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Research Paper

Dielectric Characteristics of $PbSc_{1/2}Nb_{1/2}O_3$ Prepared by Using the One-step Solid State Reaction

Yeon Jung Kim*
Center for Innovative Engineering Education, Dankook University, Yongin 448-701, Korea

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Abstract The $PbSc_{1/2}Nb_{1/2}O_3$ ceramics at a relatively low temperature of 1300°C was successful synthesized. Solid state reaction of two-step process is not necessary. The dielectric constant, dielectric loss and admittance of ceramic samples were determined. The pyroelectric characteristics are in good agreement with the dielectric properties. Ferroelectric properties of well-formed the $PbSc_{1/2}Nb_{1/2}O_3$ ceramics are in agreement with broad distribution of relaxation phenomenon. Relatively strong frequency dependent of dielectric constant is observed at about 110°C. The distinct thermal hysteresis was observed in the measurement of the dielectric constant and dielectric loss. The critical exponents of during cooling and heating measurements in the $PbSc_{1/2}Nb_{1/2}O_3$ ceramics were 1.14 and 1.59 at 1 kHz, respectively.

Keywords: $PbSc_{1/2}Nb_{1/2}O_3$, Dielectric, Pyroelectric, Admittance, Phase Transition

I. Introduction

The $AB_{1-x}B_xO_3$ ceramics are very promising for varieties of application fields such as pyro-sensors, piezoelectric transducers/actuators and FeRAM devices [1]. The $PbSc_{1/2}Nb_{1/2}O_3$ (PSN) ceramic is the classical relaxor ferroelectric. Crystal PSN appears to have the ideal structure of perovskite only above 110°C. When Sc^{3+} and Nb^{5+} ions of the PSN structure have short range ordering, it becomes a diffused ferroelectric [2]. Not every ferroelectric can be a relaxors. Relaxors are characterized by a strong frequency dispersion of the dielectric maxima, and the absence of macroscopic polarization and anisotropy at temperatures significantly below dielectric maxima. The phase transition of relaxor ferroelectrics (ceramics) effects on the physical environments, such as thermal agitation, grain size and grain boundary. And the dielectric constant of relaxors decreases with increasing frequency and the phase transition temperature is biased toward high temperature [3]. The microscopic structure of the PSN is complex. Solid-state physicists are very interested in the PSN crystal. In spite of the intensive investigations in the PSN ceramics, the mechanism responsible for relaxation process in PSN is yet to be understood [4,5].

Therefore, it attempts to analyze the mechanisms of dielectric relaxation and phase transition phenomena in these experiments. Generally, the ceramic structure is fabricated easily than the single crystal. To understand the dielectric characteristic of the PSN ceramic is discussed by carefully analyzing the experimental data. The abnormal properties of the PSN were examined by measuring the dielectric constant and dielectric loss. Understand the relaxation properties by measuring the admittance as a function of temperature and frequency.

*Corresponding author
E-mail: yjkim80@dankook.ac.kr

II. Experimental Procedure

In this study, the PSN sample at a relatively low temperature of 1300°C was successfully synthesized. Generally, the PSN fabricated by using a two-step mixed oxide method, it is clear that the formation of pyrochlore phase in PSN can be completely avoided by sintering at temperature above 1300°C [6]. In the research, when the $PbSc_{1/2}Nb_{1/2}O_3$ with a perovskite structure was produced, the B-site wolframite ($ScNbO_4$) powder was not produced first. It was precisely control the manufacturing process (mixing, drying, heating and cooling treatments) of the PSN. The PSN sample was produced by mixing the starting oxides together, such as $PbCO_3$, Sc_2O_3, and Nb_2O_5. The PSN green pellet was calcined at 900°C for 2 hours and the PSN pellet was sintered at 1300°C for 40 minutes. The XRD patterns of the PSN samples are shown in Fig. 1. The percentage of perovskite in the calcined powder PSN was 75%. The sintered sample showed complete formation of the perovskite phase. Thus, reaction of two-step process in PSN is not necessary. Fig. 2 shows the FE-SEM image of the fractured surface of the PSN ceramics. Normally, during sintering, the crystal grains of the sample composed of powder become larger with a concomitant

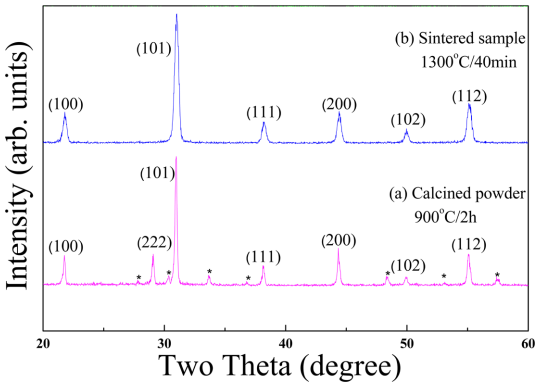

Figure 1. XRD patterns for (a) calcined powder and (b) sintered sample of the PSN.

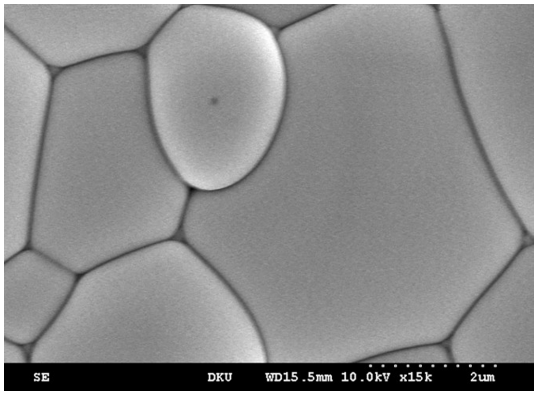

Figure 2. SEM images of the PSN sintered at 1300°C for 40 minutes.

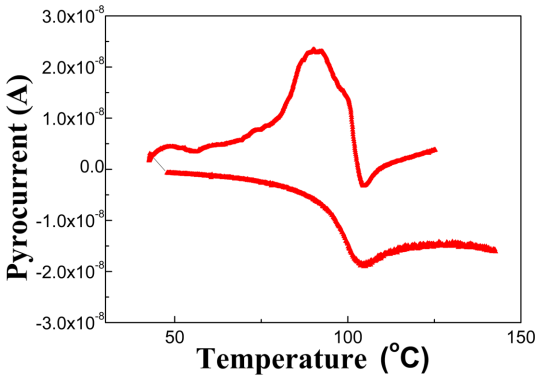

Figure 3. The pyroelectric current as a function of temperature for the PSN.

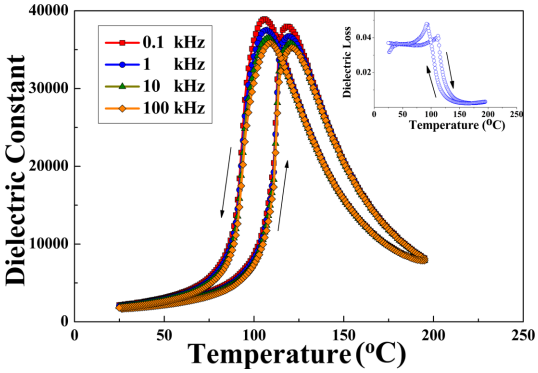

Figure 4. The dielectric constant as a function of temperature for the PSN at different frequencies. The inset figure shows dielectric loss versus temperature.

decrease in the number of pores. The grain sizes of the sintered sample are 3.5~5.5 μm and dense grains. The atomic percentage of Pb, Sc, Nb, and O in the result of EDX was 17.01%, 8.96%, 10.57%, and 63.47%, respectively. To measure the admittance and capacitance of the samples polished to a 1 mm in thick, a silver (99.9%) electrode was coated on both sides of the samples using a thermal evaporator. The admittance and capacitance of sintered PSN were examined at various temperature (R.T.~250°C) and frequency (0.1~100 kHz) with a heating and cooling rate of 2°C/min using a LCR meter (HP 4284A). Dielectric constant is routinely calculated from the well-known equation follows $\kappa = \frac{Cd}{\varepsilon_o A}$.

III. Results and Discussion

Fig. 3 shows variation of the pyroelectric current as a function of temperature in the PSN. The peak of the pyroelectric current increases initially and then decreases rapidly with increasing temperature. In particular, the change of the pyroelectric current in the vicinity of 100°C is in good agreement with the dielectric loss data (see Fig. 4). Meanwhile, Fig. 4 shows the dielectric constant and dielectric loss as a function temperature at heating and cooling measurements in the PSN. Fig. 4 shows significant thermal hysteresis between heating and cooling measurements for PSN. As shown in Fig. 4, PSN exhibits relatively strong frequency dispersion and a sharp drop of the dielectric constant at a frequency-independent temperature of 110°C on heating. On cooling, this discontinuity of dielectric constant occurs at 90°C, indicating the existence of a thermal hysteresis. These characteristics are in good agreement with the pyroelectric properties of Fig. 3. Finally, the diffuse nature of the transition in the disordered PSN composition is further suggested by the obvious thermal hysteresis between heating and cooling curves (See Fig. 4). Most of the complex perovskite ferroelectrics have several transition points. The transitions generally exhibit a large thermal hysteresis. The dielectric constant of a well-sintered ceramics is high, but dielectric loss is low. Thus, the dielectric constant of PSN was the highest. Fig. 4 shows the maximum dielectric constant decreased with increasing frequency, and the dielectric transition temperatures also increased in the PSN. Relatively large dielectric dispersion is observed at temperatures near the T_m. The PSN is rhombohedral structure in ferroelectric state. As a result of the above, the measured dielectric constant showed typical relaxor ferroelectric material properties [7]. Above the T_m the total electric dipole moment of PSN is non-zero, as though thermal energy is sufficient to make the six equilibrium positions equally in the PSN unit cell. The transition temperature corresponds to the transition from the non-polarized state into a polarized state.

The mechanism of phase transition in the PSN is

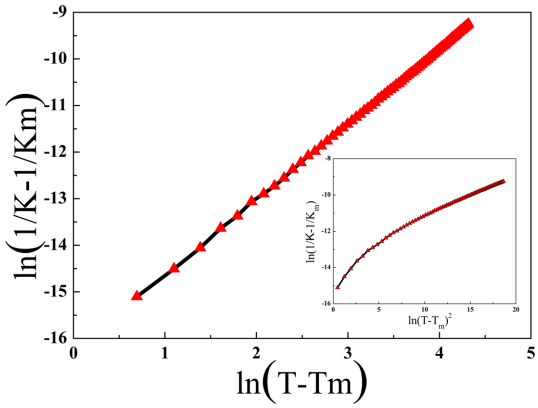

Figure 5. Plot of $\ln(1/K-1/K_m)$ versus $\ln(T-T_m)^2$ for PSN at 1 kHz.

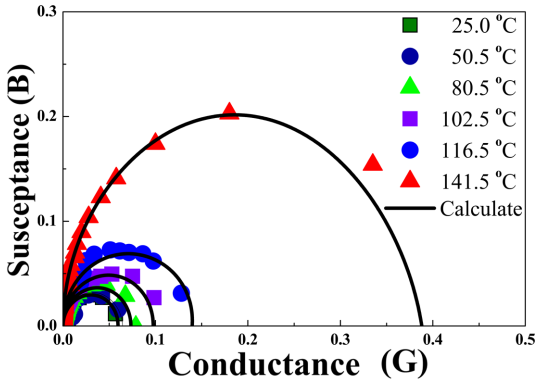

Figure 6. Variation of the conductance as a function of frequency for the PSN at different temperatures.

different from the Curie-Weiss law. Relaxors can be separated into long range ferroelectric order at T_m. The dielectric constant of relaxors near the Curie region is governed by a modified Curie-Weiss quadratic equation $\frac{1}{K} = \frac{1}{Km} + \frac{(T-T_m)^{\gamma}}{2Km\delta^2}$, where K is the dielectric constant, K_m is the maximum dielectric constant, T_m is the dielectric constant maxima temperature, δ is the diffuseness parameter and γ is the critical exponent. Quadratic equation can be solved graphically using a $\ln(1/K-1/K_m)$ versus $\ln(T-T_m)$ plot. Fig. 5 shows the $\ln(1/K-1/K_m)$ versus $\ln(T-T_m)$ and the $\ln(1/K-1/K_m)$ versus $\ln(T-T_m)^2$ relation in the PSN. The value of γ=1 in equation is the expression of the degree of dielectric relaxation in a normal ferroelectrics. When γ=1, quadratic equation express the Curie-Weiss behavior of the normal ferroelectrics, while for γ=2, quadratic equation is identical to the quadratic law [8]. For PSN systems, from the slope of plots of 1/K vs. $(T-T_m)^{\gamma}$, the values of γ were calculated. The values of critical exponent are γ=1.14 and γ=1.59 at 1 kHz showed an on cooling and heating treatments, respectively. The value of T_m and γ are decreases at cooling process than heating treatment (See table 1). Due to low symmetry of rhombohedral structure at approximately T_m, ferroelectric domains are formed. It deviation from the Curie-Weiss law in PSN systems indicates the broadening effect on the phase transition at high frequency and the decrease of the long range ferroelectric order correlation. Therefore, the PSN is determined to exhibit a more diffuse phase transition characteristics.

Fig. 6 shows the conductance and susceptance as a function of frequency of the PSN sample at various temperatures. Generally, the dielectric dispersion characteristics are analyzed by using the complex dielectric constant K*(ù) and admittance Y*(ù). And complex admittance Y*=Y'(G)+jY''(B), where Y'(G) is the conductance and Y''(B) is the susceptance. Physical defect induced dielectric relaxation would be directly related to the concentration of defects. The Y*(ω) and K*(ω) are correlated by the equation $Y^*(\omega) = Y'(G) + jY''(B) = j\omega C_0\varepsilon^*$ and $\frac{K^*(\omega)}{K_S - K_\infty} = \frac{1}{1+(j\omega\tau)^{1-\alpha}}$, where ω is the angular frequency ω=2πf, f is the circular frequency of field, $C_o=\omega_o A/d$ is the geometrical capacitance, ω_o (=8.854×10^{-12} F/m) is the permittivity of free space, d is the thickness of pellet, A is the area of electrode deposited on the pellet, K is the high frequency values of K, K_s is the low frequency values of K and á is a measure of the distribution of relaxation time τ. In this experiment, the RLC electrical equivalent circuit was used to calculate the electrical circuit elements in PSN. The calculated value of the series and parallel capacitance were 3.4×10^{-9} F, 5.4×10^{-13} F, respectively, in PSN at T_m. In the research, the maximum value of Y'(G) and Y''(B) with an increase in the measured temperature was increased. And when measuring temperature higher than T_m, it intensified the frequency dependence of the admittance. To analyze the contribution originated from microscopic quantities in PSN, Cole-Cole diagram have been made at difference temperatures. This Cole-Cole diagram provides the information about the dielectric relaxation in PSN. The Cole-Cole diagram is obtained by plotting the experimental values of Y''(B) against those of Y'(G) [9]. The value of

Table 1. The dielectric properties of the PSN ceramics.

Freq. (kHz)	Heating					Cooling				
	K_m	T_m (°C)	ΔK	ΔT (°C)	γ	K_m	T_m (°C)	ΔK	ΔT (°C)	γ
0.1	37978	119	2728	–2	1.59	38937	106	3098	–3	1.14
1	36724	120			1.59	37536	107			1.15
10	35839	120			1.61	36503	108			1.18
100	35250	121			1.63	35839	109			1.20

K_m: the maximum dielectric constant, T_m: the temperature at K_m, ΔK: K_m at 0.1 kHz-K_m at 100 kHz, ΔT: T_m at 0.1 kHz-T_m at 100 kHz, γ: the critical exponent.

Y'(G) at higher frequency for selected temperatures coincides with each other suggesting the release of space charge. The radius of the semicircle arc increases with temperature to reach a maximum. The plots show that the Y"(B) values reach a peak at all temperatures, and the magnitude of the peak increases with increasing measuring temperature. The Y'(G) of lead-type perovskite ceramics shows a similar trend. In addition, maximum Y'(G) and Y"(B) increase with increasing temperature. When the temperature was changed, the resonant frequency in the PSN changed. The broadening of Y'(G) and Y"(B) peaks on high frequency ranges with increasing temperature confirms the existence of temperature dependence of relaxation process [10]. In addition, Fig. 6 shows a distribution of relaxation times instead of a single relaxation time in the PSN. The long relaxation times part enlarged diffuse by conductivity effects with increasing temperature. At the same time, the ordering between Sc^{3+} and Nb^{5+} in PSN influences complex admittance and dielectric properties. The relaxor behavior and Pb positional fluctuation in PSN is associated with existence of polar domains in paraelectric cubic state. Such behaviors coincides with a freezing of nano-cluster occurs at low temperature than T_m (107ºC, 1 kHz) of disordered PSN on cooling.

IV. Conclusions

In conclusion, the PSN were prepared under the sintering conditions by using one-step solid state reaction. The pyroelectric characteristics are in good agreement with the dielectricic properties. The admittance spectroscopy of well-formed the PSN is in agreement with broad distribution of relaxation phenomenon such as space charge and dipoles. In addition, maximum conductance Y'(G) and susceptance Y"(B) in the PSN is increased with increasing temperature. The admittance spectroscopy of PSN is in agreement with broad distribution of relaxation phenomenon. Strong frequency dependent of dielectric constant and loss are observed at temperatures near the T_m. At approximately T_m, the phase transition of the sintered PSN occurred at a broad temperature region. Phase transitions at heating and cooling treatment in the PSN observed thermal hysteresis. The critical exponents of during cooling and heating processes in the PSN ceramics were 1.14 and 1.59 at 1 kHz, respectively, indicating a diffused phase transition for these systems.

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