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Piezoelectric and Dielectric Properties of $Pb(Zr_xTi_{1-x})O_3$-$Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$ Piezoelectric Ceramics

KEE-JOE LIM,[1] SI-YONG LEE,[2] JONG-SUB LEE,[2] MUN-JU LEE[2] & SEONG-HWA KANG[3]
[1] *School of Electrical and Computer Engineering, Chungbuk National University, Cheongju, Chungbuk 361-763, Korea*
[2] *R&D center, EMD Co., Ltd. KiroRi 97, IpjangMyun, Cheonan, ChungNam, Korea*
[3] *Department of Safety Engineering, Chungcheong University, Cheongwon, Chungbuk, Korea*

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Abstract. In this paper, piezoelectric and dielectric properties of $0.9PbZr_xTi_{1-x}O_3$-$0.1PbNi_{1/3}Sb_{1/3}Nb_{1/3}O_3$ were studied as a function of Zr/Ti mole ratio(x) for application to piezoelectric actuator. Also, microstructure and crystalline phase are investigated by using SEM and XRD, respectively. As a results, the substitution of Sb5+ to B-site increases the piezoelectric and dielectric properties, and when Zr/Ti mole ratio is 49/51 and ternary mole ration is $0.1(0.9PbZr_{0.49}Ti_{0.51}O_3$-$0.1PbNi_{1/3}Sb_{1/3}Nb_{1/3}O_3)$, the corresponding composition were found belonging to the Morphotropic Phase Boundary region with electromechanical coupling coefficient(k_p), mechanical quality factor (Q_m), permittivity(ε_r) and piezoelectric strain constant(d_{33}) equaled to 63%, 360, 2000 and 470 pC/N, respectively. Sintering temperature was about 1150°C and Curie temperature was determined around 290°C.

Keywords: piezoelectric actuator, MPB, PZT-PNSN, Piezoelectric strain constant

1. Introduction

In mobile communication devices such as mobile phone and pager, DC motor is used for silent alarm. However, silent alarms using DC motor have some problems, for example, difficulty of further reduction of thickness and high power consumption. According to these problems, the research has been focused on vibration device using piezoelectric actuators [1]. To apply piezoelectric actuators to vibration device for silent alarm, piezoelectric ceramics must have high electromechanical coupling coefficient and piezoelectric strain constant to convert efficiently electrical energy into mechanical vibration. Also, to avoid the decrease of actuator properties with time, aging ratio of piezoelectric ceramics must be lower. Indeed, piezoelectric ceramic for piezoelectric actuators who possesses these properties is lead zirconate-titanate (PZT) based ternary piezoelectric system. Complex perovskite $Pb(B',B'')O_3$ as a ternary composition is generally added to PZT piezoelectric ceramics [2, 3]. Thus, for the application of these materials to the vibration devices, donor dopant must be added in B' or B" site of $Pb(B',B'')O_3$ [4, 5]. Since Nb^{5+} or Sb^{5+} ion are well known as donor dopants, in this work, Sb^{5+} ion is added in B" site to improve the piezoelectric and dielectric properties of PZT-PNN ternary system. The piezoelectric and dielectric properties of $Pb(Zr_xTi_{1-x})O_3$-$Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$ ceramics are studied as a function of Zr/Ti mole ratio. Also, X-Ray Diffraction (XRD) and Scanning Electron Microscope (SEM) analysis are performed to determine MPB and characterize the microstructure evolution as a function of sintering temperature.

2. Experiments

The ternary piezoelectric ceramic system is designed as following:

$$0.9Pb(Zr_xTi_{1-x})O_3\text{-}0.1Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$$

where, $0.47 < x < 0.52$.

PbO, ZrO_2, TiO_2, NiO, Nb_2O_5, and Sb_2O_5 of 99.9% purity were used as raw materials. After these powders were weighed in appropriate proportions and mixed, they were calcined at 800°C for 4 hours in a magnesia-covered crucible. The calcined powders were crushed

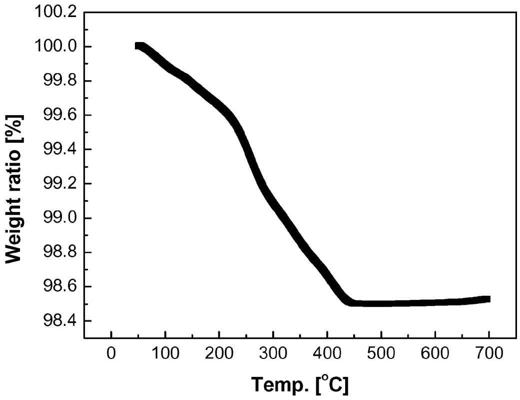

Fig. 1. Thermal Gravitation Analysis.

and then ground by ball milling for 24 hours. The ground powder had a particle size ranging from 0.06 to 2.0 μm with mean diameter of 0.6 μm. The ground powder was mixed with organic binder, PVB, and then was pressed. TGA (Thermal Gravitation Analysis) has been measured to determine the burn-out temperature of pressed specimen.

Figure 1 shows TGA measurements. As temperature increases, the gravitation critically decreases, such march is due the evaporation of water and organic binder contained in pressed sample. Accordingly, the burn-out temperature is seen located at 450°C. The rest of specimens was burnt-out in 450°C for 6 hours, and then sintered in a magnesia-covered crucible from 1100°C to 1250°C for 2 hours in PbO atmosphere. The samples were metallized by printing silver paste and firing at 800°C. After that, specimens were electrically poled under an electric field of 3 kV/mm for 20 min in heated silicon oil at 120°C.

Piezoelectric strain constant(d_{33}) was directly measured by Berlincourt d_{33}-meter(CHANNEL product). Other dielectric and piezoelectric constants were measured by impedance analyzer(HP 4194A) and calculated using resonance-antiresonance method by IRE Standard. The crystalline structure was analyzed by X-ray diffraction (XRD) in the range of $2\theta < 80°$ using Cu-Kα ($\lambda = 5.406$ Å) (SCINTAG product).

3. Results and Discussion

3.1. SEM Microstructure Observation

Figure 2 shows the SEM photographs of different sintering temperatures of $0.9Pb(Zr_{0.49}Ti_{0.51})O_3$-

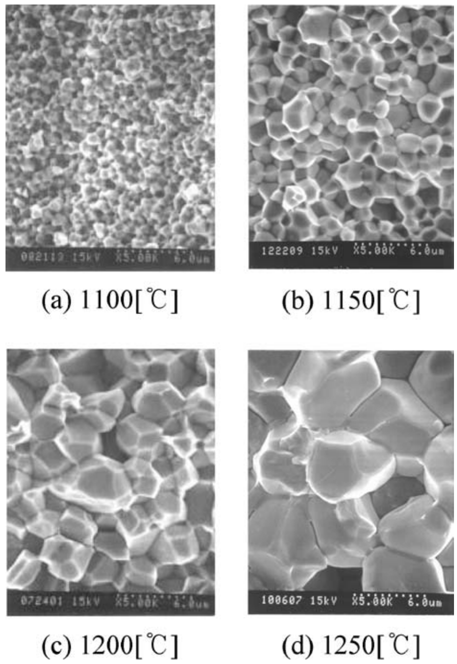

Fig. 2. SEM photographs of ceramic samples at different sintering temperatures.

$0.1Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$ ceramics. As is shown, the grain microstructure of the specimen sintered at 1100°C is not completely grown. The grain microstructure of the specimen sintered at 1150°C is completely grown and uniform, and it has a dense microstructure. Furtheremore, the grain microstructure of the specimen sintered at 1200°C and 1250°C are not uniform and have many pore. Thus, the optimal sintering temperature is assumed to be 1150°C for $0.9Pb(Zr_{0.49}Ti_{0.51})O_3$-$0.1Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$ ceramics.

3.2. Crystalline Structure Analysis by XRD

Typical XRD patterns of $0.9Pb(Zr_xTi_{1-x})O_3$-$0.1Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$ piezoelectric ceramics sintered at 1150°C as a function of Zr concentration x are depicted in Fig. 3. The figure shows a typical perovskite phase without any secondary phase such as pyrochlore phase. X-ray diffraction diagrams indicated that the phase structure for the compositions $x \leq 0.48$ are tetragonal, which are identified by the associated (002)T/(200)T and (112)T/(211)T doublet lines. For the compositions $x \geq 0.51$, the rhombohedral

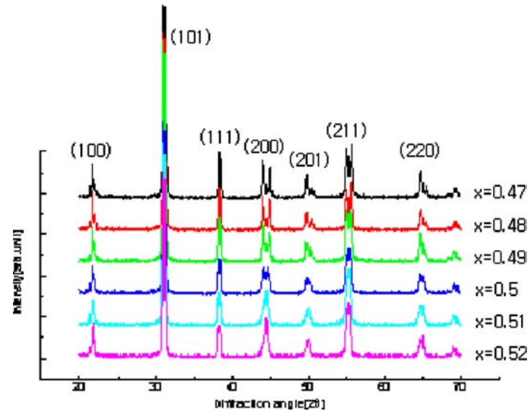

Fig. 3. XRD patterns as a function of x in $0.9Pb(Zr_xTi_{1-x})O_3$-$0.1Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$ ceramics.

phase structure is dominant as is revealed by the non splitting of (200) and (211) peaks. Whereas, in intermediate compositions comprise at $0.48 < x < 0.51$, XRD diagrams could be decomposed in tetragonal (200)T/(002)T doublet lines, and in rhombohedral (200)R single line. So, in this ternary system, the MPB is assumed to be located around $x = 0.49$ where coexists both ferroelectric phases.

3.3. *Piezoelectric and Dielectric Properties*

Figures 4 to 7 show the variations of electromechanical coupling coefficient(k_p), piezoelectric strain constant (d_{33}), permittivity($\varepsilon_{33}^T/\varepsilon_0$), and mechanical quality factor (Q_m) as a function of Zr concentration x in

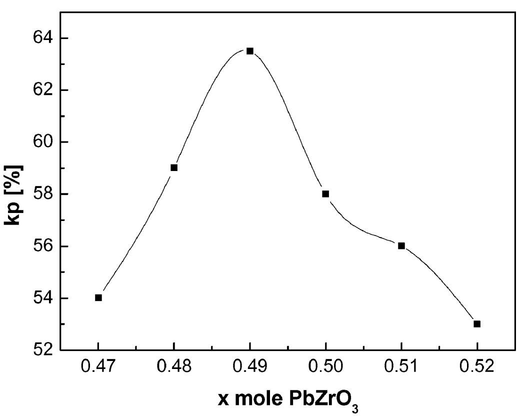

Fig. 4. Variation of k_p as a function of x mole $PbZrO_3$.

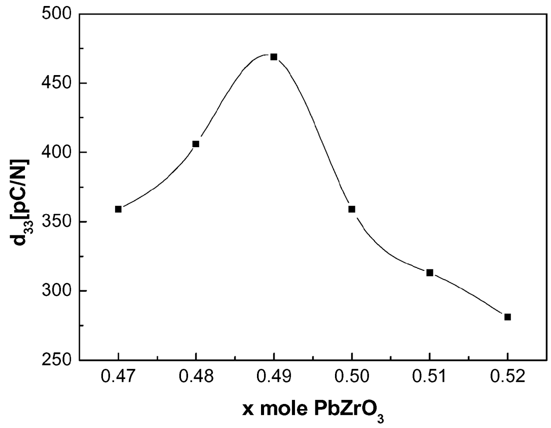

Fig. 5. Variation of d_{33} as a function of x mole $PbZrO_3$.

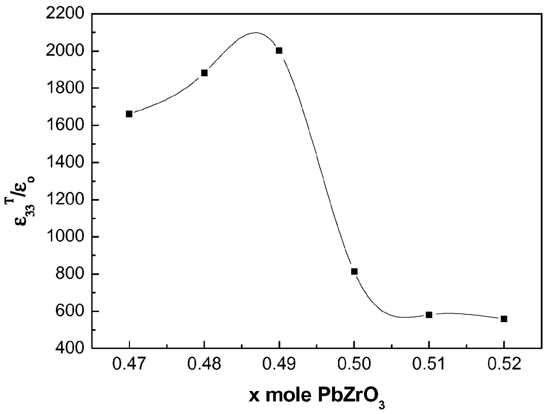

Fig. 6. Variation of $\varepsilon_{33}^T/\varepsilon_0$ as a function of x mole $PbZrO_3$.

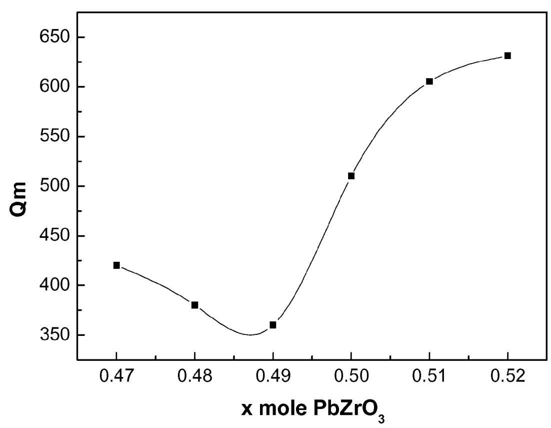

Fig. 7. Variation of Q_m as a function of x mole $PbZrO_3$.

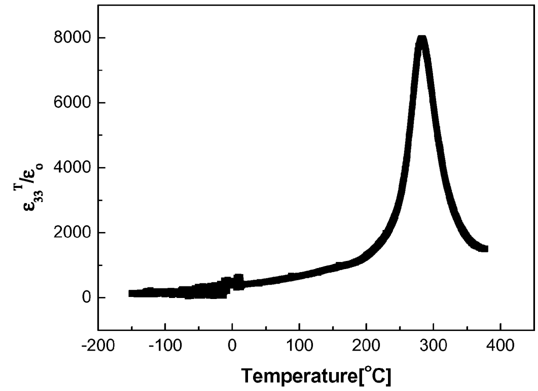

Fig. 8. Phase transition temperature.

$0.1Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$-$0.9Pb(Zr_xTi_{1-x})O_3$ ceramics. As shown in Figs. 4–6, when x is 0.49, a maximal value are reached of k_p, d_{33} and $\varepsilon_{33}^T/\varepsilon_0$, which are 63%, 470 pC/N and 2000, respectively.

In Fig. 7, a minimum value of mechanical quality factor (360) is observed at $x = 0.49$. Thus, the piezoelectric and dielectric properties results also confirm that the MPB in PZT-PNSN ternary piezoelectric ceramic system is located at $x = 0.49$, and is shifted to Ti-rich concentration, compared with the well-known MPB in pure PZT.

Figure 8 shows the evolution of permittivity as a function of temperature for ceramic with the composition $0.9Pb(Zr_{0.49}Ti_{0.51})O_3$-$0.1Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$. The maximum of permittivity is associated to the ferroelectric-paraelectric phase transition, whose the temperature corresponds to the one measured by impedance analyzer. Thus, the Curie temperature is located around 290°C.

4. Conclusions

In this paper, Sb^{5+} ion is added in B" site to improve the piezoelectric and dielectric properties of $Pb(Zr_xTi_{1-x})O_3$-$Pb(Ni_{1/3}Nb_{2/3})O_3$ ternary system. The piezoelectric and dielectric properties of $Pb(Zr_xTi_{1-x})O_3$-$Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$ ceramics are studied as a function of Zr/Ti mole ratio for piezoelectric actuators.

By SEM observations, optimal sintering temperature was assumed to be 1150°C in the ternary system. Also, from the results of XRD analysis the morphotropic phase boundary (MPB) was found located around the Zr concentration $x = 0.49$.

When x is 0.49, the piezoelectric and dielectric properties were maximum: electromechanical coupling coefficiency(k_p), piezoelectric strain constant(d_{33}), permittivity($\varepsilon_{33}^T/\varepsilon_0$) were equal to 63%, 470 pC/N and 2000, respectively. These results are well matched with the results of XRD analysis. Consequently, as Sb^{5+} ion are added in PZT–PNN ceramics, the piezoelectric and dielectric properties are improved, and $0.9Pb(Zr_{0.49}Ti_{0.51})O_3$-$0.1Pb(Ni_{1/3}Sb_{1/3}Nb_{1/3})O_3$ ceramic compositions can be an useful material for piezoelectric actuators.

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