≪**Research Paper**≫ Applied Science and Convergence Technology Vol.24 No.3, May 2015, pp.47~52
http://dx.doi.org/10.5757/ASCT.2015.24.3.47

Relaxation Characteristic of the Disordered Lead Scandium Niobate

Yeon Jung Kim*

Center for Innovative Engineering Education, Dankook University, Yongin 448-701, Korea

(Received March 30, 2015, Revised March 30, 2015, Accepted May 28, 2015)

The correlation between admittance and dielectric spectroscopy of dielectric relaxation in lead scandium noibate, have been investigated. Lead scandium niobate, with composition $PbSc_{0.5}Nb_{0.5}O_3$, was prepared by conventional solid state synthesis. Conductance Y'(G), susceptance Y"(B) and capacitance C of lead scandium niobate as a function of frequency and temperature were measured. From the temperature-dependence of RLC circuit, insight into physical significance of the dielectric properties of lead scandium niobate is obtained. The relative strong frequency dependent of dielectric properties in lead scandium niobate is observed, and the phase transition occurred at a broad temperature region. Also, the value of critical exponent γ=1.6 showed on heating process. The long relaxation times part enlarged diffuse by conductivity effects with increasing temperature, and the ordering between Sc^{3+} and Nb^{5+} in PSN influences complex admittance and dielectric properties. Confirmed the typical characteristic of lead-type relaxor in the Raman spectra of lead scandium niobate and major ranges are between 400 and 900 cm^{-1}.

Keywords : Lead scandium niobate, Ferroelectric, Admittance, Relaxation, Raman spectroscopy

I. Introduction

Lead-type polycrystalline relaxors with $PbB'_{1-x}B''_xO_3$ structure has a great advantage, which exhibits a high dielectric constant and easily preparation than single crystals and thin films. The dielectric constant and loss values of relaxors are both frequency-dependent and temperature-dependent [1]. Disordered lead scandium niobate ($PbSc_{0.5}Nb_{0.5}O_3$, PSN) appears to have the cubic structure only above 110°C. When Sc^{3+} and Nb^{5+} ions of the PSN structure have short range ordering, it becomes a diffuse phase transition [2]. PSN relaxor compared with other complex perovskites has attracted a strong interest in solid state physics for which no long-range order emerges. Complex perovskites exhibit a show enough relaxation dynamics and hence have been termed the relaxors [3-5]. Despite extensive investigations, the dielectric relaxation mechanism in PSN is yet to be understood.

In this study, the characteristic of frequency response in PSN was used to measure static method. The dielectric properties of PSN were analyzed by measuring the dielectric constant and loss as a function of temperature and frequency. Also, this study investigated the conductance Y'(G) and susceptance Y"(B) of PSN with broad distribution of relaxation phenomenon.

* [E-mail] yjkim80@dankook.ac.kr

II. Experimental Procedure

When the $PbSc_{0.5}Nb_{0.5}O_3$ with a complex perovskite structure was produced, the B-site precursor was not produced first. Instead, the PSN powder was produced by mixing the raw materials together, such as $PbCO_3$, Sc_2O_3, and Nb_2O_5, as shown in Fig. 1. The calcining and sintering were carried out at 900°C for 2 hours and at 1300°C for 30 minutes, respectively. EDX (Horiba, 6853-H) was used to analyze the atomic composition of the compounds. The fractured surfaces of sintered pellets were observed by SEM (Hitachi, S-4300). Raman spectroscopy (Horiba, T64000) was used for the room temperature structural characterization. The excitation source was used 514 nm line of Ar^+ laser. To measure the electrical properties of the PSN, a silver (99.9%) electrode was coated on both sides of the specimens using a thermal evaporator. Capacitance C, conductance Y'(G) and susceptance Y"(B) of sintered PSN were examined at various temperature between 25°C and 250°C, frequency region between 0.1 kHz and 100 kHz using a LCR meter (HP 4284A).

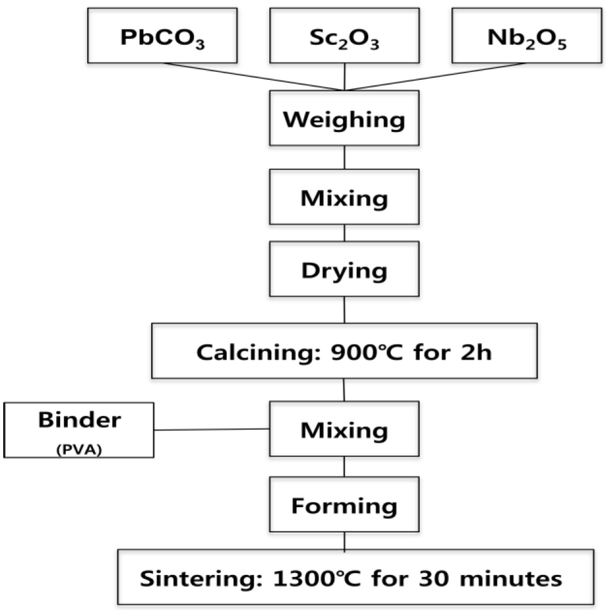

Figure 1. Schematic diagram of PSN ceramic processing.

III. Discussions

PSN was prepared by a solid state reaction at 1300°C for 30 minutes. The atomic percentage of O, Pb, Nb, and Sc in PSN was 63.47%, 17.01%, 10.57%, and 8.96%, respectively. Fig. 2 shows the fractured surfaces of PSN sintered. The specimens synthesized by solid state reaction are totally B-site disordered. Normally, during sintering, the crystal grains of the specimens become larger with a concomitant decrease in the number of pores, which means PSN was sintered well, as shown in Fig. 2.

The diffuseness characteristic of the ferroelectrics can be found by analysis of the dielectric measurements. Relaxors can be separated into long-range order at T_m and canonical relaxor which do show isotropic such as polar nano-clusters [6]. The dielectric constant of relaxor near the Curie region is defined by a quadratic law:

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{(T-T_m)\gamma}{2\varepsilon_m\delta^2} \quad (1)$$

Where ε is the dielectric constant, ε_m is the maximum dielectric constant, T_m is the temperature

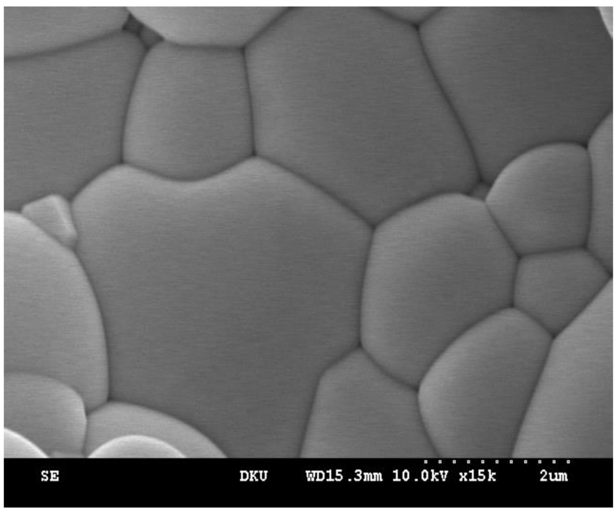

Figure 2. SEM micrograph of fractured PSN polycrystalline relaxor.

at maximum dielectric constant, δ is the diffuseness parameter and γ is the critical exponent, respectively. Quadratic equation can be solved graphically using a $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T-T_m)$ plot. Fig. 3 shows the $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T-T_m)$ and the $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T-T_m)^2$ relation in the PSN. When $\gamma=2$, this equation express the quadratic law of perfectly diffused ferroelectrics [7]. For PSN systems, from the slope of plots of $1/\varepsilon$ vs. $(T-T_m)^{\gamma}$, the values of γ were calculated. Critical exponent value was about 1.6 on heating treatments, indicating a diffused phase transition for disordered PSN. Sc and Nb ions of B-site must have a radius of different size and coordination, due to phase transition from rhombohedral to cubic structure at near T_m in PSN, ferroelectric polar domains are formed. Therefore, PSN is shown the characteristic of the more diffuse phase transition.

Most of dielectric relaxation is directly related to the dipole behaviors of polar materials. Fig. 4 shows equivalent circuit for measuring the R, L, C in PSN specimens. This RLC circuit was used to calculate the electrical circuit elements in PSN. The R, L will decrease with increasing temperature but C, C_P was increased as shown in Table 1.

Fig. 5 presents the resistance and inductance versus temperature for PSN sintered at 1300°C for 30 minutes. The calculated value of the series capacitance varies from $1.50\times10^{-10}\sim3.04\times10^{-9}$ F in PSN with increasing temperature. Also, the calculated value of the resistance, inductance, parallel capacitance varies from 16.81～2.55 Ω, $5.48\times10^{-6}\sim5.44\times10^{-6}$H, $1.58\times10^{-20}\sim4.01\times10^{-19}$ F, respectively, in PSN with increasing temperature. The admittance $Y^*(\omega)$ and dielectric constant $\varepsilon^*(\omega)$ is expressed by the following equation:

$$Y^*(\omega)=\frac{1}{Z^*}=Y'(G)+jY''(B)=j\omega C_0\varepsilon^* \quad (2)$$

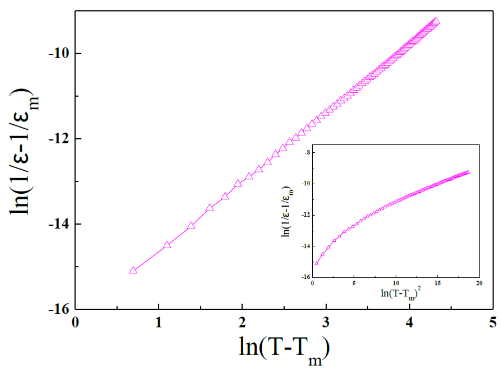

Figure 3. Plot of $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T-T_m)$ for PSN at 1 kHz. The inset figure shows $\ln(1/\varepsilon - 1/\varepsilon_m)$ versus $\ln(T-T_m)^2$.

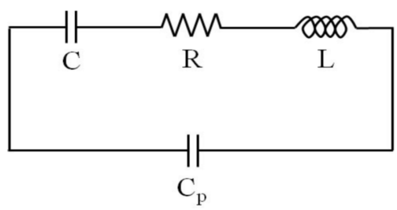

Figure 4. General equivalent circuit representation for PSN.

Table 1. Calculated values of R, L, C and C_p in the RLC circuit.

°C	R (Ω)	L (H)	C (F)	Cp (F)
25.0	16.81	5.48×10^{-6}	1.50×10^{-10}	1.58×10^{-20}
50.5	15.48	5.62×10^{-6}	1.75×10^{-10}	1.86×10^{-24}
80.5	13.61	5.61×10^{-6}	3.27×10^{-10}	1.90×10^{-24}
102.5	10.25	5.32×10^{-6}	8.17×10^{-10}	9.25×10^{-13}
116.5	7.15	5.41×10^{-6}	3.40×10^{-9}	5.40×10^{-13}
141.5	2.55	5.44×10^{-6}	3.04×10^{-9}	4.01×10^{-19}

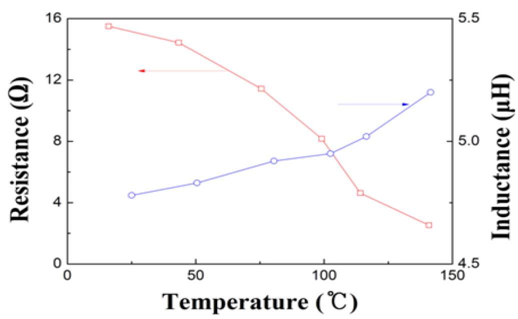

Figure 5. Resistance and inductance versus temperature for PSN.

Where Z^* is the complex impedance, Y'(G) is the conductance, Y"(B) is the susceptance, ω is the angular frequency, and C_o is the geometrical capacitance. Fig. 6(a) and 6(b) show the characteristics of Y'(G) and Y"(B) with respect to frequency for PSN in the measured temperature range. The measurement temperature range represents a significant characteristic of Y'(G) and Y"(B). Also, Y"(B) was measured in the temperature range is reached the maximum value, the maximum value with an increase in the measured temperature was increased. This phenomenon indicates that the dielectric relaxation process of the PSN depends on the temperature. Since measured temperature is changed, the value of capacitance is because of this changing resonant frequency of the PSN is also changed. The values of Y'(G) and Y"(B) in the high frequency ranges as the increasing temperature to determine what looks broadening distribution, and confirms the existence of temperature dependence of relaxation process and diffuse phase transition. Such changes in symmetry are associated with a change in the polarization's direction, as well as, with an enhancement of the polarization's magnitude and a vanishing of relaxation [8].

In order to analyze the contribution originating from microscopic quantities of PSN, Cole-Cole diagram made in other temperatures ranges. Fig. 6(c) and 6(d) show the characteristics Y'(G) versus Y"(B) of PSN for different temperatures. The value of Y'(G) in the high frequency range for the selected temperature is coincides with each other suggesting the release of space charge. PSN, showed a slight depression, which is evidence of non-Debye type relaxation. The radius of the semicircle arc is the maximum value has been increased with the temperature. In addition, Fig. 6(d) shows the distribution of relaxation time, not a single relaxation time of the PSN. The long relaxation times part enlarged diffuse by conductivity effects with increasing temperature, and the ordering between Sc^{3+} and Nb^{5+} in PSN influences complex admittance and dielectric properties. Relaxation properties and Pb-site compositional fluctuations of the PSN are represented of polar domains and associated cubic structure. This phenomenon coincides with a freezing of nano-

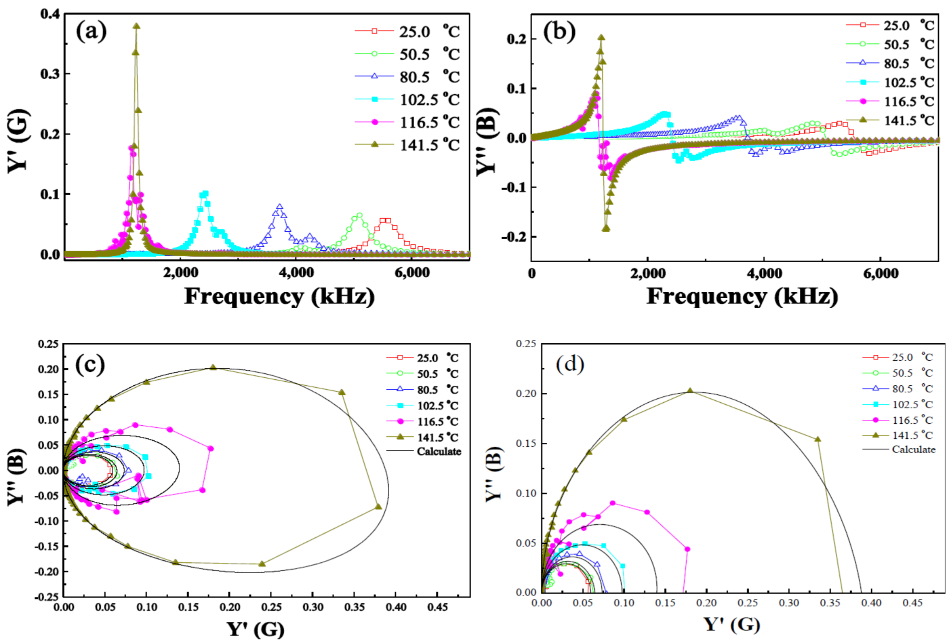

Figure 6. Conductance and susceptance of PSN ceramics at various temperatures.

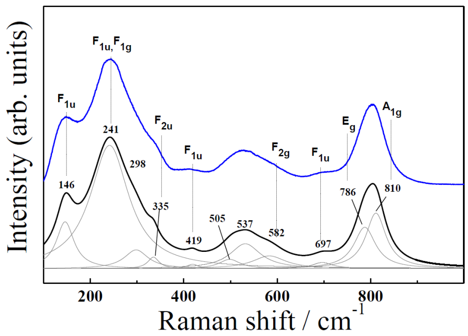

Figure 7. Raman spectra of PSN polycrystalline relaxor.

cluster occurs at low temperature than T_m (at about 120°C, 1 kHz) of disordered PSN on heating process.

Fig. 7 shows the Raman spectrum of PSN at room temperature. The major ranges in the Raman spectra of PSN are between 400 and 900 cm^{-1}. Confirmed peak band at 810 cm^{-1}, and showed the gradual enhancement of the Raman scattering at 241 cm^{-1}. The polarization of the Raman scattering are between 250 and 300 cm^{-1} rules out the possibility for F_{1u} and F_{2g} symmetry. Thus, the Fig. 7 shows the Raman spectrum that the typical characteristic of Pb-based relaxors [9].

IV. Conclusions

Lead scandium niobate, with composition $PbSc_{0.5}Nb_{0.5}O_3$, was prepared by conventional solid state synthesis. When the sintering temperature of 1300°C increased, the amount of the pores was reduced, which means PSN was sintered well. Capacitance C, conductance Y'(G) and susceptance Y"(B) of PSN as a function of temperature and frequency were measured. From the temperature-dependence of RLC circuit, insight into physical significance of the dielectric properties of PSN is obtained. The relative strong frequency-dependent of dielectric constant is observed at temperatures near T_m. The measured dielectric constant showed the typical characteristic of a relaxor ferroelectric. Moreover, increasing temperature is shown a decrease in resistance of the disordered PSN. Such behavior is indicative of a negative temperature coefficient of resistance, which is a typical characteristic of abnormal ferroelectrics. The value of critical exponent γ =1.6 showed on heating process, indicating a diffused phase transition for these systems. In addition, maximum Y'(G) and Y"(B) increase with increasing temperature. The long relaxation times part enlarged diffuse by conductivity effects with increasing temperature, and the ordering between Sc^{3+} and Nb^{5+} in PSN influences complex admittance and dielectric properties. The admittance spectroscopy of PSN is in agreement with broad distribution of relaxation phenomenon. At T_m, the capacitance value increased with increasing temperature but decreased with increasing after T_m. Also, confirmed the typical characteristic of Pb-based relaxor in the Raman spectra of PSN and major ranges are between 400 and 900 cm^{-1}.

References

[1] N. Setter, L. E. Cross, J. Appl. Phys., **51**, 4356 (1980).
[2] J. L. Tang, M. K. Zhu, Y. D. Hou, H. Wang, H. Yan, J. Cryst. Growth., **307**, 70 (2007).
[3] F. Chu, I. M. Reaney, N. Setter, J. Appl. Phys., **77**, 1671 (1995).
[4] A. A. Bokov, Z. G. Ye, J. of Advanced Dielectrics, **2(2)**, 1241010 (2012).
[5] C. Zhao, C. Z. Zhao, M. Werner, S. Taylor, P. Chalker, **8**, 456 (2013).
[6] I. M. Reaney, J. Petzelt, V. V. Voitsekhovskii, F. Chu, N. Setter, J. Appl. Phys., **76**, 2086 (1994).
[7] T. T. Huy, N. D. T. Luan, T. V. Chuong, L. V. Hong, Communications in Phys., **22**, 229 (2013).
[8] J. M. Kiat, C. Bogicevic, F. Karolak, G. Dezanneau,

N. Guiblin, W. Ren, L. Bellaiche, R. Haumont, Phys. Rev. B, **81**, 144122 (2010).

[9] A.M. Welsch, B. Mihailova, M. Gospodinov, R. Stosch, B. Guttler and U. Bismayer, J. Phys.: Condens. Matter., **21**, 235901 (2009).