

# Temperature Coefficient of Dielectric Constant in $\text{CaTiO}_3\text{-A}(\text{B}', \text{B}'')\text{O}_3$ Microwave Dielectric Ceramics (A=Ca, La, Li, B'=Al, Fe, Mg, B''=Nb, Ta)

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## ABSTRACT

The dielectric polarizability-related factors contributing to the  $\tau_\epsilon$  have been analysed in terms of dielectric permittivity  $\epsilon$ , Tolerance Factor (TF), and octahedron tilt angles in  $(1-x)\text{CaTiO}_3\text{-}x[\text{A}(\text{B}', \text{B}'')\text{O}_3]$  (A=Ca, La, Li, B'=Al, Fe, Mg, B''=Nb, Ta) and  $(\text{Sr}_{0.2}\text{Ca}_{0.8})_{1-x}\text{Zr}_x\text{O}_3$ . All the compounds have the orthorhombic Pbnm structure except the end members  $\text{A}(\text{B}', \text{B}'')\text{O}_3$  and the solid solutions of  $x \geq 0.8$ . The additional dipole field effect is suggested as a dominant factor contributing to  $\tau_\epsilon$  in  $\text{CaTiO}_3$ -based ceramics having relatively large  $\epsilon$ , which has not been generally considered in the previous reports dealing with the  $\tau_\epsilon$ . This study has been focussed on delineating the dipole field effect on the  $\tau_\epsilon$  in comparison to the octahedron tilt effect in  $\text{CaTiO}_3$ -based ceramics.

**Key words:** Temperature coefficient of dielectric constant, Crystal structure, Dipole field effect, Octahedron tilt angle,  $\text{CaTiO}_3$ -based perovskite

## 1. Introduction

Considerable amount of studies have been reported concerning the relation among the dielectric permittivity ( $\epsilon$ ), temperature coefficient of permittivity ( $\tau_\epsilon$ ), and crystal structure.<sup>1-7)</sup> The typical structure-related factors considered in the previous studies are Tolerance Factor (TF) and octahedron tilting especially in  $\text{ABO}_3$  perovskite ceramics.<sup>8-10)</sup>

Regarding the relation between the TF and the  $\tau_\epsilon$ , Reaney *et al.*<sup>6)</sup> has provided a prototypical guidance for understanding of perovskite materials. The type of octahedron tilt systems determines the overall scheme of the variation of  $\tau_\epsilon$ . And even within the same regime of tilt system, the  $\tau_\epsilon$  depends on the TF. Several reports also have confirmed the relation between the tilt system and the  $\tau_\epsilon$ .<sup>11-17)</sup>

The other important structure-related factor can be the Lorentz local field,<sup>8,9)</sup> which has not been taken into consideration in most papers. The Lorentz local field factor is not constant through perovskite lattice points but greatly enhanced at B and O1 sites due to the structurally noncubic point symmetry environment at these sites. Since the enhanced Lorentz local field originates from the interaction between the electronic and ionic polarizabilities in these sites, slight change of electronic polarizability by ionic substitution for the B-site can reduce critically the Lorentz local field. The magnitude of Lorentz local field can be material-

ized as the measurable dielectric permittivity  $\epsilon$  as described by Slater.<sup>8)</sup>

The enhanced Lorentz local field can be described as an additional dipole field to the value of  $\frac{P}{3}\epsilon_0$ , which is the dipole field of a simple cubic lattice of dipoles at one of its lattices. The effect of this additional dipole field on the  $\tau_\epsilon$  has been discussed by Wersing.<sup>4)</sup> This study is focussed on delineating the effect of the additional dipole field of Lorentz local field on the  $\tau_\epsilon$  in comparison to the effect of crystal structure-related factors, the TF and octahedron tilt.

The well known form of temperature coefficient of dielectric permittivity  $\tau_\epsilon$  derived by Bosman and Havinga<sup>1)</sup> in cubic ionic compounds is as followings.

$$\begin{aligned} \tau_\epsilon &= \frac{(\epsilon-1)(\epsilon+2)}{3\epsilon} \left[ \frac{1}{\alpha} \left( \frac{\partial \alpha}{\partial T} \right)_v + \frac{3v}{\alpha} \left( \frac{\partial \alpha}{\partial v} \right)_T \alpha_l - 3\alpha_l \right] \\ &= \frac{(\epsilon-1)(\epsilon+2)}{3\epsilon} (A+B+C) \end{aligned} \quad (1)$$

Where,  $\alpha$ ,  $\epsilon$ , and  $v$  are polarizability, permittivity, and volume, respectively.

The effect of the additional dipole field on the polarizability and local electric field  $E_{loc}$  have been studied by Slater<sup>8)</sup> and Heywang.<sup>9)</sup> Wersing<sup>4)</sup> added the additional dipole field effect term into the Eq. (1) as followings.

$$\begin{aligned} \tau_\epsilon &= \frac{(\epsilon-1)(\epsilon+2)}{3\epsilon} (A+B+C-k\Delta\alpha \alpha_l) \\ &= \frac{(\epsilon-1)(\epsilon+2)}{3\epsilon} (A+B+C+D) \end{aligned} \quad (2)$$

$\Delta\alpha$  is the additional polarizability due to the dipole field effect and  $k$  is proportionality factor. The  $\Delta\alpha$  increases and

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makes  $\tau_e$  be more negative value. As the  $\Delta\alpha$  reaches a critical value the dielectric property changes to a ferroelectric.

The crystal structure is one of the most dominating factors influencing the temperature coefficient of polarizability [term  $A$  in Eq. (1)].<sup>1,2,4)</sup> However, some of the previous papers dealing with the relation between either the  $\tau_e$  or temperature coefficient of polarizability ( $A$ ) and the TF showed quite inconsistent results compared to what has been suggested by Reaney *et al.*<sup>6)</sup> and other reports.<sup>5,7)</sup> The next two cases in the followings briefly show the necessity of the dipole field effect for rationalizing this inconsistency.

The first case is that the temperature coefficient of polarizability ( $A$ ) varies independently of the TF in the  $\text{Ca}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  and  $\text{SrZrO}_3$ , having the same Pbnm structure<sup>17)</sup>; the temperature coefficient of polarizabilities of  $\text{CaZrO}_3$  and  $\text{SrZrO}_3$  were in the range of  $0 \sim +10$  ppm/ $^\circ\text{C}$ , while those of  $\text{Ca}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  and  $(\text{Sr}_{0.2}\text{Ca}_{0.8})(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$  were about  $-30 \sim -40$  ppm/ $^\circ\text{C}$  irrespective of TF values. The second exceptional case is observed in Table 1, that shows several different groups of Ca-based perovskite ceramics. The groups of I & II show a decrease of  $\tau_e$  with an increase of TF, while the groups III & IV show a decrease of  $\tau_e$  with a decrease of TF. The microwave dielectric properties in Table 1 were taken from the previous reports<sup>10,15,16,17)</sup> and TF values were calculated using the ionic radii by Muller *et al.*<sup>26)</sup> The groups I & II follow the well-known structure- $\tau_e$  relation. But, group III & IV show the opposite behavior to groups I & II. These observations imply that the TF and the octahedron tilting

could not be the dominant factors controlling  $\tau_e$  in these Ca-based perovskites.

The additional dipole field effect on  $\tau_e$  can be exemplified by considering the relations between the  $\tau_e$  and TF in Table 1. We consider only the terms  $A$  and  $D$  since the sum ( $E + C$ ) is known to be nearly constant. According to the structure- $\tau_e$  relation by Joseph *et al.*<sup>7)</sup> and Reaney<sup>6)</sup> the decrease of TF, hence the increase of tilt angle, should result in a positive  $\tau_e$  in  $\text{CaTiO}_3$ -type materials. The  $\tau_e$  of the groups I and II (Table 1) follows this relation. However, it is not clear whether the term  $A$  is actually dominant compared to the term  $D$ , because the term  $D$  becomes less negative with the increase of  $x$ .

Contrarily to the groups I & II, the  $\tau_e$  of the groups III & IV becomes more positive values with an increase of TF. Comparing the TF's of CFN, CFT(0.975), CAT, and CAN (0.98) in groups III & IV to those of  $\text{CaTiO}_3$ (0.968) and  $\text{Ca}(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$ (0.942) in group II, it can be found that the former compounds having larger TF (CFT, CAT, and CAN) show the positive  $\tau_e$ , while the latter having smaller TF [ $\text{CaTiO}_3$  and  $\text{Ca}(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$ ] have the large and negative  $\tau_e$ . Therefore, the variations of  $\tau_e$ 's with TF in Table 1 cannot be explained simply by the structure- $\tau_e$  relation, but by the additional polarizability  $\Delta\alpha$  originating from the dipole field effect in Eq. (2).

Table 2 shows the essential idea of this study based on this discussion. Two series of  $\text{CaTiO}_3$ -based ceramics prepared in this study. The TF values of the solid solutions in the

**Table 1.** Tolerance Factor (TF), Temperature Coefficient of Dielectric Constant  $\tau_e$ , and  $\epsilon$  of  $\text{Ca}^{2+}$  and ( $\text{A}^{+1}\text{Ln}^{+3}$ )-based Microwave Ceramics

Group	Compounds	Tolerance factor	$\tau_e$ (ppm/ $^\circ\text{C}$ )	$\epsilon$	Reference
I	$(\text{Sr}_{0.2}\text{Ca}_{0.8})\text{TiO}_3$	0.973	-1375	202	17
	$(\text{Sr}_{0.2}\text{Ca}_{0.8})(\text{Ti}_{0.6}\text{Zr}_{0.4})\text{O}_3$	0.952	-945	125	
	$(\text{Sr}_{0.2}\text{Ca}_{0.8})(\text{Ti}_{0.2}\text{Zr}_{0.8})\text{O}_3$	0.931	-284	52	
	$(\text{Sr}_{0.2}\text{Ca}_{0.8})\text{ZrO}_3$	0.921	+67	31	
II	$\text{CaTiO}_3$	0.968	-1754	175	10
	$\text{Ca}(\text{Zr}_{0.4}\text{Ti}_{0.6})\text{O}_3$	0.942	-1375	118	
	$\text{Ca}(\text{Zr}_{0.8}\text{Ti}_{0.2})\text{O}_3$	0.925	-549	49	
	$\text{CaZrO}_3$	0.91	+45	27	
III	$\text{Ca}(\text{Al}_{1/2}\text{Nb}_{1/2})\text{O}_3$	0.980	+154	25	16
	$\text{Ca}(\text{Fe}_{1/2}\text{Nb}_{1/2})\text{O}_3$	0.975	+132	40	
	$\text{Ca}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$	0.945	+136	26	
	$\text{Ca}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$	0.941	+76	28	
	$\text{Ca}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3$	0.936	+66	35	
	$\text{Ca}(\text{Ca}_{1/3}\text{Nb}_{2/3})\text{O}_3$	0.900	+24	28	
IV	$\text{Ca}(\text{Al}_{1/2}\text{Ta}_{1/2})\text{O}_3$	0.980	+160	20	16
	$\text{Ca}(\text{Fe}_{1/2}\text{Ta}_{1/2})\text{O}_3$	0.975	+158	32	
	$\text{Ca}(\text{Ni}_{1/3}\text{Ta}_{2/3})\text{O}_3$	0.945	+140	22	
	$\text{Ca}(\text{Mg}_{1/3}\text{Ta}_{2/3})\text{O}_3$	0.941	+102	21	
	$\text{Ca}(\text{Zn}_{1/3}\text{Ta}_{2/3})\text{O}_3$	0.936	+112	25	
	$\text{Ca}(\text{Ca}_{1/3}\text{Ta}_{2/3})\text{O}_3$	0.900	+62	22	
V	$(\text{Na}_{1/2}\text{La}_{1/2})\text{TiO}_3$	0.959	-980	122	15
	$(\text{Na}_{1/2}\text{Sm}_{1/2})\text{TiO}_3$	0.919	-400	79	
	$(\text{Li}_{1/2}\text{Pr}_{1/2})\text{TiO}_3$	0.825	+790	92	
	$(\text{Li}_{1/2}\text{Sm}_{1/2})\text{TiO}_3$	0.816	+500	52	
-	$0.6(\text{La}_{1/3}\text{Nd}_{1/3})\text{TiO}_3-0.4\text{CaTiO}_3$	0.846	-410	102	
	$(\text{Li}_{1/2}\text{Nd}_{1/2})\text{TiO}_3$	0.821	+568	75	
	$\text{La}(\text{Mg}_{2/3}\text{Nb}_{1/3})\text{O}_3$	0.919	+112	26	

**Table 2.** Two Series of CaTiO<sub>3</sub>-based Solid Solution Systems Prepared in This Study: The Tolerance Factor in Series I (CT-CMN, CT-LMN) is Expected to Decrease with *x*, While in Series II (CT-CAN, CT-CAT) is Expected to Increase with *x*

Solid solution system	Characteristic change of dielectric property and structure-related terms with increase of <i>x</i>
Series I	$\epsilon \downarrow, \tau_\epsilon \uparrow, TF \downarrow, A \uparrow, D \uparrow$
Series II	$\epsilon \downarrow, \tau_\epsilon \uparrow, TF \uparrow, A \downarrow, D \uparrow$

<sup>†</sup> $\downarrow, \uparrow$ : Decrease and increase of the each properties with *x*.  
<sup>‡</sup>*A, L* are the terms given in Eq. (2).

Series I [(1-x)CT-x(CMN, LMN, CZ)] [LMN=La(Mg<sub>2/3</sub>Nb<sub>1/3</sub>)O<sub>3</sub>] are expected decrease with *x*, while those of in the series II [(1-x)CT-x(CAN, CAT, CFN)] are expected increase with *x*. The series II is very rare and unique in the aspect that the TF of CAN, CAT, and CFN are larger or nearly equal to that of CT so that tilt angles are expected to decrease with *x*. In both series, the  $\epsilon$  reflecting the Lorentz local field decreases to 20~40 as *x* reaches 1.

The importance of dipole field effect (term *D*) compared to the crystal structure effect (term *A*) in Eq. (2) is depicted in a qualitative manner by calculating and plotting the  $\epsilon$ ,  $\tau_\epsilon$ , TF, and the sum *M* (*A+B+C+D*) of several types of CaTiO<sub>3</sub>-based ceramics having the same Pbnm structure in this study.

## 2. Experimental

Three CaTiO<sub>3</sub>-based solid solution systems i.e., (1-x)CT-xCAN, (1-x)CT-xLMN, and (1-x)CT-xCMN, have been prepared by solid state reaction method using chemically pure (typically 99.9%) CaCO<sub>3</sub>, TiO<sub>2</sub>, MgO, Nb<sub>2</sub>O<sub>5</sub>, La<sub>2</sub>O<sub>3</sub>, and Al<sub>2</sub>O<sub>3</sub>. The CAT and (Sr<sub>0.2</sub>Ca<sub>0.8</sub>)(Ti<sub>1-x</sub>Zr<sub>x</sub>)O<sub>3</sub> were prepared only for the x-ray diffraction analysis. The raw materials were mixed into the compositional formular shown above and calcined at 1100°C for 3 h. The mixed powder added

with PVA was pressed into discs with 12 mm dia. and sintered in temperature range of 1500~1600°C for 3 h. X-ray data were collected using CuK $\alpha$  (1.5417 Å) with 0.02° step scan. The crystal structures were refined using DBWS9411 Rietveld program.<sup>18)</sup> The octahedron tilt angles about the structural axes were calculated using the relation between unit cell lengths and tilt angles ( $\alpha$ ,  $\beta$ , and  $\gamma$ ) pertaining to *c* or  $\alpha^*c^*$  tilt system according to Glazer's description.<sup>19)</sup> In the calculations, *a*<sub>o</sub>, *b*<sub>o</sub>, and *c*<sub>o</sub> were chosen in the same way as mentioned in the work by Ahtee *et al.*<sup>20)</sup> Relative dielectric constant  $\epsilon$  were measured by Hakki Colemann method. The temperature coefficient of resonant frequency was measured at -20°C and 60°C. The microwave dielectric properties of the other CaTiO<sub>3</sub>-based systems, such as CT-CAT, CT-CFN, CT-LaNT [(La<sub>1/3</sub>Nd<sub>1/3</sub>)O<sub>3</sub>], and CST [Ca<sub>1-x</sub>Sm<sub>2x/3</sub>TiO<sub>3</sub>]-LiNT [(Li<sub>1/2</sub>Nd<sub>1/2</sub>)TiO<sub>3</sub>] were obtained from the previously reported papers.<sup>11,22-25)</sup>

## 3. Results and Discussion

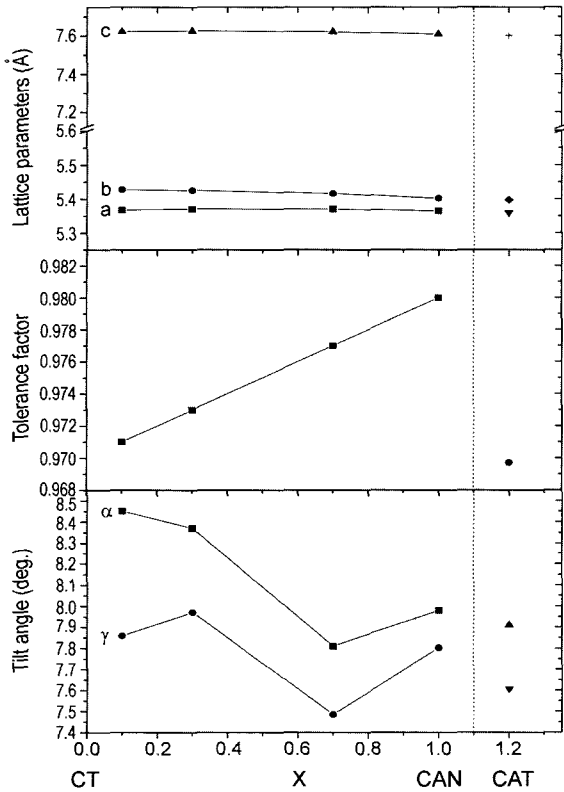
### 3.1. Crystal Structure Analysis

Crystal structures of the end members, CAN, CAT, CFN and CMN, have not been known clearly. The crystal structure of Ca<sub>2</sub>B'B''O<sub>6</sub> (B'=trivalent, B''=pentavalent ions) can be considered as either a monoclinic (*a*≠*b*≈3.9 Å,  $\beta$ ≈90.5°) or an orthorhombic structure (*a*≠*b*≈5.5 Å, *c*≈3.9 or 7.8 Å). Kagata *et al.*<sup>16)</sup> indexed the XRD pattern of CFN based on the orthorhombic CaTiO<sub>3</sub> structure. In this study, crystal structure and the tilt angles of the end members and their solid solution have been analysed using the Rietveld refinement.

Table 3 shows the results of structural refinements for CAN and CAT. The monoclinic P2<sub>1</sub>/n model produced more reliable results than the orthorhombic Pbnm. The solid solution (1-x)CT-xCAN showed a structural transition from the orthorhombic Pbnm to the monoclinic P2<sub>1</sub>/n at *x*≥0.8. The XRD patterns of other solid solution systems (1-x)CT-x

**Table 3.** Refined Crystal Structural Parameters of the CAN and CAT

Sample	Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occup.	<i>B</i> <sub>iso</sub>
CAT	Ca	0.5040(24)	0.5276(7)	0.2478(7)	1.0	1.005(109)
	Al/Ta	0.50	0	0	0.4722/0.0278(09)	0.654
	Ta/Al	0	0	0	0.5/0	0.441(085)
	O <sub>1</sub>	0.2891(23)	0.2773(21)	0.0197(42)	1.00	0.002(645)
	O <sub>2</sub>	0.2264(25)	0.8002(29)	0.0330(39)	1.0	0.831(628)
	O <sub>3</sub>	0.5787(25)	0.9852(21)	0.2557(22)	1.0	0.200(372)
Monoclinic P2 <sub>1</sub> /n, Z=4, <i>a</i> =5.3592(42), <i>b</i> =5.3970(42), <i>c</i> =7.6002(59), $\beta$ =90.04(49) <i>R</i> <sub>p</sub> =6.65, <i>R</i> <sub>wp</sub> =9.21, <i>R</i> <sub>f</sub> =6.45						
CAN	Ca	0.4913(16)	0.5252(6)	0.251(8)	1.0	1.766(8)
	Al/Nb	0.5	0	0	0.3848(3)/0.1152(3)	0.6512
	Nb/Al	0	0.5	0	0.3573(3)/0.1427(3)	0.651
	O <sub>1</sub>	0.2943(20)	0.2682(16)	0.0348(31)	1.0	-0.609(56)
	O <sub>2</sub>	0.2318(18)	0.8027(26)	0.4050(03)	1.0	0.955(71)
	O <sub>3</sub>	0.5746(9)	0.9848(21)	0.2646(02)	1.0	0.760(29)
Monoclinic P2 <sub>1</sub> /n, Z=4, <i>a</i> =5.3646(7), <i>b</i> =5.4016(7), <i>c</i> =7.6079(10), $\beta$ =89.98(1) <i>R</i> <sub>p</sub> =12.03, <i>R</i> <sub>wp</sub> =16.89, <i>R</i> <sub>f</sub> =9.79						



**Fig. 1.** Lattice parameters, tolerance factor, and tilt angles with  $x$  in  $(1-x)\text{CT}-x\text{CAN}$ .

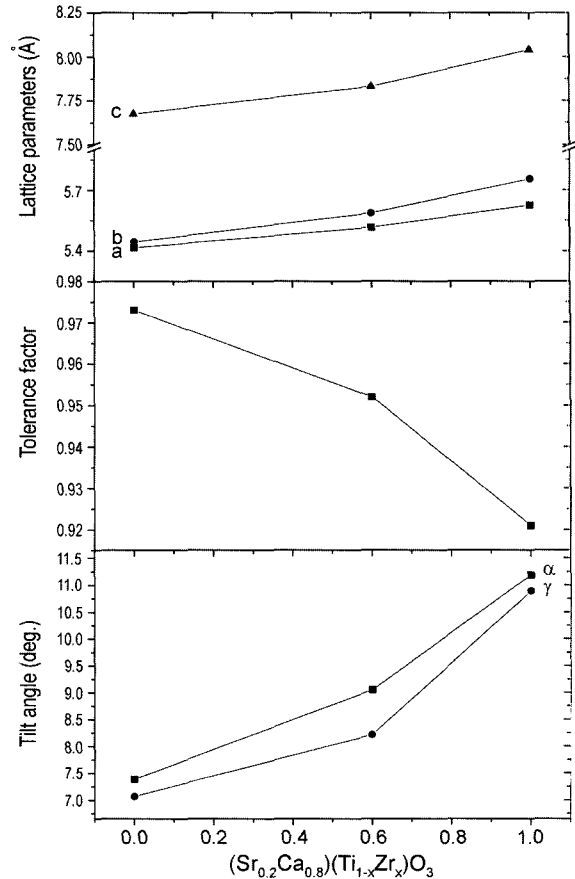
[CAT, LMN, CFN, CMN] showed a similar structural transition to the monoclinic with increase of  $x$ . The other end members, LMN and CFN could be refined by either the  $\text{P2}_1/\text{n}$  or the  $\text{Pbnm}$  model.<sup>21</sup> The B-site splits into two distinct positions and becomes ordered structure of the  $\text{P2}_1/\text{n}$ . The degree of ordering of the B-sites in CAT is larger than CAN as shown in Table 3.

Figs. 1 and 2 show the lattice parameters, Tolerance Factor (TF), and octahedron tilt angles of  $(1-x)\text{CT}-x\text{CAN}$  and  $(1-x)(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3-x(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{ZrO}_3$  solid solutions. The octahedron tilt angles follow Glazer's description. As shown in Table 1, CAN, CAT, and CFN are very rarely found compounds which have larger TF than that of CT. Hence, the tilt angles of the  $(1-x)\text{CT}-x\text{CAN}$  decrease with  $x$ . The decrease of octahedron tilt angles conforms to the TF increase with  $x$ . The other systems,  $(1-x)\text{CT}-x[\text{CAT}, \text{CFN}]$  are also expected to show the same trends with  $x$ .

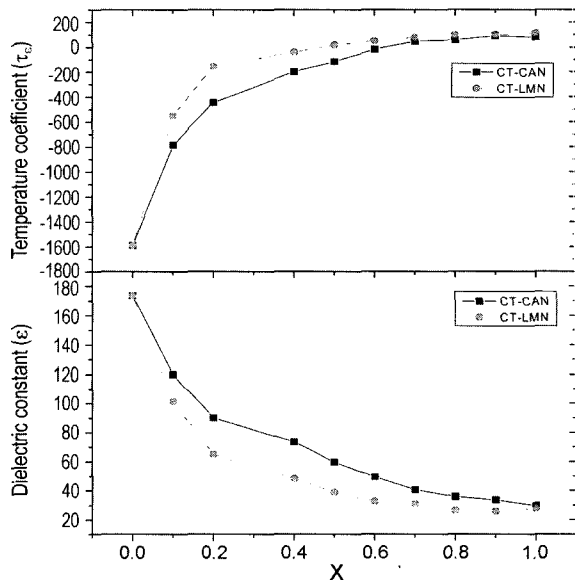
On the contrary, in  $(1-x)(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{TiO}_3-x(\text{Ca}_{0.8}\text{Sr}_{0.2})\text{ZrO}_3$  (Fig. 2) the TF and the tilt angles varied in opposite way to that of Fig. 1. The solid solutions  $(1-x)\text{CT}-x[\text{CMN}, \text{LaNT}, \text{LMN}]$  and  $\text{CST-LiNT}$  are also expected to show the same behavior as shown in Fig. 2, since the TF values of CMN, LaNT, and LMN are smaller than that of CT.

### 3.2. Temperature Coefficient of Dielectric Constant $\tau_\epsilon$

Fig. 3 shows the  $\tau_\epsilon$  and  $\epsilon$  with  $x$  in the  $(1-x)\text{CT}-x$  [CAN, LMN]. The  $\tau_\epsilon$  becomes positive values with the decrease of  $\epsilon$ . Fig. 4 shows the variation of the sum  $M$  ( $A+B+C+D$ ) in



**Fig. 2.** Lattice parameters, tolerance factor, and tilt angles with  $x$  in  $(\text{Sr}_{0.2}\text{Ca}_{0.8})(\text{Ti}_{1-x}\text{Zr}_x)\text{O}_3$ .



**Fig. 3.** Variation of temperature coefficient of dielectric constant  $\tau_\epsilon$  and  $\epsilon$  with  $x$  in  $(1-x)\text{CT}-x(\text{CAN}, \text{LMN})$ .

Eq. (2) for both the series I (CT-CMN, CT-LMN) and II (CT-CAT, CT-CAN) in relation with TF. The sum  $M$  ( $A+B+C+D$ ) is calculated using the data in Fig. 3 and the previously reported paper.<sup>11, 22-25</sup> Except the compounds of  $x \geq 0.8$ ,

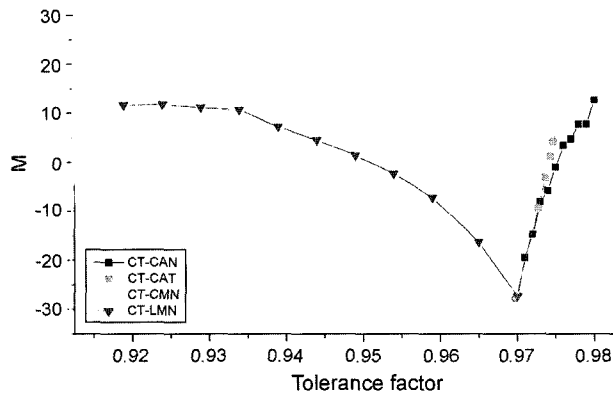


Fig. 4. The calculated  $M$  ( $A+B+C+D$ ) of the  $(1-x)\text{CT}-x(\text{CAN}, \text{CAT}, \text{CMN}, \text{LMN})$  plotted in relation to tolerance factor.

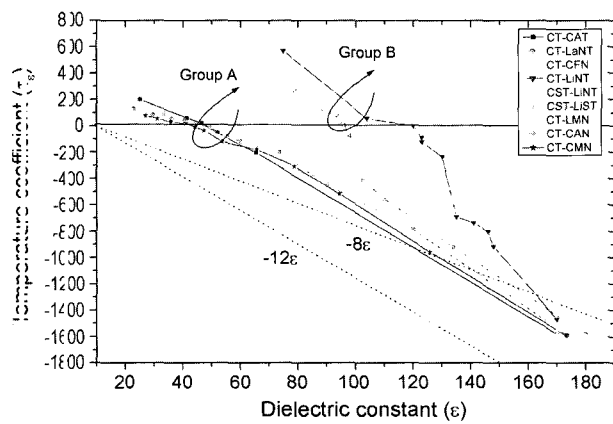


Fig. 5. The temperature coefficient ( $\tau_T$ ) of the CaTiO<sub>3</sub>-based microwave dielectric ceramics plotted as a function of  $\epsilon$ .

all the compounds have the orthorhombic Pbnm structure. The  $\tau_T$  of the CT-CAT are selected from the previously reported paper.<sup>11</sup> Fig. 4 shows that the  $M$  values does not have any relation with TF as expected in the introduction regarding the additional dipole field. The minimum point at  $\text{TF}=0.97$  simply corresponds to CT. Considering that most of the samples in Fig. 4 except the end members near the left-side and right-side has the same Pbnm crystal structure, there cannot be found any consistent trend in the variation of  $M$  values with TF among the four solid solution system.

The  $\tau_T$  (ppm/°C) as a function of the  $\epsilon$  are plotted in Fig. 5. All the compounds plotted in Fig. 5 have the Pbnm structure except the end members, such as CMN, LMN, CAN, CAT, and LiNT<sup>15</sup> and the solid solutions of  $x \geq 0.8$ . The two dotted lines represent the simple relation  $\tau_T = -\alpha_T \epsilon$  ( $\alpha_T = 8$  or  $12$  ppm). Only the CT and CST lie inside the two boundary lines. The other solid solutions substantially deviate from the simple relation. The compounds containing Li-ion (group B, such as CST-LiNT, CT-LiNT, and CST[Ca,Sm]TiO<sub>3</sub>]-LiST [Li<sub>1/2</sub>Sm<sub>1/2</sub>]TiO<sub>3</sub>) show more drastic deviation with a decrease of  $\epsilon$ .

Fig. 6 shows the variation of the  $M$  with epsilon replotted

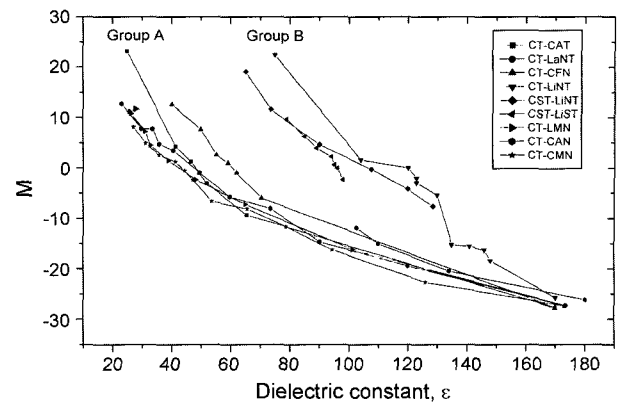


Fig. 6. The calculated  $M$  ( $A+B+C+D$ ) of the CaTiO<sub>3</sub>-based microwave dielectric ceramics plotted in relation to  $\epsilon$ .

using the data in Fig. 5. The  $M$  varies in the range of about  $-25 \sim +20$ . All of the solid solution systems in the series I (CT-CMN, CT-LMN) and II (CT-CAN, CT-CAT) in Table 2 belong to the group A in Fig. 5. The TF and tilt angles of the series I vary in opposite way to the series II. This means that the term  $A$  in the series I varies in opposite direction to that of the series II with  $x$  and  $\epsilon$ . Considering that the sum of  $(B+C)$  remains nearly constant of about  $+10 \sim +20$  ppm/K, the term  $D$  in both series can be judged to have a dominant effect rather than the term  $A$ . This result is the very expected one in the introduction.

An approximate relationship between the  $M$  and  $\epsilon$  can be obtained for the group A as followings:  $M = 421.7 - 7.94\epsilon - 0.023\epsilon^2$ . This relation suggests that both the  $M$  and  $\tau_T$  are mainly determined by the term  $D$  if the dielectrics have the same crystal structure as the CaTiO<sub>3</sub>-based compounds even though they have substantially different TF and tilt angles.

The sum  $M$  becomes negative values at  $\epsilon=40$  in the group A (CT-CMN, CT-LMN, CT-CAN, and CT-CAT) in Fig. 5 and at  $\epsilon=80$  in the group B (CT-LiNT, CST-LiNT, and CST-LiST). This implies that the sum of the three terms ( $A+B+C$ ) in the CaTiO<sub>3</sub>-based dielectric compounds is positive value in nature. And with the increase of the term  $D$  corresponding to the dipole field effect increases in a negative way the sum  $M$  ( $A+B+C+D$ ) becomes negative values. Most of the microwave dielectric compounds having near zero  $\tau_T$  show the  $\epsilon$  values in the range of  $25 \sim 45$ , such as BZT, BMT, ZST, and Ba<sub>2</sub>Ti<sub>9</sub>O<sub>20</sub>.<sup>41</sup> The compounds of the group B containing Li-ions, BNT [BaONd<sub>2</sub>O<sub>3</sub>4TiO<sub>2</sub>] of a tungsten bronze type,<sup>22</sup> and (Pb, Ca)ZrO<sub>3</sub> are exceptional case because they have zero  $\tau_T$  at  $\epsilon > 80$ . These exceptional properties are considered to originate from the characteristic features of small radius of Li ion and structural difference.<sup>15)</sup>

## 4. Conclusions

The crystal structures, temperature coefficient of dielectric constant ( $\tau_T$ ), and dipole field effect on the  $\tau_T$  have been analyzed in the complex perovskites and their solid solu-

tions with CT. The complex perovskite end members i.e., CAN, CAT, CFN, and LMN, are the monoclinic  $P2_1/n$ . The latter two compounds, CFN and LMN can be also described by the orthorhombic Pbnm model with nearly the same level of reliability. The crystal structures change to the orthorhombic Pbnm at  $0.8 \leq x$ .

The sum of the four terms  $M (A + B + C + D)$  contributing to the temperature dependence of the dielectric permittivity becomes positive at  $30 > \epsilon$  in the  $\text{CaTiO}_3$ -based perovskites (group A) and at  $80 > \epsilon$  in the Li-containing compounds (group B). The  $\text{CaTiO}_3$ -based compounds of large  $\epsilon$  have large negative value of  $M$  due to the large additional dipole field effect (term  $D$ ). The phenomenological relation between the  $\epsilon$  and the sum  $M (A + B + C + D)$  was  $M = 421.7 - 7.94\epsilon - 0.023\epsilon^2$ . The dipole field effect term  $D$  dominates the change of  $M$  in the solid solutions of both the group A and group B. The structural effect term  $A$  i.e., the effect of octahedron tilt angle was completely overwhelmed by the term  $D$  in the same Pbnm structure. The results of this study is a phenomenological but could provide a principal guide for predicting the property of other solid solution ceramics.

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