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Understanding microwave dielectric properties of Pb-based complex perovskite ceramics via bond valence

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Abstract

Correlations between microwave dielectric properties and the dielectric polarizabilities related to the bond valences of A- and B-site ions in Pb-based complex perovskite ceramics have been investigated. With the decrease of A-site bond valence, the dielectric constants were higher than those obtained from the dielectric additivity rule due to the rattling behavior of A-site ions. The temperature coefficient of the resonant frequency (TCF) depended strongly on the bond valences of the A- and B-sites, as well as the tolerance factor (t) in the perovskite structure. In the tilted region ($t < 1.0$), the tilting of the oxygen octahedra increased and the TCF decreased because of the increasing bond valence of the B-site. Also, the dependence of TCF on the bond valence of the A-site was similar to its dependence on the tolerance factor (t).

Keywords: Pb-based complex perovskite; Bond valence; Tolerance factor; Dielectric polarizability; Temperature coefficient of resonant frequency

1. Introduction

With rapid progress of the telecommunication system, several kinds of microwave dielectric materials have been investigated to meet the demand for the miniaturization, compactness and easy matching of microwave integrated circuits. Especially, complex perovskite compounds $A(B,B')O_3$ were extensively studied due to their superior dielectric properties at microwave frequencies [1–3]. Various attempts have been made to control the microwave dielectric properties of Pb-based perovskite systems such as the substitution of Ca^{2+} for Pb^{2+}, and Ti^{4+} for B^{4+} in $(Pb,Ca)BO_3$, (B = Zr, Hf, $(Fe_{1/2}Nb_{1/2})$, $(Mg_{1/2}Nb_{1/2})$, $(Ni_{1/2}Nb_{1/2})$) [4]. However, most of searches have been mainly empirical, and the compositional dependence on the dielectric constant (K) and the temperature coefficient of resonant frequency (TCF) has been explained by the dielectric mixing rule and structural change.

Microwave dielectric properties are affected by the crystal structure and the interactions between cation and anion of the compound. At microwave frequencies, K was found to be affected by the rattling effect as well as the ionic polarizability [5], and TCF was closely related with the temperature coefficient of dielectric constant (TCK), which depended on the distortion of oxygen octahedra in ABO_3 perovskite structure [6]. On the other hand, the rattling effect and the octahedral distortion were largely dependent on the bond strength and bond length of the composing ions, which could be expressed quantitatively by the bond valence [7,8].

In this study, the effects of A- and B-site bond valences on the microwave dielectric properties of Pb-based complex perovskite compound were investigated.

2. Experimental procedures

High purity (≥99.0%) oxide powders of PbO, $CaCO_3$, Fe_2O_3, Nb_2O_5, Ta_2O_5, SnO_2 and TiO_2 were used as the starting materials. They were weighed according to the compositions of $(Pb_{1-x}Ca_x)(Fe_{0.5}Ta_{0.5})O_3$ (PCFT) ($0.50 \leq x \leq 0.65$), $(Pb_{1-x}Ca_x)(Fe_{0.5}Nb_{0.5})O_3$ (PCFN) ($0.55 \leq x \leq 0.64$), $(Pb_{0.5}Ca_{0.5})((Mg_{0.33}Ta_{0.67})_{1-y}Sn_y)O_3$ (PCMTS) ($0.01 \leq y \leq 0.05$) and $(Pb_{0.5}Ca_{0.5})((Mg_{0.33}Ta_{0.67})_{1-y}Ti_y)O_3$ (PCMTT) ($0.05 \leq y \leq 0.15$). The specimens were prepared by the conventional mixed oxide method via

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the columbite route. Raw materials were ball milled and calcined at 900 °C for 3 h followed by sintering at 1150–1400 °C for 3 h. To reduce the loss of PbO and decomposition during higher-temperature sintering, the specimens were buried in powders of the same composition and placed into a platinum crucible.

X-ray powder diffraction analysis (D/Max-3C, Rigaku, Japan) was used to determine the crystalline structure and lattice parameters. The polished surface was observed using a scanning electron microscope (JEOL, JSM 820, Japan). The dielectric constant and unloaded Q value at frequencies of 5–6 GHz were measured by the post resonant method developed by Hakki and Coleman. TCF was measured by the cavity method at frequencies of 9–11 GHz and the temperature range of 25–80 °C.

The bond valence of A- and B-site in the ABO_3 perovskite was calculated from the bond valence parameters of A- and B-site cation and the distances ($d_{A–O}$, $d_{B–O}$) between A- and B-site cation and oxygen by the Eqs. (1) and (2), respectively [7]:

$$V_i = \sum_j V_{ij} \tag{1}$$

$$V_{ij} = \exp\left(\frac{R_{ij} - d_{ij}}{b'}\right) \tag{2}$$

where the bond valence of atom i, V_i was defined as the sum of all of the valences from a given atom i, R_{ij} is the bond valence parameter, which could be obtained from the literatures [8], d_{ij} is the length of a bond between atom i and j, and b' is a universal constant equal to 0.37 Å.

The observed dielectric polarizabilities (α_{obs}) of the specimens were obtained from measured dielectric constant and the unit-cell volume using the Clausius–Mossoti equation, and the theoretical dielectric polarizabilities (α_{theo}) of the specimens were calculated from the ionic polarizabilities of composing ions and the additive rule of dielectric polarizabilities by Eqs. (3) and (4) [6]:

$$\alpha_{abs} = \frac{V_m(K-1)}{b(K+2)} \tag{3}$$

$$\alpha_{theo}(ABO_3) = \alpha_A + \alpha_B + \alpha_O \times 3 \tag{4}$$

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

3. Results and discussion

It has been reported that the microwave dielectric properties depend on the secondary phases and density, as well as the compositions of the materials [9]. For the entire compositional range of PCFT, PCFN, PCMTS and PCMTT, a single phase with perovskite structure was confirmed by X-ray diffraction patterns. Also, the effect of density on the microwave dielectric properties of the specimens could be neglected because the relative density was higher than 95% in those Pb-based complex perovskite ceramics.

Microwave dielectric properties and A-site bond valence of PCFT and PCFN systems are shown in Table 1. With an increase of Ca content, the dielectric constant (K) and TCF were decreased. The tolerance factor (t) of the specimens, described the stability of perovskite structure, decreased due to the smaller ionic size of Ca^{2+} (1.34 Å, CN = 12) than that of Pb^{2+} (1.49 Å, CN = 12).

The effect of compositional change on the microwave dielectric properties could be elucidated by the change of bond valence. A-site bond valences of PCFT and PCFN were obtained from Eqs. (1) and (2). As shown in Table 1, the decrease of A-site bond valences could be explained by the decrease of the bond length of A-site with Ca content, even though the tilting of oxygen octahedral was changed with the tolerance factor (t). Therefore, TCF of the specimens depended on the bond valences of A-site, as well as the tolerance factor (t).

Similar calculations were applied to obtain B-site bond valence of PCMTS and PCMTT in Table 2. The B-site bond valence of PCMTS increased with an increase of Sn^{4+} content, while that of PCMTT decreased with an increase of Ti^{4+} content. The observed (α_{obs}) and theoretical (α_{theo}) dielectric polarizabilites were calculated by the Clausius–Mossoti equation and the additivity rule of dielectric polarizabilities in Eqs. (3) and (4). The volume of unit cell, $V_{unit\,cell}$ of Table 2, was obtained from the lattice parameters of the

Table 1
Microwave dielectric properties and A-site bond valence of PCFT and PCFN

Composition	Dielectric constant (K)	Tolerance factor (t)	$R_{A–O}$ (Å)	$d_{A–O}$ (Å)	Bond valence, V_A	TCF (ppm/°C)
$(Pb_{0.50}Ca_{0.50})(Fe_{0.5}Ta_{0.5})O_3$	82.0	0.9745	2.0395	2.7928	1.5667	−6.0
$(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Ta_{0.5})O_3$	72.0	0.9719	2.0323	2.7884	1.5547	−13.5
$(Pb_{0.40}Ca_{0.60})(Fe_{0.5}Ta_{0.5})O_3$	65.0	0.9694	2.0250	2.7840	1.5427	−16.0
$(Pb_{0.35}Ca_{0.65})(Fe_{0.5}Ta_{0.5})O_3$	60.0	0.9668	2.0178	2.7796	1.5309	−16.5
$(Pb_{0.45}Ca_{0.55})(Fe_{0.5}Nb_{0.5})O_3$	76.7	0.9719	2.0323	2.7783	1.5977	3.4
$(Pb_{0.40}Ca_{0.60})(Fe_{0.5}Nb_{0.5})O_3$	81.3	0.9694	2.0250	2.7816	1.5527	−9.19
$(Pb_{0.38}Ca_{0.62})(Fe_{0.5}Nb_{0.5})O_3$	70.8	0.9683	2.0221	2.7830	1.5347	−11.61
$(Pb_{0.36}Ca_{0.64})(Fe_{0.5}Nb_{0.5})O_3$	58.8	0.9673	2.0192	2.7866	1.5082	−12.02

Table 2
Dielectric polarizabilities and B-site bond valence of PCMTS and PCMTT

Composition	Theoretical	Observed				Δ (%) $[(\alpha_{obs} - \alpha_{theo})/\alpha_{obs} \times 100]$	Bond valence, V_B	TCF (ppm/°C)
	α_{theo}	K	$V_{unit\,cell}$	Z	α_{obs}			
$(Pb_{0.5}Ca_{0.5})(Mg_{0.33}Ta_{0.67})_{0.99}Sn_{0.01}O_3$	14.144	64	62.770	1	14.311	1.171	4.0947	−3
$(Pb_{0.5}Ca_{0.5})(Mg_{0.33}Ta_{0.67})_{0.97}Sn_{0.03}O_3$	14.128	63	62.542	1	14.249	0.846	4.1336	−5
$(Pb_{0.5}Ca_{0.5})(Mg_{0.33}Ta_{0.67})_{0.95}Sn_{0.05}O_3$	14.113	57	61.996	1	14.055	−0.414	4.2131	−9
$(Pb_{0.5}Ca_{0.5})(Mg_{0.33}Ta_{0.67})_{0.95}Ti_{0.05}O_3$	14.118	67	61.860	1	14.133	0.105	4.1785	−3
$(Pb_{0.5}Ca_{0.5})(Mg_{0.33}Ta_{0.67})_{0.90}Ti_{0.10}O_3$	14.085	73	61.953	1	14.206	0.851	4.1504	5
$(Pb_{0.5}Ca_{0.5})(Mg_{0.33}Ta_{0.67})_{0.85}Ti_{0.15}O_3$	14.052	77	62.047	1	14.257	1.442	4.1224	13

XRD patterns. With increasing Sn^{4+} and/or Ti^{4+} content, α_{theo} of the specimens decreased due to the smaller dielectric polarizabilities of Sn^{4+} (2.83 Å) and/or Ti^{4+} (2.93 Å) than that of $(Mg_{0.33}Ta_{0.67})^{4+}$ (3.59 Å). However, α_{obs} obtained from the measured K decreased for PCMTS, while α_{obs} for PCMTT increased, respectively. These differences of α_{obs} from α_{theo} could be explained by the B-site bond valence.

Figs. 1 and 2 show that the deviations of α_{obs} from α_{theo} decreased with an increase of A- and B-site bond valences in Pb-based complex perovskite ceramics. Therefore, the dielectric constant were found to depend not only on the ionic polarizabilities, but also on the rattling effect which could be evaluated by the bond valence of materials.

Although the tolerance factor (t) of perovskite structure has been reported to be closely related to the tilting of oxygen octahedra [5], it is not sufficient to explain the change of TCF by the tolerance factor because the effective size of the ion in the center of oxygen octahedra is changed with tilting [8]. It was found the TCF behavior of Pb-based complex perovskite to be related to the bond valences of A- and B-site ions. As the bond valence of A-site increased, TCF of PCFT and PCFN increased, while TCF of PCMTS and PCMTT decreased with increasing B-site bond valence. Therefore, TCF of Pb-based complex perovskite compounds was associated with the bond valences of the A- and B-sites, as well as the tolerance factor (t).

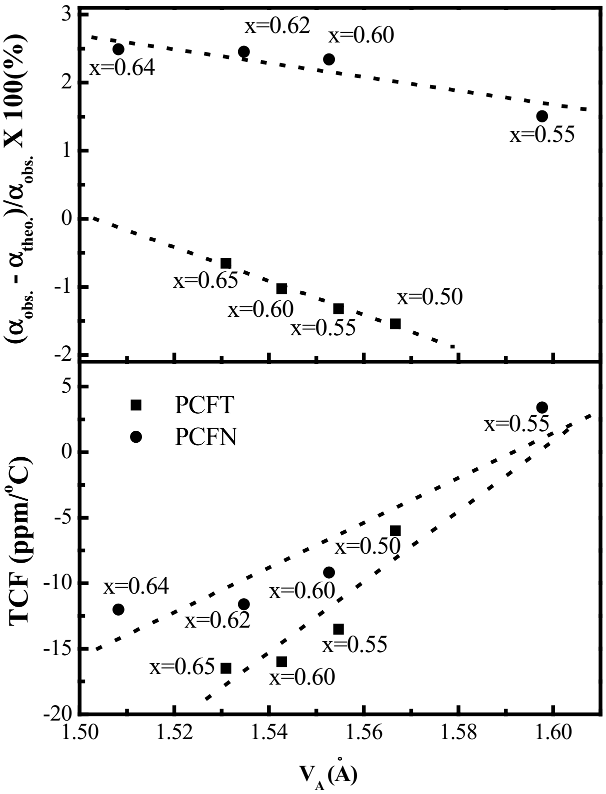

Fig. 1. Dependence of dielectric polarizabilities and TCF on A-site bond valence.

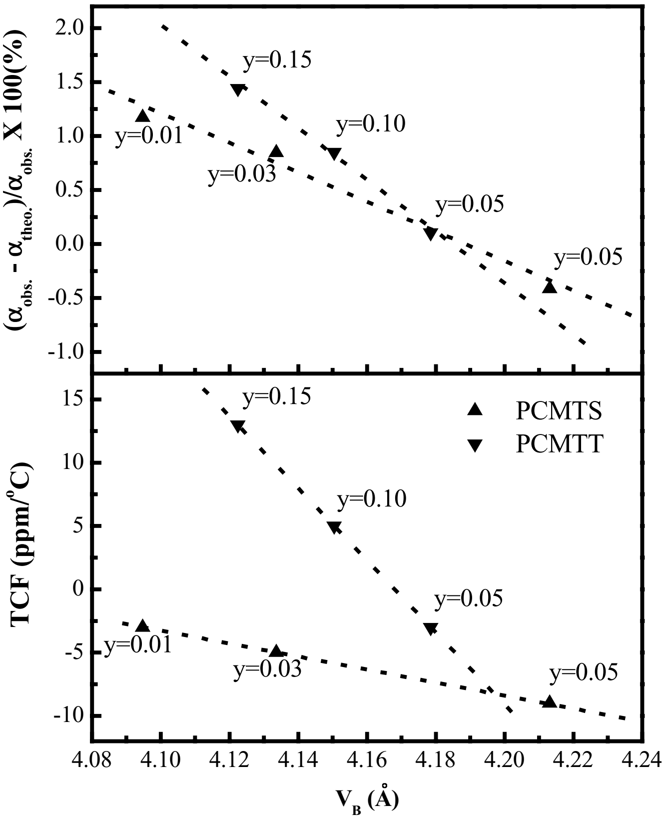

Fig. 2. Dependence of dielectric polarizabilities and TCF on B-site bond valence.

4. Conclusion

The effect of bond valence on microwave dielectric properties of Pb-based complex perovskite ceramics was investigated. The dielectric constant depended not only on the ionic polarizabilities, but also on the rattling effect, which could be evaluated by the bond valence of materials. TCF of PCFT and PCFN was related to the A-site bond valence as well as the tolerance factor (*t*), while that of PCMTS and PCMTT decreased with increasing B-site bond valence due to an increase of oxygen octahedra tilting.

References

[1] H.S. Park, K.H. Yoon, E.S. Kim, Relationship between the bond valence and the temperature coefficient of the resonant frequency in the complex perovskite $(Pb_{1-x}Ca_x)[Fe_{0.5}(Nb_{1-y}Ta_y)_{0.5}]O_3$, J. Am. Ceram. Soc. 84 (1) (2001) 99–103.

[2] J.W. Choi, J.Y. Ha, C.Y. Kang, S.J. Yoon, H.J. Kim, K.H. Yoon, Microwave dielectric properties of $(Pb,Ca)(Mg,Nb,Sn)O_3$ ceramics, Jpn. J. Appl. Phys. 39 (10) (2000) 5923–5926.

[3] H.S. Park, K.H. Yoon, E.S. Kim, Effect of bond valence on microwave dielectric properties of $(Pb_{1(x}Ca_x)(Mg_{0.33}Ta_{0.67})O_3$ ceramics, J. Mater. Res. 16 (3) (2001) 817–821.

[4] H. Kagata, J. Kato, K. Nishimoto, T. Inoue, Dielectric properties of Pb-based perovskite substituted by Ti for B-site at microwave frequencies, Jpn. J. Appl. Phys. 32 (9B) (1993) 4332–4334.

[5] I.M. Reaney, E.L. Colla, N. Setter, Dielectric and structural characteristics of Ba- and Sr-based complex perovskites as a function of tolerance factor, Jpn. J. Appl. Phys. 33 (7A) (1994) 3984–3990.

[6] R.D. Shannon, Dielectric polarizabilities of ions in oxides and fluorides, J. Appl. Phys. 73 (1) (1993) 348–366.

[7] N.B. Brese, M. O'Keefe, Bond-valence parameters for solids, Acta Cryst. B47 (1991) 192–197.

[8] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Cryst. A32 (1976) 751–767.

[9] K. Fukuda, R. Kitoh, I. Awi, Microwave characteristics of $BaPr_2Ti_4O_{12}$ and $BaPr_2Ti_5O_{14}$ ceramics, J. Mater. Res. 10 (1995) 312–319.