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Effects of the Sn^{4+} Substitution and the Sintering Additives on the Sintering Behavior and Electrical Properties of PLZT

Jeoung-Sik Choi ¹, Dong-Chul Kim ¹, Hyo-Soon Shin ^{1,*} , Dong-Hun Yeo ¹ and Joon-Hyung Lee ²

¹ Electronic Convergence Materials Division, Korea Institute of Ceramic Engineering and Technology, 101, Sohero, Jinju 52851, Korea; abcd7516@kicet.re.kr (J.-S.C.); minamdc@kicet.re.kr (D.-C.K.); ydh7@kicet.re.kr (D.-H.Y.)

² School of Materials Science and Engineering, Kyungpook National University, Daegu 41566, Korea; joonlee@knu.ac.kr

* Correspondence: hshin@kicet.re.kr

Abstract: (Pb, La)(Zr, Ti)O₃ (PLZT) with antiferroelectric properties can be applied as a capacitor whose capacitance increases in a high electric field. From this, we obtained a high sintering density at 950 °C by adding low-temperature sintering additives, 8.0 wt% of PbO and 2.5 wt% of ZnO, simultaneously to a (Pb_{0.88}, La_{0.12})(Zr_{0.86}, Ti_{0.14})O₃ composition. The change in electrical characteristics was confirmed in terms of Sn^{4+} substitution, resulting in no change in the sintering density by Sn^{4+} substitution. However, as the amount of Sn^{4+} substitution increases, the dielectric constant gradually decreases from 1300 to 700, and the grain size decreases from about 4 to 1 μm in terms of microstructure. In the crystal structure analysis, the general formation of a single perovskite structure was confirmed. The results of the hysteresis curve measurement revealed that the breakdown electric field increases from 4 to 9 $\text{kV}\cdot\text{mm}^{-1}$ as the amount of Sn^{4+} substitution gradually increases. However, polarization decreases in the same way as the permittivity trend. The composition exhibits excellent electrical properties when the ratio of Sn^{4+} is 0.4: a high energy storage density of $3.5\text{ J}\cdot\text{cm}^{-3}$, energy efficiency of 80%, and breakdown electric field of about $8.5\text{ kV}\cdot\text{mm}^{-1}$.

Keywords: antiferroelectric; MLCC; PLZST; substitution; additive

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1. Introduction

Antiferroelectric materials have a high energy storage density and low loss characteristics. Therefore, there is a growing interest in the application of multi-layer ceramic capacitors (MLCCs) in electronic and power systems used in high electric fields [1–3]. A representative ceramic composition exhibiting antiferroelectricity is (Pb, La)(Zr, Ti)O₃ (PLZT) [4]. In PLZT, La^{3+} is substituted with the Pb^{2+} site of the A-site in the PZT structure. At this time, the paraelectric, ferroelectric, and antiferroelectric properties are determined according to changes in the Pb^{2+} and La^{3+} of the A-site and the Zr^{4+} and Ti^{4+} content of the B-site. In the past, many studies were conducted on the change in electrical characteristics according to the composition change of the A- and B-sites [5–7].

The ferroelectric materials are known to have low dielectric properties at high electric fields, while in anti-ferroelectric materials, dielectric properties increase linearly in high electric fields. Therefore, many studies were conducted to apply anti-ferroelectric properties as capacitors used in high electric fields [2,8]. However, in order to be used in a high electric field, the electrical and physical destruction of the ceramic should not have occurred when the breakdown electric field of the material is high. Recently, many studies have been conducted to increase the breakdown of the electric field and energy storage density. Representatively, many research results have been reported on the composition of (Pb, La)(Zr, Sn, Ti)O₃ (PLZST) [9–11]. PLZST has a structure in which Sn^{4+} is substituted for the B-site, which is an element site with a similar ionic radius in the PLZT composition. PLZST is reported to have a high breakdown electric field. However, most of the reports mainly

investigated the characteristic change according to a small amount of Sn^{4+} substitution. In addition, in order to simultaneously sinter the Cu inner electrode to manufacture MLCC by applying the composition to the thick film process, the sintering temperature should be lowered to 950 °C [12,13]. It is necessary to systematically study additives for low-temperature sintering and the improvement in the breakdown electric field.

In the present study, we selected $(\text{Pb}_{0.88}, \text{La}_{0.12})(\text{Zr}_{0.86}, \text{Ti}_{0.14})\text{O}_3$ as the basic composition and PbO, ZnO, and NiO as low-temperature sintering additives and sintered them at 950 °C. Additives were added after the calcination process to avoid their effect on the crystal structure of PLZT. To obtain a high breakdown electric field and energy storage density, Sn^{4+} was substituted up to a content of 0.1 to 0.6 to investigate changes in electrical properties. The electrical properties of the composition were investigated by calibrating the content of Sn (0.1 to 0.6 mol ratio) to find the highest breakdown electric field and energy storage density.

2. Materials and Methods

As the starting materials, PbO (99.9%, Daejung, Siheung-si, Korea), ZrO_2 (99.6%, Daejung, Siheung-si, Korea), TiO_2 (Daejung, Siheung-si, Korea), La_2O_3 (99.7%, Daejung, Siheung-si, Korea), and SnO_2 (99.8%, Daejung, Siheung-si, Korea) were used. The raw materials were weighed according to the composition of $[(\text{Pb}_{0.88}, \text{La}_{0.12})(\text{Zr}_{1-x}, \text{Sn}_x)_{0.86}\text{Ti}_{0.14}]\text{O}_3$, then 0.4 wt% of the dispersant (DISPERBYK-111, BYK, Wesel, Germany) was added to the composition, which went through a wet ball-milling process at 120 RPM for 24 h. After that, it was dried in an oven at 100 °C for about one day, and the powder was placed into the alumina crucible and calcinated at 880 °C.

The powder was pulverized after the calcination process. Low-temperature sintering additives such as ZnO (99.5%, Daejung, Siheung-si, Korea), NiO (99.7%, Daejung, Siheung-si, Korea), and PbO (99.8%, Daejung, Siheung-si, Korea) were added to the composition. Thereafter, the mixture was pulverized and mixed by a wet ball-milling process in ethanol solvent. For sintering, the dried powder was mixed with an aqueous binder (PVA), and bulk was pressed at 10 Ø using a uniaxial pressure press. To remove the binder before sintering, the sample was heated at 600 °C for 2 h and sintered from 950 to 1100 °C for 3 h.

Density was measured using the Archimedian method to confirm whether low-temperature sintering was performed. For crystal structure analysis, X-ray diffractometer (DMAX2500, Rigaku, Tokyo, Japan) was used, and the microstructure was observed using a field emission scanning electron microscope (JSM-6700F, JEOL, Tokyo, Japan). In addition, to measure the dielectric constant, Ag electrodes were printed on both sides and annealed at 600 °C. The electrical characteristics were analyzed using an impedance analyzer (E4990A, Keysight, Santa Rosa, CA, USA) and a multiferroic tester (Precision LC, Radiant, Renton, WA, USA).

3. Results and Discussion

PLZT compositions are generally sintered at the temperature range of 1250–1350 °C. In the perovskite-based composition, CuO, NiO, Li_2O_3 , and ZnO are typically the additives that use a low melting point material to lower the sintering temperature [14–16]. Among them, ZnO and NiO were selected, and the effect of these additives on low-temperature sintering of the PLZT composition was investigated. Figure 1 shows the bulk density according to the sintering temperature of PLZT when 2.0 and 2.5 wt% of ZnO and NiO are added, respectively. As the contents of the additive increased, the sintering density increased at the same temperature. It was thought that the sintering temperature was reduced by ZnO and NiO due to their low melting point during sintering. Li [17] et al. reported that when ZnO is used as a low-temperature sintering additive in the PZT composition, the sintering temperature is lowered by the formation of a liquid phase. However, in this experiment, a relatively low density was obtained at 950 °C even when ZnO and NiO were added up to 2.5 wt%.

Figure 1. Changes in bulk density of $(\text{Pb}_{0.88}, \text{La}_{0.12})(\text{Zr}_{0.86}, \text{Ti}_{0.14})\text{O}_3$ according to the addition of NiO and ZnO.

PbO in the PZT dielectric materials has a high volatility of over 880 °C. The volatilization of PbO affects the sintering density by forming a vacancy at the A-site. It was reported that the sintering properties improved as the added PbO re-compensated for the vacancy generated after volatilization when a small amount of PbO was added. Coker [18] et al. confirmed the effect of low-temperature sintering on PZT ceramics by adding a small amount of PbO together with a low-melting additive.

Figure 2 confirms the densification behavior after sintering at 950 °C when a small amount of PbO was added simultaneously to ZnO at a fixed amount of 2.5%, the amount that effectively increases the density (Figure 1).

Figure 2. Densities and shrinkages of sintered bodies at 950 °C according to the addition of PbO in the PLZT + ZnO (2.5 wt%) composition.

As the content of PbO gradually increased, the sintered density was improved. As mentioned above, this is assumed to be the effect of the volatilization compensation of

PbO and liquefaction of ZnO. When more than 6 wt% of PbO was added, a density of $7.8 \text{ g}\cdot\text{cm}^{-3}$ and a shrinkage rate of 15% was obtained. As a result, when ZnO and PbO were simultaneously added to the PLZT composition, the densification of PLZST was completely formed at 950°C .

Based on the results in Figures 1 and 2, a composition containing 2.5 wt% of ZnO and 8.0 wt% of PbO was selected, and the change in sintering density at 950°C was observed according to the amount of Sn^{4+} substitution for Zr^{4+} . In general, when an additive is substituted, it is replaced with an ionic site with a similar ionic radius. The ionic radius of Sn^{4+} is about 0.071 nm, and the ionic radius of Zr^{4+} is about 0.079 nm, so it is assumed that the ionic radius of Sn^{4+} is similar to that of Zr^{4+} [19]. The overall change in the amount of Sn^{4+} substitution had no significant effect on the sintering density at 950°C . However, the density was slightly decreased when over 0.6 mol ratio of Sn^{4+} was substituted.

Figure 3 shows the microstructures of the body sintered at 950°C according to the substitution of Sn^{4+} . A microstructure with a uniform grain size was observed as a whole. As the amount of Sn^{4+} substitution gradually increased, the grain size decreased. The grains in which Sn^{4+} were not substituted were larger than about $4 \mu\text{m}$ but decreased to about $1 \mu\text{m}$ when the Sn^{4+} were substituted by 0.6. Wang [19] et al. reported that the particle size continuously decreased and the number of micropores increased when excessive Sn^{4+} were substituted in the PLZT composition.

Figure 3. Microstructures of $(\text{Pb}_{0.88}, \text{La}_{0.12})(\text{Zr}_{1-x}, \text{Sn}_x)_{0.86}\text{Ti}_{0.14}\text{O}_3$ sintered at 950°C according to Sn^{4+} substitution (a) $\text{Sn}^{4+} = 0$, (b) $\text{Sn}^{4+} = 0.2$, (c) $\text{Sn}^{4+} = 0.4$, (d) $\text{Sn}^{4+} = 0.6$.

The sintered density slightly decreased with the pores when Sn^{4+} was 0.6, as seen in Figure 4. A secondary phase as a needle-shaped microstructure was formed when a 0.2 mol ratio of Sn^{4+} was added to the composition. As a result of the composition analysis using EDS, this needle has relatively high ratios of Pb^{3+} and Sn^{4+} elements, so it can be estimated as the appearance of a secondary phase centered on them.

Figure 4. Sintered density of $(\text{Pb}_{0.88}, \text{La}_{0.12})(\text{Zr}_{1-x}, \text{Sn}_x)_{0.86}\text{Ti}_{0.14}\text{O}_3 + \text{ZnO}$ (2 wt%) + PbO (8 wt%) composition at 950 °C, according to Sn^{4+} substitution.

Figure 5 is an XRD diffraction pattern diagram for analyzing the structure of the PLZT sintered body for Sn^{4+} substitution. As in the microstructure figure, a secondary phase presumed to be the PbSnO_2 phase was confirmed in the XRD pattern analysis of the Sn^{4+} ion at 0.2 substitution amount. However, at other substitution amounts, a perovskite single phase without a secondary phase was obtained. A study by Dan [20] et al. also reported that a small amount of SnO_2 was precipitated when the PLZST composition was synthesized by a solid-state reaction. Based on this, it can be estimated that a small amount of unsubstituted SnO_2 and excess PbO react to generate a secondary phase. For a detailed structural analysis of the composition of PLZST, the results of a low-speed scan around 44–45° are shown in the figure on the right. Overall, a pseudocubic structure was obtained. Although the phenomenon of peak shift was confirmed with the addition of Sn^{4+} , the phenomenon of phase transition was not confirmed. Therefore, it is predicted that the addition of Sn^{4+} does not affect the phase transition.

Figure 5. Crystal structures of $(\text{Pb}_{0.88}, \text{La}_{0.12})(\text{Zr}_{1-x}, \text{Sn}_x)_{0.86}\text{Ti}_{0.14}\text{O}_3$ composition according to the substitution of Sn^{4+} (a) $\text{Sn} = 0$, (b) $\text{Sn} = 0.2$, (c) $\text{Sn} = 0.4$, (d) $\text{Sn} = 0.6$.

Figure 6 shows the dielectric constant of the PLZT sintered bodies according to the substitution of Sn^{4+} ions. The sintered body was sintered at 950 °C, and the dielectric

constant was measured at 1 KHz. The dielectric constant decreased as the substitution amount of Sn^{4+} increased. Chen [21] et al. reported that the tolerance factor is important for phase safety in perovskite structures.

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)} \quad (1)$$

Figure 6. Dielectric constant of $(\text{Pb}_{0.88}, \text{La}_{0.12})(\text{Zr}_{1-x}, \text{Sn}_x)_{0.86}\text{Ti}_{0.14}\text{O}_3$ composition according to the amounts of Sn^{4+} substitution.

R_A , R_B , and R_O are the ionic radius of A-site, B-site, and oxygen-site, respectively. It is generally known that when $t > 1$, the ferroelectric phase is stable, and when $t < 1$, the antiferroelectric phase is stable. Since the Sn^{4+} (0.069 nm) has a smaller ionic radius than the Zr^{4+} (0.072 nm), the R_B value decreases as the Sn^{4+} content gradually increases [22]. As a result, as t increases, the antiferroelectric phase becomes unstable. Therefore, as the substitution amount of Sn^{4+} increases, the polarization decreases. It is thought that this decrease in polarization causes a decrease in the dielectric constant. Additionally, as the substitution amount of Sn^{4+} increased from 0.5 to 0.6, the dielectric constant decreased sharply. This is confirmed to be related to the decrease in sintered density, as shown in Figure 3.

Figure 7 shows the electrical characteristics of the sintered PLZT according to the substitution amount of Sn^{4+} . Figure 7a is the hysteresis curve of the sintered PLZT according to the substitution of Sn^{4+} . Regardless of the substitution amount of Sn^{4+} , typical anti-ferroelectric properties are shown. As the amount of substitution of Sn^{4+} gradually increases, the breakdown electric field increases, but the polarization decreases. The above results are graphically shown in detail in Figure 7b. At 0.6, the maximum polarization decreased from about 7.5 to 4 $\mu\text{C}\cdot\text{cm}^{-2}$. It is confirmed that the polarization decreases as the tolerance factor increases due to the gradual increase in the Sn^{4+} substitution amount, thus the antiferroelectric properties become unstable, as presented in Figure 6. Therefore, the polarization and the loss were increased, as shown in Figure 7a,b. In the results in Figure 6, the dielectric constant decreased rapidly when the Sn^{4+} substitution amount was 0.6. In addition to the slightly decreased sintering density, the dielectric constant decreased rapidly due to the effect of low polarization.

Figure 7. Electrical properties of PLZST composition according to the amount of Sn^{4+} substitution (a) hysteresis curve, (b) maximum polarization and breakdown electric field, and (c) energy storage density (W) and efficiency (■).

However, as the amount of substitution of Sn^{4+} increased, the breakdown electric field increased from 4 to 9 $\text{kV}\cdot\text{mm}^{-1}$. In the results in Figure 4, the grain size decreased as the amount of Sn^{4+} substitution increased. As the grain size decreases, the number of grain boundaries increases in the same volume. Yang and Cai [23,24] et al. reported that ferroelectrics with small grain and ceramics with antiferroelectric properties had a higher breakdown electric field; therefore, the results are in good agreement.

Figure 7c is a graph in which energy density and efficiency are calculated in the hysteresis curve. The energy storage density (J) and efficiency (■) are calculated using the formulas below:

$$J = \int E dP \quad (2)$$

$$\blacksquare = \frac{J}{J + J_{\text{loss}}} \quad (3)$$

E = applied electric field and P = polarization, where J_{loss} is the energy-loss density. The energy-loss density was calculated by the numerical integration of closed area of the hysteresis loop [25].

The energy density increased as the amount of substitution gradually increased, but the amount of substitution of Sn^{4+} decreased from 0.6. This is considered to be a result of an increase in loss caused by an increase in the tolerance factor value and a decrease in the sintering density. As a result, when the substitution amount of Sn^{4+} was 0.4, an energy density of about $3.5 \text{ J}\cdot\text{cm}^{-3}$ and high energy efficiency of 80% was obtained.

4. Conclusions

In the $(\text{Pb}_{0.88}, \text{La}_{0.12})(\text{Zr}_{0.86}, \text{Ti}_{0.14})\text{O}_3$ composition, 8.0 wt% of PbO and 2.0 wt% of ZnO were added to obtain a high sintered density at 950 °C. PbO and ZnO, which are additives with relatively low melting points, are liquefied during the sintering process, thereby lowering the sintering temperature.

As the amount of Sn^{4+} substitution increased, the sintered density did not change significantly, and the crystal structure also maintained the perovskite phase well. However, as the Sn^{4+} substitution amount increased, the dielectric constant decreased. This is confirmed as a result of a decrease in the polarization due to an increase in the tolerance factor as the amount of Sn^{4+} substitution gradually increased.

In the measurement of the hysteresis curve, the breakdown electric field rapidly increased as the amount of Sn^{4+} substitution gradually increased. As a result, when

Sn^{4+} is 0.4, a high energy storage density of $3.5 \text{ J}\cdot\text{cm}^{-3}$, energy efficiency of 80%, and breakdown electric field of about 8.5 kV/mm are obtained.

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