Effect of Manganese Addition on 94NBT-6BT Lead Free Multilayer Ceramics

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Abstract In this study, lead-free $94\text{Bi}_{0.5}\text{Na}_{0.5}\text{TiO}_3\text{-}6\text{BaTiO}_3$ (94NBT-6BT) ceramics were fabricated by solid-state synthesis method at ambient atmosphere. Glassy phase and rounded particles in 94NBT-6BT was observed with increasing Mn content. The effects of doping manganese on the ferroelectric properties of 94NBT-6BT bulk ceramics were evaluated. From the XRD results of the calcined powders, peaks were slightly changed to higher 2 theta value while increasing manganese ratio. Multivalence additive Mn ions act as acceptor dopant in 94NBT-6BT structure at ambient atmosphere. Samples were sintered from 1075 °C to 1175 °C for 2 hours to obtain highest piezoelectric values. SEM results show that glassy phase and rounded particles in 94NBT-6BT was observed with increasing Mn content so, bulk density was enhanced up to 1125C. From the results, 0.3 wt% manganese doped 94NBT-6BT samples have highest electromechanical coupling factor about 0.23, mechanical coupling factor (Q_m) 150 and d_{33} 110 pC/N respectively. Further work, 94NBT-6BT and Mn-doped 94NBT-6BT multilayer actuators were manufactured by water-based tape casting technique. The active area was 49 mm² MLA and was fabricated by using Ag-Pd internal electrode without Pd-Bi reaction at the electrode-ceramic interface. Hysteresis loop measurements of manufactured lead free actuators were done by using Aixact CMA module. Remnant polarization values of Mn-doped 94NBT-6BT MLA for a layer were higher than 6 $\mu\text{C}/\text{cm}^2$.

Keywords Lead-Free, 94NBT-6BT, Manganese Doped, Multilayer, Electrical Properties

1. Introduction

Piezoelectric multilayer ceramics have a wide range of

applications from aerospace, medical, satellite to defense, automotive and manufacturing industries [1]. The products used are generally PZT based ceramics [2]. Instead of these lead-based products, it is desired to use lead-free products due to RohS standards, and the research goes on about the alternative materials [3]. In this context, actuators produced from the 94NBT-6BT around MPB composition, whose actuator performance is relatively good, have begun to be developed [4].

94NBT-6BT has a potential for multilayer actuators depending on their high strain and high polarization values [5]. Most of the manufacturing method for multilayer ceramic production is tape casting [6]. Although generally solvent-based production route has been chosen due to alkali solubility in water for NBT based compositions in tape casting method, Nd-doped BNKLT tapes have been prepared, 7/3 Ag/Pd electrode paste has been applied on to the surface and successfully multilayer sample produced [7]. Ag/Pd paste was not preferred for reaction potential with Bismuth to occur BiPd₃ phase [8].

94NBT-6BT based compositions are researching with modifying compositions such as KNN [9], BKT [10, 11] and oxides like manganese oxide [12], CuO [13], Nb₂O₅ [14], La₂O₃, CO₂O₃ [15, 16] Li₂CO₃ [17], Ta₂O₅ [18] that affects piezoelectric properties depending on their valance. Manganese oxide is multivalence additive so, its effects have been changed to its valance and temperature. Manganese can be added to NBT-based system as MnO₂ and MnCO₃ form [19]. It increases the density, d_{33} , k_p , Q_m values of 94NBT-6BT composition at 1140-1160 °C [12].

Manganese addition causes oxygen vacancies in the lattice and provides grain growth by the phenomena of mass diffusion in polycrystal materials [20]. In addition, manganese atoms replace B-site atoms in the ABO₃ perovskite structure so behaves like acceptor doping [19,21].

There were some studies about doping manganese to 94NBT-6BT system [22, 23] to achieve an extended working range by investigating the BaTiO₃ ratio from 0 to 0.9 and to keep the manganese ratio constant.

For single crystals, manganese doping provides grain growth and decrease in especially leakage current density in 94NBT-6BT composition. For this reason, studies are going in this manner [24]. Although manganese addition to 94NBT-6BT multilayer sample has been studied by Guo et al and showed that Mn-doped-94NBT-6BT multilayer materials can be used as low voltage power supply, effect of manganese has not been mentioned [25].

In this work, manganese amount has been optimized in bulk form of 94NBT-6BT composition, small and large electrical field analysis has been carried out. After decision of manganese ratio in 94NBT-6BT composition, water-based slurry has been prepared, tape casting has been performed and multilayer ceramics produced by using 7/3 Ag/Pd internal electrode to compare with undoped 94NBT-6BT multilayer ceramics.

2. Experimental

In this study, Na₂CO₃ (Carlo Erba 99,5%), Bi₂O₃ (ABCR 99%), BaCO₃ (Carlo Erba 99%), TiO₂ (Fopol Chemicals 99.9%) and MnO₂ (Merck 90%) were used to obtain 94NBT-6BT+x wt%MnO₂ (x=0.2, x=0.3, x=0.5, x=0.7, x=1.0) powders by using conventional solid-state synthesis method. Abbreviations of the compositions were given in Table 1. BaCO₃ has been milled in pulverisette milling to get equiaxed particles. Reagent grade oxides and carbonates were weighted according to stoichiometry and milled for 24 hours. After milling, slurry was dried with rotary evaporator. The powder was calcined at 925 °C for 2 hours to obtain perovskite structure. Then milled for 24 hours with dispersant Darvan-C. The milled slurry was dried at 60 °C in an oven for 12 hours. For producing pellet samples, these powders were granulated with binder PVA and pressed as pellets. Pellets were cold isostatically pressed under 180 MPa to achieve density and sintered at different sintering temperatures from 1075 °C to 1175 °C for 2 hours. Sintered pellets were ground and polished to 1 mm for small signal measurements and 0,6 mm for large-signal

measurements. The crystal structure was analyzed using an X-ray diffractometer (XRD, RAD III, Rigaku, Japan). The surface morphology was observed with a field-emission scanning electron microscope (FE-SEM, Jeol, JSM-650FF, Japan). d₃₃ measurements were done by using Sinocera YE2730A d₃₃ meter, small-signal measurements were done by using Agilent 4294A gain-phase analyzer.

Table 1. Abbreviation of the 94NBT-6BT ceramics with amount of MnO₂ doped

Abbreviation	Amount of MnO ₂ doped wt%
94NBT-6BT	0
B	0.2
C	0.3
E	0.5
G	0.7
J	1.0

For multilayer production, mixed oxides were calcined and milled above. 94NBT-6BT and % wt 0,3 manganese doped 94NBT-6BT powders were manufactured for multilayer ceramics. Then WB4101 binder, distilled water, plasticizer, defoamer, thickener polymers were used to make tape casting slurry. Mars Haake Rheostress 6000 rheometer was used to measure the viscosity of slurry. Prepared slurries were tape cast in KEKO equipment tape caster CAM-L252 that thickness about 50-60 micrometers. Then sheets were dried and cut into 6-inch samples to screen printed with 7/3 Ag/Pd Gwent inner electrode thickness about 3-4 microns and 49 mm² active areas. Electroded sheets were stacked to have interdigital electrode with the stacker pressure 50 Bar and temperature about 60 °C. After stacking, green multilayer ceramics have been warm isostatically pressed to densify composite structure under 15 MPa at 50 °C for 3 minutes. Then green dense multilayer ceramics have been cut and sintered at furnace from 1110 °C to 1125 °C for 2-4-6 hours to obtain multilayer ceramics. After sintering, surface finishing has been made to get flat and parallel surfaces. Electrical connections have been made with silver electrode termination paste. Aixacct TF Analyzer 2000 has been used to attain large-signal measurements.

Figure 1. Schematic view of multilayer structure

3. Results and Discussions

Figure 2 shows X-ray diffraction patterns of 94NBT-6BT+x wt%MnO₂ ceramics for x=0, 0.2, 0.3, 0.5, 0.7 and 1.0. It can be seen from the image, no secondary phase has been observed. The peaks shift to the higher angle with increasing amount of Manganese. That shows the tetragonality (c/a) decreases and, perovskite lattice is shortening by obeying Bragg law [20].

Figure 3 shows the density of 94NBT-6BT ceramics as

a function of Mn contents. The density value of sintered samples was increased while increasing manganese addition and sintering temperature. When sintering temperature increases above 1125 °C, density of the samples was decreased depending on the loss of Bi₂O₃ [12].

Manganese addition increases grain growth due to mass diffusion. Oxygen deficiency causes mass diffusion easier [26]. Figure 4 shows the microstructures of the samples that sintered at 1125 °C for 2 hours as a function of manganese contents.

Figure 2. XRD patterns for 94NBT-6BT+x wt% Mn pellets doped with different amounts of Mn.

Figure 3. Density values of 94NBT-6BT samples as a function of sintering temperature and amount of Mn dopant

a. Undoped 94NBT-6BT ceramics

b. 0.2 wt% Mn-doped 94NBT-6BT

c. 0.3 wt% Mn-doped 94NBT-6BT

Figure 4. SEM images of a) 94NBT-6BT b) 0,2%wt Mn-doped 94NBT-6BT c) 0,3%wt Mn-doped 94NBT-6BT samples sintered @ 1125C-2s

SEM images show the effect of manganese addition on grain growth of 94NBT-6BT ceramics. As manganese ratio increases, the size of grains increased. Also grains have rounded shape while manganese doped. Manganese behaves like sintering agent.

d_{33} and k_p values of the samples were shown in figure 5. d_{33} increases up to 100 pC/N and k_p increases to 0,25 when 0,3wt% manganese added to the system. These values are optimum values for the manganese addition on the 94NBT-6BT MPB system for the limits of solubility in the lattice. When manganese ratio increases above the solubility limits, manganese atoms pinch the domains by accumulating to the grain boundaries and deteriorate the piezoelectric properties in PZT [27] and 94NBT-6BT [12].

Figure 5. d_{33} and k_p results (a-b) of 94NBT-6BT ceramics as a function of temperature and amount of Mn dopant

As shown in figure 6, the mechanical quality factor of manganese doped 94NBT-6BT samples was increased. The following equation mechanical quality factor is the figure of merit defined as internal friction of domain walls under high power conditions [28].

$$Q_m = \frac{f_a^2}{2\pi C f_r (f_a^2 - f_r^2) Z_m} \quad (1)$$

f_a is antiresonance frequency (Hz), f_r is resonance frequency (Hz), C is the capacitance (F), Z_m is the minimum impedance (ohm) at the resonance frequency. Increasing the mechanical quality factor indicates that manganese atoms are located at B site in the lattice due to oxygen deficiency. Domain walls and motion effects also remanent polarization

Figure 6. Mechanical quality factor values of different amount Mn-doped 94NBT-6BT samples depending on sintering temperature

Figure 7. Hysteresis loops for Mn-doped and undoped 94NBT-6BT samples

All the electrical values support the literature to confirm the effect of manganese to 94NBT-6BT [12, 19]. Ceramics exhibit saturated hysteresis loops (figure 7). Manganese doped 94NBT-6BT composition exhibit larger polarization. If manganese ratio increases up to optimum value of 0,3 wt%, not only hysteresis can exhibit saturated value but also samples go into breakdown. Therefore, measurable hysteresis results obtained only from B, C and E compositions.

Doping manganese has increased the conductivity of samples when the amount is increasing to the solubility limits, leakage current increases [29]. For this reason, 0,3 wt% Mn-doped ceramics have been selected to produce ML ceramics.

Figure 8. a) Photograph of a multilayer ceramic actuator b) cross-sectional SEM

The behavior of NBT materials was not fully resolved in water-based tape casting slurry due to possible alkali

solubility in water, but process can be applied [7]. The 8x7x1 mm³ size 0,3wt% Manganese doped and undoped 94NBT-6BT MLAs were fabricated by water-based tape casting technique that is shown in figure 8.

These MLAs were sintered at different sintering temperatures and time. Internal electrode behavior changes depending on sintering conditions. Thermal mismatch of electrode and ceramic causes deformation on inner electrode and delamination defect while sintering [30] and decrease in polarisation loop [31]. Also Ag-Pd electrode was not preferred before it was known that the presence of excess bismuth exists in the composition and would cause the reaction with palladium [32].

It can be clearly seen that homogenous floating of electrode of Mn-doped 94NBT-6BT multilayer samples from figure 9 (d-f) that sintered at 1115 °C-2 hours. Optimum sintering conditions for multilayer materials can be found to obtain max values of polarization to electrical field applied [33]. Figure 10 a-b presents room temperature polarization-electric field (P-E) hysteresis loops of the 94NBT-6BT multilayer ceramics sintered at 1115 °C and 1120 °C for different hours. Remnant polarization (P_r) values of samples were about 5µC/cm². Increasing sintering time causes decrease in coercive electric field. Figure 10c shows Mn-doped 94NBT-6BT multilayer samples sintered at 1115 °C for 2-4-6 hours. Remnant polarization value for 2 hours sintered samples were above 6µC/cm². Increasing sintering time causes increase in coercive electrical field in NBT-H-ML samples.

Figure 9. SEM analysis for 94NBT-6BT multilayer ceramics sintered @ 1115 °C a-c) 94NBT-6BT samples 2-4-6 hours d-f) Mn-doped 94NBT-6BT samples 2-4-6 hours

Figure 10. Hysteresis loops of 94NBT-6BT multilayer samples sintered at different temperatures and time a) 1115 °C b) 1120 °C c) Mn-doped 1115 °C

4. Conclusions

Manganese doped 94NBT-6BT ceramics synthesized by solid-state method was investigated. According to obtained small and large signal results of bulk samples, amount of manganese has been optimized about 0.3 wt%. Remnant polarization value has been increased to 40 $\mu\text{C}/\text{cm}^2$ by optimizing manganese ratio. Based on the obtained results, multilayer samples of 94NBT-6BT and doped 94NBT-6BT compositions have been produced successfully and measurements have been done. Sintering temperature and time for sintering the ceramic and metal-ceramic interaction has been optimized for 94NBT-6BT and Mn-doped 94NBT-6BT multilayer structures. As expected, Mn-doped 94NBT-6BT multilayer ceramics have higher remnant polarization values than 94NBT-6BT multilayer ceramics apart from size effect. In future works, electrical switching performance of 94NBT-6BT and Mn-doped 94NBT-6BT multilayer ceramics will be held and compared.

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