

Contribution of Structure to Temperature Dependence of Resonant Frequency in the $(1 - x)La(Zn_{1/2}Ti_{1/2})O_3 \cdot xATiO_3$ (A = Ca, Sr) System

Seo-Yong Cho,[†] Hyuk-Joon Youn,[†] Hyo-Jong Lee,^{*,‡} and Kug Sun Hong[†]

School of Materials Science and Engineering, Seoul National University, Seoul, 151-742, Korea and

Micro-Radiowave Technology, Ltd., Seoul, 150-010, Korea

The crystal structure and microwave dielectric properties of the (1 - x)La(Zn_{1/2}Ti_{1/2})O₃:xSrTiO₃ and (1 - x)La(Zn_{1/2}Ti_{1/2})-O₃:xCaTiO₃ system were investigated. X-ray powder diffraction showed that cation ordering disappeared at x > 0.3 for both systems. However, infrared spectra demonstrated that short-range cation ordering could exist at x = 0.4. Permittivity and the temperature coefficient of the resonant frequency (τ_f) of both systems exhibited nonmonotonic variations with composition. Both systems exhibited a $\tau_{\rm f}$ of zero at the same composition of x = 0.5 although the τ_f of SrTiO₃ was about two times larger than that of CaTiO₃. The behavior of the permittivity and $\tau_{\rm f}$ were described by the tilting of oxygen octahedra and cation ordering. The relation between $\tau_{\rm f}$ and cation ordering of La(Zn_{1/2}Ti_{1/2})O₃ was discussed in conjunction with the experimental results on metal halides. It is suggested that cation ordering induced a negative $\tau_{\rm f}$ and suppressed the increase of permittivity for compositions between x = 0 to x = 0.5for $(1 - x)La(Zn_{1/2}Ti_{1/2})O_3$:xSrTiO₃ and $(1 - x)La(Zn_{1/2}Ti_{1/2})$ -O3:xCaTiO3 systems.

I. Introduction

THE dielectric properties of perovskite compounds are strongly I related to their structural characteristics, such as cation ordering and the orientation of the oxygen octahedra.^{1,2} Recently, complex perovskites and their solid solutions were investigated and found to be promising dielectrics for microwave applications.^{3,4} Dielectric materials for microwave applications should, in general, satisfy three conditions: high permittivity, low dielectric loss, and small temperature coefficient of resonant frequency ($\tau_{\rm f}$). These properties can be understood in terms of the structural characteristics. The permittivity of dielectrics can be calculated using the Clausius–Mossotti relation and additivity rule;⁵ however, structural factors, such as cation compression or rattling, can induce a difference between the calculated and measured permittivity.^{5,6} Cation ordering has a great effect on the dielectric loss and phase transition characteristics of complex perovskites.¹

 $\tau_{\rm f}$ is mainly determined by the temperature coefficient of permittivity $(\tau_{\varepsilon})^3 \tau_{\varepsilon}$ can be divided into three terms: A, B, and $C^{7-9}A$, B, and C terms are related to a decrease in the number of polarizable particles per unit volume as the temperature increases, the increase of the polarizability of a constant number of particles with the increase of temperature, and the dependence of polarizability on temperature with constant volume, respectively. The C

term depends on the structure of the compound.⁷ In the case of perovskites, compounds having a tilt of the oxygen octahedra appear to exhibit a positive $\tau_{e}^{,10}$ For example, the correlation between the tilt of oxygen octahedra and τ_{ϵ} was investigated for $(Ba,Sr)(Mg_{1/3}Ta_{2/3})O_3$ and $(Ba,Sr)(Zn_{1/3}Nb_{2/3})O_3$ systems.^{2,11} The sign and magnitude of τ_{ϵ} changed rapidly near the composition at which antiphase tilting appeared. $Sr(Zn_{1/3}Nb_{2/3})O_3$, which has octahedral tilting, shows positive τ_{ϵ} , while Ba(Zn_{1/3}Nb_{2/3})O₃ without tilting exhibits a negative τ_{ϵ} .² Such coincidence between positive τ_{ϵ} and octahedral tilting was also found in several $A^{2+}B^{4+}O_3$ type complex perovskites compounds.¹² It is suggested that the existence of octahedral tilting reduces the restoring force and makes the C term less negative.¹⁰ More recently, a short-range modulation of the crystal structure rather than a change in oxygen octahedral tilting was suggested as the origin of the τ_{e} and the permittivity variation in the (Ba,Sr)(Zn_{1/3}Nb_{2/3})O₃ system.13

Structurally, tilting of oxygen octahedra has similar effects as cation ordering in 1:1 type complex perovskites. These factors result in doubled unit cells and face-center symmetry.¹ Hence, if the C term is affected by octahedral tilting because of a structural change, then it is also possible that cation ordering could induce a positive τ_{ϵ} . However, the relation between cation ordering and τ_{ϵ} (or τ_f) is still unclear.

 $La(Zn_{1/2}Ti_{1/2})O_3$ (LZT) is a promising microwave dielectric material with a dielectric constant of 34 and low dielectric loss (tan $\delta < 10^{-4}$ at 6 GHz), but its large $|\tau_f| > 50~ppm/^\circ C$ requires modification for applications as a dielectric resonator. 14 SrTiO $_3$ (ST) and CaTiO₃ (CT) have a positive τ_f , so mixing LZT with ST and CT is expected to adjust the τ_f of LZT near zero. The above-mentioned relation between octahedral tilting and τ_f does not apply to CaTiO₃. That is, CaTiO₃ has inphase and antiphase octahedral tilting, but its τ_f is positive.¹⁰ In a structural aspect, ST is cubic but CT is orthorhombic with octahedra tilting. LZT has cation ordering and octahedral tilting. Therefore, when the LZT-ST system is compared to LZT-CT system, their structural changes with composition should be quite different. It is the purpose of this article to discuss the relation between structure and microwave dielectric properties of LZT-ST and LZT-CT. In particular, the behavior of $\tau_{\rm f}$ is discussed in terms of cation ordering.

II. Experimental Procedure

Powders of $(1 - x)La(Zn_{1/2}Ti_{1/2})O_3-xSrTiO_3$ and (1 - x)- $La(Zn_{1/2}Ti_{1/2})O_3 - xCaTiO_3$ with compositions from x = 0 to 1 were prepared using the conventional mixed oxide method. La_2O_3 , CaCO₃, SrCO₃, ZnO, and TiO₂ with high purity (>99.9%) were weighed and mixed for 24 h with stabilized ZrO₂ media and ethyl alcohol. The mixed powders were calcined at 1200°C for 2 h and then ball-milled for 24 h. The milled powders were pressed into disks 8 mm in diameter and 2-4 mm thick under a pressure of 1000 kg/cm². Pellets were sintered at 1550°C for 2 h in air.

X-ray diffraction (XRD, Model M18X, Mac Science, Tokyo) data was collected using $CuK\alpha$ radiation and a graphite monochromator in the 2θ range of 10° – 60° . Step scanning was used with a

H. Chan-contributing editor

Manuscript No. 189487. Received March 18, 1999; approved January 28, 2000. Supported by the Korea Science and Engineering Foundation (KOSEF) through the Research Center for Thin Film Fabrication and Crystal Growing of Advanced Materials (RETCAM) at Seoul National University.

Member, American Ceramic Society. School of Materials Science and Engineering, Seoul National University. [‡]Micro-Radiowave Technology.

step size of 0.005° and a count time 1 s/step to investigate the existence of $\frac{1}{2}$ (111) superlattice reflections. For infrared (IR) reflectivity measurement, samples were ground and polished using 1 μ m diamond paste. IR reflectivity in the 30–4000 cm⁻¹ range was measured using FTIR spectroscopy (Model DA8-12, BOMEM, Canada). The reflectivity spectra were evaluated by means of standard Kramers–Kronig analysis.

Microwave dielectric properties of sintered samples were measured using a network analyzer (Model 8720C, Hewlett Packard, Palo Alto, CA). Permittivity was measured using the post-resonator method.¹⁵ An Invar cavity was used for the measurement of the temperature coefficient of resonant frequency because of its low thermal expansion coefficient ($< 2 \text{ ppm/}^{\circ}$ C).

III. Results

(1) X-ray Diffraction Analysis

In Fig. 1, XRD patterns of the $(1 - x)La(Zn_{1/2}Ti_{1/2})O_3$ xSrTiO₃ [LZT-ST] samples are shown. The reflections were indexed on the basis of the doubled pseudocubic perovskite subcell. Several superlattice reflections were observed in the XRD pattern of $La(Zn_{1/2}Ti_{1/2})O_3$. The origin of each superlattice reflection was explained in the previous paper.¹⁶ $\frac{1}{2}$ (111) superlattice reflections were due to the cation ordering in $La(Zn_{1/2}Ti_{1/2})O_3$. $^{1\!\!/_{\!\!2}}(\mathbf{311})$ and $^{1\!\!/_{\!\!2}}(\mathbf{310})$ reflections resulted from antiphase and inphase tilting of the oxygen octahedra, respectively.¹⁷ From the XRD patterns in Fig. 1, approximate structure changes were suggested and listed in Table I. 1/2 (111) superlattice reflections disappeared at x > 0.3, which indicated that cation ordering was disrupted at compositions of x > 0.3, however, short-range cation ordering could exist at x > 0.3 since the XRD method is generally sensitive to long range ordering. Figure 2 shows the variation with composition of $\frac{1}{2}$ (111) and $\frac{1}{2}$ (210) superlattice reflections of LZT-ST system in more detail.

Figure 3 shows the XRD pattern of the $(1 - x)La(Zn_{1/2}Ti_{1/2})$ -O₃- $xCaTiO_3$ [LZT-CT] system. Superlattice reflections were also found but their variation with composition was quite different from those of the LZT-ST system, that is, $\frac{1}{2}$ (210), $\frac{1}{2}$ (311), and $\frac{1}{2}$ (310) reflections existed in the entire range of composition.



Fig. 1. XRD patterns of the (1 - x)La $(Zn_{1/2}Ti_{1/2})O_3$ -xSrTi O_3 system.

Table I. Approximate Structure Change in $(1 - x)La(Zn_{1/2}Ti_{1/2})O_3 - xSrTiO_3^{\dagger}$

	Cation	Cation	Inphase	Antiphase
	ordering	displacement	tilting	tilting
	½ (111)	¹ / ₂ (210)	½ (310)	½ (311)
$0 \le x \le 0.3 \\ 0.3 < x \le 0.5 \\ 0.5 < x \le 0.9$	Х	X X	X X	X X X

[†]Based on XRD data only.



Fig. 2. $\frac{1}{2}$ (111) and $\frac{1}{2}$ (210) superlattice reflections of (1 - x)La(Zn_{1/2}-Ti_{1/2})O₃-xSrTiO₃ system ((a) x = 0.2, b) x = 0.3, c) x = 0.4, d) x = 0.5, e) x = 0.6).

Table II shows the approximate structure change in the LZT–CT system. This difference was related to the fact that $CaTiO_3$ has a distorted structure with tilting of oxygen octahedra and cation displacements, whereas $SrTiO_3$ had an ideal cubic structure.¹⁷ The $\frac{1}{2}$ (**111**) reflection disappeared at x > 0.3, as it did in the LZT–ST system.

The dielectric properties of perovskites have been explained by the tilt scheme of oxygen octahedra.^{2,10,12} If the tilt scheme of oxygen octahedra determines the τ_f of the LZT–ST and LZT–CT systems, then the dielectric behaviors of the LZT–CT and LZT–ST systems should exhibit different trends with compositions.

(2) Microwave Dielectric Properties

Figures 4 and 5 show the permittivity and the $\tau_{\rm f}$ of the LZT–ST and LZT–CT systems, respectively. The trend of permittivity variation with composition can be described using the mixture rule, i.e., $1/\varepsilon_{\rm total} = v_1/\varepsilon_1 + v_2/\varepsilon_2$ where v_i and ε_i are the volume fractions and permittivity of each phase *i*, respectively.¹⁶ The dotted line in the figures of permittivity indicates the calculated values. As can be seen in the figure, calculated values coincide with the measured values. The variation of $\tau_{\rm f}$ with composition also shows mixturelike behavior.

It is interesting that the dielectric behaviors with composition of the LZT–ST and LZT–CT systems exhibit similar trends. The $\tau_{\rm f}$ of CaTiO₃ is ~600 ppm/°C, less than half of the value for SrTiO₃



Fig. 3. XRD patterns of the (1 - x)La $(Zn_{1/2}Ti_{1/2})O_3$ -xCaTiO₃ system.

Table II. Approximate Structure Change in $(1 - x)La(Zn_{1/2}Ti_{1/2})O_3-xCaTiO_3^{\dagger}$

	Cation	Cation	Inphase	Antiphase
	ordering	displacement	tilting	tilting
	¹ / ₂ (111)	¹ / ₂ (210)	½ (310)	½ (311)
$0 \le x \le 0.3$ $0.3 < x \le 1$	Х	X X	X X	X X

[†]Based on XRD data only.

(> 1100 ppm/°C). However, the composition having a zero $\tau_{\rm f}$ value is the same, x = 0.5, for the two systems. The $\tau_{\rm f}$ values of LZT–ST system in the composition range from x = 0 to x = 0.5 do not change significantly, i.e. from -52 ppm/°C to 0 ppm/°C, whereas those from $x = 0.5 \sim 1$ exhibit a rapid increase from 0 ppm/°C to 1100 ppm/°C. This indicates that certain factors suppressed the increase of $\tau_{\rm f}$ in the composition range from x = 0 to x = 0.5.

(3) Far-IR Spectroscopy

Far-infrared spectroscopy work was done on the LZT–ST and LZT–CT samples to examine the short-range structure variation. Figure 6 shows the reflectivity spectra for the LZT–ST system. In the case of simple perovskite structures (*Pm3m*), three IR active modes were observed, as can be seen in the IR spectra of SrTiO₃ (x = 1) in Fig. 6. The lowest-frequency mode corresponded to A—BO₃ translations, the second mode to BO₆ bending, and the third mode corresponded to B—O₆ stretching.¹⁸ The IR spectra of LZT were more complex than that of ST. Several new modes could be found in the range from 200 to 500 cm⁻¹. The general shape of the spectra did not change within the composition range from x = 0 to x = 0.5. Figure 7 shows the results of Kramer–Kronig analysis. Existence of modes between 200 and 500 cm⁻¹ was found at x = 0.5.

The exact mode assignment of LZT was beyond the scope of this work but possible reasons for some modes could be suggested by considering the IR spectra and XRD patterns together. Structurally, LZT has three additional characteristics compared to ST:



Fig. 4. Permittivity and $\tau_{\rm f}$ of the $(1-x)La(Zn_{1/2}Ti_{1/2})O_3\text{-}xSrTiO_3$ system.

cation ordering, cation displacement, and tilting of oxygen octahedra. Cation ordering and octahedral tilting are known to induce extra modes in the IR spectra.11 Through the comparison of BaZrO₃ (cubic) and SrZrO₃ (orthorhombic with octahedra tilting), it is suggested that the appearance of the additional infrared active mode at $\sim 300 \text{ cm}^{-1}$ is a common characteristic of the perovskite compounds with tilted oxygen octahedra.¹¹ The mode assignment of the ordered Ba $(B'_{1/2}B''_{1/2})O_3$ (Fm3m) was recently suggested.¹⁹ According to the authors, modes in the $280-320 \text{ cm}^{-1}$ range were assigned to B' - B'' stretching and the strength of this mode was used as a measure for the degree of B-site ordering. Considering these works, the new modes found in LZT between 200 and 500 cm^{-1} could be related to cation ordering and tilting of oxygen octahedra. These modes were found at $0 \le x \le 0.5$, which indirectly indicates that short-range cation ordering might exist at x = 0.4, although an unambiguous interpretation of each mode cannot be provided yet.

Figure 8 depicts the IR spectra of LZT–CT system. The lowest-frequency mode at 150 cm⁻¹ corresponds to Ca—TiO₃ translations, the second mode at 180 cm⁻¹ to Ti—O₆ stretching, the resonance mode at 440 cm⁻¹ to Ti—O₃ torsion, and the resonance mode at 550 cm⁻¹ to BO_6 bending.¹⁸ The modes between 200 and 500 cm⁻¹ exhibited nearly the same tendency as those in LZT–ST system within the composition between x = 0 and x = 0.5. This phenomenon was confirmed by the results of Kramer–Kronig analysis shown in Fig. 9. If the modes between 200 and 500 cm⁻¹ were originated by only oxygen octahedra tilting, then the modes should be found at x > 0.5 because $\frac{1}{2}$ (**310**) and $\frac{1}{2}$ (**311**) superlattice reflections were found at x > 0.5 in the XRD pattern of Fig. 3.

Consequently, from the XRD and IR results, it can be said that cation ordering existed within the composition range of x = 0 to x = 0.5 in the LZT–ST and LZT–CT system.



Fig. 5. Permittivity and $\tau_{\rm f}$ of the $(1-x)La(Zn_{1/2}Ti_{1/2})O_3\text{--}xCaTiO_3$ system.

IV. Discussion

Temperature coefficient of resonant frequency (τ_f) is given by the equation $\tau_f = -(\alpha + \tau_{e'}2)$ where α is the linear thermal expansion coefficient and τ_e the temperature coefficient of permittivity.³ In the case of ceramics, τ_f is directly influenced by τ_e since the magnitude of α is generally constant and insignificant compared to that of τ_e , τ_e is composed of three terms: *A*, *B*, and *C*:⁷

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

The *A* and *B* terms indicate the direct effect of volume expansion due to a temperature increase, and the *C* term represents a dependence of the polarizability on temperature with a constant volume. A relative magnitude of the *C* term to (A + B) generally determines the sign and magnitude of τ_{e} .^{2,7} Literature on metal halides and oxides shows that the *C* term depends on the structure of the compounds rather than composition.^{7,8} For example, halides having CsCl structure (*Pm3m*) have a negative τ_{e} and those having NaCl structure (*Fm3m*) exhibit a positive τ_{e} .

Perovskite structures can be described by three components: tilting of anion octahedra, displacements of cations, and distortions of the octahedron.¹⁷ Cation ordering should be added in the case of complex perovskites. Among these components, only the tilting of oxygen octahedra have been investigated in conjunction with τ_{e} .^{2,11,20} For example, in the case of Ba_{1-x}Sr_x(Zn_{1/3}Nb_{2/3})O₃ system, the sign of τ_{e} changes from negative to positive when the structure changes from an untilted structure to a tilted structure.

Three structural components were commonly found in the LZT–ST and LZT–CT system, but their variations with compositions were quite different. In the case of the LZT–ST system, the sign of τ_f changed at x = 0.5 and the $\frac{1}{3}$ (**310**) superlattice reflections, showing in phase octahedra tilting, also disappeared at this composition, as shown in Fig. 4 and Table I. That is, the



Fig. 6. Infrared reflectivity spectra of the $(1 - x)La(Zn_{1/2}Ti_{1/2})O_3 - xSrTiO_3$ system.

coincidence of the tilted structure and sign change of τ_e was found in the LZT–ST system. However, in contrast to the case of the LZT–ST system, in phase and antiphase octahedra tilting existed in the entire range of compositions for the LZT–CT system, so the sign change of τ_f could not be related to the tilting of oxygen octahedra. In fact, as mentioned earlier, the criterion of oxygen octahedral tilting could not be applied to CaTiO₃ itself because it has a positive τ_f with octahedra tilting. These results imply that there could be another factor controlling the τ_f of the LZT–CT system. In addition, it is very important that the sign of τ_f changes at the same composition (x = 0.5) for LZT–ST and LZT–CT system, despite of the large difference in the τ_f values between ST and CT. This meant that the τ_f of the LZT–CT systems at the composition of $x \le 0.5$ was determined by a certain structural property of LZT.

Then, what structural features changed near x = 0.5 for the two systems? Through a comparison of Tables I and II, cation displacement can be ruled out at x = 0.5 because the $\frac{1}{2}$ (**210**) reflection was found at x > 0.5 in the LZT–CT system, whereas it disappeared at >0.5 in the LZT–ST system. Cation ordering disappeared at the same composition of x > 0.3 for the two systems, but the τ_f of the two systems changed at x = 0.5. However, the structure classifications in Tables I and II are based on XRD results and IR spectra in Figs. 6–9 demonstrated that short-range ordering could exist at $0.3 < x \le 0.5$ and disappeared at x > 0.5. This indicates that cation ordering should be considered as a critical factor which could determine the sign of τ_f .

The question of interest is how $\tau_{\rm f}$ or $\tau_{\rm e}$ can be associated with cation ordering. Structurally, cation ordering in 1:1-type perovskites such as Pb(Sc_{1/2}Ta_{1/2})O₃ (PST) has two effects. First, the cation ordering in PST induces a doubled unit cell with face-centered symmetry.¹ That is, ordered PST has *Fm3m* symmetry and disordered PST exhibits *Pm3m*. Second, cation ordering in PST reduces the space for the rattling of the Pb²⁺ cation.²¹ These two effects can be related to the variation of $\tau_{\rm e}$.

(A) Effect of Symmetry Change: Cation ordering in LZT induces a symmetry change from Pm3m to Fm3m. In the case of metal halides, the symmetry change is matched to the variation of



Fig. 7. Infrared conductivity spectra $\sigma(\omega)$ obtained from Kramer–Kronig analysis for the LZT–ST system.

the sign of the *C* term and τ_{e} , as is the case for NaCl and CsCl. Their composition and permittivities are almost the same but the sign of τ_{e} is opposite.⁸ The space group of CsCl is *Pm3m* and that of NaCl is *Fm3m*. The effect of symmetry on τ_{e} is more evident for RbBr.⁸ It has the NaCl structure and a positive τ_{e} under normal conditions. This transforms to the CsCl structure at high pressure and the τ_{e} also changes to a negative value. This relation between structure and τ_{e} is applicable to the LZT–CT and LZT–ST systems. That is, the disappearance of cation ordering of LZT at x = 0.5 resulted in a symmetry change from *Fm3m* to *Pm3m*, and τ_{e} changes from positive to negative (τ_{f} changes from negative to positive value) at the same composition.

(B) Effect of Compression: Most perovskite compounds exhibit a constant value of the (A + B) term.² Therefore, the sign and magnitude of τ_e is determined by the magnitude of the *C* term. The origin of the *C* term is explained by an ion moving in a potential well.⁸ As temperature increases, the restoring force constant (f) increases because the ions move from a potential minimum to a displaced position. The magnitude of the *C* term decreases as the restoring force increases, since the polarizability is proportional to 1/f.

It was reported that the ordering of cations with different sizes reduces the rattling space for cations, compared to a disordered state.²¹ Differences in rattling space between ordered and disordered states increases with the size difference of the cations. The ion size of Zn^{2+} and Ti^{4+} is 0.74 and 0.605 Å,²² respectively, and the size difference is ~22%. This indicates that cations in ordered LZT are under stress, compared to those in the disordered state. Therefore, the magnitude of the *C* term in the ordered state could be smaller than that in the disordered state, which means the sign of τ_{e} of an ordered LZT is dominated by the (*A* + *B*) term and is therefore positive.



Fig. 8. Infrared reflectivity spectra of the $(1 - x)La(Zn_{1/2}Ti_{1/2})O_3 - xCaTiO_3$ system.

The hypothesis of reduced rattling space could also explain the behavior of permittivity in the LZT–ST and LZT–CT systems at 0 < x < 0.5. Permittivity of oxides at microwave frequencies can be calculated using Clausius—Mossotti relations and ion additivity rules⁵ but several compounds showed discrepancies between the measured and calculated values.^{6,23} Properties of the compounds such as ionic or electronic conductivity, ferroelectricity, or cation compression/rattling were suggested as possible explanations.^{5,6} For example, the measured permittivity of La(Mg_{1/2}Ti_{1/2})O₃ and LnAlO₃ (Ln = lanthanide) were much smaller than the calculated values.^{6,23} This phenomenon was explained by cation compression. In the case of LZT–ST and LZT–CT systems, the degree of increase of permittivity is much smaller at 0 < x < 0.5 than those at 0.5 < x < 1. This can be explained by the reduced rattling space with the cation ordering at 0 < x < 0.5.

Considering the above explanations, how can the cation ordering in the LZT–ST and LZT–CT systems be maintained at x = 0.5? The solid solution between a complex perovskite and a simple perovskite has been widely studied. Typical examples are Ba(Zn_{1/3}-Ta_{2/3})O₃–SrTiO₃, Ba(Mg_{1/3}Ta_{2/3})O₃–BaSnO₃, and Pb(Sc_{1/2}Ta_{1/2})-O₃–PbTiO₃.^{24–26} In all these cases, cation ordering is disrupted by the small addition, a few mole percent, of a simple perovskite. In this experiment, cation ordering was found even with the addition of several tens of percent. The maintenance of cation ordering in LZT–CT and LZT–ST systems can be explained as follows.

First, 1:1-type cation ordering is generally an easier process than 1:2-type ordering. For example, ordering of $Ba(Mg_{1/3}Ta_{2/3})$ - O_3 is hard to achieve.²⁷ This system needs more than a 10 h annealing at 1600°C. Cation ordering of LZT has been found in the samples sintered even at 1300°C for 2 h, which means that the cation ordering of LZT is less sensitive to the addition of foreign atoms than that of $Ba(Mg_{1/3}Ta_{2/3})O_3$. Second, the charge difference between the two B-site cations $(Zn^{2+} \text{ and } Ti^{4+})$ is not changed when $CaTiO_3$ or $SrTiO_3$ has been added to LZT. The driving forces for cation ordering are the size and valence difference between cations.²⁸ In the case of $Pb(Sc_{1/2}Ta_{1/2})O_3$ -PbTiO₃, introducing Ti⁴⁺ onto the shared $Sc^{3+} + Ta^{5+}$ B-site reduces the valence difference between B-site ions. However, in



Fig. 9. Infrared conductivity spectra $\sigma(\omega)$ obtained from Kramer–Kronig analysis for the LZT–CT system.

the case of LZT–CT and LZT–ST systems, the valence difference in B-site ions does not change with increasing CT and ST contents, so the driving force for ordering could be maintained.

V. Conclusion

The behavior of permittivity and $\tau_{\rm f}$ in $(1 - x){\rm La}({\rm Zn}_{1/2}{\rm Ti}_{1/2}){\rm O}_3-x{\rm SrTiO}_3$ and $(1 - x){\rm La}({\rm Zn}_{1/2}{\rm Ti}_{1/2}){\rm O}_3-x{\rm CaTiO}_3$ was discussed in conjunction with structural changes. Dielectric properties of both systems exhibited mixturelike behavior, which was characterized as suppressed increase of permittivity and $\tau_{\rm f}$ in the composition range 0 < x < 0.5. The composition at which the sign of $\tau_{\rm f}$ changed was x = 0.5 for both systems. XRD results showed that cation ordering disappeared at x > 0.3 for both systems, but IR spectra demonstrated that short-range cation ordering were suggested as the determining factor for the sign of $\tau_{\rm f}$ in ${\rm La}({\rm Zn}_{1/2}{\rm Ti}_{1/2}){\rm O}_3$ -based perovskite systems. Effects of cation ordering on $\tau_{\rm e}$ may be understood in terms of the symmetry change and the reduced space for cation rattling.

References

¹N. Setter and L. E. Cross, "The Contribution of Structural Disorder to Diffuse Phase Transitions in Ferroelectrics," *J. Mater. Sci.*, **15**, 2478–82 (1980).

²E. L. Colla, I. M. Reaney, and N. Setter, "Effect of Structural Changes in Complex Perovskites on the Temperature Coefficient of the Relative Permittivity," *J. Appl. Phys.*, **74**, 3414–25 (1993).

³W. Wersing, "High Frequency Ceramic Dielectric and Their Application for Microwave Components"; pp. 67–119 in *Electronic Ceramics*, Edited by B. C. H. Steele. Elsevier, New York, 1991.

⁴M. Furuya and A. Ochi, "Microwave Dielectric Properties for $Ba(Mg_{1/3}Ta_{2/3})O_3$ " $A(Mg_{1/2}Ta_{1/2})O_3$ (A = Ba, Sr, and Ca) Ceramics," *Jpn. J. Appl. Phys.*, **33**, 5482–87 (1994).

⁵R. D. Shannon, "Dielectric Polarizabilities of Ions in Oxides and Fluorides," J. Appl. Phys., **73**, 348–66 (1993).

⁶V. J. Fratello and C. D. Brandle, "Calculation of Dielectric Polarizabilities of Perovskite Substrate Materials for High-Temperature Superconductors," *J. Mater. Res.*, **9**, 2554–60 (1994).

⁷A. J. Bosman and E. E. Havinga, "Temperature Dependence of Dielectric Constants of Cubic Ionic Compounds," *Phys. Rev.*, **129**, 1593–1600 (1963).

⁸E. E. Havinga and A. J. Bosman, "Temperature Dependence of Dielectric Constants of Crystals with NaCl and CsCl Structure," *Phys. Rev.*, **140**, A292–A302 (1965).

⁹G. A. Samara, "Temperature and Pressure Dependence of the Dielectric Constants of the Thallous Halides," *Phys. Rev.*, **165**, 959–69 (1968).

¹⁰R. C. Kell, A. C. Greenham, and G. C. E. Olds, "High-Permittivity Temperature-Stable Ceramic Dielectrics with Low Microwave Loss," *J. Am. Ceram. Soc.*, **56**, 352–54 (1973).

¹¹T. Nagai, M. Sugiyama, M. Sando, and K. Niihara, "Anomaly in the Infrared Active Phonon Modes and Its Relationship to the Dielectric Constant of $(Ba_{1-x})Sr_x(Mg_{1/3}Ta_{2/3})O_3$ Compound," *Jpn. J. Appl. Phys.*, **35**, 5163–67 (1996).

¹²I. M. Reaney, E. L. Colla, and N. Setter, "Dielectric and Structural Characteristics of Ba- and Sr-based Complex Perovskites as a Function of Tolerance Factor," *Jpn. J. Appl. Phys.*, 33, 3984–90 (1994).
¹³J. S. Kim, J. H. Lee, Y. S. Lim, J. W. Jang, and I. T. Kim, "Revisit to the

¹³J. S. Kim, J. H. Lee, Y. S. Lim, J. W. Jang, and I. T. Kim, "Revisit to the Anomaly in Dielectric Properties of (Ba₁₋₃Sr_x)(Zn_{1/3}Nb_{2/3})O₃ Solid Solution System," *Jpn. J. Appl. Phys.*, **36**, 5558–61 (1997).

¹⁴S. Y. Cho, M. K. Seo, K. S. Hong, and S. J. Park, "Influence of ZnO Evaporation on the Microwave Dielectric Properties of La(Zn_{1/2}Ti_{1/2})O₃," *Mater. Res. Bull.*, **32**, 725–35 (1997).

¹⁵B. W. Hakki and P. D. Coleman, "A Dielectric Resonator Method of Measuring Inductive Capacities in the Millimeter Range," *IRE Trans. Microwave Theory Tech.*, [July] 402–10 (1960).

¹⁶S. Y. Cho, I. T. Kim, and K. S. Hong, "Crystal Structure and Microwave Dielectric Properties of (1 - x)La(Zn_{1/2}Ti_{1/2})O₃-xSrTiO₃ System" *Jpn. J. Appl. Phys.*, **37**, 593–96 (1998).

¹⁷A. M. Glazer, "Simple Ways of Determining Perovskite Structures," *Acta Crystallogr., Sect. A*, A31, 756–61 (1975).

¹⁸C. H. Perry, D. J. McCarthy, and G. Rupprecht, "Dielectric Dispersion of Some Perovskite Zirconates," *Phys. Rev.*, **138**, A1537–A1538 (1965).

¹⁹I. M. Reaney, J. Petzelt, V. V. Voitsekhovskii, F. Chu, and N. Setter, "B-site Order and Infrared Reflectivity in A(B'B")O₃ Complex Perovskite Ceramics," *J. Appl. Phys.*, **76**, 2086–92 (1994).

²⁰V. Sivasubramanian, V. R. K. Murthy, and B. Viswanathan, "Microwave Dielectric Properties of Certain Simple Alkaline Earth Perovskite Compounds as a Function of Tolerance Factor," *Jpn. J. Appl. Phys.*, **36**, 194–97 (1997).

²¹K. Uchino, L. E. Cross, R. E. Newnham, and S. Nomura, *J. Phase Transitions*, **1**, 333 (1980).

²²R. D. Shannon, "Revised Effective Ionic Radii and Systematic Studies of Interatomic Distances in Halides and Chalcogenides," *Acta Crystallogr., Sect. A*, A32, 751–67 (1976).

²³R. Guo, A. S. Bhalla, R. Roy, and L. E. Cross, "Ion Polarizability Additivity Rule and Its Application on HTSC Substrate Materials," *Ferroelectrics*, **155**, 43–48 (1994).

²⁴H. Matsumoto, H. Tamura, and K. Wakino, "Ba(Mg,Ta)O₃·BaSnO₃ High-Q Dielectric Resonator," Jpn. J. Appl. Phys., **30**, 2347–49 (1991).

²⁵H. Tamura, T. Konoike, Y. Sakabe, and K. Wakino, "Improved High-*Q* Dielectric Resonator with Complex Perovskite Structure," *J. Am. Ceram. Soc.*, **67**, C59–C61 (1984).

 26 J. R. Giniewicz, A. S. Bhalla, and L. E. Cross, "An Investigation of the Structural and Dielectric Properties of the Solid Solution System $(1 - x)Pb(Sc_{1/2}Ta_{1/2})O_3-xPbTiO_3,"$ *Ferroelectr. Lett. Sect.*, **12**, 35–42 (1990).

 $^{27}R.$ Guo, A. S. Bhalla, and L. E. Cross, "Ba(Mg_{1/3}Ta_{2/3})O₃ Single Crystal Fiber Grown by the Laser Heated Pedestal Growth Technique," *J. Appl. Phys.*, **75**, 4704–08 (1994).

²⁸N. Setter and L. E. Cross, "The Role of *B*-site Cation Disorder in Diffuse Phase Transition Behavior of Perovskite Ferroelectrics," *J. Appl. Phys.*, **51**, 4356–60 (1980).