Kidate, Y. Nishihara, and M. Itoh: Jpn. J. Appl. Phys. **50** (2011) 09ND10.
7. F. Izumi and K. Momma: Solid State Phenom., **130** (2007) 15.