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Sintering Behavior, Structures, and Microwave Dielectric Properties of $(Li_xNb_{3x})Ti_{1-4x}O_2$

Li-Xia Pang, Hong Wang,† Di Zhou, and Xi Yao

Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, China

$(Li_xNb_{3x})Ti_{1-4x}O_2$ ($0.05 \le x \le 0.23$) ceramics were synthesized by conventional solid-state reaction method. The sintering behavior, structures, and microwave dielectric properties were investigated as a function of the content of $(Li_{1/4}Nb_{3/4})^{4+}$ substitution for Ti^{4+}. Tetragonal rutile solid solutions were observed when $0.05 \le x \le 0.15$, while $LiNb_3O_8$ phase coexisted with rutile phase when $0.20 \le x \le 0.23$. Without sintering aids, $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics were well densified at 960°–1020°C. Dielectric constant (ε_r) changed from 91 to 39 and temperature coefficient of the resonant frequency (TCF) shifted from +320.5 ppm/°C to −72.7 ppm/°C with the amount of $(Li_{1/4}Nb_{3/4})^{4+}$ substitution increasing. $(Li_{0.215}Nb_{0.645})Ti_{0.14}O_2$ ceramic sintered at 1020°C showed excellent microwave dielectric properties with $\varepsilon_r \sim 43$, $Q \times f$ value ~ 14 500 GHz and TCF ~ −15 ppm/°C. The relationship between structure parameter (tetragonality ratio) and dielectric constant or/and TCF value of $Li_xNb_{3x}Ti_{1-4x}O_2$ rutile solid solutions was also studied in this work.

I. Introduction

Recent progress in mobile and satellite telecommunications has increased the demands on the development of microwave components. Dielectric resonators with small size, low insertion loss, and good temperature stability at microwave frequency are required. Thus, there are three main requirements for dielectric resonator materials. Firstly, the dielectric loss (tanδ) should be very low. Secondly, the dielectric constant (ε_r) should be high, to aid the miniaturization. Thirdly, the temperature coefficient of the resonant frequency (TCF) should be approximately zero (a few ppm/°C). In addition, it is desirable that the TCF value should be able to be "tuned" by small variation in the composition. Achieving all these three requirements in one material is still formidable.

Rutile TiO_2 which possesses high dielectric constant (105) and high quality factor ($Q \approx 1/\tan\delta$) (9200 at 5 GHz) at microwave frequency has been most popularly used as dielectrics of resonators since 1960s.[1–4] However, the large TCF value (+465 ppm/°C) and high sintering temperature (1500°C)[5] of TiO_2 ceramic limited its practical applications. Many works on the low-temperature sintering and microwave dielectric properties in TiO_2-rutile system were reported.[6,7] Kim *et al.*[6] reported the low-temperature sintering and microwave dielectric properties of TiO_2–CuO system for low-temperature cofired ceramics technology devices. Two weight percent CuO addition could lower the sintering temperature of TiO_2-rutile ceramic to about 900°C, but unfortunately the TCF value was still high (+374 ppm/°C).

To obtain a microwave material with good temperature stability of the resonant frequency, a way by combining a large negative TCF material with a large positive one was usually used, for example TiO_2–$Bi_2Ti_4O_{11}$[8] and $CaTiO_3$–$Li_{1/2}Sm_{1/2}TiO_3$.[9] Another way to modify the properties of materials is to form solid solution. Solid solution is basically a crystalline phase that can have variable compositions. Certain material properties such as conductivity and ferromagnetism have often been modified by changing the composition in such a way to form solid solution, which can be used to design new materials with specific characteristics. There are a great number of papers[10–13] dealing with solid-solution synthesis focused on the rutile structures, while only a few papers[14–19] reported on the microwave dielectric properties of these rutile solid solutions.

$Li_xTi_{1-4x}M_{3x}O_2$ (M = Nb, Ta, and Sb) is a set of rutile solid solutions. The previous study[11] showed that the $(Li_xNb_{3x})Ti_{1-4x}O_2$ system remained tetragonal rutile phase when $x \le 0.17$, while $LiNb_3O_8$ phase coexisted with rutile phase when $0.17 < x < 0.25$. Yoon *et al.*[20] reported the microwave dielectric properties ($\varepsilon_r \sim 34$, $Q \times f \sim 58\,000$ GHz, TCF ~ −96 ppm/°C) of $LiNb_3O_8$ ceramic. This work focused on the $(Li_xNb_{3x})Ti_{1-4x}O_2$ system. Their phase structures, lattice parameters, and microstructures were studied. The microwave dielectric properties and sintering behavior of $(Li_xNb_{3x})Ti_{1-4x}O_2$ system were reported. The relationship between microwave dielectric properties and structures was also discussed in detail.

II. Experimental Procedure

The compositions of $(Li_xNb_{3x})Ti_{1-4x}O_2$ were prepared by conventional solid state reaction method using high purity reagent-grade raw materials of Li_2CO_3 (>99%, Guo-Yao Co. Ltd., Shanghai, China), Nb_2O_5 (>99%, Zhu-Zhou Harden Alloys Co. Ltd., Zhuzhou, China) and rutile TiO_2 (>99%, Linghua Co. Ltd., Zhaoqing, China). The raw materials were weighted according to the compositions of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ($x = 0.05$, 0.10, 0.15, 0.20, 0.215, 0.23) and ball milled using a planetary mill (Nanjing Machine Factory, Nanjing, China) with Zirconia balls (2 mm in diameter) as milling media. The mixtures were calcined at 850°C for 12 h and then remilled for 5 h using Zirconia balls in deionized water. The milled powders were dried and granulated with PVA binder and pressed into cylinders (6 mm in diameter and 3 mm in height) in a steel die under uniaxial pressure of 20 kN/cm^2. The cylinders were sintered in air at 900°–1170°C for 8 h.

The crystalline phases of the samples were investigated using an X-ray diffractometry (XRD) with Cu$K\alpha$ radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Accurate lattice parameters of the solid solutions of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ($0.05 \le x \le 0.15$) were calculated from the XRD patterns obtained by step scanning measurement. The apparent densities were measured by Archimedes' method. The microstructures of the fracture surface of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics were observed by scanning electron microscopy (SEM) (JSM-6360LV, JEOL, Tokyo, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS). The dielectric behaviors at microwave

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†Author to whom correspondence should be addressed. e-mail: hwang@mail.xjtu.edu.cn

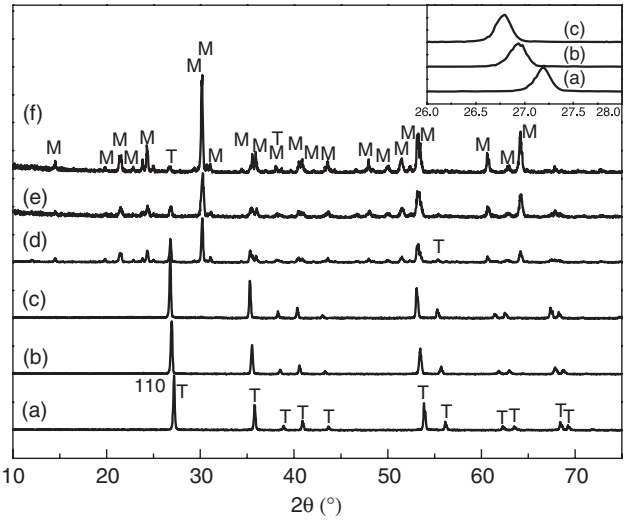

Fig. 1. XRD patterns for powders of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics: (a) $x = 0.05$; (b) $x = 0.10$; (c) $x = 0.15$; (d) $x = 0.20$ sintered at 1020°C; (e) $x = 0.215$; (f) $x = 0.23$ sintered at 1080°C (T: Tetragonal rutile phase; M: Monoclinic $LiNb_3O_8$ phase).

frequency of the samples were measured by the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (DELTA 9023, Delta Design, Poway, CA). The TCF was calculated by the following formula:

$$TCF = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \quad (1)$$

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85° and 25°C, respectively.

III. Results and Discussion

The powder diffraction patterns of the sintered samples in Fig. 1 showed that single tetragonal rutile phase has been obtained when x value was <0.2 in $(Li_xNb_{3x})Ti_{1-4x}O_2$ $(0.05 \le x \le 0.23)$ system. The lattice parameters of the samples with single tetragonal rutile phase were calculated and listed in Table I. The lattice parameters of both a and c increased (as shown in Table I) and the diffraction peaks shifted to lower angle (as shown in the insert of Fig. 1) as the content of the substitution of $(Li_{1/4}Nb_{3/4})^{4+}$ for Ti^{4+} increased. Tetragonal rutile phase and monoclinic $LiNb_3O_8$ phase coexisted in $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics when $x \ge 0.2$, and the amount of $LiNb_3O_8$ phase increased greatly as the x value increased. The result agreed well with that reported by Shin *et al.*[7]

Figure 2 shows the bulk densities of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics as a function of sintering temperature. The relative densities of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics for $x = 0.05$ and $x = 0.10$ were above 96% at 990°–1140°C and the bulk density of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics for $x = 0.15$ reached its saturated value at about 960°C. Comparing with the sintering temperature

Table I. Lattice Parameters, Theoretic Bulk Density (ρ_{calc}), Tetragonality (c/a) and TCF Obtained from XRD Patterns of $(Li_xNb_{3x})Ti_{1-4x}O_2$ Ceramics in Fig. 1

Samples	a (Å)	c (Å)	ρ_{calc} (g/cm^3)	Tetragonality (c/a)	TCF (ppm/°C)
$x = 0.05$	4.62147	2.97468	4.4224	0.64366	320.58
$x = 0.10$	4.65681	2.99461	4.5670	0.64306	235.17
$x = 0.15$	4.68684	3.01273	4.7176	0.64281	199.56

TCF, temperature coefficient of the resonant frequency.

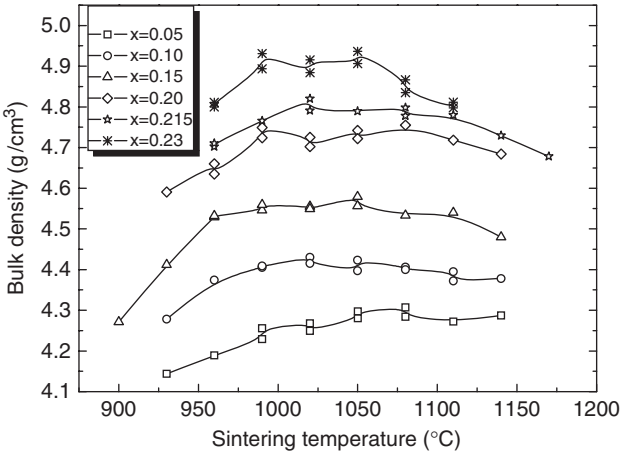

Fig. 2. Bulk densities of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics as a function of sintering temperature.

of pure rutile TiO_2 (1500°C),[5] the sintering temperature was lowered to about 960°–990°C for $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics with the remained single tetragonal rutile phase. The bulk densities of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics for $0.20 \le x \le 0.23$ reached saturated values at about 990°–1020°C. That indicated the sintering temperature increased slightly when monoclinic $LiNb_3O_8$ phase appeared in the $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics. The sintering temperature of $LiNb_3O_8$ ceramic was 1075°C.[20] Thus, the sintering temperature of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics with the co-existing tetragonal rutile phase and monoclinic $LiNb_3O_8$ phase increased slightly accordingly. Comparing with the sintering temperature of pure rutile TiO_2 (1500°C)[5] and that of $LiNb_3O_8$ ceramic (1075°C),[20] the sintering temperature of the tetragonal rutile solid solutions $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics for $0.05 \le x \le 0.15$ were much lower. That is to say the solid solution is much effective on lowering the sintering temperature of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics.

Figure 3 shows the SEM micrographs of fracture surface of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics. $(Li_xNb_{3x})Ti_{1-4x}O_2$ $(0.05 \le x \le 0.15)$ ceramics sintered at 990°C showed dense microstructures with a small amount of pores in the grains (as shown in Fig. 3(a–c)). The grain size of $(Li_xNb_{3x})Ti_{1-4x}O_2$ $(x = 0.05)$ ceramic sintered at 990°C (Fig. 3(a)) lied between 2 and 2.5 μm, and the average grain size increased to 5 and 9 μm, respectively for $(Li_{0.1}Nb_{0.3})Ti_{0.6}O_2$ and $(Li_{0.15}Nb_{0.45})Ti_{0.4}O_2$ sintered at 990°C. That means the grain size of $(Li_xNb_{3x})Ti_{1-4x}O_2$ $(0.05 \le x \le 0.15)$ ceramic sintered at the same temperature increased as the content of substitution of $(Li_{x/4}Nb_{3x/4})^{4+}$ for Ti^{4+} increased. The grain size of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramic was sensitive to sintering temperature. Comparing with $(Li_xNb_{3x})Ti_{1-4x}O_2$ $(x = 0.15)$ sintered at 930°C (Fig. 3(d)) showing average grain size of 2.5 μm, the average grain size of $(Li_xNb_{3x})Ti_{1-4x}O_2$ $(x = 0.15)$ ceramic increased to 9 μm when sintered at 990°C (Fig. 3(c)). Backscattered electron images of $(Li_xNb_{3x})Ti_{1-4x}O_2$ $(0.15 \le x \le 0.23)$ ceramics (Fig. 3(e–h)) showed that a secondary phase (lighter grains) appeared in $(Li_xNb_{3x})Ti_{1-4x}O_2$ $(0.2 \le x \le 0.23)$ ceramics and the content of the secondary phase increased greatly as the content of substitution of $(Li_{x/4}Nb_{3x/4})^{4+}$ for Ti^{4+} increased. EDS analysis in Fig. 4 showed that the lighter grains were rich in Nb element and the content of Ti element was higher in the darker grains than that in the lighter grains. Combining with XRD analysis in Fig. 2, it was regarded that the lighter grains and the darker grains were $LiNb_3O_8$ and rutile solid solution grains, respectively.

Microwave dielectric properties of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics as a function of x value are shown in Fig. 5. The dielectric constant of $(Li_xNb_{3x})Ti_{1-4x}O_2$ $(0.05 \le x \le 0.15)$ ceramics decreased from 91 ($(Li_{0.05}Nb_{0.15})Ti_{0.8}O_2$ sintered at 990°C) to 82 ($(Li_{0.15}Nb_{0.45})Ti_{0.4}O_2$ sintered at 990°C) as the x value increased from 0.05 to 0.15 although the ionic polarizability of $(Li_{x/3}Nb_{2x/3})^{4+}$ (3.28 Å^3) is higher than that of Ti^{4+} (2.93 Å^3).[21]

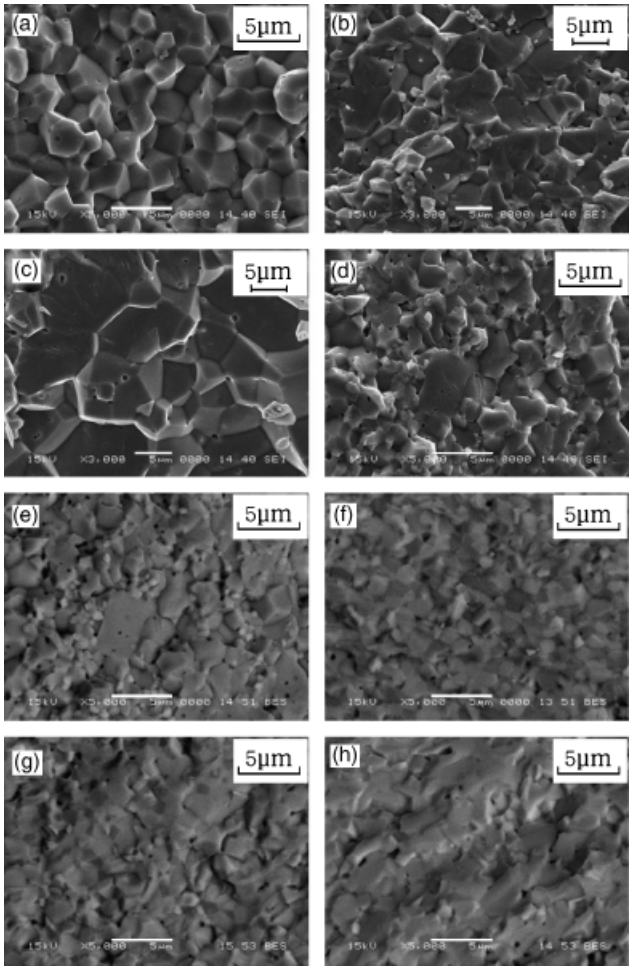

Fig. 3. SEM micrographs of the fracture surface of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics: second electron images of (a) $x = 0.05$, (b) $x = 0.10$, (c) $x = 0.15$ sintered at 990°C, and (d) $x = 0.15$ sintered at 930°C; back-scattered electron images of (e) $x = 0.15$, (f) $x = 0.20$, (g) $x = 0.215$, and (h) $x = 0.23$ sintered at 990°C.

It was due to that the dielectric constant of rutile TiO_2 system depends mainly on the structure.[22] The dielectric constant of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramic decreased greatly from 82 to 52 ($(Li_{0.2}Nb_{0.6})Ti_{0.2}O_2$ sintered at 1020°C) when the secondary phase ($LiNb_3O_8$ phase) appeared in the ceramic and it decreased to 39 ($(Li_{0.23}Nb_{0.69})Ti_{0.08}O_2$ sintered at 1050°C) as the x value increased to 0.23, which can be explained by the logarithmic mixing rule of dielectric constant in composite ceramic between $LiNb_3O_8$ having a dielectric constant of 34[20] and TiO_2 having a dielectric constant of 105.[5] The $Q \times f$ value of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramic decreased from 9000 GHz ($(Li_{0.05}Nb_{0.15})Ti_{0.8}O_2$ sintered at 990°C) to 6700 GHz ($(Li_{0.15}Nb_{0.45})Ti_{0.4}O_2$ sintered at 990°C) and then increased to 24 000 GHz ($(Li_{0.23}Nb_{0.69})Ti_{0.08}O_2$ sintered at 1050°C) because of the high $Q \times f$ value (58 000 GHz) of $LiNb_3O_8$ phase.[20]

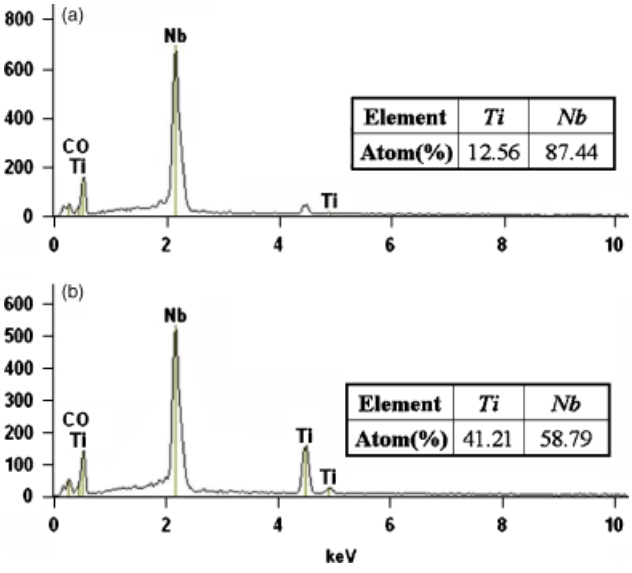

Fig. 4. EDS spectrum of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ($x = 0.20$) ceramics sintered at 990°C for 8 h: (a) the light grains; (b) the dark grains.

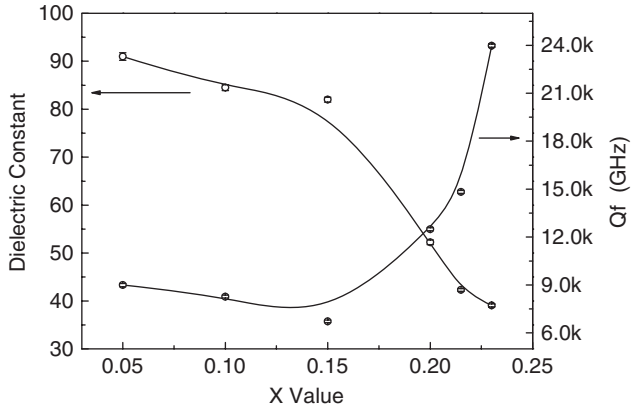

Fig. 5. Microwave dielectric properties (dielectric constant and $Q \times f$ value) of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics as a function of x value.

Figure 6 presents the temperature coefficients of resonant frequencies (TCF) of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics as a function of x value. The TCF value of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramic shifted from +320 ppm/°C to +200 ppm/°C when the x value increased from 0.05 to 0.15, and then shifted greatly towards negative when the x value increased to 0.20 because of the appearance of $LiNb_3O_8$ phase (TCF ~ −96 ppm/°C[20]). The TCF value of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramic shifted from +52 ppm/°C to −73 ppm/°C when the x value increased from 0.20 to 0.23. The TCF value of $(Li_{0.215}Nb_{0.645})Ti_{0.14}O_2$ ceramic sintered at 1020°C was −15 ppm/°C, which could be used as a temperature stable microwave dielectric material.

The relationship between structure parameter and dielectric constant and/or TCF value of $(Li_xNb_{3x})Ti_{1-4x}O_2$ rutile solid solution was also studied. For tetragonal rutile solid solutions, the dielectric constant and TCF value depend greatly on the octahedral distortion[15] or the tetragonality ratio (c/a).[16] The distortion of the oxygen octahedra surrounding each Ti atom is governed by the oxygen positional parameter (μ), the tetragonality ratio (c/a) and a.[23] The relationship between tetragonality

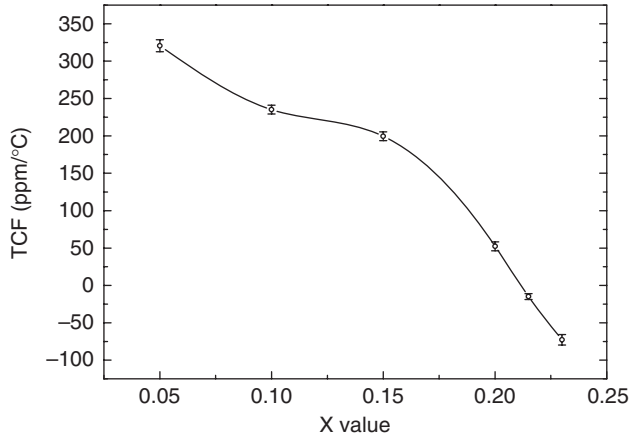

Fig. 6. Temperature coefficients of resonant frequencies (TCF) of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics as a function of x value.

ratio (c/a) and oxygen positional parameter (μ) could be described as in the following equation[16]:

$$\mu = \frac{2 - \left(4 - 2\left(1 - \left(\frac{d_e}{d_a}\right)^2\right)\left(\left(\frac{c}{a}\right)^2 + 2\right)\right)^{\frac{1}{2}}}{4\left(1 - \left(\frac{d_e}{d_a}\right)^2\right)} \quad (2)$$

where d_a and d_e were the lengths of two apical Ti–O bonds and four equatorial Ti–O bonds, respectively, which could be calculated from a, c, and μ[23]:

$$d_a = a\mu\sqrt{2} \quad (3)$$

$$d_e = \frac{1}{2}a\left[2(2\mu - 1)^2 + \left(\frac{c}{a}\right)^2\right]^{\frac{1}{2}} \quad (4)$$

The apical and equatorial bonds are equal when μ takes the special value of $\mu^* = \frac{1}{4}\left[1 + \frac{1}{2}(c/a)^2\right]$.[23] Perfect octahedral symmetry would require lattice parameter of $(c/a)_{ideal} = 2 - \sqrt{2} \approx 0.586$ and $\mu_{ideal} = \frac{1}{2}(c/a)_{ideal} \approx 0.293$, giving all twelve O–O bonds equal lengths. To some extent, the tetragonality ratio (c/a) indicates the octahedral distortion. Meanwhile the dielectric constant and/or TCF value depended greatly on the octahedral distortion. Thus the present work studied the relationship between tetragonality ratio (c/a), dielectric constant and/or TCF value of $(Li_xNb_{3x})Ti_{1-4x}O_2$ rutile solid solutions. The tetragonality ratio (c/a) of $(Li_xNb_{3x})Ti_{1-4x}O_2$ rutile solid solution was obtained from the XRD patterns in Fig. 1 and the data were listed in Table I. Figure 7 presents the relationship between tetragonality ratio (c/a) and TCF value and/or dielectric constant of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ($0 \le x \le 0.15$) solid solutions. It is observed that the tetragonality ratio (c/a) of $(Li_xNb_{3x})Ti_{1-4x}O_2$ solid solution decreased as the content of the substitution of $(Li_{1/4}Nb_{3/4})^{4+}$ for Ti^{4+} increased (as shown in Table I). The TCF value and/or dielectric constant of $(Li_xNb_{3x})Ti_{1-4x}O_2$ solid solution shown in Fig. 7 decreased linearly with the tetragonality ratio (c/a) decreasing. The dependence of TCF value on the tetragonality ratio (c/a) could be explained as in the following. The tetragonality ratio (c/a) of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ($0 \le x \le 0.15$) solid solution was higher than $(c/a)_{ideal}$ (0.586), which indicated that the octahedra distorted in $(Li_xNb_{3x})Ti_{1-4x}O_2$ solid solutions. When the temperature increased, the increase of thermal energy was supposed to be absorbed completely in recovering the octahedral distortion rather than in restoring the direct dependence of the polarizability on temperature.[15] That is to say the tetragonality ratio would change towards $(c/a)_{ideal}$ (0.586). For $(Li_xNb_{3x})Ti_{1-4x}O_2$ solid solutions, c/a would decrease when the temperature increased. The dielectric constant of $(Li_xNb_{3x})Ti_{1-4x}O_2$ solid solutions decreased as c/a decreased as shown in Fig. 7. For the same sample, the decrease of c/a with temperature resulted in the decrease of dielectric constant with temperature and then the resonant frequency would shift towards high frequency when temperature increased, which was the reason why $(Li_xNb_{3x})Ti_{1-4x}O_2$ solid solution possessed high positive TCF value. The nearer to $(c/a)_{ideal}$ (0.586) of tetragonality ratio (c/a), the smaller change of c/a when the temperature increased from 25° to 85°C (measure temperature of TCF value), and the nearer to zero of TCF value, which could explain why the TCF value of $(Li_xNb_{3x})Ti_{1-4x}O_2$ solid solution decreased with the tetragonality ratio (c/a) decreasing.

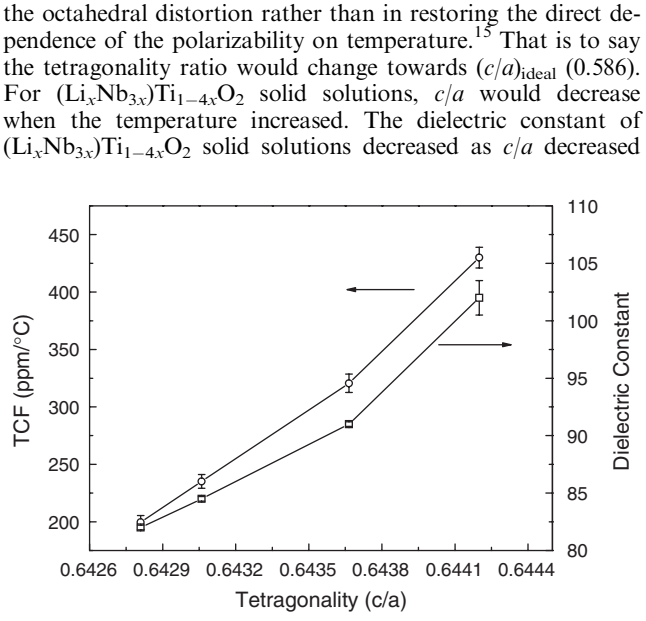

Fig. 7. Relationship between tetragonality ratio (c/a) and TCF value and/or dielectric constant of $(Li_xNb_{3x})Ti_{1-4x}O_2$ ($0 \le x \le 0.15$) solid solution.

IV. Conclusions

In $(Li_xNb_{3x})Ti_{1-4x}O_2$ system, the microwave dielectric properties can be tuned by the substitution of $(Li_{1/4}Nb_{3/4})^{4+}$ for Ti^{4+}. Tetragonal rutile solid solutions were obtained when $0.05 \le x \le 0.15$, while $LiNb_3O_8$ phase and tetragonal rutile phase coexisted when $0.20 \le x \le 0.23$. Without sintering aids, $(Li_xNb_{3x})Ti_{1-4x}O_2$ ceramics could be densified well at 960°–1020°C. Dielectric constant (ε_r) changed from 91 to 39 and TCF shifted from +320.5 ppm/°C to −72.7 ppm/°C with the amount of $(Li_{1/4}Nb_{3/4})^{4+}$ substitution increasing. For $(Li_xNb_{3x})Ti_{1-4x}O_2$ tetragonal rutile solid solutions, the dielectric constant and TCF value depended greatly on the tetragonality ratio (c/a). $(Li_{0.215}Nb_{0.645})Ti_{0.14}O_2$ ceramic sintered at 1020°C showed excellent microwave dielectric properties with $\varepsilon_r = 43$, quality factor ($Q \times f$) = 14 500 GHz and TCF = −15 ppm/°C, which could be used as a temperature stable microwave dielectric material.

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