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Effects of CuO-doping and Quenching on Electrical Properties of $(Bi_{1/2}Na_{1/2})TiO_3$-based Solid Solution Ceramics

$(Bi_{1/2}Na_{1/2})TiO_3$系固溶体セラミックスの電気的特性に対するCuO添加と急冷の効果

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1. INTRODUCTION

$(Bi_{1/2}Na_{1/2})TiO_3$ (BNT) ceramics are expected to be one of the superior candidates for lead-free piezoelectric materials owing to their friendly for current manufacturing process, low materials cost, and relatively high piezoelectric properties [1]. Also, BNT-based solid solution system among $BaTiO_3$ and $(Bi_{1/2}K_{1/2})TiO_3$ with tetragonal symmetry show excellent piezoelectric properties on their MPB compositions [2,3]. For example, 0.90BNT-0.06$BaTiO_3$ - 0.04$(Bi_{0.5}Li_{0.5}TiO_3$ (BNLBT4-6) of MPB composition is said to have relatively high piezoelectric constant d_{33} of approximately 140 pC/N among BNT-based ceramics [4]. However, the d_{33} values are still not as large as these of PZT-based ceramics. To cover the low d_{33} values of BNT, it is generally considered that a multilayer structure is very effective for actuator and high-power applications because the total displacement can be increased proportionally to the layer number of the multilayer structure. For fabricating the MLCA low-temperature sintering of BNT-based ceramics is indispensable in order to co-firing with internal electrodes (Ag-Pd) and BNT-based ceramics [5-7].

Among several sintering additives used for dielectric ceramics, CuO, NiO and B_2O_3 have a low melting point and is often used because a liquid phase is formed. [8−9]. We have already done the preliminary works about doping effects of these additives to BNLBT4-6 ceramics for lowering their sintering temperatures. And, then, CuO doping was effective for lowering the sintering temperatures (down to 940^{o}C) of BNLBT4-6 without the deterioration of relative densities, >90%. However, the investigations about electrical properties such as depolarization temperature T_d and piezoelectric properties such as piezoelectric constants d_{33} have not been enough conducted yet. Therefore, in this study, piezoelectric properties and T_d for CuO doped BNLBT4-6 ceramics were investigated. Additionally, CuO-doped BNLBT ceramics were fabricated by using the quenching treatment for increasing the T_d.

2. EXPRIMENTAL PROCEDURE

Ceramic samples of BNLBT4-6 as a base-composition were prepared by a conventional solid-state reaction. High purity raw materials were used as the starting materials. Doping amounts of CuO was changed from 0 to 1.5 wt% (BNLBT4-6+CuO *x* wt%). These materials were mixed by ball milling and calcined at 850°C for 2 h. After the calcination, CuO was added to the 2 h. After the calcination, CuO was added to the main powders. The ground and ball-milled powders were pressed into 20 mm in diameter and about 10 mm in thickness. The discs were then sintered in air at temperature of 940-1140°C for 2 h. The crystal structures and lattice constants of the sintered ceramics were determined using an XRD (Rigaku; RINT2000). These ceramics were cut and polished for various physical and electrical measurements. For the obtained ceramics, densities were measured by the Archimedes method and microstructures were observed by SEM, Hitachi S-2400. Electrodes of fired-on Ag paste were formed for electrical measurements. After the poling treatment, piezoelectric properties were evaluated by resonance and antiresonance method by using an impedance analyzer (HP4294A). Also, temperature dependences of electromechanical coupling factor k_{33} were measured using the heat chamber to determine the depolarization temperature T_d.

3. RESULTS and DISCUSSION

Prior to the measurement of piezoelectric properties (poling treatment), the resistivities of BNLBT4-6+CuO *x* wt% ceramics were checked, and then all samples showed relatively high resistivities of over 10^{12} Ω・cm which were regardless of the CuO-doping amount and sintering temperature. Therefore, the same poling conditions were able to be applied to CuO-doped samples even sintered at 940^{o}C. From the resonance and antiresonance curves, electromechanical coupling

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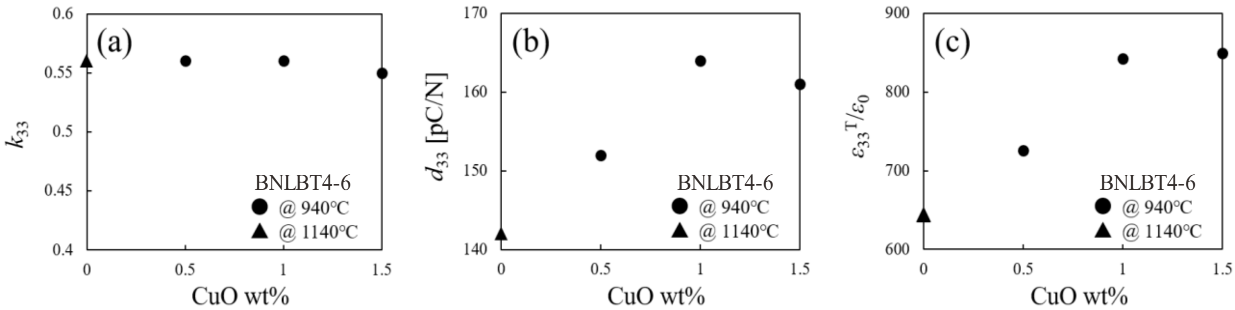

Fig. 1 Various piezoelectric characteristics (a) k_{33}, (b) d_{33}, and (c) $\varepsilon_{33}^{T}/\varepsilon_0$ of BNLBT4-6+CuO x wt% as a function of doped CuO amount of x.

factor k_{33} and piezoelectric strain constant d_{33} were calculated and summarized in Fig. 1. Fig. 1(a) shows k_{33} as a function as CuO content of x in BNLBT4-6 ceramics, indicating the same values of ~0.56 for all samples with different CuO amounts. Speaking of the d_{33} as shown in Fig. 1(b), surprisingly, the d_{33} increased with increasing the CuO amount and showed the maximum value of d_{33}= 164 pC/N at x=1.0 wt% of CuO. This improvement of the d_{33} is considered to be due to the improvement of the free dielectric constant $\varepsilon_{33}^{T}/\varepsilon_0$ while keeping k_{33} by the addition of CuO as shown in Fig. 1 (a) and (c). From the temperature characteristic of k_{33} on the undoped BNLBT4-6 sintered at 1140°C and BNLBT4-6+ CuO x wt% sintered at 940°C, it can be seen that a depolarization temperature T_d is reduced by the addition of CuO. Figure 2 shows relationship between the amount of doped CuO and T_d of BNLBT4-6+x with a sintering temperature of 940°C From this figure, it can be seen that the T_d decreases with increasing the CuO amount. This result suggests that Cu ions substitute the A/B site of perovskite structure, because the phase transition temperature T_d was dramatically changed. From the laboratory-level XRD measurements, significant changes in the lattice parameters were not observed.

To increase the T_d, BNLBT4-6+CuO 1.0 wt% ceramic was quenched after the sintering at 940°C. Quenching process and effects for the T_d on BNT-based ceramics were described in elsewhere [10]. The T_d of quenched BNLBT4-6+CuO 1.0 wt% was 143°C, which was higher than non-doped BNLBT4-6 sintered at 1140°C. The k_{33} and d_{33} of quenched BNLBT4-6+CuO 1.0 wt% sintered at 940°C were 0.57 and 137 pC/N, respectively. Those values are still higher than those on the non-doped BNLBT4-6 ceramic sintered at 1140°C. From these results, CuO doping is quite effective for decreasing the sintering temperature about 200°C on BNLBT ceramics

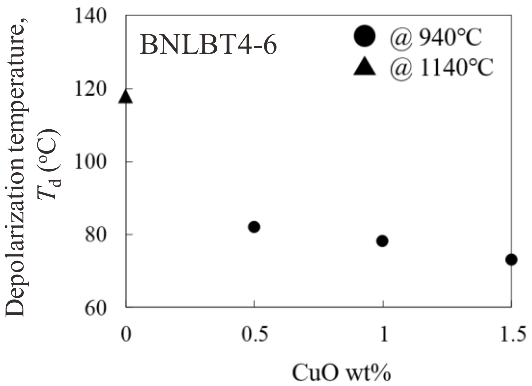

Fig. 2 Depolarization temperature T_d of BNLBT4-6 +CuO x wt% sintered at 940°C as a function of CuO content x.

without any deterioration of the piezoelectric properties and depolarization temperature by combining the quenching treatment.

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