

Microwave Dielectric Properties of $0.95\text{Ca}_{0.85}\text{Nd}_{0.1}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy, Er) Ceramics

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ABSTRACT

Microwave dielectric properties of $0.95\text{Ca}_{0.85}\text{Nd}_{0.1}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy, Er) were investigated as a function of sintering temperature and lanthanide ion type. A single perovskite phase with an orthorhombic structure was obtained throughout the entire range of composition. The dielectric constant (K) was dependent upon the dielectric polarizabilities and the B-site bond valence in the ABO_3 perovskite structure. The quality factor (Qf) of the specimens with ErAlO_3 was smaller than those with SmAlO_3 and/or DyAlO_3 due to the smaller grain size. The temperature coefficient of resonant frequency (TCF) could be controlled from 107.28 ppm/°C at Ln=Sm to 87.23 ppm/°C at Ln=Er due to the changes of B-site bond valence in the ABO_3 perovskite structure.

Key words: $\text{Ca}_{0.85}\text{Nd}_{0.1}\text{TiO}_3$, LnAlO_3 (Ln=Sm, Dy, Er), Bond valence, Microwave dielectric properties

1. Introduction

Although the perovskite titanates,¹⁾ $(\text{Ca}_{1-x}\text{Nd}_x)\text{TiO}_3$ (CNT) show good microwave dielectric properties, such as a high dielectric constant (K) and quality factor (Qf), their temperature coefficient of resonant frequencies (TCF) is too large to warrant their practical application.²⁾ Though much effort has been invested to improve the microwave dielectric properties of CNT, the dependence of microwave dielectric properties on composition and crystal structure must be studied in order to effectively predict and control the microwave dielectric properties of these perovskite titanates. It is well known that ABO_3 perovskite compounds have oxygen octahedra composed of an octahedral cation with six oxygen ions, and that a distortion of oxygen octahedra arises if the ionic radii of the A-site are too small to fully occupy the available volume.³⁾

Microwave dielectric properties are largely dependent on the structural characteristics of materials. In the case of TCF , changes are closely related to the structural characteristics of oxygen octahedra such as the bond length between the octahedral cation and oxygen ions,⁴⁾ and the distortion of the oxygen octahedra,⁵⁾ which could be evaluated by the B-site bond valence⁶⁾ in the ABO_3 perovskite structure.

Since the B-site bond valence is inversely proportional to the bond length between the B-site cation and oxygen ions,⁷⁾ the B-site bond valence could be increased with a reduction

of the unit-cell volume through substitution of ions with a smaller ionic radius than that of the A-site and/or B-site ion. As to the perovskite titanate $\text{Ca}_{0.85}\text{Nd}_{0.1}\text{TiO}_3$, the unit-cell volume could be reduced through the substitution of the smaller-sized ion Al^{3+} ion (0.535 Å) for the larger Ti^{4+} ion (0.605 Å) in the B-site ion, and by substitution of the smaller-sized Ln^{3+} ion (Sm=1.079 Å, Dy=1.027 Å, Er=1.004 Å) for $(\text{Ca}_{0.85}\text{Nd}_{0.10})^{2+}$ (1.2499 Å) in the A-site ion.⁴⁾

Therefore, the microwave dielectric properties of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy, Er) were investigated as a function of sintering temperature and Lanthanide (Ln) ion type in order to control the TCF of $\text{Ca}_{0.85}\text{Nd}_{0.1}\text{TiO}_3$. The effects of bond valence on the microwave dielectric properties of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy, Er) ceramics are also discussed.

2. Experimental Procedure

$\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3$ and LnAlO_3 (Ln=Sm, Dy, Er) powders were separately prepared by a conventional solid-state reaction from oxide powders with purities above 99%. To obtain a single phase of each composition, $\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3$ was calcined at 1100°C for 3 h and SmAlO_3 was calcined at 1400°C for 3 h, while DyAlO_3 and ErAlO_3 were each calcined at 1450°C for 24 h. These calcined powders were mixed according to the formula $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy, Er). The mixed powders were pressed isostatically into 10 mm-diameter disks at 1500 kg/cm². The resultant pellets were sintered in air for 4 h at temperatures of 1300 °C to 1400°C.

X-ray powder diffraction (XRD, D/Max-3C, Rigaku, Japan) analyses were used to determine the phase identifi-

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cation. The lattice parameters, unit-cell volumes and atomic positions were obtained from Rietveld refinements of XRD patterns. The Rietveld refinements were performed using the RIETAN-2000 program.⁸⁾ The microstructure of the specimens was observed using a scanning electron microscope (SEM, Hitachi S-4200, Japan). The microwave dielectric properties were measured by Hakki and Coleman's method⁹⁾ with the TE₀₁₁ mode at 5~7 GHz. The *TCF* of specimens was measured by the cavity method¹⁰⁾ in a temperature range of 25°C to 80°C at 9-11 GHz.

The bond valences between the A-, or B-site cation and the oxygen ion, $v_{(A,B)-O}$ were calculated from eq. (1).⁷⁾

$$v_{(A,B)-O} = \exp[(R_{(A,B)-O} - d_{(A,B)-O}) / b'] \quad (1)$$

where $R_{(A,B)-O}$ is the bond valence parameter, $d_{(A,B)-O}$ is the bond length between A-, or B-site cation and oxygen ion, and b' is commonly taken to be a universal constant equal to 0.37 Å.¹¹⁾ The bond valence parameters followed the values in the previous report.⁷⁾ A- and B-site bond valences with coordination numbers of 8 and 6, V_A , V_B were calculated from eqs. (2) and (3), respectively.

$$V_A = v_{1A-O} \times 2 + v_{2A-O} \times 2 + v_{3A-O} \times 2 + v_{4A-O} + v_{5A-O} \quad (2)$$

$$V_B = v_{1B-O} \times 2 + v_{2B-O} \times 2 + v_{3B-O} \times 2 \quad (3)$$

3. Results and Discussion

For the specimens of 0.95Ca_{0.85}Nd_{0.10}TiO₃-0.05LnAlO₃ (Ln = Sm, Dy, Er) sintered in air for 4 h from 1300°C to 1400°C, the complete solid solutions were formed with the orthorhombic perovskite structure through the given range of compositions. With an increase of the sintering temperature, the crystallinity of the specimens was slightly increased. Fig. 1 shows the Rietveld refinement plots of XRD data for the specimens sintered at 1400°C in air for 4 h. Solid lines are the observed intensities, overlying dots are calculated intensities, and bottom lines are the difference between the observed and calculated intensities. Short vertical bars indicate the Bragg reflections which are allowed for the ordered orthorhombic perovskite structure. All peaks in the XRD patterns fit well with the orthorhombic perovskite structure, *Pnma*. The lattice parameters, unit-cell volume and atomic positions of the sintered specimens obtained from the Rietveld refinement are shown in Fig. 2

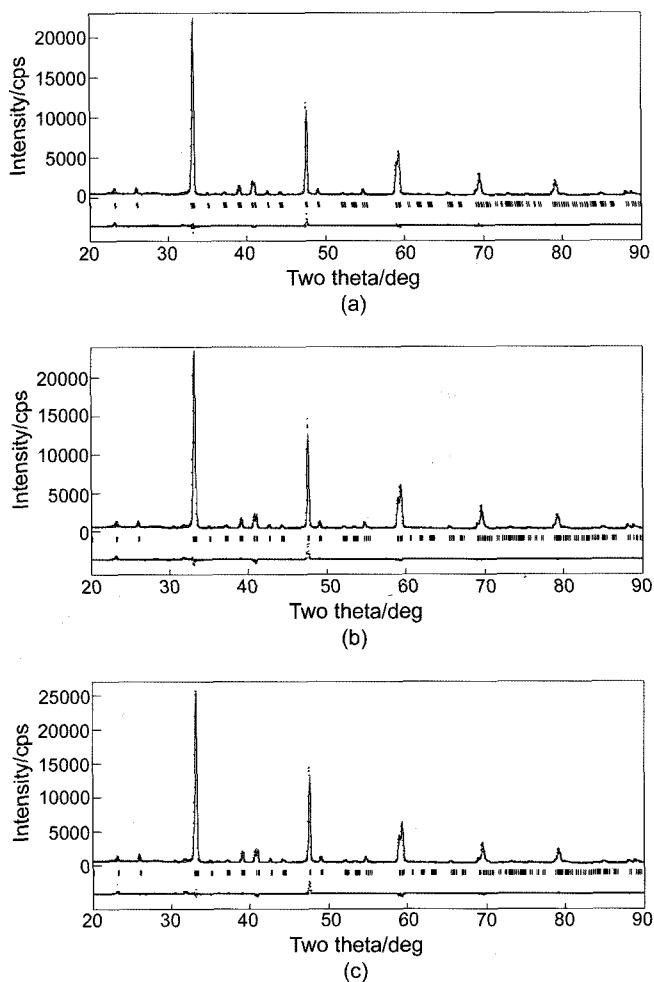


Fig. 1. Rietveld refinement patterns of 0.95Ca_{0.85}Nd_{0.10}TiO₃-0.05LnAlO₃ specimens sintered at 1400°C for 4 h; (a) Ln=Sm, (b) Ln=Dy, (c) Ln=Er.

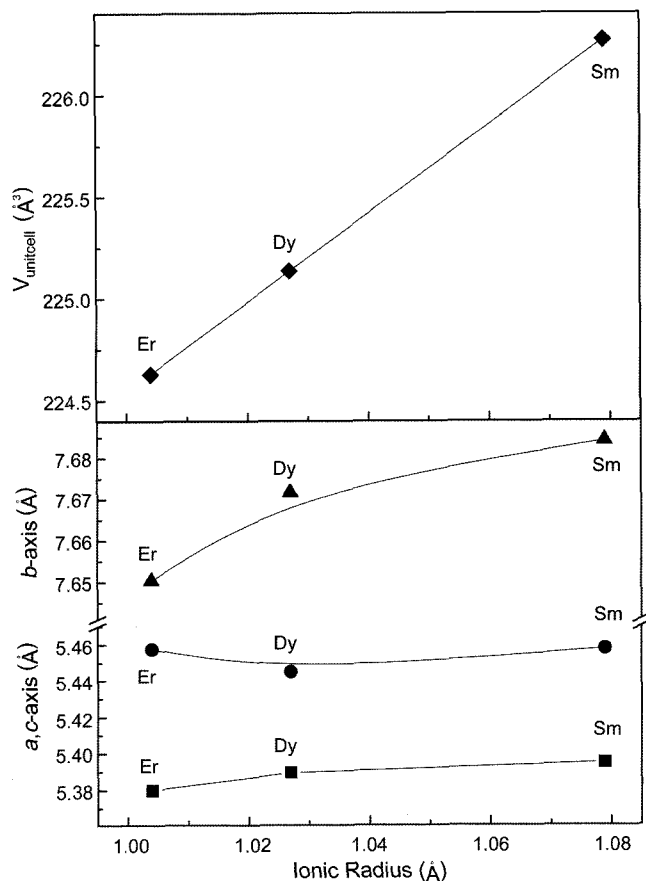


Fig. 2. Lattice parameters and unit-cell volume of 0.95Ca_{0.85}Nd_{0.10}TiO₃-0.05LnAlO₃ (Ln=Sm, Dy and Er) specimens sintered at 1400°C for 4 h.

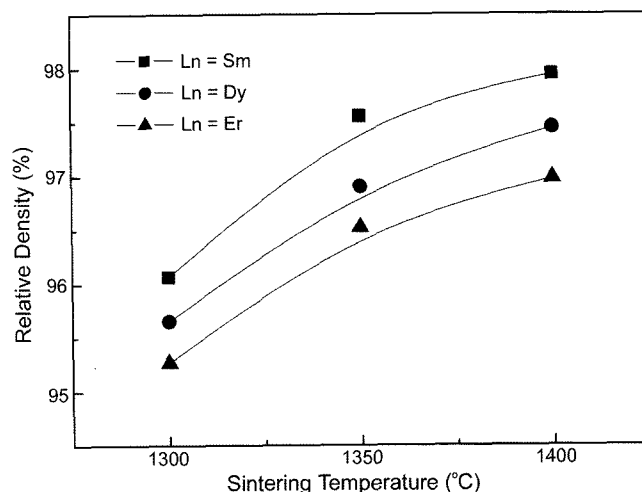
Table 1. Atomic Position of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy and Er) Specimens Sintered at 1400°C for 4 h

Ln	Position	x	y	z
Sm	A	0.0314	0.2500	0.9937
	B	0.5000	0	0
	O1	0.4820	0.2500	0.0774
	O2	0.2911	0.0333	0.7117
Dy	A	0.0346	0.2500	0.9887
	B	0.5000	0	0
	O1	0.4843	0.2500	0.0746
	O2	0.2883	0.0347	0.7156
Er	A	0.0331	0.2500	0.9907
	B	0.5000	0	0
	O1	0.4868	0.2500	0.0690
	O2	0.2877	0.0320	0.7123

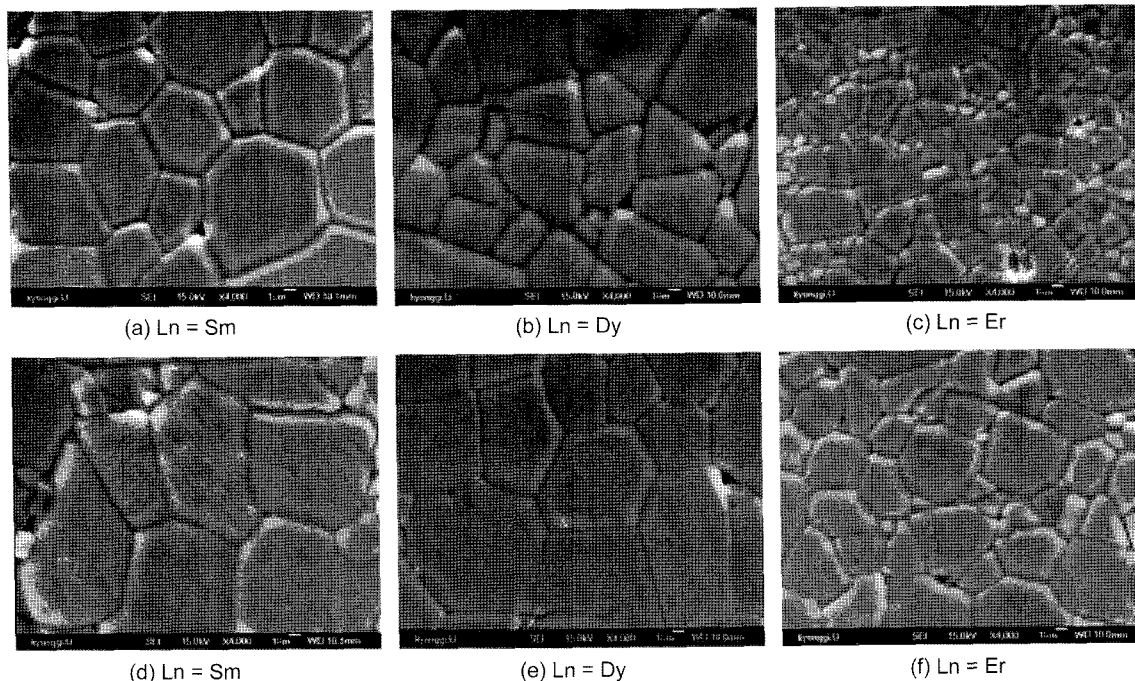
and Table 1. The unit-cell volume of the specimen with SmAlO_3 was larger than those with DyAlO_3 and ErAlO_3 , which was due to the larger ionic size of Sm^{3+} (1.079 Å) than those of Dy^{3+} (1.027 Å) and Er^{3+} (1.004 Å) at the same coordination number.⁴⁾

Fig. 3 shows SEM micrographs of the specimens sintered in air for 4 h from 1300°C to 1400°C . The grain size of the specimen increased as sintering temperature increased. The grain size of the specimen with ErAlO_3 was smaller than those with SmAlO_3 and/or DyAlO_3 at the same sintering temperature; however, the relative densities of the specimens were higher than 95% of the theoretical density throughout the entire composition range, as shown in Fig. 4.

The microwave dielectric properties of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}$


Fig. 4. Relative density (%) of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy and Er) specimens sintered from 1300°C to 1400°C for 4 h.

0.05LnAlO_3 (Ln=Sm, Dy, Er) specimens sintered in air for 4 h from 1300°C to 1400°C are shown in Fig. 5. It has been reported that at microwave frequencies both the Qf value and K are dependent upon not only the composition, the relative density and any secondary phase, but also upon the crystal structure, lattice defects and dielectric polarizability. Since the relative density was higher than 95% and there was no secondary phase in the given compositions, as confirmed in Fig. 1 and 4, the Qf value and K were not significantly affected by either the relative density or a secondary phase. Therefore, the changes in Qf value could be attributed to the effect of Lanthanide (Ln) ions, and K was largely affected by the dielectric polarizability of the specimens. Qf


Fig. 3. SEM micrographs of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ specimens sintered at 1300°C ((a), (b), (c)) and 1400°C ((d), (e), (f)) for 4 h, respectively.

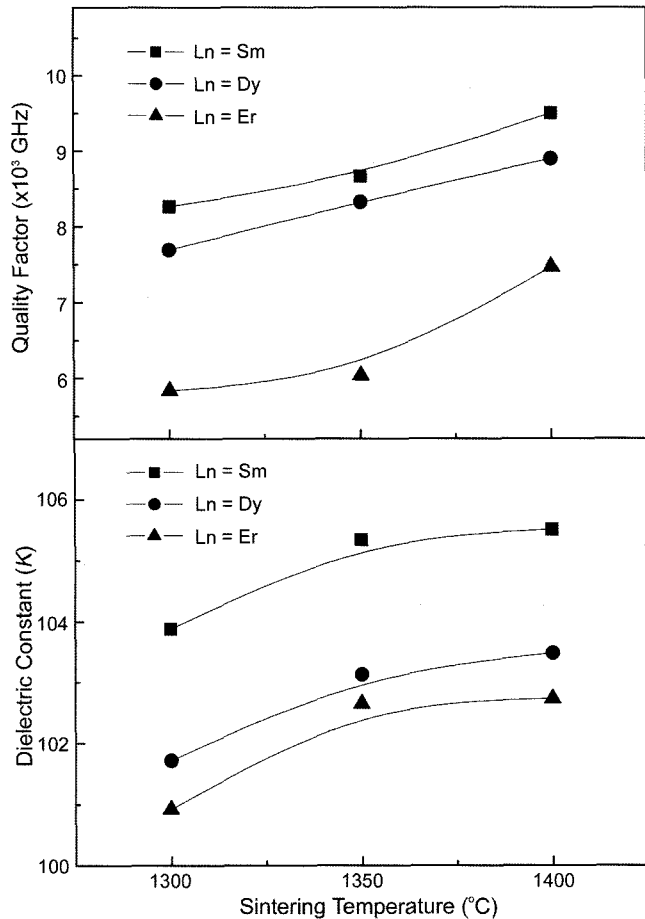


Fig. 5. Microwave dielectric properties of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ ($\text{Ln} = \text{Sm}, \text{Dy}$ and Er) specimens sintered from 1300°C to 1400°C for 4 h.

value of the specimens with ErAlO_3 was smaller than that of those with SmAlO_3 and DyAlO_3 at the same sintering temperature, which was consistent with the grain size as confirmed in Fig. 3. K of the specimen with SmAlO_3 was higher than those of specimens with DyAlO_3 and ErAlO_3 , as shown in Fig. 5. These results could be attributed to the larger ionic polarizability of Sm^{3+} (4.74 \AA) than those of Dy^{3+} (4.07 \AA) and Er^{3+} (3.81 \AA).¹²⁾

As shown in Table 2, the theoretical dielectric polarizabilities (α_{theo}) obtained from the additive rule¹²⁾ and the observed dielectric polarizabilities (α_{obs}) obtained from the measured dielectric constants using the Clausius-Mosotti equation¹²⁾ decreased with the type of Ln ions ($\text{Ln} = \text{Sm}, \text{Dy}, \text{Er}$). Also, the deviation of α_{obs} from α_{theo} decreased with the

Table 3. B-site Bond Valence (V_B) of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ ($\text{Ln} = \text{Sm}, \text{Dy}$ and Er) Specimens Sintered at 1400°C for 4 h

	Ln		
	Sm	Dy	Er
$R_{\text{A-O}}$	1.8939	1.8913	1.8900
$d1_{\text{A-O}} \times 2$	2.6520	2.6710	2.6460
$d2_{\text{A-O}} \times 2$	2.6440	2.3870	2.3950
$d3_{\text{A-O}} \times 2$	2.3800	2.5990	2.6310
$d4_{\text{A-O}}$	2.3240	2.3630	2.3810
$d5_{\text{A-O}}$	2.4880	2.4860	2.5000
$R_{\text{B-O}}$	1.8068	1.8068	1.8068
$d1_{\text{B-O}} \times 2$	1.9450	1.9110	1.9250
$d2_{\text{B-O}} \times 2$	1.9190	1.9460	1.9310
$d3_{\text{B-O}} \times 2$	1.9370	1.9320	1.9260
V_A	1.5721	1.5367	1.5027
V_B	4.2602	4.3079	4.3320

type of Ln ions ($\text{Ln} = \text{Sm}, \text{Dy}, \text{Er}$). These results are due to the changes of bond strength between the A- or B-site cation and the oxygen ion, because the dielectric constant (K) was affected by the rattling or compression effect resulting from the changes of bond strength. The bond strength between cation and anion was closely related to bond valence which is a function of the bond length and bond valence parameter.⁶⁾ Therefore, the bond valence could be applied to the estimation of bond strength.

Table 3 summarizes the B-site bond valence of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ ($\text{Ln} = \text{Sm}, \text{Dy}, \text{Er}$) specimens sintered at 1400°C in air for 4 h. B-site bond valence increased according to Ln ion type ($\text{Ln} = \text{Sm}, \text{Dy}, \text{Er}$). This resulted from a decrease of unit-cell volume as the ionic size of the Ln ions decreased, as confirmed in Fig. 2. The rattling effect was subsequently decreased with the increase of B-site bond valence, which in turn decreased the deviation of α_{obs} from α_{theo} , as shown in Fig. 6.

In the ABO_3 perovskite structure, the TCF was closely related with the distortion of the oxygen octahedra, which could be evaluated from the bond valence.⁶⁾ The TCF of specimens sintered in air at 1400°C for 4 h decreased with the increase of B-site bond valence, as shown in Fig. 7. Therefore, a large positive value of TCF in the ABO_3 perovskite structure could be controlled by the increase of B-site bond valence, which in turn resulted from the decrease of unit-cell volume.

Table 2. Comparison of Observed and Theoretical Polarizabilities of $0.95\text{Ca}_{0.85}\text{Nd}_{0.10}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ ($\text{Ln} = \text{Sm}, \text{Dy}$ and Er) Specimens Sintered at 1400°C for 4 h

Ln	Theoretical $\alpha_{\text{theo}} (\text{\AA}^3)$	Observed				$\Delta, \%$ $(\alpha_{\text{obs}} - \alpha_{\text{theo}}) / \alpha_{\text{obs}} \times 100$
		K	$V_{\text{unitcell}} (\text{\AA}^3)$	Z	$\alpha_{\text{obs}} (\text{\AA}^3)$	
Sm	12.1177	105.51	226.2684	4	13.1276	7.6927
Dy	12.0842	103.48	225.1366	4	13.0547	7.4340
Er	12.0712	102.73	224.6302	4	13.0226	7.3057

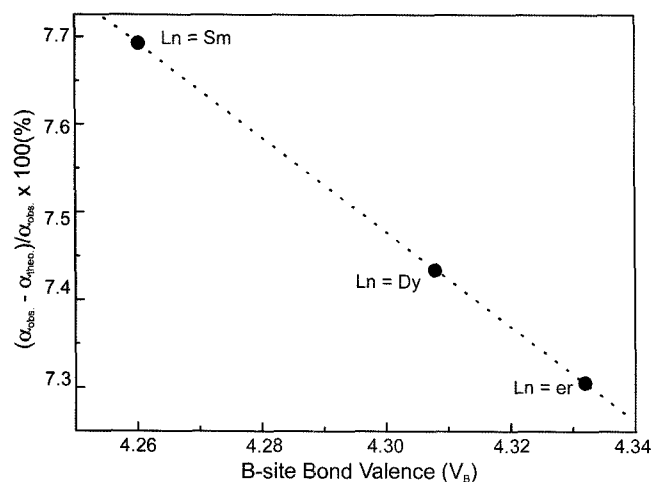


Fig. 6. Deviation and B-site bond valence (V_B) of $0.95\text{Ca}_{0.85}\text{Nd}_{0.1}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy and Er) specimens sintered at 1400°C for 4 h.

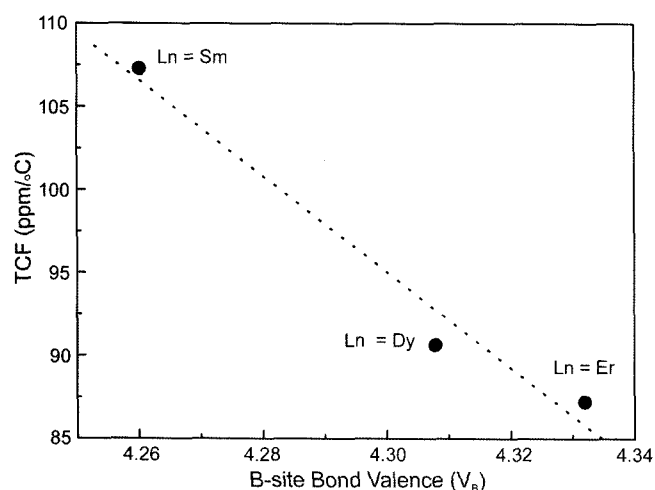


Fig. 7. Variation of TCF with B-site bond valence (V_B) of $0.95\text{Ca}_{0.85}\text{Nd}_{0.1}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy and Er) specimens sintered at 1400°C for 4 h.

4. Conclusions

For specimens of $0.95\text{Ca}_{0.85}\text{Nd}_{0.1}\text{TiO}_3\text{-}0.05\text{LnAlO}_3$ (Ln=Sm, Dy, Er), a single phase with the orthorhombic perovskite structure was detected. With the increase of the sintering temperature, the dielectric constant (K) and quality factor (Qf) were increased due to the increase of the density and grain size. K was decreased due to the decrease of dielectric polarizability, according to Ln ion type (Ln=Sm, Dy, Er). The rattling effect decreased as B-site bond valence increased. Qf value of the specimens with ErAlO_3 was smaller than those with SmAlO_3 and DyAlO_3 at the same sintering temperature. These results could be attributed to

the decrease of grain size. In the ABO_3 perovskite structure, a large positive TCF value could be controlled through manipulation of B-site bond valence.

Acknowledgements

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