

Microwave Dielectric Properties of $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ Ceramics

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ABSTRACT

Microwave dielectric properties of $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ (PCFMN) ceramics were investigated as a function of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content ($0.1 \leq x \leq 0.8$). A single perovskite phase with the cubic structure was obtained through the given composition range. The unit cell volume was increased with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content, due to the larger average ionic size of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ than that of $(\text{Fe}_{1/2}\text{Nb}_{1/2})^{4+}$ for B-site ion. Dielectric constant (K) and Temperature Coefficient of Resonant Frequency (TCF) of PCFMN ceramics were dependent on $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content due to the decrease of ionic polarizability and B-site bond valence, respectively. Qf value was decreased with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content due to the decrease of grain size. Typically, K of 73.56, Qf of 5,074 GHz and TCF of -6.45 ppm/°C were obtained for the specimens with $x=0.4$ sintered at 1250°C for 3 h.

Key words: $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$, Microwave dielectric properties, Dielectric polarizability, B-site bond valence, Rattling effect

1. Introduction

Extensive studies¹⁻³⁾ have been carried out on the Pb-based perovskite compounds to meet the requirements of microwave dielectric materials in advanced communication systems. Although several kind of Pb-based perovskite compounds with good microwave dielectric properties have been reported, it is still necessary to study the basic relationships between the crystal structure and dielectric properties, especially thermal stability at microwave frequencies, which is available to control and predict the microwave dielectric properties of Pb-based perovskite compounds.

In our preliminary research for materials with high dielectric constant, $(\text{Pb}_{0.4}\text{Ca}_{0.6})(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PCFN) showed a good microwave dielectric properties, $K=80$, $Qf=6,110$ GHz and $\text{TCF}=-25$ ppm/°C, however, the Temperature Coefficient of Resonant Frequency (TCF) should be controlled for the practical applications. TCF of ABO_3 perovskite with tilted oxygen octahedral ($t \leq 1$) increased with the decrease of B-site bond valence. Thus, TCF of PCFN could be improved by a decreasing of B-site bond valence. The B-site bond valence of ABO_3 perovskite could be reduced by an increasing of the unit-cell volume or the bond valence parameters on B-site, because B-site bond valence is a function of bond length between B-site cation and oxygen.^{4,5)}

The unit-cell volume of PCFN can be increased by the sub-

stitution of tetra-valent ions with larger ionic radius than that of $(\text{Fe}_{1/2}\text{Nb}_{1/2})^{4+}$ for B-site. Therefore, TCF of PCFN can be improved by the substitution of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ for $(\text{Fe}_{1/2}\text{Nb}_{1/2})^{4+}$, because the average ionic radius of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ (0.667 \AA)⁶⁾ is larger than that of $(\text{Fe}_{1/2}\text{Nb}_{1/2})^{4+}$ (0.643 \AA).⁶⁾

In this study, $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ ($0.1 \leq x \leq 0.8$, PCFMN) system was investigated to search the effect of B-site bond valence on the thermal stability, and to improve TCF of Pb-based perovskite materials. The dependence of dielectric polarizability on the B-site bond valence was also discussed.

2. Experimental Procedures

PbO , CaCO_3 , Fe_2O_3 , MgO , and Nb_2O_5 powders with high-purity (>99.9%) were used as starting materials. The mixture of Fe_2O_3 , MgO , and Nb_2O_5 was calcined at 1100°C for 4 h and 1000°C for 3 h to prepare FeNbO_4 and MgNb_2O_6 powders, respectively. They were weighed according to the compositions $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ ($0.1 \leq x \leq 0.8$), and then milled with ZrO_2 balls for 24 h in distilled water. The mixtures were dried and calcined at 900°C for 4 h, and then pressed into 10 mm diameter disks under the pressure of 1450 kg/cm^2 , isostatically. These disks were sintered at 1250°C for 3 h in air. Burying the specimens in powder of the same compositions and placing them into a platinum crucible inhibited the loss of PbO and decomposition during sintering process.⁷⁾

X-Ray Diffraction (XRD) was used to determine the phase identification and lattice parameter measurements.⁸⁾ The apparent densities of the sintered specimens were measured by ASTM 373-C.⁹⁾ The dielectric constant (K) and

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unloaded Q in the microwave frequency range (5–7 GHz) were measured by Hakki-Colemans method.¹⁰ The Temperature Coefficient of Resonant Frequency (TCF) at microwave frequencies was measured in the temperature range from 25 to 80°C by Cavity method.¹¹

The bond valence of atom i , V_i was defined as the sum of all of the valences from a given atom i , and that was calculated by Eqs. (1) and (2).¹²

$$V_i = \sum_j v_{ij} \quad (1)$$

$$v_{ij} = \exp\{(R_{ij} - d_{ij})/b'\} \quad (2)$$

where, R_{ij} is the bond valence parameter, d_{ij} is the bond length between atoms i and j , and b' is commonly taken to be a universal constant equal to 0.37 Å.¹² The bond valence parameters were followed the values in the previous report.¹² Also the theoretical and observed dielectric polarizabilities were obtained using the additivity rule of dielectric polarizabilities and the Clausius-Mosotti equation in Eqs. (3) and (4), respectively.¹² The theoretical dielectric constant K' was obtained from Eq. (5).¹³

$$\alpha_{theo.}(ABO_3) = \alpha_A + \alpha_B + \alpha_O \times 3 \quad (3)$$

$$\alpha_{obs.} = \frac{V_m(K-1)}{b(K+2)} \quad (4)$$

$$K' = (3V_m + 8\pi\alpha_{theo.}) / (3V_m - 4\pi\alpha_{theo.}) \quad (5)$$

where, $\alpha_{theo.}$ and $\alpha_{obs.}$ are the theoretical and observed polarizabilities. α_A , α_B , and α_O are the ionic polarizabilities of A- and B-site ions and oxygen, respectively. K is the measured dielectric constant and K' is the theoretical one. b is $4\pi/3$ and V_m is molar volume.

3. Results and Discussion

The X-ray diffraction patterns of $(Pb_{0.4}Ca_{0.6})(Fe_{1/2}Nb_{1/2})_{1-x}(Mg_{1/3}Nb_{2/3})_xO_3$ (PCFMN) specimens sintered at 1250°C for 3 h are shown in Fig. 1. Only perovskite phase with cubic structure was obtained through the given composition range. With an increase of $(Mg_{1/3}Nb_{2/3})^{4+}$ content, the lattice parameters were increased from 3.9449 Å to 3.9567 Å. These results are due to the larger average ionic radius of $(Mg_{1/3}Nb_{2/3})^{4+}$ (0.667 Å, C.N.=6)⁶ than that of $(Fe_{1/2}Nb_{1/2})^{4+}$ (0.643 Å, C.N.=6)⁶ for B-site ion in ABO_3 perovskite structure.

Table 1 shows the B-site bond valence of the specimens sintered at 1250°C for 3 h. With the increase of $(Mg_{1/3}Nb_{2/3})^{4+}$ content, the lattice parameter of unit cell was increased, while the B-site bond valence obtained from Eqs. (1) and (2) was decreased. Therefore, the B-site bond valence was effectively controlled by the change of unit-cell volume due to the substitution of $(Mg_{1/3}Nb_{2/3})^{4+}$ for $(Fe_{1/2}Nb_{1/2})^{4+}$ in B-site, as shown in Fig. 2.

Fig. 3 shows the dependence of TCF on the B-site bond valence (V_B) of PCFMN specimens sintered at 1250°C for 3 h. It has been reported that the temperature coefficient of

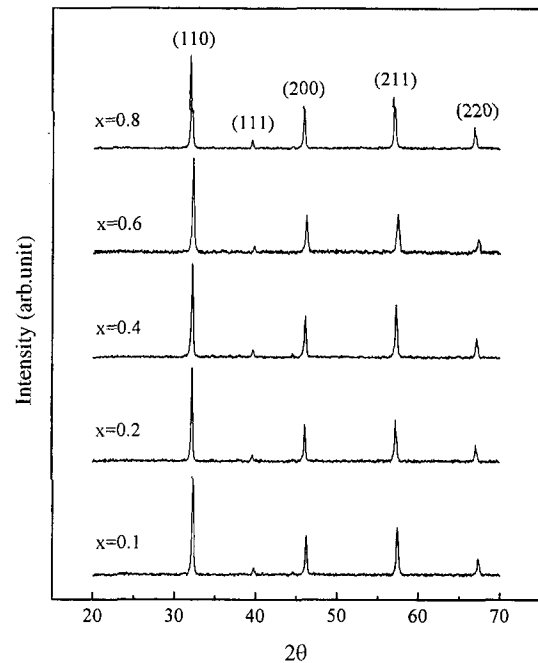


Fig. 1. X-ray diffraction patterns of $(Pb_{0.4}Ca_{0.6})(Fe_{1/2}Nb_{1/2})_{1-x}(Mg_{1/3}Nb_{2/3})_xO_3$ specimens sintered at 1250°C for 3 h.

Table 1. B-site Bond Valence of the $(Pb_{0.4}Ca_{0.6})(Fe_{1/2}Nb_{1/2})_{1-x}(Mg_{1/3}Nb_{2/3})_xO_3$ Specimens Sintered at 1250°C for 3 h

x (mol)	Lattice parameter (Å)	$R_{(B-O)}$ (Å)	$d_{(B-O)}$ (Å)	b	v_B (Å)	V_B (Å)
0.1	3.9449	1.8353	1.9725	0.37	0.6902	4.1416
0.2	3.9480	1.8357	1.9740	0.37	0.6881	4.1286
0.4	3.9507	1.8363	1.9754	0.37	0.6868	4.1205
0.6	3.9535	1.8370	1.9768	0.37	0.6854	4.1125
0.8	3.9567	1.8377	1.9784	0.37	0.6837	4.1022

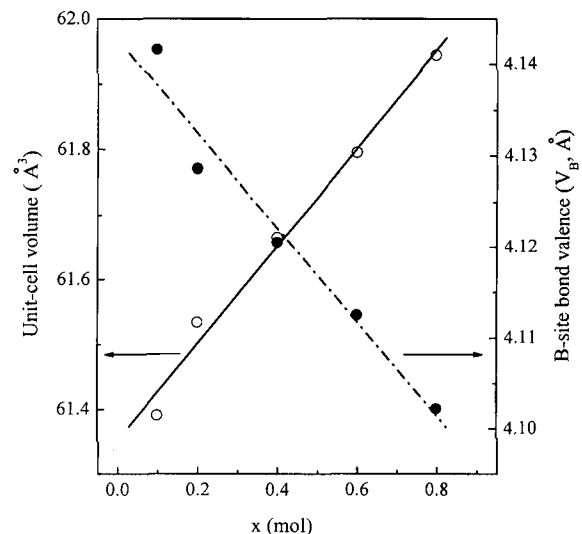


Fig. 2. Unit-cell volume and B-site bond valence (V_B) of $(Pb_{0.4}Ca_{0.6})(Fe_{1/2}Nb_{1/2})_{1-x}(Mg_{1/3}Nb_{2/3})_xO_3$ specimens sintered at 1250°C for 3 h.

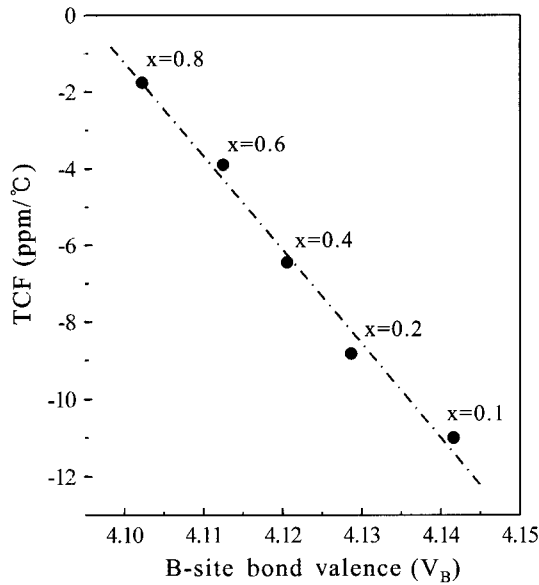


Fig. 3. Dependence of TCF on B-site bond valence (V_B) of $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ specimens sintered at 1250°C for 3 h.

dielectric constant (TCK) was depended on the degree of tilting and bond strength on oxygen octahedra in ABO_3 perovskite, and TCF is a function of TCK. Moreover, the degree of tilting and bond strength on oxygen octahedra were closely related to the B-site

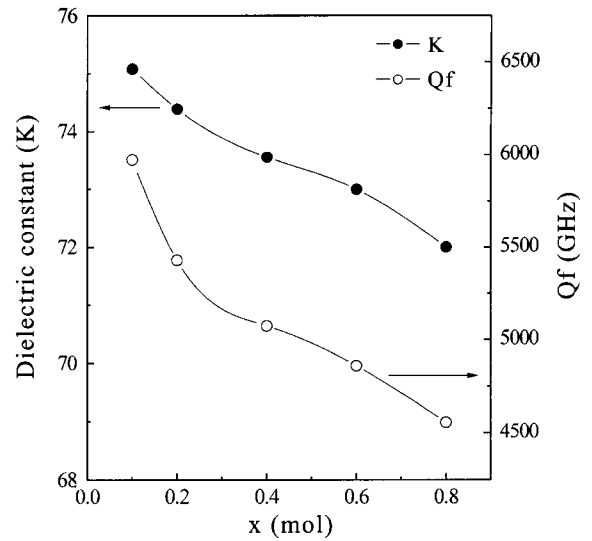


Fig. 4. Microwave dielectric properties of $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ specimens sintered at 1250°C for 3 h.

bond valence is a function of bond length and bond strength on oxygen octahedra.^{4,13} With an increase of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content, TCF increased due to the decrease of degree of tilting and/or bond strength on oxygen octahedra resulted from the decrease of B-site bond valence. Therefore, TCF was depended on the B-site bond valence, as shown in Fig. 3.

Fig. 4 shows the microwave dielectric properties of

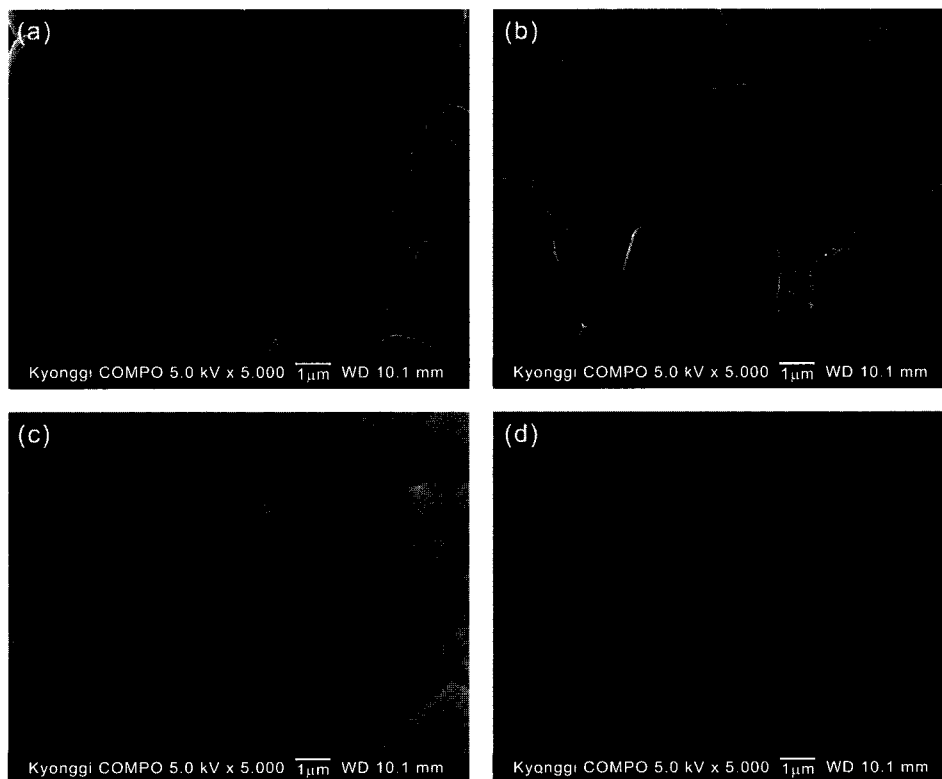


Fig. 5. SEM photographs of $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ specimens sintered at 1250°C for 3 h; (a) $x=0.2$, (b) $x=0.4$, (c) $x=0.6$, and (d) $x=0.8$.

Table 2. Comparison of the Theoretical and Observed Polarizabilities of $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ Specimens Sintered at 1250°C for 3 h

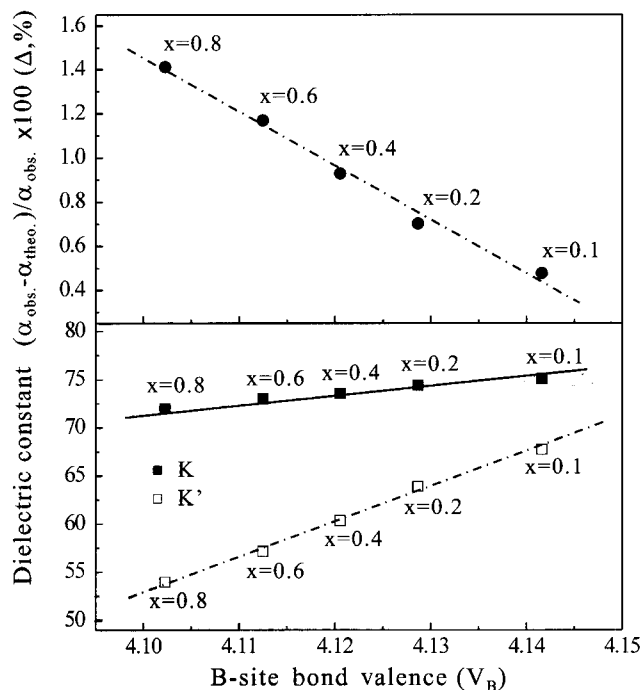
x (mol)	Theoretical		Observed				Δ , % $(\alpha_{\text{obs.}} - \alpha_{\text{theo.}}) / \alpha_{\text{obs.}} \times 100$
	$\alpha_{\text{theo.}}$ (Å)	K'	K	$V_{\text{unit cell}}$	Z	$\alpha_{\text{obs.}}$ (Å)	
0.1	14.026	67.7	75.1	61.391	1	14.093	0.477
0.2	14.021	63.9	74.4	61.534	1	14.120	0.702
0.4	14.013	60.3	73.6	61.665	1	14.144	0.929
0.6	14.004	57.1	73	61.795	1	14.170	1.169
0.8	13.995	54.0	72	61.944	1	14.196	1.412

PCFMN specimens sintered at 1250°C for 3 h. The dielectric constant (K) and Qf value decreased with increasing of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content. Generally, Qf values are significantly influenced by the density, impurity, secondary phases, and grain size.^{14,15} The effect of density on the Qf value of PCFMN, which has a relative density higher than 93%, could be neglected because the Qf value was independent on the relative density when it is greater than 90%.¹⁶ Also there is no secondary phase in the entire composition range, as confirmed in XRD patterns of Fig. 1. Therefore, Qf value decreased with increase of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content due to the decrease of grain size, as confirmed in Fig. 5.

The dielectric constant (K) of the specimens was also decreased with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content. In general, K was depended on the ionic polarizability at microwave frequencies. As shown in Table 2, the theoretical ionic polarizabilities ($\alpha_{\text{theo.}}$) obtained from the additivity rule using Eq. (3) was decreased with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content due to the smaller ionic polarizability of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ (3.09 Å)¹² than $(\text{Fe}_{1/2}\text{Nb}_{1/2})^{4+}$ (3.13 Å).¹² However, the observed ionic polarizabilities ($\alpha_{\text{obs.}}$) obtained from the measured dielectric constants (K) using Eq. (4) was increased with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content. Also, the deviations of $\alpha_{\text{obs.}}$ from $\alpha_{\text{theo.}}$ increased with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content. These results could be explained by the change of B-site bond valence with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content. With an increase of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content, B-site bond valence decreased, which means the decrease of bond strength between B-site ions and oxygen and finally, the increase of the rattling effect of B-site ions.⁵ Therefore, $\alpha_{\text{obs.}}$ showed larger value than that of $\alpha_{\text{theo.}}$ and the deviations of $\alpha_{\text{obs.}}$ from $\alpha_{\text{theo.}}$ were increased with the decrease of B-site bond valence, as shown in Fig. 6. Also, the effects of B-site bond valence on the dielectric polarizability were clearly confirmed from the changes of dielectric constant with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content in Fig. 6. Even though the theoretical dielectric constant (K') obtained from Eq. (5) was drastically decreased with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content due to the decrease of B-site bond valence, the measured dielectric constant (K) was slightly decreased with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content due to the increase of rattling effect.

4. Conclusions

For $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ ($0.1 \leq x \leq 0.8$) ceramics sintered at 1250°C for 3 h, only perovskite phase with cubic structure was obtained through the given compo-

**Fig. 6.** Deviations of the dielectric polarizabilities (Δ , %) and B-site bond valence (V_B) of $(\text{Pb}_{0.4}\text{Ca}_{0.6})[(\text{Fe}_{1/2}\text{Nb}_{1/2})_{1-x}(\text{Mg}_{1/3}\text{Nb}_{2/3})_x]\text{O}_3$ specimens sintered at 1250°C for 3 h.

sition range. Temperature Coefficient of Resonant Frequency (TCF) was strongly dependent on the B-site bond valence, which was effectively controlled by the change of unit-cell volume resulted from the increase of $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content. Dielectric constant (K) was dependent on the dielectric polarizabilities as well as B-site bond valence in ABO_3 perovskite structure. Qf value was decreased with $(\text{Mg}_{1/3}\text{Nb}_{2/3})^{4+}$ content due to the decrease of grain size.

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