Microwave dielectric properties of $(1-x)\mathrm{CaTiO_3}-x\mathrm{Li_{1/2}Sm_{1/2}TiO_3}$ ceramics

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Abstract

The effect of the bond valence on microwave dielectric properties of $(1-x)\mathrm{CaTiO_3}-x\mathrm{Li_{1/2}Sm_{1/2}TiO_3}$ ceramics was investigated in the range of $0.0 \leqslant x \leqslant 1.0$. A complete solid solutions was formed with the orthorhombic perovskite structure in the entire composition range. As the $\mathrm{Li_{1/2}Sm_{1/2}TiO_3}$ content increased, the deviation of the observed dielectric polarizabilities calculated by the Clausius–Mosotti equation from the theoretical values, calculated by the additivity rule of dielectric polarizability, decreased with increasing bond valence of the B-site in $\mathrm{ABO_3}$ perovskite compound. The temperature coefficient of the resonant frequency (TCF) of the specimens decreased, depending on the B-site bond valence in the tilted region ($t < 1$). Typically, the dielectric constant $K = 114$, $Q \cdot f = 3700$ GHz, and TCF = 11.5 ppm/°C for the $x = 0.7$ composition sintered at 1300 °C for 3 h.
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1. Introduction

Numerous dielectric materials have been investigated for microwave application in advanced telecommunication systems. These materials require a high dielectric constant (K) to reduce the size of components, a high quality factor ($Q \cdot f$) for good frequency selectivity, and a small temperature coefficient of the resonant frequency (TCF) in order to have frequency stability.

In particular, CaTiO$_3$-based materials have attracted considerable interest due to their high dielectric constant. However, they have a large TCF.[1] Various attempts have been undertaken to control TCF of CaTiO$_3$-based materials. However, most of them were mainly based in the empirical approach, such as the addition of materials with negative TCF value. TCF of ABO$_3$ perovskites mainly results from the temperature dependence of the dielectric constant (TCK) related with the structural change. Although TCK is largely dependent on the tolerance factor and the tilting of oxygen octahedra of the ABO$_3$ perovskite, the change of TCK with the tolerance factor could not be fully explained by the tilting of oxygen octahedra alone due to the changes of the effective ionic size in the center of the oxygen octahedra with tilting.[2] Therefore, the bond valence of oxygen octahedra is considered important and should be taken into account in order to predict the TCF of ABO$_3$ perovskites with the tilting of oxygen octahedral. It has been reported that TCF decreases with the increase of B-site bond valence in the tilted region ($t < 1$) of ABO$_3$ perovskites.[3] Due to the dependence of B-site bond valence on the bond length between B-site cation and oxygen, the B-site bond valence could be increased with the reduction of unit-cell volume, which could be achieved by the substitution of divalent ion with smaller ionic radius than that of Ca^{2+} for A-site ion.

Therefore, $(1-x)\mathrm{CaTiO_3}-x\mathrm{Li_{1/2}Sm_{1/2}TiO_3}$ $(0.0 \leqslant x \leqslant 1.0)$ system was investigated to control the TCF of CaTiO$_3$-based materials. The relationship between the microwave dielectric properties of these CaTiO$_3$-based materials and the bond valence is also discussed.

2. Experimental procedure

$(1-x)\mathrm{CaTiO_3}-x\mathrm{Li_{1/2}Sm_{1/2}TiO_3}$ $(0.0 \leqslant x \leqslant 1.0)$) ceramics were prepared by a conventional solid-state reaction

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from reagent grade powders of $CaCO_3$, TiO_2, Li_2CO_3, and Sm_2O_3. Raw materials were weighed in the desired compositions and ground with ethanol for 24 h in a ball-mill. Mixed powders were dried at 120 °C and calcined at 1100 °C for 3 h in air. The calcined powders were ground again in a ball-mill, and then cold-isostatically pressed at 1500 kg/cm². To prevent the volatilization of Li, the pressed specimens were buried in powders of the same composition and sintered at 1300 °C for 3 h.

Crystalline phases of the specimens were identified from powder X-ray diffraction patterns (D/Max-3C, Rigaku, Japan). Lattice parameters of the sintered specimens were determined from the X-ray diffraction patterns by the least square method.[4] Microstructures of the specimens were observed using a scanning electron microscope (JEOL, JSM 820, Japan). The dielectric constant and unloaded Q value at frequencies of 4–6 GHz were measured by the post resonant method developed by Hakki and Coleman.[5] The TCF was measured by the cavity method[6] at frequencies of 9–11 GHz and the temperature range of 25–80 °C.

The bond valence of the B-site in ABO_3 perovskite was obtained from the reported bond valence parameters (R_{Ti-O}: 1.85 Å) and the summation of all the valences from the B-site ions.[7] From the Clausius–Mosotti equation and the additivity rule of dielectric polarizabilities, the observed ($\alpha_{obs.}$) and theoretical ($\alpha_{theo.}$) dielectric polarizabilities were calculated respectively.[6]

3. Results and discussion

It has been reported that $Li_{1/2}Sm_{1/2}TiO_3$ has an orthorhombic perovskite structure with four formula units per unit-cell similar to $CaTiO_3$.[1] However, the superstructure reflection lines of $Li_{1/2}Sm_{1/2}TiO_3$ were also observed for the specimens sintered at 1300 °C for 3 h due to the ordering of Li^{1+} and Sm^{3+} ions along the c-axis.[8] From the XRD patterns of the $(1-x)CaTiO_3-xLi_{1/2}Sm_{1/2}TiO_3$ $(0.0 \leqslant x \leqslant 1.0)$, a single phase with orthorhombic perovskite was obtained and well crystal-

lized through the entire composition range. For the formation of complete solid solutions, a linear change of the unit-cell parameters could be expected by the Vegard's law.[9] Some of the crystallographic data are listed in Table 1. Because the effective average ionic radius of $(Li_{1/2}Sm_{1/2})^{2+}$ (0.9995 Å) ion is smaller than that of the Ca^{2+} (1.1200 Å) ion at the same coordination number,[10] the lattice parameters of b and c axes decreased linearly, while the lattice parameter of a-axis remained nearly the same value. Therefore, the unit-cell volume of the solid solutions decreased with $Li_{1/2}Sm_{1/2}TiO_3$ content. For the entire composition range, the relative densities of the specimens were higher than 95% even though the grain size was slightly decreased with $Li_{1/2}Sm_{1/2}TiO_3$ content.

To obtain the B-site bond valence, the interatomic distances between Ti and O were calculated from the lattice parameters obtained from the XRD patterns by the least square method, as follows;

$$d_{(Ti-O)} = \frac{a}{2} \tag{1}$$

where, $d_{(Ti-O)}$ is the distance between Ti and O, a is the lattice parameter. The cube root of the cell volume per formula unit is applied to a in the case of orthorhombic structure.

With the increase of $Li_{1/2}Sm_{1/2}TiO_3$ content, the interatomic distance between Ti and O decreased, while the valence of Ti increased. Finally, the B-site bond valence of $(1-x)CaTiO_3-x$ $Li_{1/2}Sm_{1/2}TiO_3$ increased from 4.6126 ($x = 0$) to 4.6977 ($x = 1.0$), as shown in Fig. 1. These results are due to the decrease of unit cell volume with the substitution of $(Li_{1/2}Sm_{1/2})^{+2}$ ion for Ca^{2+} ion in A-site.

The temperature coefficient of resonant frequency (TCF) is related to the temperature coefficient of dielectric constant (TCK) and the thermal expansion coefficient (α), as given in Eq. (2)

$$TCF = -\left(\frac{TCK}{2} + \alpha_L\right) \tag{2}$$

where α_L is the linear thermal expansion coefficient. TCF is affected directly by TCK, because the magnitude

Table 1
Lattice parameter and unit-cell volume of $(1-x)CaTiO_3-xLi_{1/2}Sm_{1/2}TiO_3$ specimens sintered at 1300 °C for 3 h

x (mol)	Lattice parameter (Å, axis)			Unit-cell volume (Å³)	X-ray density (g/cm³)	Relative density (%)
	a	b	c			
0	5.4424	7.6417	5.3807	223.7789	4.0351	95.41
0.3	5.4420	7.6348	5.3684	223.0494	4.3929	95.15
0.5	5.4417	7.6304	5.3605	222.5805	4.6324	96.06
0.7	5.4415	7.6260	5.3520	222.0913	4.8733	98.50
1.0	5.4420	7.6190	5.3400	221.4103	5.2355	97.41

of α_L is generally constant in the ceramics. The temperature dependence of the dielectric constant (TCK) can be divided into three terms of A, B and C, in Eq. (3)[11]:

$$TCK = \frac{(\varepsilon - 1)(\varepsilon + 2)}{\varepsilon}$$

$$\times \left[\frac{1}{\alpha_m}\left(\frac{\partial \alpha_m}{\partial T}\right)_V + \frac{1}{\alpha_m}\left(\frac{\partial \alpha_m}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P - \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P \right]$$

$$= \frac{(\varepsilon - 1)(\varepsilon - 2)}{\varepsilon}(A + B + C)$$

$$(3)$$

where α_m and V denote the polarizability and volume, respectively. The term A, (commonly negative) represents the direct dependence of the polarizability on temperature. B and C represent the increase of the polarizability and the decrease of the number of polarizable ions in the unit-cell respectively; the unit cell volume increased with an increase in temperature. The B and C terms are normally the largest ones but have similar value with opposite signs. Hence, (B+C) has a small positive value. TCK is increased by an increase of the tilting of oxygen octahedra in the perovskite structure,[12] which correspond to a decrease of TCF by Eq. (2). These could be explained by the fact that the increase of thermal energy is supposed to be absorbed completely in recovering the octahedral tilting rather than restoring the A term, and therefore (B+C) terms are expected to be larger than the A term. With an increase of B-site bond valence, the bond strength between the B-site cation and oxygen, and/or the degree of tilting on oxygen octahedra were increased, because B-site bond valence is a function of the bond strength and the distance between the B-site cation and oxygen. Finally, the restoring force for recovering the tilting increased with an increase of B-site bond valence, and then TCF decreased. Therefore, TCF could be effectively evaluated by the B-site bond valence in the perovskite structure. The dependence of TCF on the B-site bond valence is shown in Fig. 2. Therefore, TCF of CaTiO3-based ceramics can be controlled by the substitution of divalent ion with smaller ionic radius than that of Ca^{2+} for the A-site, because the B-site bond valence is affected by the unit-cell volume due to the change of ionic radius for the A-site in ABO3 perovskite.

Fig. 3 shows the microwave dielectric properties of $(1-x)CaTiO_3-xLi_{1/2}Sm_{1/2}TiO_3$ specimens sintered at 1300 °C for 3 h. Both dielectric constant (K) and Qf decreased with an increase of $Li_{1/2}Sm_{1/2}TiO_3$ content. In general, K was dependent not only on the density and secondary phases, but also on the ionic polarizabilities.[13] The relative densities of all the $(1-x)CaTiO_3-xLi_{1/2}Sm_{1/2}TiO_3$ specimens were higher than 95%. Hence, the dielectric constant was not significantly affected by the density, because the relative density was above 95% for all of the specimens,[13] and there were no secondary phases through the entire composition range. Therefore, the dielectric constant was largely dependent on the ionic polarizabilities. As shown in Table 2, the theoretical ionic polarizabilities ($\alpha_{theo.}$) obtained from the additive rule decreased with
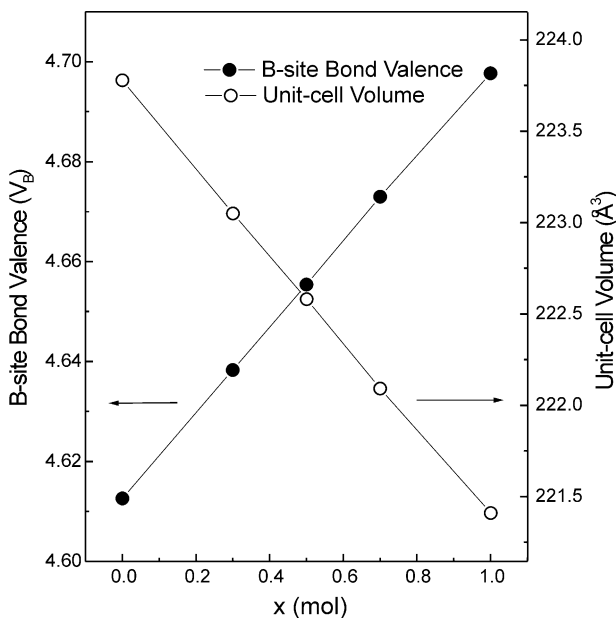

Fig. 1. B-site bond valence and unit-cell volume of $(1-x)CaTiO_3-x$ $Li_{1/2}Sm_{1/2}TiO_3$ specimens sintered at 1300 °C for 3 h.
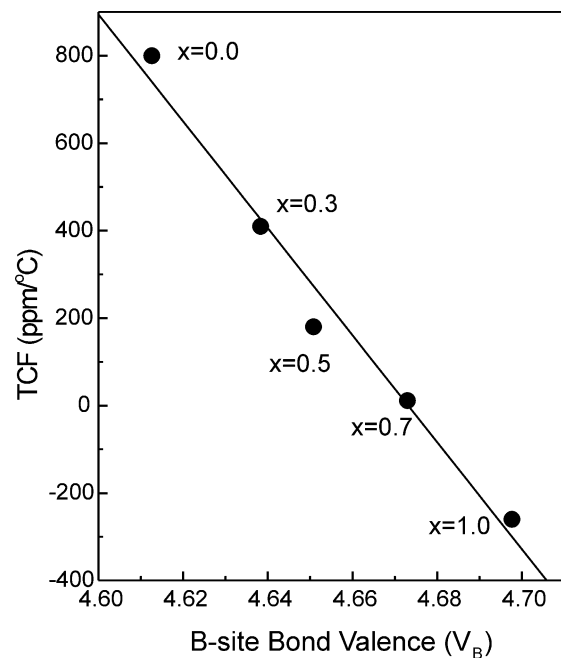

Fig. 2. Dependence of TCF on B-site bond valence of $(1-x)CaTiO_3-x$ $Li_{1/2}Sm_{1/2}TiO_3$ specimens sintered at 1300 °C for 3 h.

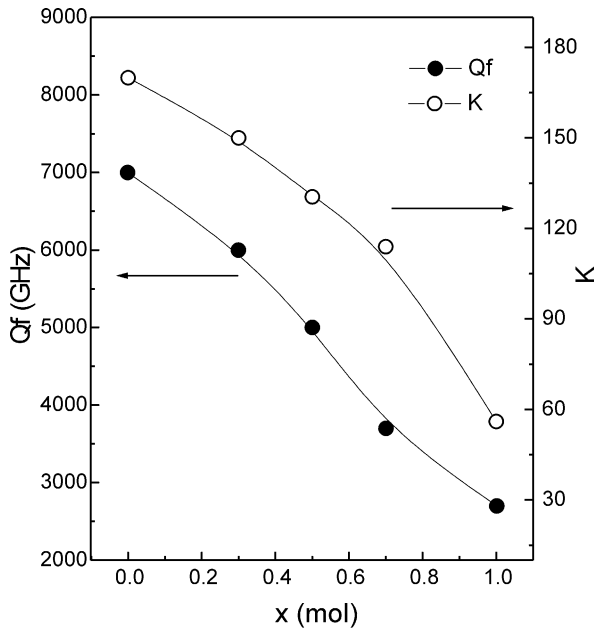Fig. 3. Dielectric constant (K) and Qf value of $(1-x)CaTiO_3-x$ $Li_{1/2}Sm_{1/2}TiO_3$ specimens with variation of x, sintered at 1300 °C for 3 h.

Fig. 4. Deviations of the ionic polarizabilities and B-site bond valence of $(1-x)CaTiO_3-xLi_{1/2}Sm_{1/2}TiO_3$ specimens sintered at 1300 °C for 3 h.

increasing $Li_{1/2}Sm_{1/2}TiO_3$ content due to the smaller ionic polarizability of $Li_{1/2}Sm_{1/2}TiO_3$ (11.93 Å^3) than that of $CaTiO_3$ (12.12 Å^3).[2] The observed ionic polarizabilities ($\alpha_{obs.}$) obtained from the measured dielectric constants using the Clausius–Mosotti equation also decreased with $Li_{1/2}Sm_{1/2}TiO_3$ content. However, $\alpha_{obs.}$ was higher than $\alpha_{theo.}$ due to the rattling effect of the B-site ion in the ABO_3 perovskite, and the deviations of $\alpha_{obs.}$ from $\alpha_{theo.}$ decreased with $Li_{1/2}Sm_{1/2}TiO_3$ content. These results could be explained by the increase of the B-site bond valence, because B-site bond valence and rattling effect are a function of bond strength. Hence, the deviations of $\alpha_{theo.}$ from $\alpha_{obs.}$ were dependent on the B-site bond valence of the ABO_3 perovskite, as shown in Fig. 4. Therefore, K decreased with an increase of $Li_{1/2}Sm_{1/2}TiO_3$ content due to, not only the smaller ionic polarizability of $Li_{1/2}Sm_{1/2}TiO_3$ (11.93 Å^3) than that of $CaTiO_3$ (12.12 Å^3), but also to an increase of B-site bond valence resulting in the decrease of rattling effect.
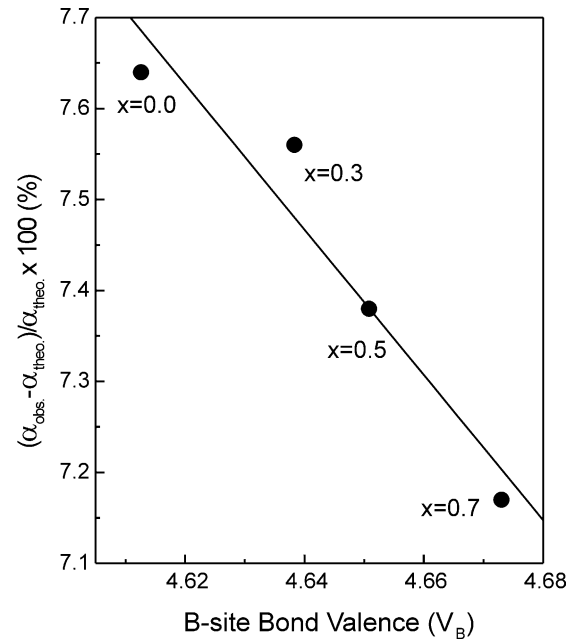
4. Conclusions

Due to an increase of the B-site bond valence, resulting from the decrease of unit-cell volume, TCF of the specimens could be controlled from +800 to −250 ppm/°C by the substitution of a smaller effective ionic radius $(Li_{1/2}Sm_{1/2})^{2+}$ (0.9995 Å) ion compared with that of Ca^{2+} (1.1200 Å) at the same coordination number, for the A-site in the ABO_3 perovskite structure. With an increase of $Li_{1/2}Sm_{1/2}TiO_3$ content, the dielectric constant decreased, and the deviations of the observed ionic polarizability ($\alpha_{obs.}$) from the theoretical ($\alpha_{theo.}$) decreased due to an increase of the B-site bond valence. Dielectric constant was dependent not only on the ionic polarizability, but also the B-site bond valence. Typically, dielectric properties of $K=114$, $Q \cdot f = 3700$ GHz, and TCF = 11.5 ppm/°C were obtained for the $0.3CaTiO_3-0.7Li_{1/2}Sm_{1/2}TiO_3$ specimens sintered at 1300 °C for 3 h.

Table 2

Comparison of observed and theoretical polarizabilities of $(1-x)CaTiO_3-xLi_{1/2}Sm_{1/2}TiO_3$ specimens sintered at 1300 °C for 3 h

x (mol)	Theoretical $\alpha_{theo.}$ (Å^3)	Observed				$\Delta,\%$ $(\alpha_{obs.}-\alpha_{theo.})/\alpha_{obs.} \times 100$
		K	$V_{unitcell}$	Z	$\alpha_{obs.}$(Å^3)	
0	21.2100	170	223.8	4	13.1229	7.84
0.3	12.0630	150	223.1	4	13.0500	7.56
0.5	12.0250	130.5	222.6	4	12.9835	7.38
0.7	11.9870	114	222.1	4	12.9123	7.17

Acknowledgements

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