



# Microwave dielectric characterization of the perovskite series $A_{1/2}Ln_{1/2}TiO_3-NaNbO_3$ ( $A = Na, Li$ ; $Ln = La, Nd, Sm$ )

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## ABSTRACT

Structure and microwave dielectric characterization of the perovskite series  $A_{1/2}Ln_{1/2}TiO_3-NaNbO_3$  ( $A = Na, Li$ ;  $Ln = La, Nd, Sm$ ) have been investigated by XRD, SEM, and microwave resonator method in this paper. All samples exhibited single perovskite phase.  $0.5Na_{1/2}Ln_{1/2}TiO_3-0.5NaNbO_3$  ( $Ln = Nd, Sm$ ) adopted  $Pbnm$  space group, whereas  $0.5Na_{1/2}La_{1/2}TiO_3-0.5NaNbO_3$  adopted  $Cmcm$  space group. The relative permittivity decreased and  $Qf$  value increased with the decrease of rare earth metal ionic radii, respectively. All samples exhibited large positive  $\tau_f$  value. For  $(1-x)Li_{1/2}Ln_{1/2}TiO_3-xNaNbO_3$  ( $Ln = Nd, Sm$ ) series, the relative permittivity increased with increasing  $x$ , whereas  $Qf$  value decreased with the increase of  $x$ . The  $\tau_f$  value changed from the negative to positive value with the increase of  $x$ . Near zero  $\tau_f$  value could be obtained by tuning the composition of  $x$ . Good complex microwave dielectric properties could be obtained:  $\epsilon_r = 120$ ,  $Q \times f = 2300$  GHz,  $\tau_f = 9.3$  ppm/°C for  $(1-x)Li_{1/2}Sm_{1/2}TiO_3-xNaNbO_3$  with  $x = 0.2$  and  $\epsilon_r = 103$ ,  $Q \times f = 2120$  GHz,  $\tau_f = -3.4$  ppm/°C for  $(1-x)Li_{1/2}Nd_{1/2}TiO_3-xNaNbO_3$  with  $x = 0.1$ .

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## 1. Introduction

Compounds with perovskite structure have been widely studied not only because of interest in their crystal structural behavior, but also their wide variety of technologically important properties and applications, ranging from high-temperature superconductivity to ionic conduction and microwave dielectrics [1–3]. It is well known that several perovskite compounds have excellent microwave dielectric properties [4–6], and they constitute a large share of the microwave dielectric materials commercially used as dielectric resonators in microwave communications. Since the perovskite structure can accommodate a variety of ions at both of the cation sites due to the high tolerance of the structural distortion, the formulations of the perovskite compounds are very diverse. Substitution of cations of similar size in distorted derivatives commonly does not cause a change in space group but can result in changes in cell dimensions, tilt angles of BO<sub>6</sub> polyhedron and displacement of A-cations [7]. These changes can produce significant variations in physical properties. For example, the temperature coefficient of dielectric permittivity (TC $\epsilon$ ) for the perovskite compound is strongly related to the tilting of the oxygen octahedron [5]. Temperature stable microwave dielectric ceramics with high dielectric permittivity are strongly desired for application as negative-positive zero (NPO) chips or the min-

inaturization of MW device under low frequency (<900 MHz). In general, dielectric ceramics with high dielectric constant have large positive temperature coefficient of resonant frequency and high dielectric loss. Hence, there has been a continuous effort to improve the dielectric properties of perovskite-based oxides or discover new dielectric materials by alloying at A and/or B sites. After the initial report of dielectric property of  $(A^{1+}_{1/2}A^{3+}_{1/2})TiO_3$  system [8], several high dielectric constant microwave ceramics with near zero temperature coefficient of resonant frequency have been reported [9–13]. High  $Q \times f$  value could be obtained in some A-site deficient titanate based perovskites [14,15]. Recently we have investigated the microwave dielectric properties of  $La_{(1-x)/3}Na_xNbO_3$  ( $0.0 \leq x \leq 0.4$ ) [16], and found that the niobate perovskites have much higher dielectric constant than that of titanate counterpart. However its  $\tau_f$  value is still large positive. The  $\tau_f$  value of perovskite can usually be tuned by varying the tolerance factor which can be achieved by co-substitution at A and/or B sites with different size of cations. Sodium niobate ( $NaNbO_3$ ) has antiferroelectric phase with space group  $Pbcm$  at room temperature and exhibits a series of phase transitions as a function of temperature change [17]. It is well known that solid solutions of  $NaNbO_3$  with other perovskite-structured compounds result in changes in space group as a function of composition. Therefore the  $A_{1/2}Ln_{1/2}TiO_3-NaNbO_3$  ( $A = Na, Li$ ;  $Ln = La, Nd, Sm$ ) system may be useful to obtain a material with both near zero  $\tau_f$  value and high dielectric constant. Microwave dielectric properties of  $A_{1/2}Ln_{1/2}TiO_3-NaNbO_3$  ( $A = Na, Li$ ;  $Ln = La, Nd, Sm$ ) were investigated in this paper.

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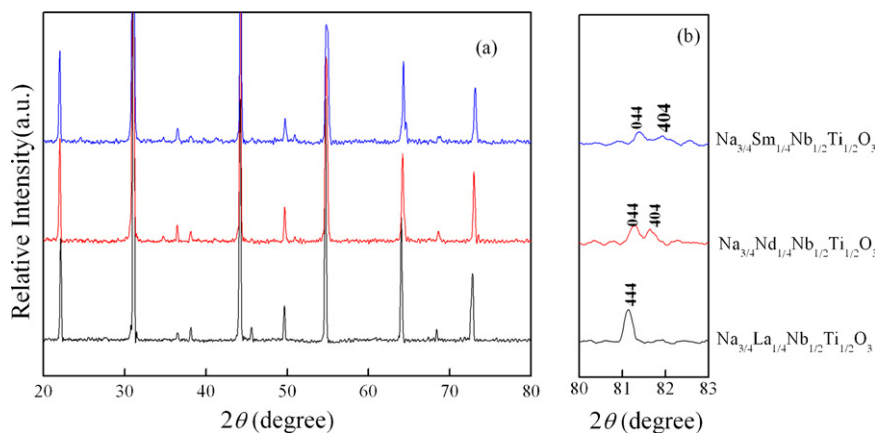


Fig. 1. XRD patterns of  $0.5\text{Na}_{1/2}\text{Ln}_{1/2}\text{TiO}_3\text{--}0.5\text{NaNbO}_3$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ ) ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$  in the  $2\theta$  range from (a)  $20\text{--}80^\circ$  and (b)  $80\text{--}83^\circ$ .

## 2. Experimental

$0.5\text{Na}_{1/2}\text{Ln}_{1/2}\text{TiO}_3\text{--}0.5\text{NaNbO}_3$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ ) and  $(1-x)\text{Li}_{1/2}\text{Ln}_{1/2}\text{TiO}_3\text{--}x\text{NaNbO}_3$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $x = 0.1\text{--}0.5$ ) ceramic samples were prepared by conventional solid-state reaction process from the starting materials including  $\text{Na}_2\text{CO}_3$  (99.9%),  $\text{Li}_2\text{CO}_3$  (99.9%),  $\text{TiO}_2$  (99.7%),  $\text{La}_2\text{O}_3$  (99.9%),  $\text{Nd}_2\text{O}_3$  (99.9%),  $\text{Sm}_2\text{O}_3$  (99.9%) and  $\text{Nb}_2\text{O}_5$  (99.9%). The raw materials were weighed according to the above formula and milled with  $\text{ZrO}_2$  balls in ethanol for 24 h. The wet mixed powders were dried and calcined at the temperature of  $1050\text{--}1100^\circ\text{C}$  for 2 h. In order to suppress the volatilization of lithium or sodium the compacts were muffled with powder of the same composition. The sintering conditions were optimized to get best densification and microwave dielectric properties.

Bulk densities of the sintered specimens were identified by the Archimedes' method. The phases were identified by room temperature X-ray diffraction (XRD) with Ni-filtered  $\text{CuK}\alpha$  radiation (40 kV and 20 mA, Model Dmax-RC, Japan). The microstructure of the sintered sample was characterized by scanning electron microscopy (SEM) (Model XL20, Philips Instruments, Netherlands). All samples were polished and thermally etched at a temperature which was  $200^\circ\text{C}$  lower than its sintering temperature.

Microwave dielectric properties of the sintered samples were measured between 2 and 5 GHz using network analyzer (Hewlett Packard, Model HP8720C, USA). The quality factor was measured by the transmission cavity method by using  $\text{TE}_{018}$  resonant mode. A cylindrical copper cavity having the same aspect ratio as the cylindrical sample and a ratio of the cavity diameter over the sample diameter between 2 and 3 was used here. The sample was placed in the cavity on a low-loss Teflon spacer. The conductor losses can be neglected even for very high  $Q$  values of the dielectric material. The relative dielectric permittivity ( $\epsilon_r$ ) was measured according to the Hakki–Coleman method using the  $\text{TE}_{011}$  resonant mode, and the temperature coefficient of the resonator frequency ( $\tau_f$ ) was measured using invar cavity in the temperature range from  $20$  to  $80^\circ\text{C}$ .

## 3. Results and discussion

Fig. 1 shows the powder XRD patterns of  $0.5\text{Na}_{1/2}\text{Ln}_{1/2}\text{TiO}_3\text{--}0.5\text{NaNbO}_3$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ ) ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$ .

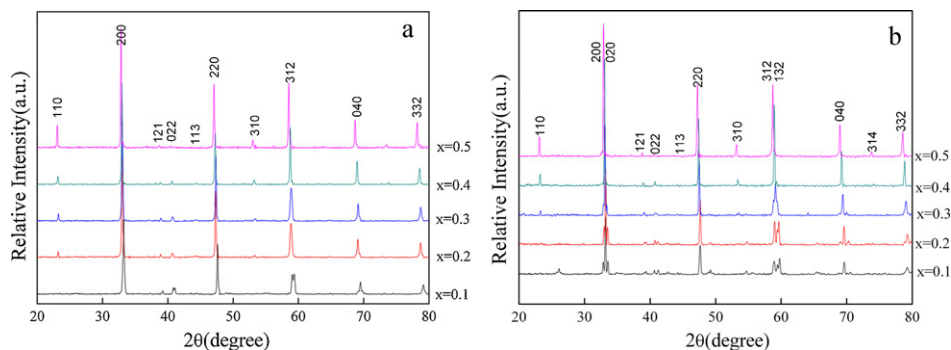


Fig. 2. XRD patterns of (a)  $(1-x)\text{Li}_{1/2}\text{Nd}_{1/2}\text{TiO}_3\text{--}x\text{NaNbO}_3$  and (b)  $(1-x)\text{Li}_{1/2}\text{Sm}_{1/2}\text{TiO}_3\text{--}x\text{NaNbO}_3$  ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$ .

All samples exhibit single perovskite phase. Inspection of the powder XRD patterns in the  $80\text{--}83^\circ$   $2\theta$  range indicated that the La-compound adopted a different space group compared with the other compounds. The La compound exhibits single peak, whereas the Nd and Sm compounds show doublet, which is in agreement with the results of Mitchell and Liferovich [18]. The space group of  $0.5\text{Na}_{1/2}\text{Ln}_{1/2}\text{TiO}_3\text{--}0.5\text{NaNbO}_3$  could be identified as  $\text{Cmcm}$  and the Nd, Sm compounds is  $\text{Pbnm}$  according to the results of Mitchell and Liferovich [18]. The XRD patterns of  $(1-x)\text{Li}_{1/2}\text{Ln}_{1/2}\text{TiO}_3\text{--}x\text{NaNbO}_3$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $x = 0.1\text{--}0.5$ ) ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$  are shown in Fig. 2. All patterns could be indexed on the basis of single orthorhombic perovskite phase. The samples seem to exhibit a different type of perovskite structural distortion evidenced by the splitting of higher angle peaks. The trend in such distortions is obviously related to the variation of tolerance factor  $t$  with the change of the A-site ionic radii. SEM images of  $(1-x)\text{Li}_{1/2}\text{Ln}_{1/2}\text{TiO}_3\text{--}x\text{NaNbO}_3$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $x = 0.1\text{--}0.5$ ) ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$  are shown in Fig. 3. All samples exhibit dense microstructure.

The microwave dielectric properties and relative densities of  $0.5\text{Na}_{1/2}\text{Ln}_{1/2}\text{TiO}_3\text{--}0.5\text{NaNbO}_3$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ ) ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$  are illustrated in Table 1. All samples exhibited high relative densities. The relative permittivity increased from 181 to 231 as the  $\text{Ln}^{3+}$  changed from  $\text{Sm}^{3+}$  to  $\text{La}^{3+}$ , which is due to the increase of ionic polarizability ( $\alpha_{\text{La}^{3+}} = 6.07(\text{\AA})$ ,  $\alpha_{\text{Nd}^{3+}} = 5.01(\text{\AA})$ , and  $\alpha_{\text{Sm}^{3+}} = 4.74(\text{\AA})$ ) [19]. All samples exhibit large positive  $\tau_f$  value. The varying trend of  $Q \times f$  value is opposite to that of relative permittivity. Maximum  $Q \times f$  value of  $2550\text{ GHz}$  was obtained for  $0.5\text{Na}_{1/2}\text{Sm}_{1/2}\text{TiO}_3\text{--}0.5\text{NaNbO}_3$ . Variations of relative permittivity and  $Q \times f$  value of  $(1-x)\text{Li}_{1/2}\text{Ln}_{1/2}\text{TiO}_3\text{--}x\text{NaNbO}_3$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $x = 0.1\text{--}0.5$ ) ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$  with  $x$  are shown in Figs. 4 and 5, respectively. The relative permittivity increased

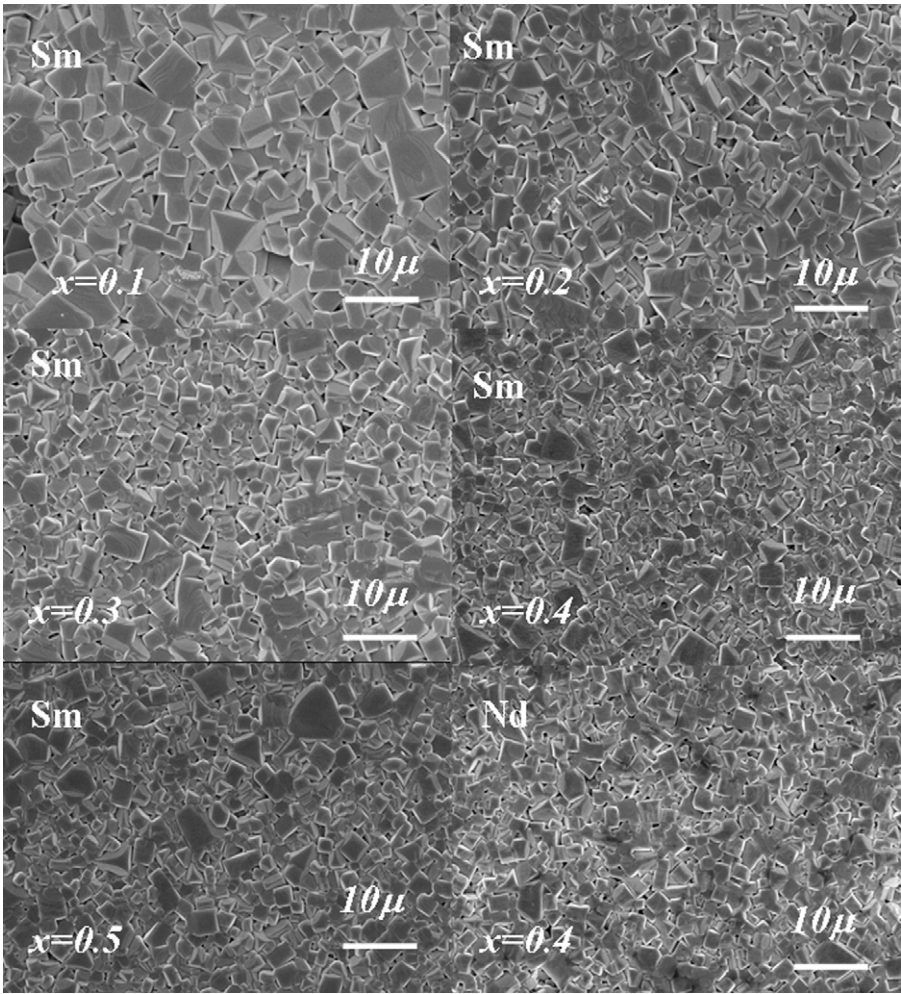


Fig. 3. SEM images of  $(1-x)\text{Li}_{1/2}\text{Ln}_{1/2}\text{TiO}_3-x\text{NaNbO}_3$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ) sintered at  $1300^\circ\text{C}/2\text{ h}$ .

**Table 1**  
Microwave dielectric properties and relative density of  $0.5\text{Na}_{1/2}\text{Ln}_{1/2}\text{TiO}_3-0.5\text{NaNbO}_3$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ ) sintered at  $1300^\circ\text{C}/2\text{ h}$ .

Composition	S.T. ( $^\circ\text{C}$ )	$\epsilon_r$	$Q \times f$ (GHz)	$\tau_f$ (ppm/ $^\circ\text{C}$ )	Tolerance factor ( $t$ )	TD (%)
$0.5\text{Na}_{1/2}\text{La}_{1/2}\text{TiO}_3-0.5\text{NaNbO}_3$	1300/2 h	231	1136	571	0.9741	98.9
$0.5\text{Na}_{1/2}\text{Nd}_{1/2}\text{TiO}_3-0.5\text{NaNbO}_3$	1300/2 h	192	2431	491	0.9681	99.3
$0.5\text{Na}_{1/2}\text{Sm}_{1/2}\text{TiO}_3-0.5\text{NaNbO}_3$	1300/2 h	181	2550	447	0.9665	99.6

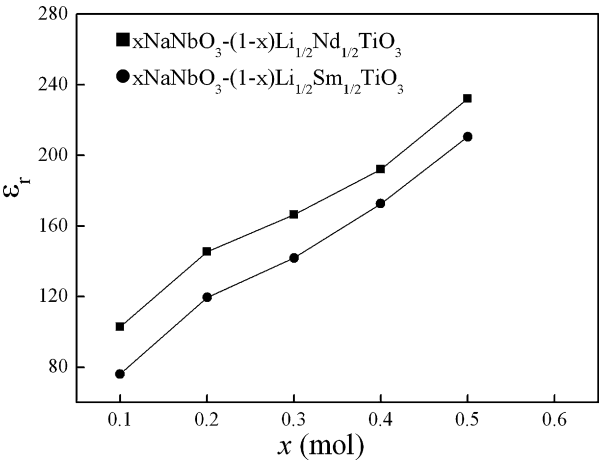


Fig. 4. Variation of relative permittivity with  $x$  for  $(1-x)\text{Li}_{1/2}\text{Ln}_{1/2}\text{TiO}_3-x\text{NaNbO}_3$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $x = 0.1-0.5$ ) ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$ .

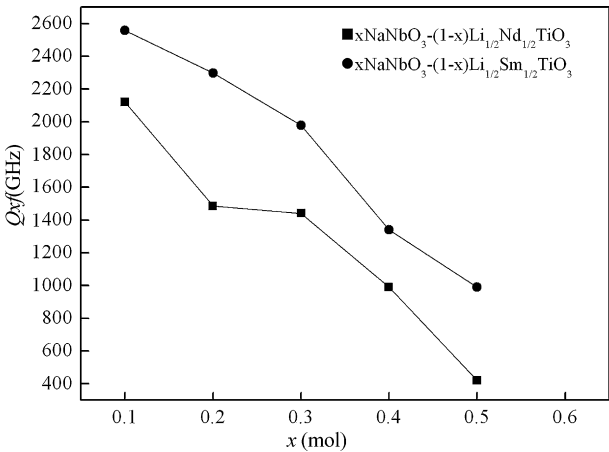


Fig. 5. Variation of  $Q_f$  value with  $x$  for  $(1-x)\text{Li}_{1/2}\text{Ln}_{1/2}\text{TiO}_3-x\text{NaNbO}_3$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $x = 0.1-0.5$ ) ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$ .



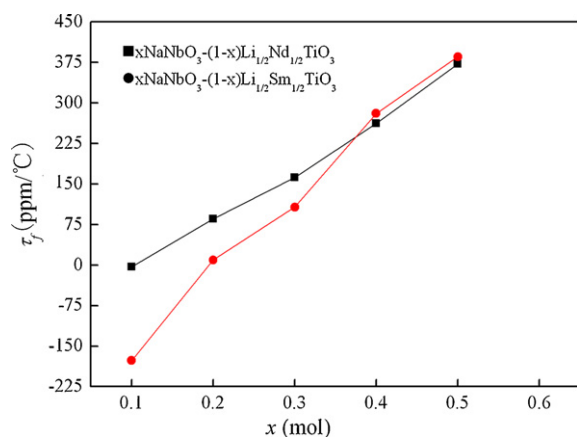


Fig. 6. Variation of  $Q \times f$  value with  $x$  for  $(1-x)\text{Li}_{1/2}\text{Ln}_{1/2}\text{TiO}_3-x\text{NaNbO}_3$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $x = 0.1-0.5$ ) ceramics sintered at  $1300^\circ\text{C}/2\text{ h}$ .

linearly, whereas the  $Q \times f$  value decreased, with the increase of  $\text{NaNbO}_3$  content. The dielectric constant of  $\text{Sm}$  compound is lower than that of the  $\text{Nd}$  counterpart as expected. In contrast the  $Q \times f$  value of  $\text{Sm}$  compound is larger than that of the  $\text{Nd}$  counterpart. Variation of  $\tau_f$  value with  $x$  is shown in Fig. 6. The  $\tau_f$  value changed from negative to positive with the increase of  $\text{NaNbO}_3$ . The  $\tau_f$  value could be tuned to near zero when  $x = 0.1$  for  $\text{Nd}$  compound and  $x = 0.2$  for  $\text{Sm}$  compound, respectively. Good combined microwave dielectric properties could be obtained:  $\epsilon_r = 120$ ,  $Q \times f = 2300\text{ GHz}$ ,  $\tau_f = 9.3\text{ ppm}/^\circ\text{C}$  for  $(1-x)\text{Li}_{1/2}\text{Sm}_{1/2}\text{TiO}_3-x\text{NaNbO}_3$  with  $x = 0.2$  and  $\epsilon_r = 103$ ,  $Q \times f = 2120\text{ GHz}$ ,  $\tau_f = -3.4\text{ ppm}/^\circ\text{C}$  for  $(1-x)\text{Li}_{1/2}\text{Nd}_{1/2}\text{TiO}_3-x\text{NaNbO}_3$  with  $x = 0.1$ .

The variation of  $\tau_f$  value for perovskites is generally considered to be related to the variation of octahedral tilting which is manifested by changing of tolerance factor  $t$ . The prototypical relationship among temperature coefficient of permittivity ( $\tau_\epsilon$ ), tolerance factor ( $t$ ) and octahedral tilting was proposed by Reaney et al. for  $\text{Sr}$  and  $\text{Ba}$ -based perovskites [20]. It has been found that smaller  $t$  correlates with the more negative  $\tau_f$  value in a variety system. We calculated the tolerance factors for all compositions. The  $t$  values for  $0.5\text{Na}_{1/2}\text{Ln}_{1/2}\text{TiO}_3-0.5\text{NaNbO}_3$  ( $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ ) series change from 0.9741 to 0.9665 (Table 1), which are in the antiphase tilted region. The  $t$  values for  $(1-x)\text{Li}_{1/2}\text{Ln}_{1/2}\text{TiO}_3-x\text{NaNbO}_3$  ( $\text{Ln} = \text{Nd}, \text{Sm}$ ;  $x = 0.1-0.5$ ) series vary from 0.902 to 0.934, which should be in the both antiphase and inphase tilted region. We tried to append the estimated  $\tau_\epsilon$  values for the above compositions to the  $\tau_\epsilon-t$  relationship plotted by Reaney et al. However, we found they substantially deviated from what has been suggested by Reaney et al. Similar inconsistent results were observed in many cases [10]. It indicates that the relationship between tolerance factor and  $\tau_f$  value is not universal. The  $\tau_\epsilon-t$  relationship plotted by Reaney et al. was obeyed well for the perovskites with relative permittivity less than  $\sim 45$ . For high permittivity perovskites, other important structure factor such as Lorentz local field, which can be described as an additional dipole field to the value of  $(P/3)\epsilon_0$ , should be taken into consideration.

The effect of the Lorentz local field on the  $\tau_\epsilon$  has been discussed by Wersing [21] and [10] Kim, respectively. The increase in dipole field effect, which increases with permittivity, makes the  $\tau_\epsilon$  more negative value or corresponding more positive  $\tau_f$  value. This leads to the phenomenological relation noticed by Harrop between  $\tau_\epsilon$  and permittivity ( $\tau_\epsilon \approx -\alpha_1 \epsilon_r$ ) [22]. Therefore the variation of  $\tau_f$  value with composition for  $\text{A}_{1/2}\text{Ln}_{1/2}\text{TiO}_3-\text{NaNbO}_3$  ( $\text{A} = \text{Na}, \text{Li}$ ;  $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ ) perovskite series can mainly be ascribed to the effect of local dipole field, which dominate over the effect of octahedral tilting.

#### 4. Conclusions

The microwave dielectric properties of  $\text{A}_{1/2}\text{Ln}_{1/2}\text{TiO}_3-\text{NaNbO}_3$  ( $\text{A} = \text{Na}, \text{Li}$ ;  $\text{Ln} = \text{La}, \text{Nd}, \text{Sm}$ ) have been characterized. The dielectric permittivity decreased and  $Qf$  value increased with the decrease of rare earth metal ionic radii, respectively. The relative permittivity increased with increasing  $\text{NaNbO}_3$  content, whereas  $Qf$  value decreased with the increase of  $\text{NaNbO}_3$  content. The  $\tau_f$  value changed from the negative to positive value with the increase of  $\text{NaNbO}_3$  content. Near zero  $\tau_f$  value could be obtained by tuning the composition of  $x$ . Good complex microwave dielectric properties could be obtained:  $\epsilon_r = 120$ ,  $Q \times f = 2300\text{ GHz}$ ,  $\tau_f = 9.3\text{ ppm}/^\circ\text{C}$  for  $(1-x)\text{Li}_{1/2}\text{Sm}_{1/2}\text{TiO}_3-x\text{NaNbO}_3$  with  $x = 0.2$  and  $\epsilon_r = 103$ ,  $Q \times f = 2120\text{ GHz}$ ,  $\tau_f = -3.4\text{ ppm}/^\circ\text{C}$  for  $(1-x)\text{Li}_{1/2}\text{Nd}_{1/2}\text{TiO}_3-x\text{NaNbO}_3$  with  $x = 0.1$ .

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