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DESIGN OF MICROWAVE DIELECTRICS BASED ON CRYSTALLOGRAPHY

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ABSTRACT

The authors have been studying correlation between crystal structure and microwave dielectric properties based on crystallography. New dielectric materials were designed based on the origins of the properties clarified as presented in following three categories. (I) Low loss microwave dielectrics designed by low internal strain due to compositional ordering, perfect crystallinity without defects and impurities, and high symmetry and high crystallographic densities. (II) Dielectric constants due to large unit cell with inversion symmetry *i*, large rattling factor accompanying expanding polyhedron. On the other hand, low dielectric constant due to tight polyhedron due to covalence such as silicates. (III) Low temperature coefficients of resonant frequencies (*TCf*) are affected by the tilted octahedra depending on the crystal transitions. The *TCf* is designed generally by combination positive and negative *TCf*, which might be clarified the origin of *TCf*. In this paper, some examples with relationship between crystal structure and microwave dielectric properties are presented, and origin of the properties are clarified.

INTRODUCTION

The authors have been studying correlation between crystal structure and microwave dielectric properties based on crystallography[1-3]. Microwave dielectrics are expected following properties: high quality factor Q for resonate with microwave, dielectric constant ε_r of high for shortage wavelength, and low for millimeter wave, and near zero temperature coefficient of resonate frequency *TCf* for stability usage on wide temperature range. These properties are depending on the crystal structure. So, after relationship between crystal structure and properties has been studied and the origin of the properties is clarified, new dielectrics with high properties have been designed.

New dielectric materials improved the properties were designed based on the origins of the properties clarified as presented in following three categories. (I) Low loss microwave dielectrics designed by low internal strain due to compositional ordering, perfect crystallinity without defects and impurities, and high symmetry and high crystallographic densities. (II) High dielectric constants due to large unit cell with inversion symmetry *i*, accompanying large rattling factor on the expanding polyhedron. On the other hand, low dielectric constant due to tight polyhedron due to covalence such as silicates. (III) Near zero temperature coefficient of resonant frequency *TCf* designed generally by combination positive and negative *TCf* which has clarified the origin of *TCf*.

In this paper, examples with relationship between crystal structure and microwave dielectric properties of the microwave dielectrics are presented, and origins of the properties are clarified.

EXPERIMENTAL

These compounds are almost fabricated by solid state reactions, identified and obtained the lattice parameters by X-ray powder diffraction (XRPD)[4]. The crystal structures were analyzed by RADY program[5] for single crystal, or by Rietveld method[6] for powder patterns. And the microwave dielectric properties were evaluated by Hakki and Colleman's method[7-8], as presented previous papers[1-2].

RESULTS AND DISCUSSIONS

Three microwave dielectric properties are presented in the order of High Q, ε_r and *TCf*.

1) High Q

1-1) (a) High Q by compositional ordering

The pseudo-tungstenbronze $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = rare earth) solid solutions shows the highest Qf value at x = 2/3 as shown in Fig. 1(a)[1,9], which internal strain is the smallest at the composition as shown in Fig. 1(b).

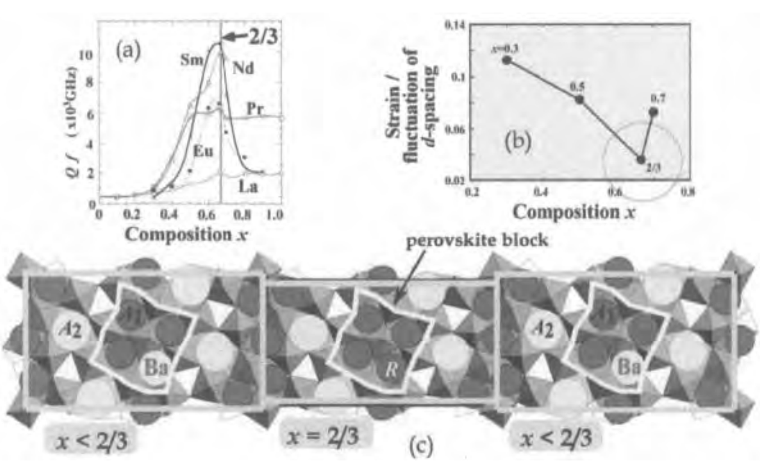

Fig. 1. (a) The Qf of pseudo-tungstenbronze $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ (R = Sm, Nd, Pr, Eu and La) as a function of composition x. (b) Strain/fluctuation of d-spacing of the Sm-analogous as a function of x. (c) Crystal structure with different occupation in the perovskite blocks in x < 2/3 case.

At the $x = 2/3$ composition of the solid solutions, the crystal structure show compositional ordering for R ions occupying A_1 site in perovskite block as shown in a part of $x = 2/3$ on Fig. 1(c). At the $x < 2/3$, Ba ions occupy statistically at A_1 sites in the perovskite block such as $[R_{8+2x}Ba_{2-3x}V_x]_{A1}$ as shown in a part of $x < 2/3$ on Fig. 1(c). The internal strains as shown in Fig. 1(b) are explained as the fluctuation of d-spacing of lattice constants. At $x < 2/3$, the fluctuation of d-spacing becomes large depending on the statistical occupation of Ba ions in perovskite blocks. On the other hand, at $x = 2/3$, the fluctuation of d-spacing becomes to be reduced depending on the all unit cells with the same size.

(b) Design more compositional ordering on the pseudo-tungstenbronze compounds

Low Qf value of ca. 200 GHz on the $Ba_6R_8Ti_{18}O_{54}$ (R = Nd) composition in the vicinity of $x = 0$ for $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$ as shown in Fig. 1(a) was improved to 6,000 GHz by substitution of Sr for Ba in the perovskite blocks of $[Nd_8B_{a2-\alpha}Sr_\alpha]_{A1}[Ba_4]_{A2}Ti_{18}O_{54}$ as shown in Fig. 2[10]. The substitution of Sr with smaller ionic radius than Ba ion must reduce the internal strain decreasing the fluctuation of d-spacing. This substitution of Sr for Ba also introduces a kind of the compositional ordering in A_1 and A_2 sites.

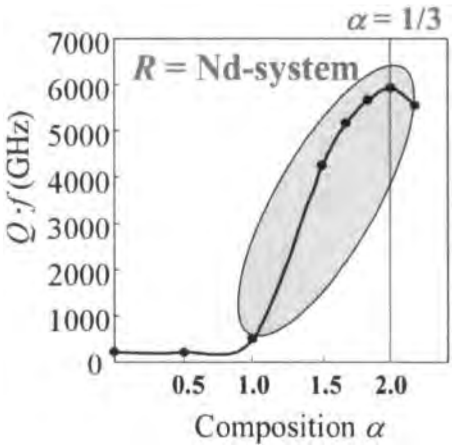

Fig. 2. Qf values of the Nd-analogy with $x = 0$ were improved from 200 to 6,000 GHz by substitution of Sr for Ba[10].

I-2) High Q by high symmetry

As presented at previous section, compositional ordering on the pseudo- tungsten bronze solid solutions brings high Q. And many researchers presented ordering of complex perovskite such as $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT), $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) and $Ba(Zn_{1/3}Nb_{2/3})O_3$

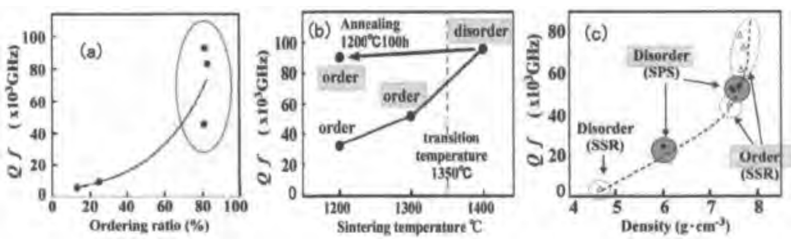

Fig. 3. (a) Qf of BZT ceramics as a function of ordering ratio, (b) Qf of BZN with order-disorder phase transition at 1350 °C as a function of sintering temperature, (c) Qf of BZT as a function of density by solid state reaction (SSR) and spark plasma sintering (SPS). Order: ordered perovskite, Disorder: disordered perovskite.

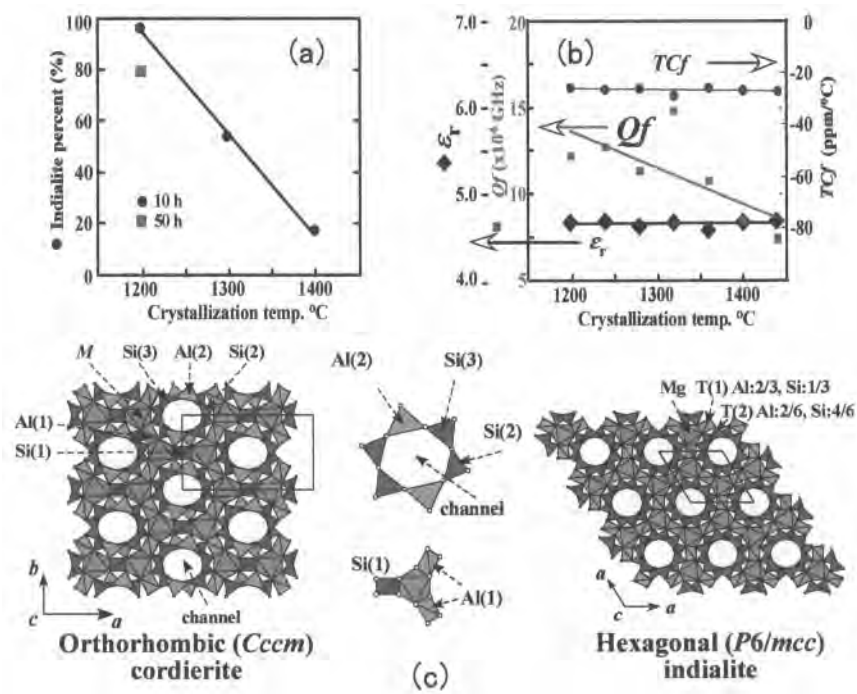

Fig. 4. (a) Indialite percentage sintered for 10 h as a function of temperature, (b) Qf, ε_r and TCf of indialite/cordierite glass ceramics sintered at1200 °C for 10 h as a function of crystallized temperature, (c) polymorph of indialite/cordierite: cordierite is ordered form with orthorhombic, and indialite is disorder form with hexagonal.

(BZN) brings high Q[11-12]. On the other hand, Koga et al.[13-17] found another factor instead of ordering, and Ohsato et al. presented high symmetry brings high Q instead of ordering on the compounds with order-disorder transition[18-20]. This conclusion has been derived from following five examples: (1) in the case of BZT, the Q values are not depended on the ordering ratio[13-15] as shown in Fig. 3(a). (2) In the case of BZN[17] with an clear order-disorder transition at 1350 °C, the low temperature form with high ordering ratio did not show higher Q than the high temperature form with high symmetry as shown in Fig. 3(b). (3) The disordered BZT samples synthesized by spark plasma sintering (SPS) showed the same high Q as ordered ones synthesized by solid state reaction (SSR)[16] as shown in Fig. 3(c). (4) Ni-doped cordierite[21-23] changing to disordered high temperature form was improved in the Q value. (5) In the case of indialite/cordierite glass ceramics, indialite with high symmetry (*P6/mcc*) shown higher Q than cordierite (*Cccm*) as shown in Fig. 4. Si/AlO_4 tetrahedra of indialite and cordierite are disordered and ordered, respectively[24].

The authors resume about the order of crystal structure and microwave dielectric properties. There are two categories of order: one is compositional ordering without order-disorder transition, another is ordering with order-disorder transition. The former case is pseudo-tungstenbronze solid solutions, the latter case is complex perovskite such as BMT, BZT and BZN, as presented above. The ordering of former yield on the same crystal symmetry, but that of the latter on the different symmetry, that is, ordered complex perovskite on the hexagonal and disordered one on the cubic. In the case of complex perovskite with *A*-site ordering, effect of symmetry might be dominant more than that of ordering.

I-3) High Q by perfect crystal structure

As an example of microwave dielectrics with defect, complex perovskite BZT on the BaO side in the vicinity of BZT as shown in Fig. 5(a) is presented here[15-16]. The phase is a single solid solution with disordered structure and has defects in *B*- and O-sites, as presented by Koga et al. The Qf values of the side become low in order of A, Q, R and S on the ③ line as shown in Fig. 5(b). Kugimiya[25] also presented a defect phase in the region $\alpha > 5g/4$ in $Ba_\alpha Ta_g O_\alpha + 5g/2$ as shown in Fig. 5(c), the composition denoted by $Ba_{1+\alpha}(Mg_{1/3}Ta_{2/3+\gamma}V_{\alpha-\gamma})O_{3+\alpha+5\gamma/2}V_{2\alpha-5\gamma/2}$ has *B*- and O-site vacancies with holes and electrons.

Though the crystal structural origins of Q factors stated above are intrinsic, extrinsic origin such as impurities, grain growth also degregate the Q values. The forsterite ceramics are improved from 10,000 to 240,000 GHz by means of using high purity raw materials as shown in Fig.6(a). The grains of forsterite are very clear and there is no glassy phase among the grains as shown in Fig. 7(c) [26-29].

Grain growth without rough microstructure sometimes improves Q values as shown in Fig. 7, which shows Qf of Al_2O_3 as a function of grain size. Q of Al_2O_3 was improved from

335,000 to 680,000 GHz by grain growth[30]. The *Qf* value of single crystal of Al_2O_3 shows 1,890,000 GHz on // *c*-axis[31]. So, grain growth might be in the process to single crystal with superior *Qf*.

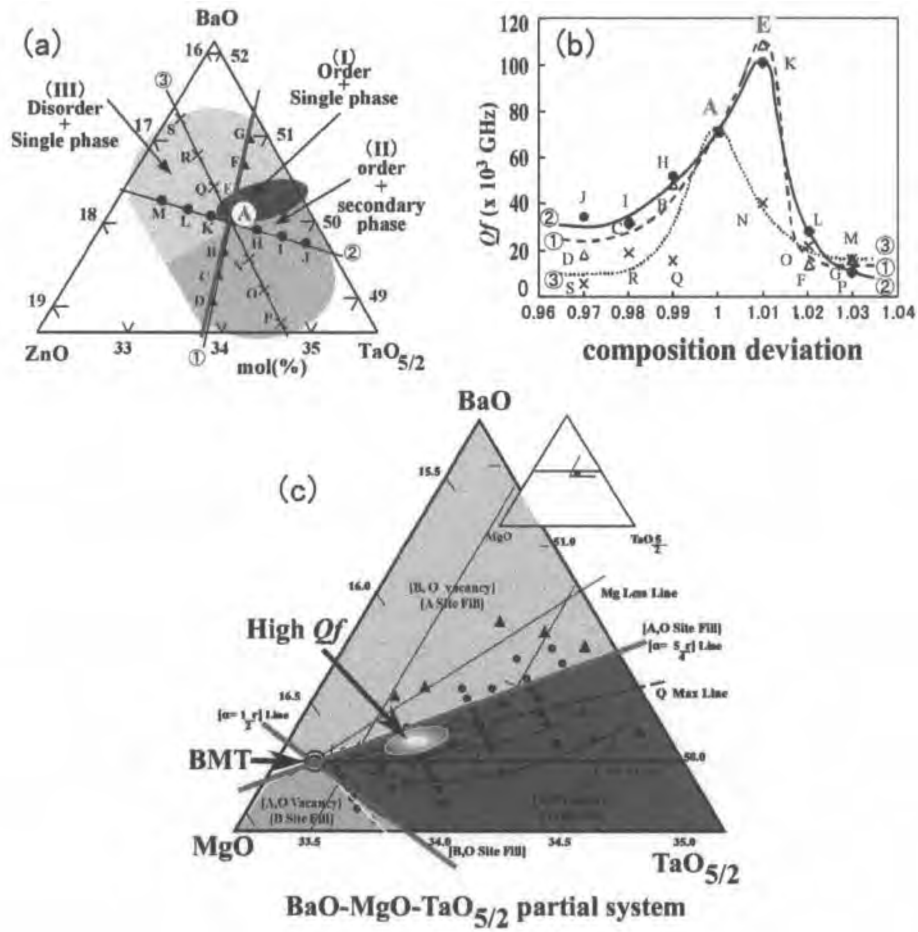

Fig. 5. (a) Partial ternary phase diagram around BZT. Three area are shown as (I) for order/single phase, (II) for order/secondary phase, (III) for disorder/single phase. (b) *Qf* as a function of composition deviation. On the line ③ , disordered single phase region (III) shows low *Qf*. (c) On the partial ternary system in the vicinity of BMT presented by Kugimiya. Highest *Qf* value is located near the line of BMT-$BaTa_{4/5}O_3$.

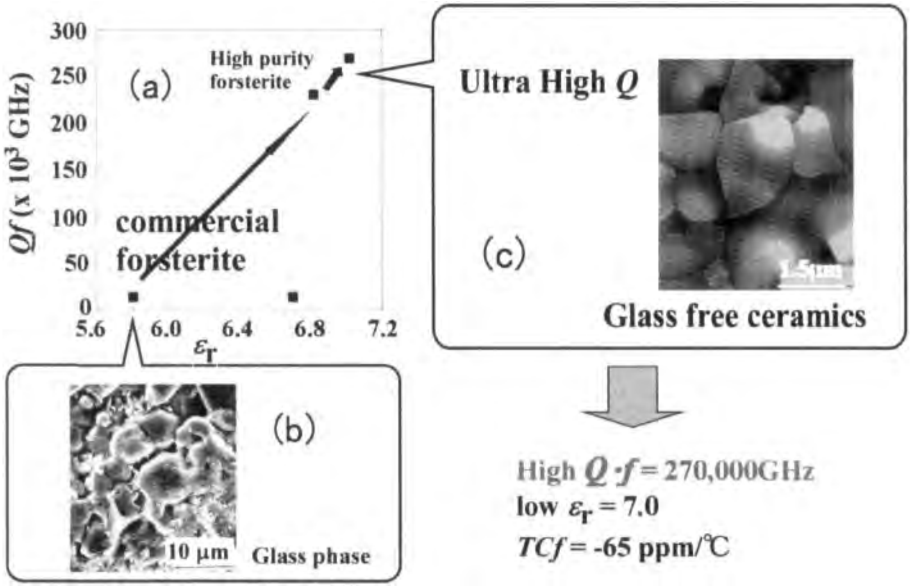

Fig. 6. (a) Qf improved by means of using high purity raw materials. (b) commercial forsterite with glass phase. (c) improved glass free forsterite with high Q.

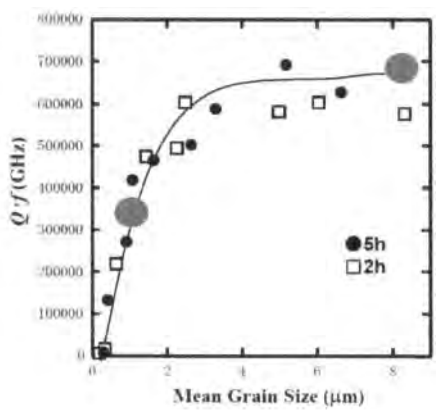

Fig. 7. Qf of Al_2O_3 as a function of mean grain size. Miyauchi improved the Qf of Al_2O_3 from 335,000 to 680,000 GHz.

II) Dielectric constant ε_r

Usually, high dielectric constant induces high dielectric loss, because the both properties are proportional to fluctuation of ions. So, *Qf* values decrease as a function of dielectric constants as shown in Fig. 8(a)[31-32]. Pseudo-tungstenbronze solid solutions with high *Qf* of ca. 10,000 GHz are examples for high dielectric constants of 80-90[34]. The dielectric constants are almost proportional to the unit cell volumes as shown in Fig. 8(b)[33]. This compound has large unit cell volume of over 2,000 Å^3 and 1/8 of the unit cell is an asymmetric unit, which space group is *Pnma* (No.62), and multiplicity/Wyckoff letter is 8*d*[1]. The large dielectric constants are produced from the 4.5 TiO_6 octahedra in an asymmetric unit as shown in Fig. 8(c).

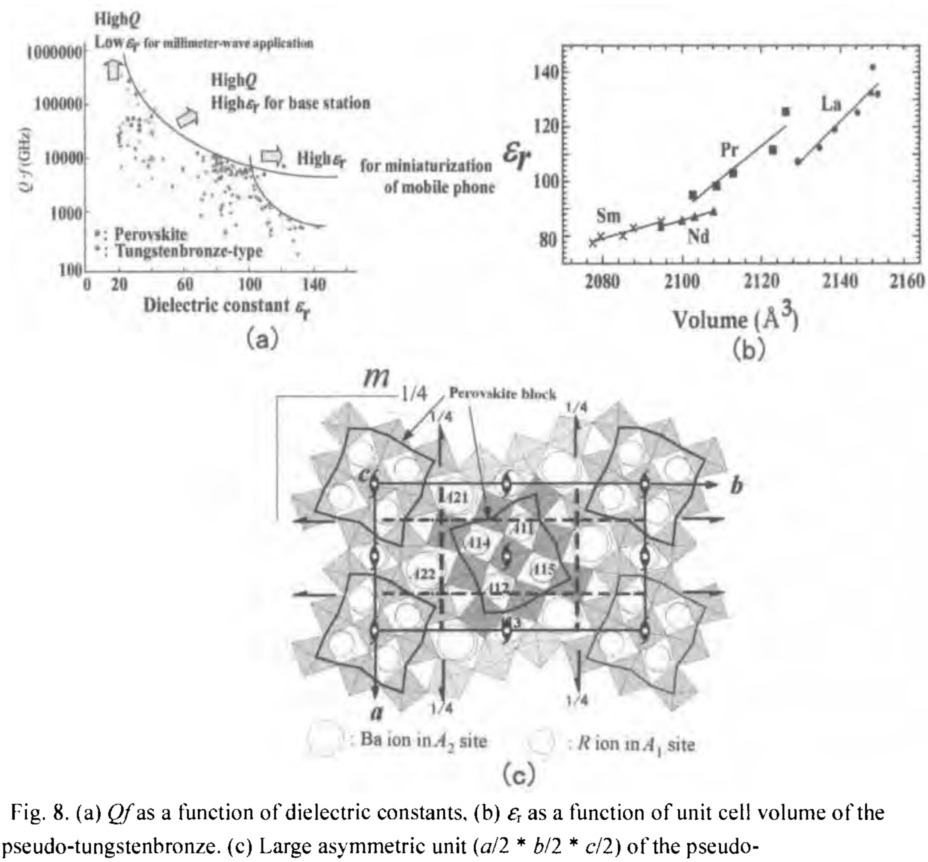

Fig. 8. (a) *Qf* as a function of dielectric constants, (b) ε_r as a function of unit cell volume of the pseudo-tungstenbronze. (c) Large asymmetric unit ($a/2 * b/2 * c/2$) of the pseudo-tungstenbronze.

The TiO_6 octahedra of the pseudo-tungstenbronze structure are tilting forming super structure of two times of c-axis[1]. The tilting affects to dielectric constant. Fig. 9 and Table 1 show schematic figures and angles of tilting from c-axis, respectively. The tilting angles are depending on the composition and R cations. As the composition x of 0.5 has much more cations in A_2 sites than $x = 0.7$, the tilting angle decreases and dielectric constant increases. TiO_6 octahedron reached the straight to the c-axes that is the tilting angle of 0° yields large dielectric constants.

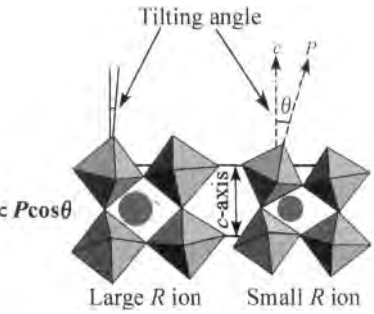

Fig. 9. Corelationship between dielectric constant and tilting angle.

Table 1. Tilting angles θ from c-axis on $x = 0.5$ and 0.7 for $Ba_{6-3x}R_{8+2x}Ti_{18}O_{54}$.

X	0.5	0.7
Sm	9.990°	10.63°
Nd	9.687°	8.961°

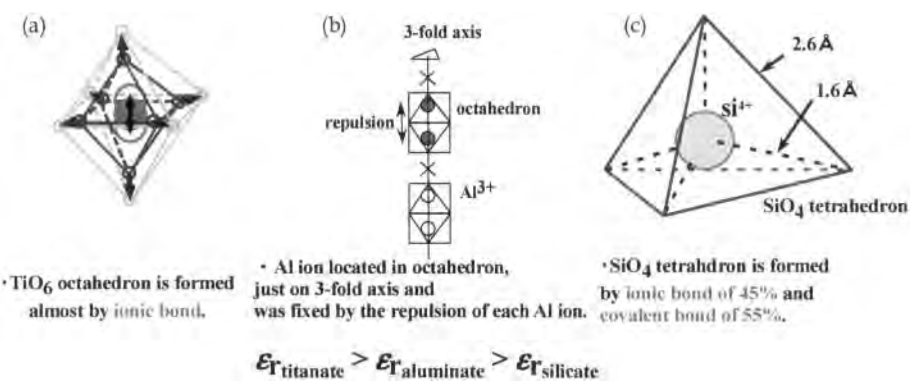

Fig. 10. Dielectric constant due to crystal structure: TiO_6 octahedron (a), octahedra of Al_2O_3 (b), and SiO_4 tetrahedron (c).

Rattling of the cations also affects the dielectric constant. Fig. 10 compared with the effects of rattling on the titanate with TiO_6 octahedron, Al_2O_3 and silicates[35]. As the titanates have large rattling effect because of large space around Ti cation as shown in Fig. 10(a). As silicates composed by SiO_4 tetrahedron which combined a half by covalency, the cation of Si was bonded hard as shown in Fig. 10(c). So, as the rattling effects are reduced, the dielectric constant is small, which is suitable for millimeter wave dielectrics. The dielectric constant of rutile TiO_2 is about 10, although the structure composed by TiO_6 octahedra. As the octahedra of Al_2O_3 occupied by 2/3 by Ti atoms as shown in Fig. 10(b), Ti ions occupied two adjacent octahedra repulse to the corner of octahedron each other. So, the rutile shows medium dielectric constants.

III) Temperature coefficient of resonant frequency (*TCf*)

The *TCf* is defined as following equation:

$$TCf = (f_T - f_{ref})/f_{ref}(T - T_{ref}) \text{ ppm/}^{o}\text{C} \quad (1)$$

Here, f_T and f_{ref} (GHz) are resonant frequencies on the temperature T, and the reference temperature T_{ref}, respectively. $T_{ref} = -40$ °C and $T = 85$ °C on JIS R 1627-1996[36]. The *TCf* is very difficult to estimate the value, but it is depending on the crystal structure. Reaney *et al.*[37] presented the relationship between temperature coefficient of dielectric constant ($TC\varepsilon$) and tolerance factor t, given by eq. (2) on the complex perovskite as shown in Fig. 11[38].

$$t = (R_A + R_O)/\sqrt{2}\ (R_B + R_O) \quad (2)$$

Here, R_A, R_B and R_O are ionic radii of A, B and O ions on ABO_3 perovskite, respectively. There is a relationship between *TCf* and $TC\varepsilon$ given by eq. (3).

$$TCf = -[\alpha + TC\varepsilon/2] \quad (3)$$

Here, α is a coefficient of thermal expansion. The t is affected by tilting of octahedron: the octahedron is untilted, in the range of t between 1.055 and 0.985, antiphase tilted in 0.964 and 0.985, and in phase and antiphase tilted in 0.964 and 0.92 as shown in Fig. 11. BMT and $Sr(Mg_{1/3}Nb_{2/3})O_3$ (SMN) located near zero $TC\varepsilon$ at $t = 1.033$ and 0.964, respectively. Solid solutions such as $Ba_xSr_{1-x}(Mg_{1/3}Ta_{2/3})O_3$ (BSMT) also show the same trend. In the case of pseudo-tungstenbronze with tilted octahedra, *TCf* of Sm-compound is minus as opposite to Nd-, Pr-, and La-compounds with plus *TCf*. Sm-Nd- and Sm-La-pseudo-tungstenbronze solid solutions yield near zero *TCf*[39]. As seen in these examples, the resonant frequencies are affected by tilting of octahedra. On the other hand, usually, near zero *TCf* achieved adding different compound with opposite sign of *TCf*, and the adding ratio is in inverse proportion to the *TCf*. The *TCf* should be considered on the resonation which is affected by tilting of octahedron, and volume of additional compound for reducing of *TCf*.

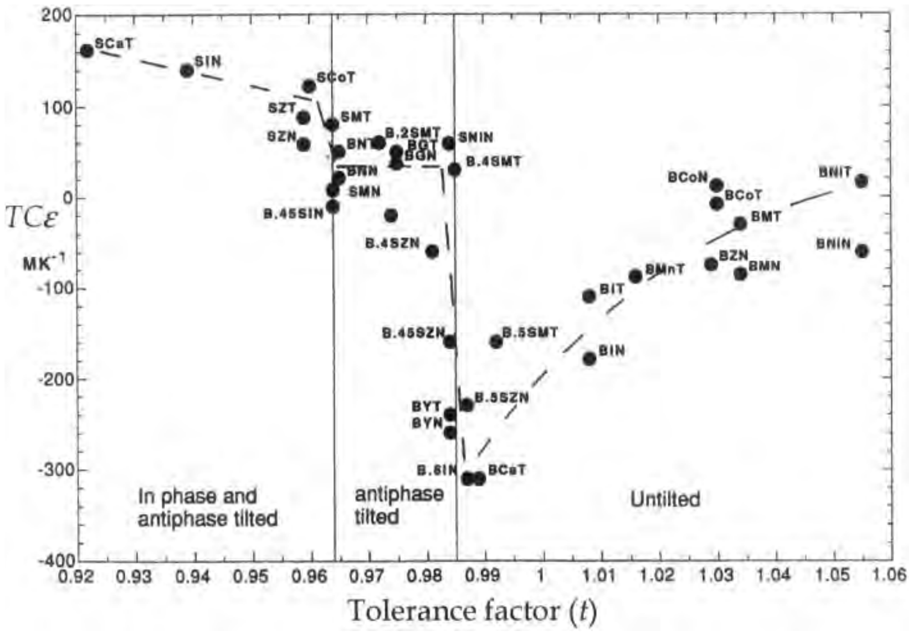

Fig. 11. The $TC\varepsilon$ as a function of tolerance factor t for Ba- and Sr-based complex perovskite[39].

SUMMARY

1) Compositional ordering and high symmetry yield high Qf which indicate the perfect crystal. And as defects and impurity degrade the perfect crystal, Qf should be reduced. As grain growth without rough microstructure is transient state to single crystal, it brings high Qf.

2) The pseudo-tungstenbronze solid solutions with high dielectric constant of 80 to 90 have asymmetric large unit. Tilting of octahedron also affects the dielectric constant. Rattling effects in polyhedra such as TiO_6 octahedron and Al_2O_3, and SiO_4 tetrahedron.

3) The temperature coefficient of resonant frequency might be considered on the resonation which is affected by tilting of octahedron, and volume of additional compound for reducing of TCf.

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