

Effect of Alkaline-Earth Ion Substitution on Phase Development and Dielectric Properties of $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$

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알칼리-토륨이온 치환에 따른 PIN 세라믹스의 상발달 및 유전특성

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초 록 Pb^{2+} ion in $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PIN) ceramics was partially replaced by Ca^{2+} , Sr^{2+} or Ba^{2+} ions, and resultant phase development and dielectric characteristics were studied. Optimum preparation conditions of PIN with only perovskite phase was investigated in terms of calcination, species and amount of substituents, sintered density, and dielectric properties. For the development of perovskite phase in PIN, Ba^{2+} ion was found to be the most effective among the three substituents.

Abstract $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PIN) 세라믹스에서 Pb^{2+} 이온 대신에 Ca^{2+} , Sr^{2+} , Ba^{2+} 이온을 부분적으로 치환하여 상합성 과정 및 유전특성을 조사하였다. 페로브스카이트 PIN을 얻기 위한 최적조건을 도출하기 위하여 하소, 치환 이온의 종류 및 그량, 소결민물, 유전특성의 관점에서 관찰하였다. 페로브로스카이트 PIN상을 합성하기 위해서는 Ba^{2+} 이온의 치환이 가장 효과적이었다.

1. Introduction

Lead indium niobate, $\text{Pb}(\text{In}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PIN), is a ferroelectric compound with a dielectric constant of 550 at room temperature^{1). PIN possesses a pseudocubic perovskite structure ($a = 4.11 \text{ \AA}$) at room temperature and exhibits broad dielectric maxima around 90°C ^{1). The dispersion of dielectric constant (diffuse phase transition, DPT) is considered to be due to microstructural inhomogeneities arising from compositional disorder in the B-site occupation between In^{3+} and Nb^{5+} ions. The resultant DPT behavior of temperature-stable dielectric characteristics would allow for PIN to be utilized as potential capacitive elements, if the dielectric constant could be increased sufficiently. PIN also exhibits a relaxor character,}}

which is typified by a frequency dependence of dielectric constant and loss, *i.e.*, dielectric constant decrease and temperature of maximum dielectric constant (T_{max}) increase, with the increase of measuring frequency. In lead indium niobate-lead titanate (PIN-PT) solid solution, the dielectric constant of 2000 and electromechanical coupling coefficient of 0.4 were reported at the morphotropic phase boundary (37mol% of PT) between pseudocubic and tetragonal structure^{2).}

The synthesis of lead-based perovskite compounds based on $\text{Pb}(\text{B}_1, \text{B}_2)\text{O}_3$ is difficult. Metastable pyrochlore phases that are detrimental to the dielectric properties are generally formed in the reaction process. The columbite method proposed by Swartz and Shrout³⁾ showed that the intermediate pyrochlore phase reac-

Table 1. Compositions studied in $Pb_{1-x}M_x(In_{1/2}Nb_{1/2})O_3$ [$M = Ca, Sr, Ba$] system.

Specimens		Batch Composition (by mol)					
		PbO	MCO ₃			In ₂ O ₃	Nb ₂ O ₅
			CaCO ₃	SrCO ₃	CaCO ₃		
I-0		1.00	-	-	-	1/4	1/4
MI	CI-1	0.90	0.10			1/4	1/4
	CI-2	0.75	0.25			1/4	1/4
	CI-3	0.50	0.50			1/4	1/4
	SI-1	0.90		0.10		1/4	1/4
	SI-2	0.75		0.25		1/4	1/4
	SI-3	0.50		0.50		1/4	1/4
	BI-1	0.90			0.10	1/4	1/4
	BI-2	0.75			0.25	1/4	1/4
	BI-3	0.50			0.50	1/4	1/4

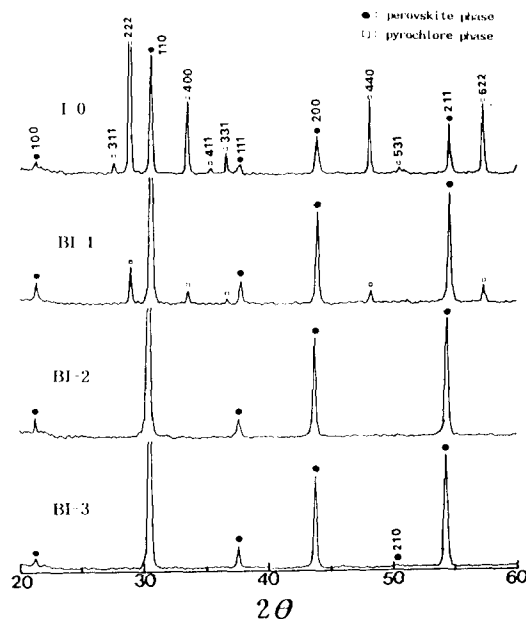


Fig. 1. XRD patterns of specified composition, fired at 1150°C for 2h.

tion can be bypassed, but this method also failed to yield pure perovskite phase. In our recent research, considerable improvements in the sinterability and the extent of perovskite formation were observed with increasing the Ba²⁺ ion substitution for Pb²⁺ ion on $Pb(Cd_{1/3}Nb_{2/3})O_3$ ⁴⁾ and $Pb(Zn_{1/3}Nb_{2/3})O_3$ ⁵⁾ compounds.

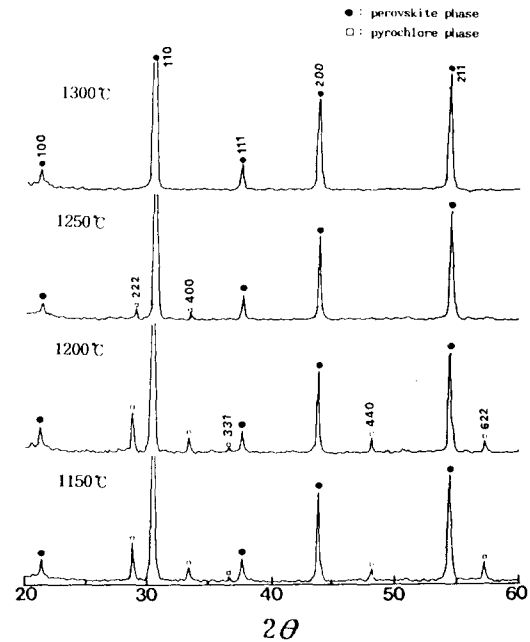


Fig. 2. XRD patterns of BI-1 specimen, fired for 2h at specified temperatures.

So far, however, preparation of PIN in pure perovskite phase has not been accomplished by conventional mixed oxide or columbite processes either^{3, 6)}. In the current study, therefore, stoichiometric composition of PIN as well as modified compositions by alkaline-earth ion of Ca, Sr or Ba was examined to investigate

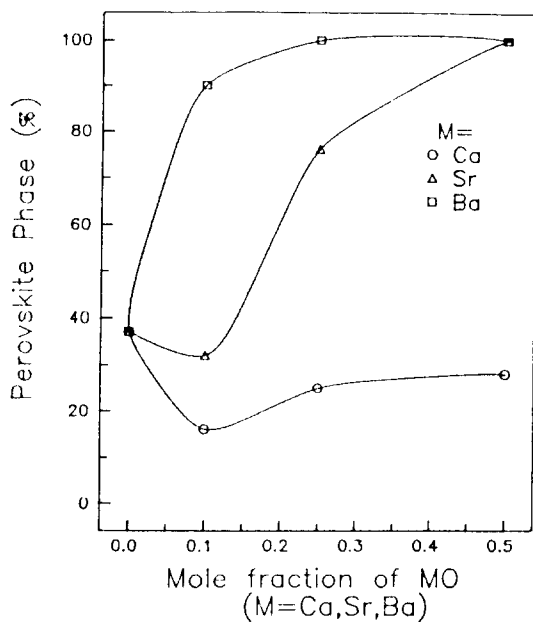


Fig. 3. Change in relative amount of perovskite phase with mole fraction of MO[M = Ca, Sr, Ba] in MI system, fired for 2h at 1075°C for pure PIN and at 1250°C for the others.

the development of perovskite phase and the effect of substituents on dielectric properties.

2. Experimental Procedure

Starting materials were analytical reagent grade chemicals of PbO, In₂O₃, Nb₂O₅, CaCO₃, SrCO₃ and BaCO₃, with purity of over 99%, Table 1 lists the nomenclature of compositions studied. Raw chemicals were weighed accordingly and wet-milled for 24 hours in ethyl alcohol in a polyethylene jar with ZrO₂ media. Three different sized of balls(5, 10 and 15φ) were used to promote mixing efficiency. After mixing, the slurries were dried for 24 hours in an electric oven and calcined in an MgO crucible at 750°C for 8 hours. Calcined product was then crushed, pulverized, granulated with 5wt % PVA solution, and uniaxially pressed into pellets of 15φ at a pressure of 300MPa. The pellets were then heated in two stages; first stage of binder Burn-out at 500°C for 2hours and second stage of sintering at 1000-1350°C for 2hours.

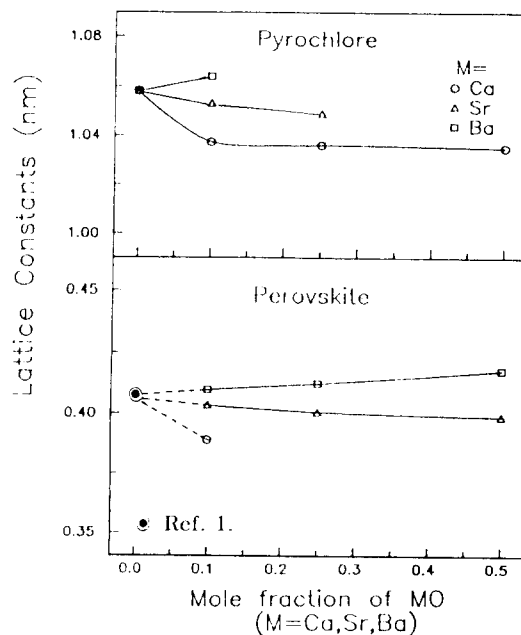


Fig. 4. Variation of lattice constant with mole fraction of MO[M = Ca, Sr, Ba] in MI system.

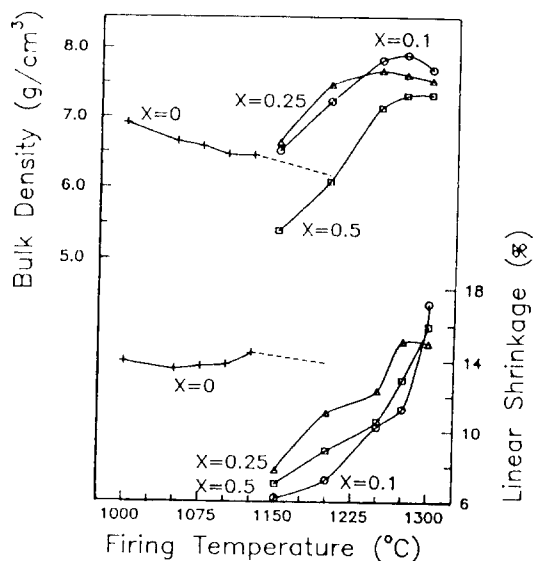


Fig. 5. Changes in bulk density and linear shrinkage of BI-series with firing temperature.

Sintered specimens as well as calcined powders were analyzed by X-ray diffraction (XRD) to examine the phase development and to obtain lattice parameters. Densities of sintered pellets were estimated by Archimedes method (ASTM standard C373-72) with dis-

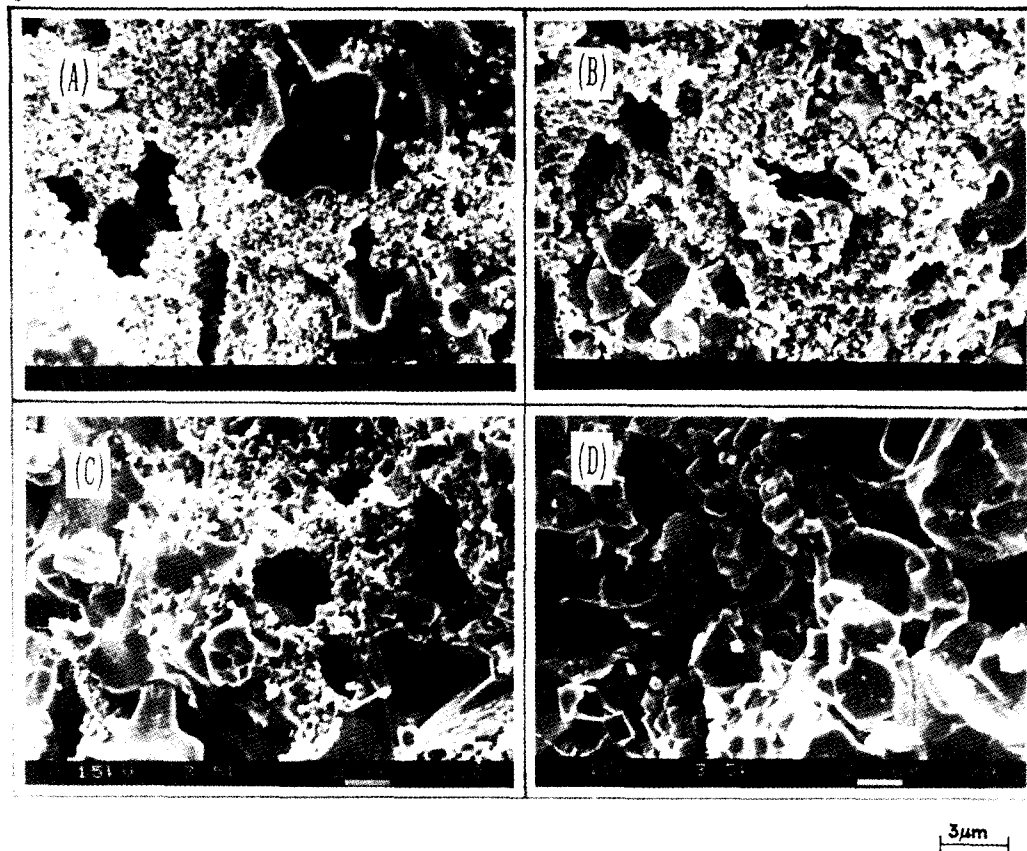


Fig. 6. Fractographs of I-0 specimen, fired for 2h at (A) 1000°C, (B) 1075°C, (C) 1125°C, (D) 1200°C.

tilled water as displacement liquid. Microstructure and regional composition of the sintered bodies were examined by using scanning electron microscope (SEM) with EDAX.

Circular pattern electrodes of silver paste were applied to the sintered, face-polished, and ultrasonically cleaned specimens by screen printing and were heat-treated for 10min at 600°C for curing. Dielectric constants and losses were measured at 1, 10 and 100kHz using a computer(HP 9826) interfaced low-frequency impedance analyzer (HP 4192A) over a temperature range of -10°C to 120°C at an interval of 5°C on heating. Capacitance change with temperature($\Delta C/C$) was also measured over a range of -30°C to 100°C at the same interval.

3. Results and Discussion

In case of pure PIN composition(I-0), in

creasing firing temperature(within range of 1000-1200°C) was observed to hinder the formation of perovskite phase and a relative amount of pyrochlore($Pb_3Nb_2O_{13}$) phase was calculated to be as high as 70%. Ca substitution up to 50mol% also seemed to hinder the development of perovskite phase. On the contrary, replacement by Sr or Ba enhanced the phase formation and only the perovskite phase was detected by XRD in both cases when 50mol% of Pb was substituted. In Figure 1, XRD patterns of B1-series specimen are presented, where well-developed perovskite phase can only be seen in both B1-2 and B1-3 specimens. The case of Sr substitution showed patterns similar to Figure 1. Figure 2 shows development of phases in B1-1 specimen, where disappearance of pyrochlore phase with firing temperature increase can easily be seen. After firing at 1300°C, only the clean pattern of

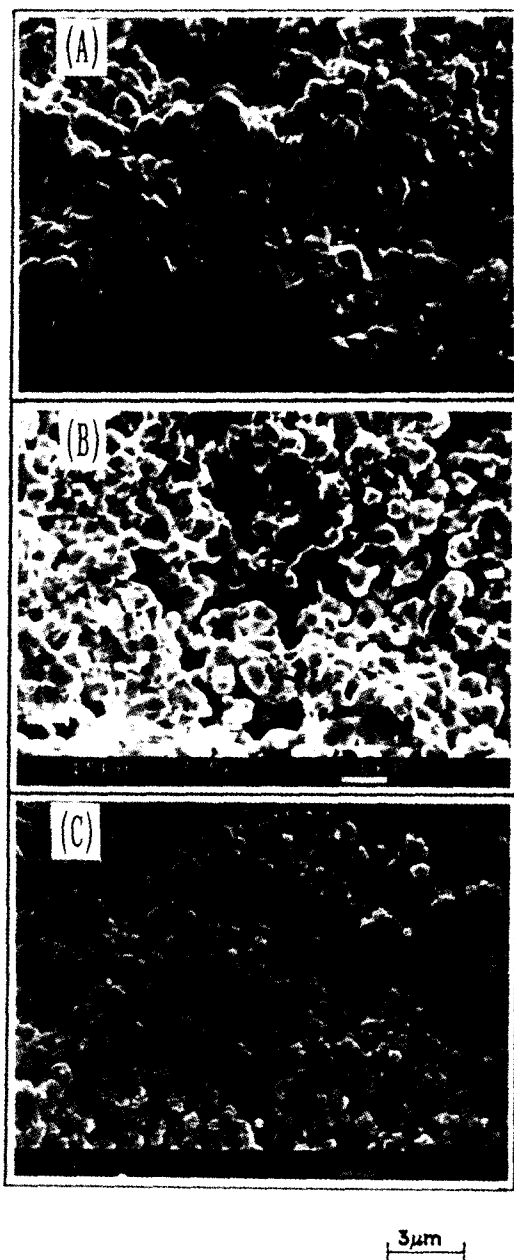


Fig. 7. Fractographs of (A) BI-1, (B) BI-2, and (C) BI-3 specimen, fired at 1150°C for 2h.

perovskite phase resulted. From the XRD data of each composition, relative amounts of perovskite phase were estimated, by comparing the diffraction peak heights between perovskite(110 and pyrochlore (222) peaks, and are plotted in Figure 3 against species and mole fraction of the substituents. The eliminated results of pyrochlore phase by substituting

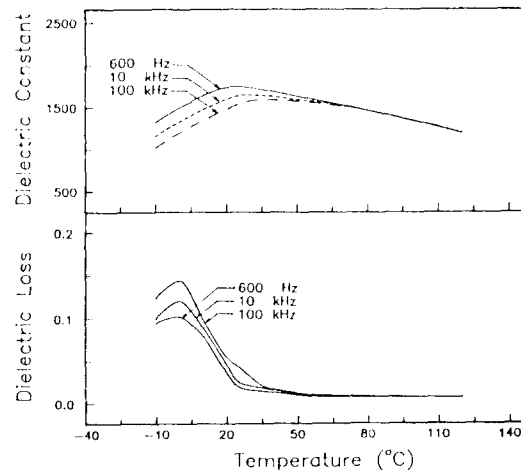


Fig. 8. Temperature and frequency dependence of dielectric constant and loss of BI-1 specimen, fired at 1200°C for 2h.

Sr^{2+} and Ba^{2+} ion is due to the increase of tolerance factor and electronegativity difference. Actually, by substituting Pb-complex perovskite compounds with A-site ions such as Sr^{2+} and Ba^{2+} , tolerance factor and electronegativity difference increase, it is coincided with the result that stable perovskite phase was gained^{4,5}. Also from the XRD data, lattice constants of pyrochlore and perovskite phases were calculated and the results are presented in Figure 4. Though both Sr and Ba played affirmative roles in the development of perovskite phase in PIN, as shown in Figure 3, the lattice parameter increased with Ba substitution while decreased with Sr and decreased by a greater degree with Ca. The opposite trend of lattice parameter change with substitution can be interpreted in terms of ionic size: $r_{\text{Pb}}(1,06 \text{ \AA}) > r_{\text{Pb}}(1,49 \text{ \AA}) > r_{\text{Sr}}(1,44 \text{ \AA}) > r_{\text{Ca}}(1,35 \text{ \AA})$ ².

Substituent amount and firing temperature dependencies of bulk density and linear shrinkage of BI-series specimen are plotted in Figure 5. As shown, bulk density of pure PIN sample decreased gradually with increasing firing temperature. When Ca was substituted, overall densification became worse with substitution. In contrast, Ba replacement promoted

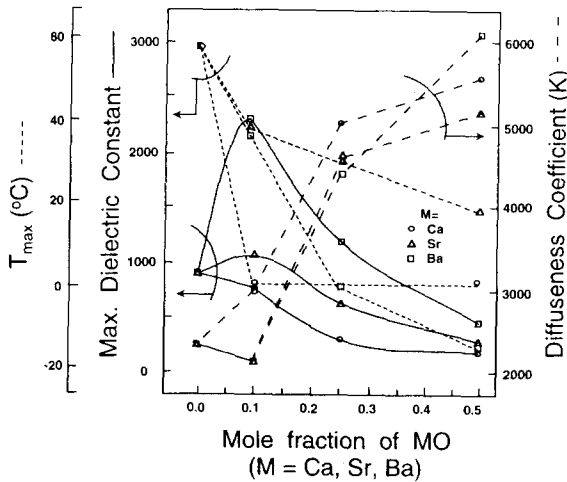


Fig. 9. Species and amount of substituent dependence of temperature of maximum dielectric constant (T_{max}), maximum dielectric constant, and diffuseness coefficient at 1kHz.

densification by increasing the values of density and linear shrinkage (Figure 5). Results of SI-series specimen were quite similar to the BI-series.

Sintered specimens were examined using SEM to observe the microstructure morphology. Figure 6 shows the microstructure of pure PIN composition where internal microstructure was observed not to be improved much with firing temperature increase up to 1200°C. When Ca was substituted into, pyrochlore phase was observed to develop, as confirmed by EDAX. In contrast, substitution of Ba enhanced the densification and internal microstructure comprised entirely of uniformly sized grains (Figure 7). The Sr-substituted case showed similar trend.

Figure 8 illustrates a relaxor behavior, observed in the BI-1 specimen, T_{max} variation as functions of amount and species of substituents is presented in Figure 9, where decrease T_{max} is prominent in the cases of Sr and Ba substitution. Figure 9 is also plotted the amount and species of substituent dependencies of maximum dielectric constant and diffuseness coefficient, where Ba definitely and Sr somewhat increases the dielectric constant

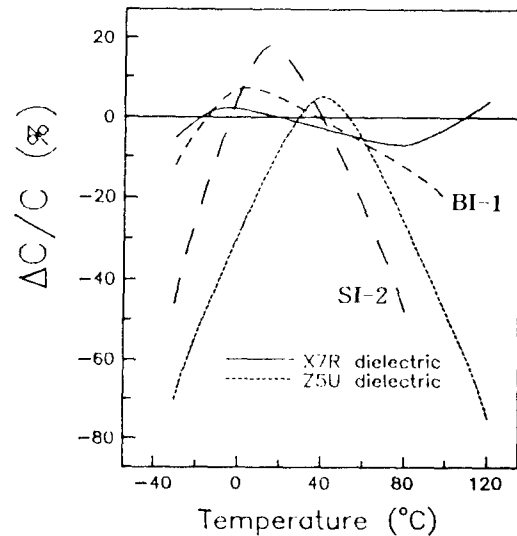


Fig. 10. Capacitance change with temperature of SI-2 and BI-1 specimen.

at a substitution level of 0.1mol. When more amount of Ba or Sr was replaced into, the dielectric constant decreased afterwards. Meanwhile, Ca substitution decreased the maximum dielectric constant monotonously.

Diffuseness coefficient is the measurement of broadness in the dielectric constant-temperature relationship (e.g., Figure 9), and has been defined in several ways⁸⁻⁹. In the paraelectric region, dielectric constant of DPT materials decreases at a different mode, as compared with normal ferroelectric materials with Curie-Weiss behavior. Assuming that $K \propto 1/(T-T_c)^2$ and also distribution of phase transition temperature near the Curie temperature (T_c) follows the Gaussian distribution¹⁰, dielectric constant (K) of DPT material at a temperature (T) can be expressed as follows,

$$K = K_m / \left[1 + \frac{1}{2} \left(\frac{T - T_c}{\delta} \right)^2 \right] \quad (1)$$

where K_m is the maximum dielectric constant and δ is the diffuseness coefficient. In Figure 9, diffuseness coefficient was observed to increase gradually, in general, with substitution.

Two representative cases of capacitance

change with temperature of specimens are presented in Figure 10, together with two characteristics of X7R and Z5U. BI-1 specimen was observed to almost satisfy the less rigorous Z5U requirement, while SI-2 was deviated significantly.

4. Conclusion

Preparation of PIN of only perovskite phase, which has not yet been reported in the stoichiometric composition using conventional mixed oxide or columbite process, was accomplished by partial replacement of Sr or Ba into Pb-site. Ca substitution, on the contrary, was harmful and increased the deleterious pyrochlore phase. The two substituents were also found to enhance densification during sintering process. Among the two, however, Ba was more effective in increasing dielectric constant. Diffuseness coefficient was observed to increase, in general, with substitution by all of the three elements.

Acknowledgements

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