Piezoelectric Properties of $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{--PbTiO}_3\text{--PbZrO}_3$ Ceramics Near the MPB

Masao KONDO, Masaharu HIDA, Mineharu TSUKADA, Kazuaki KURIHARA and Nobuo KAMEHARA

Fujitsu Laboratories Ltd., Inorganic Materials & Polymers Laboratory, 10-1, Morinosato-Wakamiya, Atsugi-shi 243-01

$\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{--PbTiO}_3\text{--PbZrO}_3$ セラミックスの相境界付近における圧電特性

近藤正雄・肥田勝春・塚田峰春・栗原和明・亀原伸男

(株)富士通研究所材料技術研究所無機・高分子材料研究部, 243-01 神奈川県厚木市森の里若宮 10-1

The change in the electromechanical coupling factor, k_{33} , was investigated as a function of $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{--PbTiO}_3\text{--PbZrO}_3$ (PNN-PT-PZ) piezoelectric ceramic composition near the morphotropic phase boundary. Ceramics were sintered both in air and in a powder-bed. The average grain size of the PNN-PT-PZ ceramics obtained by sintering in the powder-bed was larger than that in air. Utilizing the powder-bed sintering technique, a high performance PNN-PT-PZ ceramic with a k_{33} of 80.8% was obtained.

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1. Introduction

Piezoelectrics are materials which have attracted much interest, both from fundamental and applied aspects, such as a multilayer ceramic actuator. Electromechanical coupling factor (k) is the most important factor to evaluate the performance of piezoelectric ceramics.¹⁾ This factor represents the conversion efficiency of electric energy into mechanical energy qualitatively. The factor has several different vibration modes. The 33 mode represents the strain direction which is parallel to the polar axis. The 33 mode (k_{33}) is most important factor for multilayer ceramic actuators.²⁾

Lead-based perovskites are known to have excellent piezoelectric properties. For example, $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramics has the highest electromechanical coupling factor with a planar mode (k_p) of 77% in the piezoelectric ceramics.³⁾ $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3\text{--PbTiO}_3\text{--PbZrO}_3$ (hereafter designated as PNN-PT-PZ) ceramics are also known to have high piezoelectric properties. The piezoelectric property of the $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ ceramics increases as the composition approaches the morphotropic phase boundary (MPB). Banno et al. formed the PNN-PT-PZ piezoelectric ceramics with the various compositions and determined the MPB composition of the PNN-PT-PZ system.⁴⁾ The composition range investigated in their research was relatively large. The piezoelectric properties near the MPB composition are not clear, because their objective was to make a phase diagram. Luff et al. also investigated the change of the piezoelectric property with the composition and reported that the composition with the highest performance ($d_{33}=1100 \text{ pm/V}$) was 0.5PNN-0.35PT-0.15PZ.⁵⁾ However, they did not report a change of k_{33} with composition near MPB.

Other published research have focuses on the processing factors of PNN-PT-PZ ceramics, such as the influences of particle size of the calcined powder,⁶⁾ of the additives (CdO , MnO_2 , SiO_2),⁷⁾ sintering atmosphere (O_2 , N_2 , air)⁸⁾ and so on. Thus, an investigation of the composition near the MPB has not yet been published in the research literature.

As a result in this study, the effect of the environment in the sintering process on grain growth was investigated. Then, the effect of composition on the piezoelectric ceramics particularly the PZ/PT ratio near the MPB was investigated.

2. Experimental

Oxide powders of PbO , NiO , Nb_2O_5 , TiO_2 and ZrO_2 of which purities are above 99.9% were used. 1 mol NiO and 1 mol Nb_2O_5 were mixed by ball milling for 20 h. The mixture were calcined at 1000°C for 4 h. The phase of the calcined powder, determined by X-ray diffraction (XRD) was single phase of NiNb_2O_6 . PbO , NiNb_2O_6 , TiO_2 and ZrO_2 were mixed by ball milling for 20 h. The mixtures were dried and calcined at $850\text{--}1100^\circ\text{C}$ for 3–6 h. The green compacts ($30 \text{ mm}\phi \times 5 \text{ mm}$) of the calcined powders were obtained by die pressing at 120–130 MPa after an addition of a binder. The binder was burned out at 500°C for 1–3 h. The green compacts were sintered at 1100°C for 3 h in air (closed container) or in the same composition powder (powder-bed method). The 33 mode specimens ($4 \times 4 \times 15 \text{ mm}$) were made from the sintered bodies. The specimens were metallized with Ag paste and were poled under a DC field of 2 kV/mm at room temperature in a silicone oil bath.

The compositions of the calcined powders were measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES). The molar regions of the composition at $\text{PNN}=0.5$, $0.335 < \text{PT} < 0.355$ and $0.145 < \text{PZ} < 0.165$ ($0.408 < \text{PZ/PT} < 0.493$). The compositions obtained by ICP-AES are almost the same as starting material composition.

The phase structure of PNN-PT-PZ ceramics was also established by X-ray diffraction (XRD) using $\text{Cu K}\alpha$. In order to carry out an accurate determination of the peak position (2θ), the X-ray peaks were recorded step by step with $0.01^\circ/\text{steps}$ for a 5 s measuring period. The background and the diffraction of $\text{K}\alpha_2$ were removed from the peaks.

The densities of the piezoelectric ceramics were measured by the Archimedeian method. The microstructure of fractured surface of the piezoelectric ceramics was observed by scanning electron microscope (SEM). Electromechanical coupling factor (k_{33}) were measured by the resonant-antiresonant frequency method with an impedance analyzer.

3. Results and discussion

The XRD peaks of the (200) tetragonal, (002) tetragonal and (200) pseudocubic (rhombohedral) crystal occurred around 45° in 2θ of the PNN-PT-PZ ceramics of which the composition is close to the MPB.⁷⁾ Figure 1 shows the XRD

Fig. 1. Changes of XRD patterns of PNN-PZ-PZ powder (PNN=0.5) after the calcination at 1100°C for 3 h with PZ/PT molar ratio, T: Tetragonal and PC: Pseudocubic.

peaks of PNN-PT-PZ powder (PZ/PT=0.43, 0.45 and 0.47) calcined at 1100°C for 3 h again after the calcination at 850°C for 3 h. The calcination at 1100°C was done to increase the crystallinity of PNN-PT-PZ powder. Each sample consists of both tetragonal and pseudocubic crystals. The peaks of the (002) tetragonal and (200) pseudocubic crystals overlapped, although the (200) peak of tetragonal crystal can be separated (Figs. 1(a) and (b)). However, the intensity of the peaks for the tetragonal (200) can be estimated because the intensity is almost two times larger than that of the (002) tetragonal crystal. The quantity of the tetragonal crystal phase decreases with the increase of PZ/PT molar ratio and that of the pseudocubic crystal phase increase with it. The quantity of the tetragonal is more than that of the pseudocubic with PZ/PT=0.43. However, the quantity of the pseudocubic with PZ/PT=0.45 is more than that of PZ/PT=0.43. The tetragonal peak is diminished with PZ/PT=0.47. We believe that the PNN-PT-PZ ceramics with a composition of PZ/PT=0.45 was on the MPB, although the phase boundary is not entirely clear.

Figure 2 shows the microstructures of the fractured surface of the PNN-PT-PZ ceramics sintered in an air (hereafter specimen A) and a powder-bed method (hereafter specimen B). The density of specimen A (8.14 g/cm³) is almost same as that of specimen B (8.17 g/cm³) and it is considered that the effect of k_{33} on the density of piezoelectric ceramics is negligible.

Each specimen shows pore-less and high density microstructure. It is thought that the PNN-PT-PZ powder sintered under a self-generated PbO atmosphere in air, be-

Fig. 2. Microstructures of fractured surfaces of PNN-PT-PZ piezoelectric ceramics sintered at 1100°C for 3 h in (a) air and (b) powder-bed.

cause the densities are relatively high. However, the average grain size of the specimen B is larger than that of specimen A. The PbO did not deposit on the surfaces of the specimens, because only a perovskite single phase was observed by XRD of the surfaces of specimens A and B.

For Pb-based piezoelectric ceramics, the atmosphere oxygen partial pressure influenced the density.^{9),10)} With a sintering temperature of around 1100°C, the PbO vapor pressure evaporation-recondensation reaction is in equilibrium,¹¹⁾

Thus, the partial vapor pressure of oxygen in powder-bed sintering is higher than that in air. Kudo et al. reported that the grain growth of Pb-based ceramics sintered in oxygen is also larger than that in air.¹⁰⁾ The small grain size of specimen A is probably due to lower PbO and oxygen partial pressure near the end of the sintering process. The PbO atmosphere significantly influenced to the grain growth process, although it does not influence to a lesser extent the densification in the sintering PNN-PT-PZ powder.

Figure 3 shows the changes of k_{33} for the specimens A and B as a function of PZ/PT molar ratio. The values of k_{33} of specimen B are larger than those of specimen A with the same PZ/PT molar ratio. The values of k_{33} of the specimens A and B show a maximum at PZ/PT=0.45–0.475. The maximum value of k_{33} for specimen B is 80.8% with PZ/PT=0.45. The molar ratio of PZ/PT with a maximum of k_{33} agreed with that of MPB in Fig. 1. This value is the largest k_{33} which has ever been reported except for single crystal ferroelectrics.¹²⁾ This high performance is due to carefully controlling the composition of specimen B near the MPB.

The composition with maximum k_{33} value of sample A slightly differs from that of sample B. This reason is not

Fig. 3. Changes of coupling factors (k_{33}) of PNN-PT-PZ (PNN=0.5) piezoelectric ceramics sintered in air and in a powder-bed as a function of PZ/PT molar ratio.

clear at present.

The maximum value of k_{33} of sample A is smaller than that of sample B. The microstructure of ceramics influences on the coupling factor. The coupling factor of the piezoelectric ceramics having large grains is higher than that having small grains.¹⁰⁾ It is also supported that the coupling factor of piezoelectric single crystal is higher than that of ceramics.¹²⁾ Thus, the difference of maximum value of k_{33} between the two types of sintering appears to be due to the

size effect of the grains.

To summarize, the highest performance piezoelectric ceramics ($k_{33}=80.8\%$) in PNN-PT-PZ system were produced in this study. The high k_{33} appears to be due to the growth of the grain in the ceramic by powder-bed sintering method and to careful control of the composition of the ceramics near the MPB.

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