Temperature Stabilized Piezoceramics of (Li_{0.5}Bi_{0.5})-Modified PZT System in the Morphotropic Region

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1. Introduction

Lead zirconate-lead titanate ceramics, Pb(Zr_{y}Ti_{1-y})O_{3} (PZT), are very important piezoelectric materials, because the piezoelectric ceramics near the morphotropic phase boundary (MPB) show extremely strong piezoelectric activities. However, the temperature dependence of the frequency constant and the electromechanical coupling factor of these materials in the vicinity of the MPB indicate complex behavior, because of the minimum Young's modulus at the MPB. Stable temperature dependence of frequency constant is desired for piezoelectric ceramic devices such as ceramic filters, actuators, and so forth. For ceramic filters it is further essential that the piezoelectric ceramics should have a large electromechanical coupling factor that will allow the realization of the required bandwidth. In the PZT system, the MPB has a slight tilt to the PbZrO_{3} side and the degree depends on the ratio of the modified A-site ions. The tilt of the MPB was used to improve the temperature dependence of frequency constant of the piezoelectric ceramics with composition near the MPB without decreasing the high value of the coupling factor. In this study, the temperature dependence of the piezoelectric properties of (Li_{0.5}Bi_{0.5})_{x}Pb_{1-x}(Zr_{y}Ti_{1-y})O_{3} system were discussed from the viewpoint of a tilt of the MPB.

2. Temperature Compensated Composition Near the MPB

For most materials, the temperature coefficient of the frequency constant is negative because the Young's modulus decreases with increasing temperature. At structural phase changes, however, the Young's modulus often show anomalous behavior "softening" or a positive temperature coefficient.

In the PZT system, the MPB has a slight tilt to the PbZrO_{3} side and the degree depends on the concentration ratio of the modified A-site ions (Fig. 4). However, the temperature dependence of frequency constant and electromechanical coupling factor of these materials in the vicinity of the MPB indicate complex behavior, because of the minimum Young's modulus at the MPB.

Figure 1 shows a schematic diagram for TCN as a function of y and related phase diagram of the PZT system in the vicinity of the MPB. In the following, we shall consider only materials near the MPB between tetragonal (F_{4}) and rhombohedral (F_{3}) phases. This phase boundary shifts a little toward a higher zirconate content as the temperature increases. Therefore, with tetragonal ceramics near the MPB, positive TCN are found, whereas with rhombohedral ceramics the TCN are negative. Thus in searching for zero TCN, materials with unusual elastic properties are needed. In particular, it is important to find materials with positive TCN. If the composition is chosen corresponding to optimum tetragonal side yn, the required compensated TCN (=0) is realized with the aid of elastic anomalies in the tilted MPB.
3. Experimental

Raw oxide of carbonate materials, Bi\textsubscript{2}O\textsubscript{3}, Li\textsubscript{2}CO\textsubscript{3}, PbO, ZrO\textsubscript{2} and TiO\textsubscript{2} were used for the composition

\[(Li_{0.5}Bi_{0.5})_{x}Pb_{-x}(Zr_{y}Ti_{-y})O_{3}\] (PZT 100x/100y).

The composition range of 0.05 \leq x \leq 0.15 and 0.49 \leq y \leq 0.55 was examined. The weighed components were completely wet-mixed for 10 hours with acetone and zirconia balls using the ball milling method. After drying, the pressed mixtures were calcined at 850°C for 1 hour. After ground by alumina mortar, they were well-milled by the ball milling method until the particle size had submicron orders. Then they were pressed into a disk of 20mm in diameter and about 1mm in thickness. Pressed disks for samples in a magnesia crucible were sintered at 1020 - 1040°C for 2 hours in an air atmosphere after burning out the binder at 500°C for 2 hours. The density ratio of sintered specimens was about 95% of the theoretical value.

The phases in each sample were identified from the X-ray diffraction (XRD) patterns using a diffractometer with CuK\textalpha radiation.

Specimens for piezoelectric measurement were poled at 100°C in a stirred silicone oil bath by applying a dc electric field of 3KV/mm for 5 minutes. Piezoelectric properties (temperature dependences of Np and kp) were measured by the resonance-antiresonance method on the basis of the IRE standard using the automated piezoelectric measurement system with the impedance analizer (YHP-4192A) and the desktop computer (HP-9816S).

4. Results and Discussion

The variations of planar coupling factor kp and planar frequency constant Np as a function of composition are given in Fig.2. The MPB is characterized by a moderately sharp peak in kp and a minimum in Np. The maximum values of kp, 55 to 65%, were obtained for composition y=0.52. The MPB values of kp decreased gradually with the (Li\textsubscript{0.5}Bi\textsubscript{0.5}) content x. The MPB is nearly independent of the compositional parameter x of this system.

Figure 3 shows the variation of Np and kp in this system as a function of temperature(T) and the compositional parameter y. For y=0.53 (5/100y system), the temperature gradient of Np is negative at 20°C; and for y=0.52 and 0.51, the gradients are positive. For x=0.50 and 0.49, Np's are nearly constant from 20°C to 120°C.

To make clear the y dependence of the temperature gradient, the temperature coefficient averaged over the range between 20 to 120°C, denoted as TCNp, is calculated from the following equation

\[TCNp = \frac{N_{p,120}-N_{p,20}}{\Delta T \times N_{p,30}} \times 10^6 \quad (\text{ppm/}^\circ\text{C})\]

where N\textsubscript{p,20}, N\textsubscript{p,30} and N\textsubscript{p,120} represent the values of Np at 20, 30 and 120°C, respectively. The temperature difference is \Delta T(=100°C). The values of TCNp are plotted against y in Fig.5. It is seen that TCNp is -16 ppm/°C for y=0.49 and 0.51(PZT 10/100 y system). The improved ceramics with composition near the MPB have high kp of more than 60%, from room temperature to 120°C (Fig. 6). The temperature coefficient of the kp(TCkp) is -70 ppm/°C.
Fig. 1. Schematic diagrams for (a) temperature coefficient of $N$, $TCN$, as a function of $y$ in the PZT system, (b) phase diagram of the PZT system in the vicinity of MPB.

Fig. 2. Frequency constant $N_p$ and electromechanical coupling factor $k_p$ as a function of $y$ in the PZT 100 $x/100$ $y$ system.

Fig. 3. Temperature dependence of frequency constant $N_p$ and electromechanical coupling factor $k_p$ for (a) PZT 5/100 $y$ system and (b) PZT 10/100 $y$ system.
5. Conclusions

The temperature dependence of the piezoelectric properties of \((Li_{0.5}Bi_{0.5})_xPb_1-x(Zr_{y}Ti_{1-y})O_3\) system were discussed from the viewpoint of a tilt of the MPB. The tilt of the MPB was used to improve the temperature dependence of frequency constant of the piezoelectric ceramics with composition near the MPB without decreasing the high value of the coupling factor.

The TCNp of the improved ceramics was \(-16\text{ppm/°C}\) at 30°C while the kp kept over 60%, from room temperature to 120°C.