Relationship between tolerance factor and temperature coefficient of permittivity of temperature-stable high permittivity BaTiO₃–Bi(Me)O₃ compounds

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The temperature coefficient of permittivity (TC ϵ) of BaTiO₃–Bi(Me)O₃ solid solutions were investigated. It was determined that as the tolerance factor was decreased with the addition of Bi(Me)O₃, the TC ϵ shifted from large negative values to TC ϵ values approaching zero. It is proposed that the different bonding nature of the dopant cation affects the magnitude and temperature stability of the permittivity. This study suggests that the relationship between tolerance factor and TC ϵ can be used as a guide to design new dielectric compounds exhibiting temperature-stable high permittivity characteristics, which is similar to past research on perovskite and pyrochlore-based microwave dielectrics.

Keywords: Tolerance factor; temperature coefficient of permittivity; dielectric; temperature stable; titanate perovskite.

1. Introduction

The perovskite (ABO₃) structure is well known to exhibit excellent electrical properties that make it suitable for a variety of electronic applications. Most importantly, the electrical properties can be engineered via chemical modifications in order to obtain insulating, semiconducting, and conducting characteristics.^{1–5} In the perovskite structure, the tolerance factor (t) is often used to determine the structural stability, which can be calculated from Eq. (1).

$$t = \frac{R_A + R_O}{\sqrt{2}(R_B + R_O)}, \quad (1)$$

where R_A , R_B , and R_O are the ionic radii of A-cation, B-cation, and oxygen ion, respectively. For ideal cubic perovskites such as SrTiO₃ the tolerance factor equals 1.00. Stable perovskites with noncubic symmetry can be obtained when the tolerance factor deviates from 1.00. For example, BaTiO₃ with a tolerance factor of 1.06 exhibits tetragonal symmetry and CaTiO₃ with a tolerance factor of 0.97 exhibits orthorhombic symmetry. However, the perovskite structure is no longer stable when the tolerance factor greatly deviates from the ideal value ($t = 1.00$) such as for MgTiO₃ ($t = 0.81$), which is stabilized in the ilmenite structure.

The tolerance factor can also be applied to complex perovskites in which more than one cation occupies the A and/or

B sites (A'A'')(B'B'')O₃. Complex perovskites exhibit structural changes as predicted from the tolerance factor but additional improvement in the electrical properties can be observed.^{6–8} For example, the substitution of Zr onto the Ti-site of PbTiO₃ results in excellent piezoelectric properties in the widely used material Pb(Zr_{0.52}Ti_{0.48})O₃ (PZT).⁹ Substitution of Sr onto the Ba-site in BaTiO₃ results in a tunable dielectric capacitor (Ba,Sr)TiO₃ (BST).¹⁰ Lead-free piezoelectric ceramics with large piezoelectric coefficients can also be obtained in complex perovskites such as the Ba(Ti_{0.8}Zr_{0.2})O₃–(Ba_{0.7}Ca_{0.3})TiO₃ system.¹¹

Recent research has been focused on the development of high permittivity dielectrics with temperature-stable performance characteristics for capacitor applications requiring high temperatures (> 200°C). Complex perovskites based on BaTiO₃–Bi(Me)O₃ solid solutions have been found to be suitable candidates with promising electrical properties for compounds where the Me cation possesses an average charge of 3+. An increase in the mole content of Bi(Me)O₃ (with compounds such as Bi(Zn_{1/2}Ti_{1/2})O₃, Bi(Mg_{1/2}Ti_{1/2})O₃, Bi(Ni_{1/2}Ti_{1/2})O₃, BiScO₃) leads to an increase in the temperature stability of the permittivity at high temperatures.^{12–15} In particular, the BaTiO₃–Bi(Zn_{1/2}Ti_{1/2})O₃–BiScO₃ solid solution exhibits a temperature-stable high permittivity with ϵ_r greater than 1000 over the temperature range 100–400°C.^{16,17}

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This family of compounds ($\text{BaTiO}_3\text{--Bi(Me)O}_3$) exhibits weak relaxor ferroelectric behavior which governs the low-field and high-field dielectric behavior.¹⁵ The low-field (i.e., $E < 10$ kV/cm) dielectric response is characterized by a broad and diffuse temperature dependence of the permittivity. The high-field (i.e., $E > 10$ kV/cm) dielectric behavior shows a pseudo-linear dielectric response with a high permittivity and negligible saturation.

For capacitor applications, it is desirable to use dielectrics with temperature-stable permittivity characteristics, therefore the capacitor can be operated over a wide temperature range. The temperature coefficient of permittivity ($\text{TC}\epsilon$) is a useful characteristic for determining the temperature stability of dielectric materials and can be obtained from Eq. (2).

$$\text{TC}\epsilon = \frac{1}{\epsilon} \left(\frac{\partial \epsilon}{\partial T} \right). \quad (2)$$

In this work, the tolerance factor of the $\text{BaTiO}_3\text{--Bi(Me)O}_3$ system will be discussed and the low-field dielectric properties will be analyzed in terms of the temperature stability as defined by the $\text{TC}\epsilon$. The important relationship between the tolerance factor and $\text{TC}\epsilon$ will be discussed based on data obtained from the $\text{BaTiO}_3\text{--Bi(Me)O}_3$ compounds as well as relevant phenomenological theories.

2. Experimental Procedure

Solid solutions based on $\text{BaTiO}_3\text{--Bi(Me)O}_3$ are the focus of this study, including the solid solutions $\text{BaTiO}_3\text{--Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (BT-BZT), $\text{BaTiO}_3\text{--Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--BiInO}_3$ (BT-BZT-BI), $\text{BaTiO}_3\text{--Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--BiScO}_3$ (BT-BZT-BS), and $\text{BaTiO}_3\text{--Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--BiScO}_3\text{--NaNbO}_3$ (BT-BZT-BS-NN). The specific compositions selected for this study are listed in Table 1. All samples were prepared by using the solid state reaction technique.¹⁷ The dielectric data from previous studies were utilized for further analysis, including measurements at various frequencies from room temperature up

Table 1. Compositions and calculated tolerance factor (t) of $\text{BaTiO}_3\text{--Bi(Me)O}_3$ solid solutions.

Composition	t
0.80 $\text{BaTiO}_3\text{--}0.20\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$	1.0256
0.80 $\text{BaTiO}_3\text{--}0.10\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.10\text{BiInO}_3$	1.0192
0.75 $\text{BaTiO}_3\text{--}0.125\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.125\text{BiInO}_3$	1.0116
0.60 $\text{BaTiO}_3\text{--}0.20\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.20\text{BiScO}_3$	0.9943
0.55 $\text{BaTiO}_3\text{--}0.225\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.225\text{BiScO}_3$	0.9875
0.50 $\text{BaTiO}_3\text{--}0.25\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.25\text{BiScO}_3$	0.9807
0.70 $\text{BaTiO}_3\text{--}0.10\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.10\text{BiScO}_3\text{--}0.10\text{NaNbO}_3$	1.0249
0.60 $\text{BaTiO}_3\text{--}0.15\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.15\text{BiScO}_3\text{--}0.10\text{NaNbO}_3$	1.0114
0.50 $\text{BaTiO}_3\text{--}0.10\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.10\text{BiScO}_3\text{--}0.30\text{NaNbO}_3$	1.0060
0.50 $\text{BaTiO}_3\text{--}0.15\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.15\text{BiScO}_3\text{--}0.20\text{NaNbO}_3$	1.0019
0.45 $\text{BaTiO}_3\text{--}0.175\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.175\text{BiScO}_3\text{--}0.20\text{NaNbO}_3$	0.9951
0.40 $\text{BaTiO}_3\text{--}0.20\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.20\text{BiScO}_3\text{--}0.20\text{NaNbO}_3$	0.9883

to 500°C.^{17–19} The dielectric properties of these solid solutions exhibited a broad and diffuse dielectric peak and it was shown previously that minor modification by the introduction of Ba vacancies could improve the dielectric properties and insulation resistance of the materials.¹⁸ Thus, all compounds selected in this study were nominally A-site nonstoichiometric with a batch composition fixed at 0.02 mol Ba-deficient. The presence of A-site vacancies in the complex perovskite structure will be taken into account in the tolerance factor calculation. The ionic radii required for the calculations were obtained from the data of Shannon and Prewitt.²⁰ To determine the $\text{TC}\epsilon$, the permittivity data was selected over an appropriate temperature range for analysis. In this study, the common temperature range that exhibited a monotonic trend in permittivity for all compositions was above the temperature at which the permittivity was maximum (T_{max}), which was over the range of 100°C to 400°C. However, to avoid anomalous permittivity variations near T_{max} and at high temperatures due to conduction losses, the permittivity measured at 1 kHz over temperature range 200–400°C was chosen for calculating the $\text{TC}\epsilon$.

3. Results and Discussion

The tolerance factor of selected complex perovskite $\text{BaTiO}_3\text{--Bi(Me)O}_3$ compounds is shown in Table 1. Due to the relatively small cation size of Bi^{3+} (1.36 Å), it can be seen that Bi(Me)O_3 end-members have low values of the tolerance factor. For example, the tolerance factor values of $\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$, BiInO_3 and BiScO_3 are equal to 0.9417, 0.8871, and 0.9098, respectively, as compared to that of the BaTiO_3 end-member ($t = 1.0615$). Thus, with a decreasing mole fraction of BaTiO_3 or increasing mole fraction of Bi(Me)O_3 , the result is a decrease in the tolerance factor of the solid solution. In terms of ion size, the increase in concentration of larger B-cations (Zn^{2+} , In^{3+} , and Sc^{3+}) and the decrease in concentration of larger A-cation (Ba^{2+}) result in a lowering of the tolerance factor in $\text{BaTiO}_3\text{--Bi(Me)O}_3$. It is noted that the ionic radii of Ba^{2+} and Bi^{3+} occupying the 12-fold coordinated site are 1.61 Å and 1.36 Å, respectively, and the ionic radii of Ti^{4+} , Zn^{2+} , In^{3+} , and Sc^{3+} occupying six-fold coordinated site are 0.605, 0.740, 0.800, and 0.745 Å, respectively.^{20,21}

The tolerance factor of $\text{BaTiO}_3\text{--Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$, $\text{BaTiO}_3\text{--Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--BiInO}_3$, $\text{BaTiO}_3\text{--Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--BiScO}_3$, and $\text{BaTiO}_3\text{--Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--BiScO}_3\text{--NaNbO}_3$ compounds was varied from greater than 1 to lower than 1, which suggests a noncubic crystal structure. However, structural characterization by X-ray diffraction showed that the compounds exhibited a pseudocubic crystal structure, which could also be found in other related systems with similar tolerance factors, for example, $\text{BaTiO}_3\text{--BiScO}_3$,¹⁵ $\text{BaTiO}_3\text{--Bi(Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$,¹³ and $\text{BaTiO}_3\text{--Bi(Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$.¹⁴ In-depth structural characterizations of $\text{BaTiO}_3\text{--Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3$ by using high resolution synchrotron X-ray diffraction (HRXRD) and neutron pair distribution function (NPDF) techniques indicated that long-range structure of

the compounds are indeed pseudocubic, however, the local structure (nanoscale) was found to be noncubic. This is likely a common occurrence in $\text{BaTiO}_3\text{--Bi(Me)O}_3$ solid solutions. It can be seen that the structure suggested from tolerance factor considerations and the structure observed by using high resolution diffraction techniques were in a good agreement in considering short-range structure.

The $\text{TC}\epsilon$ of compounds listed in Table 1 was found to be in the range of $-2441 \text{ ppm}/^\circ\text{C}$ to $-182 \text{ ppm}/^\circ\text{C}$.¹⁷ As the concentration of the Bi(Me)O_3 component increased, the $|\text{TC}\epsilon|$ decreased reaching values close to zero indicating that compositions with high concentrations of Bi(Me)O_3 exhibited stable dielectric properties. In this case, the composition with the optimum $\text{TC}\epsilon$ was $0.50\text{BaTiO}_3\text{--}0.25\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.25\text{BiScO}_3$ with a value of $\text{TC}\epsilon = -182 \text{ ppm}/^\circ\text{C}$. It should be noted that this composition was near the solubility limit of this solid solution. Similar behavior was observed in the $\text{BaTiO}_3\text{--Bi(Me)O}_3$ system with different Bi(Me)O_3 end-members,^{12–16} however, $\text{TC}\epsilon$ values were not reported for these systems. The variation of $\text{TC}\epsilon$ as a function of tolerance factor of selected $\text{BaTiO}_3\text{--Bi(Me)O}_3$ compositions is shown in Fig. 1. A monotonic trend could be observed in which the $\text{TC}\epsilon$ values ($-2441 \text{ ppm}/^\circ\text{C}$ to $-182 \text{ ppm}/^\circ\text{C}$) approach zero as the tolerance factor decreased from 1.0256 to 0.9807. The pseudo-quaternary compounds of BT-BZT-BS- NaNbO_3 showed the same trend with the tolerance factor and the $\text{TC}\epsilon$, as shown in Fig. 1. It should be noted that BT-BMO labeled in Fig. 1 represents both pseudo-binary and pseudo-ternary compounds.

A dispersion of $\text{TC}\epsilon$ values could be observed for compositions exhibiting tolerance factor greater than 1.01. By comparing the $0.8\text{BT}\text{--}0.2\text{BZT}$ ($t = 1.0256$) and the $0.7\text{BT}\text{--}0.1\text{BZT}\text{--}0.1\text{BS}\text{--}0.1\text{NN}$ ($t = 1.0249$) compositions, the differences in the $\text{TC}\epsilon$ values could be due to the interruption of long range order of polar regions by multi-cations occupying B-site of the latter compound as compare to the former

compound. However, the BT-BZT-BS-NN system produces dielectrics with overall lower relative permittivities compared to the other compositions presented in this investigation. Compositions with more BaTiO_3 exhibited higher dielectric constants and tolerance factors but also higher temperature dependence of permittivity.

Based on the trend observed in Fig. 1, it is clear that further reduction of tolerance factor could potentially lead to an improvement in $\text{TC}\epsilon$ to obtain temperature-stable high permittivity dielectrics ($\text{TC}\epsilon \approx 0$). However, further increasing the Bi(Me)O_3 concentration from the $0.50\text{BaTiO}_3\text{--}0.25\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.25\text{BiScO}_3$ composition is not possible as it would exceed the solubility limit of the system, leading to the formation of secondary phases and a consequent degradation in electrical properties. Therefore, to avoid the formation of secondary phases in the system, A-cation (Ba or Bi) substitutions with an isovalent cation was considered. Specifically, the cations Sr and Ca were selected as dopant elements to substitute for the Ba ion in the $0.50\text{BaTiO}_3\text{--}0.25\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.25\text{BiScO}_3$ compositions. This resulted in lowering the tolerance factor from 0.9807 (undoped) to 0.9749 (Sr-doped) and 0.9714 (Ca-doped). Secondary phases were not detected by X-ray diffraction within the resolution limit of the laboratory scale instrument. Since the ionic radii of Sr^{2+} (1.44 Å) and Ca^{2+} (1.34 Å) were smaller than that of Ba^{2+} (1.61 Å), thus, it led to the reduction in the average $R_A - R_O$ distance resulting in a decrease in tolerance factor for the Sr and Ca-substituted compounds.

The temperature dependence of the relative permittivity of Sr-doped and Ca-doped $0.50\text{BaTiO}_3\text{--}0.25\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.25\text{BiScO}_3$ compounds is shown in Fig. 2. Temperature stable behavior was maintained for both materials as the $\text{TC}\epsilon$ values of Sr-doped and Ca-doped compositions approached zero as compared to that of the undoped composition. The substitution of Sr had only a moderate effect on improving the temperature stability, however, the $\text{TC}\epsilon$ values transitioned from $-100 \text{ ppm}/^\circ\text{C}$ to $+100 \text{ ppm}/^\circ\text{C}$ in the Ca-doped compositions. For both cases, the permittivity decreased as the doping concentration increased. The permittivity of all Sr-doped compounds remained higher than 1000. However, permittivity values of less than 1000 were obtained in the Ca-doped compounds. These results suggest that Ca is an effective dopant in the $0.50\text{BaTiO}_3\text{--}0.25\text{Bi(Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.25\text{BiScO}_3$ system for achieving temperature stable dielectric properties.

These results show that decreasing the tolerance factor via the substitution of Sr and Ca ions for Ba successfully shifted the $\text{TC}\epsilon$ closer to zero. A different rate of the change in the value of $\text{TC}\epsilon$ and the unit cell volume was observed for Sr-doped and Ca-doped compositions as shown in Fig. 3. Comparatively, at approximately the same tolerance factor for Sr-doped and Ca-doped compositions, the difference in $\text{TC}\epsilon$ value was significant ($\sim 60 \text{ ppm}/^\circ\text{C}$). Following the model proposed by Levin, see Ref. 21, this difference can be

Fig. 1. $\text{TC}\epsilon$ versus tolerance factor of selected $\text{BaTiO}_3\text{--Bi(Me)O}_3$ compounds.

Fig. 2. Temperature dependence of permittivity of (a) Sr-doped and (b) Ca-doped $0.50\text{BaTiO}_3\text{--}0.25\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.25\text{BiScO}_3$ compounds.

Fig. 3. (a) $\text{TC}\epsilon$ versus tolerance factor and (b) unit cell volume as a function of doping concentration for Sr-doped and Ca-doped $0.50\text{BaTiO}_3\text{--}0.25\text{Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--}0.25\text{BiScO}_3$ compounds.

explained by the different bonding nature of the substituting ions (Sr and Ca).²² In the case of Sr substitution for Ba in BaTiO_3 , a reduction in unit cell volume is observed as well as a more relaxed bonding nature for Sr-O in $[\text{SrO}_{12}]$ coordination. The substitution of the Ca ion for Ba in BaTiO_3 resulted in a reduced unit cell volume and an off-center position for Ca, resulting in a strained Ca-O bond, in $[\text{CaO}_{12}]$ coordination, similar to the results obtained by Zheng.²³ This strained Ca-O bond can induce stress in the lattice, which could interrupt or clamp the polarization dynamics resulting in a reduction in permittivity and a stabilization of the permittivity over a wide temperature range.²⁴ Based on this analysis, it is suggested that the unit cell volume reduction and the strained Ca-O bonding characteristic played a major role in the significant reduction of permittivity. This could also mean that the presence of the strained Ca-O bond helped further stabilize the permittivity as the temperature increased. This result supports the correlated rattling-ion model recently proposed by Krayzman *et al.* with the $\text{BaTiO}_3\text{--BiScO}_3$ solid

solution. This model would suggest that the substitution of Sr or Ca for Ba impacts the Bi off-centering and split-site separation therefore resulting in a modification of the dielectric behavior.²⁵

The temperature dependence of the relative permittivity of $\text{BaTiO}_3\text{--Bi}(\text{Zn}_{1/2}\text{Ti}_{1/2})\text{O}_3\text{--BiScO}_3\text{--NaNbO}_3$ compounds is shown in Fig. 4. The addition of NaNbO_3 was effective in shifting the temperature of the dielectric maximum (T_{max}) to temperatures as low as -50°C . While this shift resulted in lower room temperature dielectric loss values it was also accompanied with a lower permittivity. These results show that decreasing the tolerance factor in this system lowers the $\text{TC}\epsilon$. Dielectric constant, dielectric loss at room temperature and $\text{TC}\epsilon$ determined from $30^\circ\text{C}\text{--}200^\circ\text{C}$ are shown in Table 2.

The $\text{TC}\epsilon$ and tolerance factor relationship has been studied in detail for $(\text{Ba}/\text{Sr})(\text{Me}_{1/3}(\text{Nb}/\text{Ta})_{2/3})\text{O}_3$ microwave dielectrics ($\epsilon_r \approx 40$) with similar results to the present work.²⁶ Reaney *et al.* showed that as the tolerance factor

Fig. 4. Temperature dependence of permittivity of BaTiO₃-Bi(Zn_{1/2}Ti_{1/2})O₃-BiScO₃-NaNbO₃ compounds at (a) low temperatures and (b) high temperatures.

Table 2. BaTiO₃-Bi(Zn_{1/2}Ti_{1/2})O₃-BiScO₃-NaNbO₃ compounds with permittivity and dielectric loss ($\tan \delta$) at room temperature and TC ϵ .

Compounds	Permittivity (room temperature)	$\tan \delta$ (room temperature)	TC ϵ (ppm/°C) (30–200°C)
70BT-10BZT-10BS-10NN	706	0.011	–789
60BT-15BZT-15BS-10NN	670	0.052	–476
50BT-10BZT-10BS-30NN	439	0.003	–818
50BT-15BZT-15BS-20NN	563	0.014	–412
45BT-17.5BZT-17.5BS-20NN	537	0.028	–231
40BT-20BZT-20BS-20NN	536	0.048	159

decreased ($t < 0.9900$), the TC ϵ values transitioned from negative to positive values. Additionally, it was found that the microwave dielectric compounds with tolerance factors in the range of 0.9850 to 0.9650 exhibited the TC ϵ values close to zero, which corresponded to structures with anti-phase octahedral tilting. Compared to this study, as shown in Fig. 3(a), the compounds with $t < 0.9900$ exhibited the TC ϵ values close to zero with a negative to positive transition. This finding suggests that both groups of materials share a common relationship between the TC ϵ and the tolerance factor.

The temperature dependence of the permittivity of (Ba/Sr)(Me_{1/3}(Nb/Ta)_{2/3})O₃ microwave dielectrics and other cubic compounds was explained by Colla *et al.*,²⁷ Bosman and Havinga,²⁸ Cockbain and Harrop,²⁹ and Harrop.³⁰ The analysis of the macroscopic Clausius–Mossotti formula with respect to temperature showed that three physical processes contribute to the temperature dependence of permittivity in cubic compounds. First, there is an increase in macroscopic polarizability due to volume expansion. Second, there is a decrease in the number of polarizable particles per unit volume as the temperature increases because of the effect of volume expansion. Third, at constant volume, there is an intrinsic temperature dependence of the macroscopic polarizability. Based on these mechanisms, the macroscopic

polarizability plays a major role in controlling the temperature dependence of the permittivity. However, due to the complicated contribution of the polarizability from multiple mechanisms in complex perovskites,^{28,29} a revised analysis of the Clausius–Mossotti relationship is needed in order to successfully explain the temperature dependence of permittivity of high permittivity complex perovskites such as the dielectric materials in this work.

Pyrochlore-based dielectrics are known to exhibit temperature-stable permittivity characteristics, similar to perovskite, with permittivities of approximately 200 or less. Researchers have focused on the development of Bi-based pyrochlores due to their excellent electrical properties for microwave dielectric applications.^{31–37} The TC ϵ of Bi-based pyrochlores was found to be in the range of –1330 ppm/°C to values close to zero. Valant and Davies showed that the TC ϵ values approached zero as the ratio of A-cation and B-cation radii (R_A/R_B) decreased in a manner such that R_A/R_B was used to represent the stability of pyrochlore.³⁷ Due to difference in structural characteristics between pyrochlore and perovskite, the tolerance factor used for perovskite cannot be directly applied to pyrochlore. Recently, Cai *et al.* re-defined the tolerance factor of pyrochlore by considering the two distinct tetrahedra (A₂B₂ and A₄ with oxygen inside) that comprise the pyrochlore

structure.³⁸ Two tolerance factors were determined by Eqs. (3) and (4), as follows:

$$t_1 = \frac{\sqrt{(x - \frac{1}{4})^2 + \frac{1}{32}}}{\sqrt{(x - \frac{1}{2})^2 + \frac{1}{32}}} \left(\frac{R_A + R_O}{R_B + R_O} \right), \quad (3)$$

$$t_2 = a \left(\frac{3\sqrt{3}}{8(R_A + R_O)} \right), \quad (4)$$

where t_1 represents tolerance factor of the A_2B_2 tetrahedra with O inside, x represents the Wyckoff position of oxygen at 48f (x , 1/8, 1/8), t_2 represents the tolerance factor of the A_4 tetrahedra with O' inside, and a represents the lattice parameter of the pyrochlore unit cell. Previous works by Kamba *et al.*³³ and Nino³⁹ suggested that dominant dielectric response of Bi-based pyrochlores originates from O'-A-O' bonding dynamics. Therefore, it is suggested to consider t_2 as the parameter to correlate with the dielectric response of pyrochlore structures since it is closely related to A-O' bonding. The linear relationship between t_2 and R_A/R_B was determined in which t_2 decreased linearly as R_A/R_B increased.³⁸ It should be noted that the majority of pyrochlore compounds possess t_2 values in between 0.8800 to 0.9200. However, the relationship between the TC ϵ and the t_2 was not presented. Thus, in order to investigate this relationship, the t_2 and the TC ϵ of (Bi,Zn)(Ti,Nb)O₇ pyrochlores were extracted from Cai *et al.*³⁸ and Valant and Davies,³⁶ respectively, and is shown in Table 3. It could be seen that as the t_2 increased the TC ϵ values approached zero. Since t_2 showed a linear relationship with R_A/R_B as previously mentioned, for pyrochlores the TC ϵ approached zero when t_2 increased or R_A/R_B decreased.

In general, the relationship between the tolerance factor and the TC ϵ was established for temperature-stable high permittivity BaTiO₃-Bi(Me)O₃ compounds, i.e., as the tolerance factor decreased, the TC ϵ approached zero. This relationship was found to be similar to that of microwave dielectric Ba- and Sr-based perovskites. In comparison with Bi-based pyrochlore compounds, the TC ϵ approached zero when the tolerance factor (t_2), defined differently as compared to perovskites, increased or R_A/R_B decreased. Overall, the established structure-property relationships for high permittivity perovskites, microwave dielectric perovskites, and microwave dielectric pyrochlores can be a useful guide for developing new high-permittivity materials with temperature-stable behavior.

Table 3. Bi-based pyrochlore compounds and associated tolerance factor (t_2), and TC ϵ .

Compounds	t_2 ³⁸	TC ϵ (ppm/°C) ³⁶
(Bi _{1.65} Zn _{0.35})(Ti _{1.65} Nb _{0.35})O ₇	0.8970	-1330
(Bi _{1.50} Zn _{0.50})(Ti _{1.50} Nb _{0.50})O ₇	0.9030	-1300
(Bi _{1.00} Zn _{1.00})(Ti _{1.00} Nb _{1.00})O ₇	0.9260	-870

4. Conclusions

As the tolerance factor decreased from 1.0256 to 0.9807 due to the addition of Bi(Me)O₃ in BaTiO₃-Bi(Me)O₃ compounds, the result was a shift in the temperature dependence of permittivity (TC ϵ) to values approaching zero (from -2441 ppm/°C to -182 ppm/°C). This suggests that the TC ϵ can be optimized by engineering the tolerance factor by designing the composition of perovskite solid solutions. The substitution of Ba in the 0.50 BaTiO₃-0.25Bi(Zn_{1/2}Ti_{1/2})O₃-0.25BiScO₃ solid solution with Sr or Ca resulted in a decrease in tolerance factor, a decrease in the unit cell volume, and a decreased permittivity. However, the temperature stability of the permittivity for Sr-doped and Ca-doped was significantly improved. The bonding nature of Sr-O (relaxed) and Ca-O (strained) played a significant role in governing the magnitude of the permittivity and the TC ϵ . The range of tolerance factors that shifted TC ϵ values close to zero was found to be similar to that observed in high permittivity perovskite-based microwave dielectrics ($t \approx 0.9750-0.9800$). This study suggests a general relationship between TC ϵ and the tolerance factor, which can be used as a guide to design new high permittivity compounds with temperature-stable permittivity characteristics.

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