

Article

Temperature Stable, High-Quality Factor $\text{Li}_2\text{TiO}_3\text{-Li}_4\text{NbO}_4\text{F}$ Microwave Dielectric Ceramics

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Abstract: In this work, $(1-x)\text{Li}_2\text{TiO}_3\text{-}x\text{Li}_4\text{NbO}_4\text{F}$ ceramics were prepared by the conventional solid-state ceramic route. With the increase of $\text{Li}_4\text{NbO}_4\text{F}$ content, the phase structure transformed from ordered monoclinic to disordered cubic. By increasing $\text{Li}_3\text{NbO}_4\text{F}$ content, the temperature coefficient of resonant frequency (τ_f) was successfully adjusted closer to zero, while the dielectric constant (ϵ_r) and microwave quality factor (Qf) decreased to some degree. Outstanding microwave dielectric properties with a $\epsilon_r = 18.7$, $Qf = 61,388 \text{ GHz}$ (6.264 GHz), and $\tau_f = 0.9 \text{ ppm}/^\circ\text{C}$ were obtained for $0.9\text{Li}_2\text{TiO}_3\text{-}0.1\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at 1050°C for 2 h, which indicated that these ceramics are suitable for practical applications in the field of microwave substrates and components.



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Keywords: microwave dielectric properties; quality factor; Li_2TiO_3 ; $\text{Li}_4\text{NbO}_4\text{F}$

1. Introduction

With the rapid development of wireless and mobile communication, new microwave dielectric ceramics with a suitable dielectric constant (ϵ_r), high microwave quality factor values (Qf , low dielectric loss), and near-zero temperature coefficient of resonant frequency ($\tau_f \approx 0 \text{ ppm}/^\circ\text{C}$) are desired for microwave device applications [1–6]. Recently, lithium-based microwave dielectric ceramics with rock salt, such as Li_2TiO_3 , Li_3NbO_4 , Li_2WO_4 , and Li_2CeO_3 , have gained plenty of attention because of their relatively low sintering temperature and excellent dielectric properties [7–9]. Among these ceramics, Li_2TiO_3 ceramics sintered at 1300°C for 2 h showed superior microwave dielectric properties with a ϵ_r of 22, Qf value of 63,500 GHz (8.6 GHz), and τ_f value of $+20.3 \text{ ppm}/^\circ\text{C}$ [10]. However, its practical applications were hindered because of the high sintering temperature as well as the positive τ_f value. In a previous study, B_2O_3 was added to $\text{Li}_2\text{TiO}_3\text{-Li}_3\text{NbO}_4$ ceramics to decrease the sintering temperature, and the results showed that the sintering temperature was decreased to 900°C with the deterioration of the Qf value to 44,000 GHz [11]. On the other hand, LiF, as a kind of sintering aid, was reported to successfully decrease the sintering temperature in several microwave dielectric ceramic systems [12–14]. As reported, $\text{Li}_4\text{NbO}_4\text{F}$ with a high Qf , low sintering temperature, and negative τ_f was studied extensively [15]. Therefore, in this work, $\text{Li}_4\text{NbO}_4\text{F}$ ceramics were implemented as a sintering aid to adjust the τ_f value and decrease the sintering temperature for Li_2TiO_3 ceramics. $(1-x)\text{Li}_2\text{TiO}_3\text{-}x\text{Li}_4\text{NbO}_4\text{F}$ ($x = 0.05, 0.10, 0.15, 0.20$) ceramics, compared with non-lithium based ceramics [16–18], were investigated in order to reduce the sintering temperature and achieve a near-zero τ_f value as well as a high Qf value. Their outstanding properties made the widespread application in a satellite communication and global positioning system antenna possible to achieve [19]. The phase structure, microstructure,

and microwave dielectric properties of $(1-x)\text{Li}_2\text{TiO}_3\text{-}x\text{Li}_4\text{NbO}_4\text{F}$ ($x = 0.05, 0.10, 0.15, 0.20$) were studied in detail.

2. Experimental Procedure

$(1-x)\text{Li}_2\text{TiO}_3\text{-}x\text{Li}_4\text{NbO}_4\text{F}$ ceramics were prepared by a conventional solid-state route. TiO_2 (99.9%, Sinopharm, China), Li_2CO_3 (99%, Sinopharm, China), N_2O_5 (99.9%, Zibo Weijie, China), and LiF (98%, Sinopharm, China) powders were used as starting materials. Stoichiometric Li_2CO_3 and TiO_2 were mixed according to the formula of Li_2TiO_3 and milled with ZrO_2 balls in ethanol for 6 h. Then, the mixtures were dried and calcined at $800\text{ }^\circ\text{C}$ for 2 h in air. At the same time, stoichiometric Li_2CO_3 , N_2O_5 , and LiF were mixed, milled, dried, and calcined at $700\text{ }^\circ\text{C}$ for 2 h in air in another furnace. The obtained Li_2TiO_3 and $\text{Li}_4\text{NbO}_4\text{F}$ powders were weighed according to the designed molar ratios, mixed with 30 mL ethanol, and milled by balls for 8 h, dried, and sieved. Subsequently, the powders were sieved through 60 mesh. Then, the powder (the particle size at a scale of $4\text{--}10\text{ }\mu\text{m}$) was granulated with 5 wt% PVA as binder and uniaxially pressed into cylindrical disks under a pressure of 100 MPa. These samples were buried by mixed powder with the same composition and sintered at $1000\text{--}1125\text{ }^\circ\text{C}$ for 2 h at a heating rate of $3\text{ }^\circ\text{C}/\text{min}$.

The bulk densities of the sintered ceramics were measured by Archimedes method. The crystal structure was analyzed using X-ray diffraction (XRD) with $\text{Cu K}\alpha$ radiation (D8-Advanced, Bruker, Germany). The microstructures were observed by a scanning electron microscope (SEM) (JSM 6510LV, JEOL Japan). Microwave dielectric properties were measured using a network analyzer (E5071C, Agilent, USA) with $\text{TE}_{01\delta}$ resonant mode. The temperature coefficient of the resonant frequency (τ_f) was calculated with the following formula:

$$\tau_f = \frac{(f_{80} - f_{25})}{f_{25}(80 - 25)} \times 10^6 \quad (1)$$

where f_{80} and f_{25} were the resonant frequencies at $80\text{ }^\circ\text{C}$ and $25\text{ }^\circ\text{C}$, respectively.

3. Results and Discussion

The XRD patterns of the $(1-x)\text{Li}_2\text{TiO}_3\text{-}x\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at $1050\text{ }^\circ\text{C}$ for 2 h are shown in Figure 1. It is well known that the Li_2TiO_3 phase has three modifications: the metastable cubic phase $\alpha\text{-Li}_2\text{TiO}_3$, ordered monoclinic phase $\beta\text{-Li}_2\text{TiO}_3$, and disordered cubic phase $\gamma\text{-Li}_2\text{TiO}_3$. The $\alpha\text{-Li}_2\text{TiO}_3$ phase transforms to the monoclinic $\beta\text{-Li}_2\text{TiO}_3$ phase at $670\text{ }^\circ\text{C}$, after which the reversible transition of the $\beta\text{-Li}_2\text{TiO}_3$ phase to the $\gamma\text{-Li}_2\text{TiO}_3$ phase occurs at $1150\text{--}1215\text{ }^\circ\text{C}$ [20,21]. With the increase of x , the intensity of peaks, which belonged to the monoclinic phase, decreased, and there were only peaks belonging to cubic phase in the composition $x = 0.20$. The intensity of the (002) supercell peak, which was considered to indicate the degree of long-range order [22], decreased with the increase of x and finally faded away. At $x = 0.05$, the (311) and (222) supercell peaks were observed with low intensity, which belonged to cubic phase. This phenomenon showed that a true solid solution did not exist at $x = 0.05$. With the increase of x , the intensity of (200) and (220) supercell peaks was conspicuously enhanced, while (002) supercell peak vanished, showing that the ordered monoclinic phase transformed to the disordered cubic phase and totally transformed to the cubic phase between $x = 0.10$ and $x = 0.15$, which was consistent with the data in Table 1.

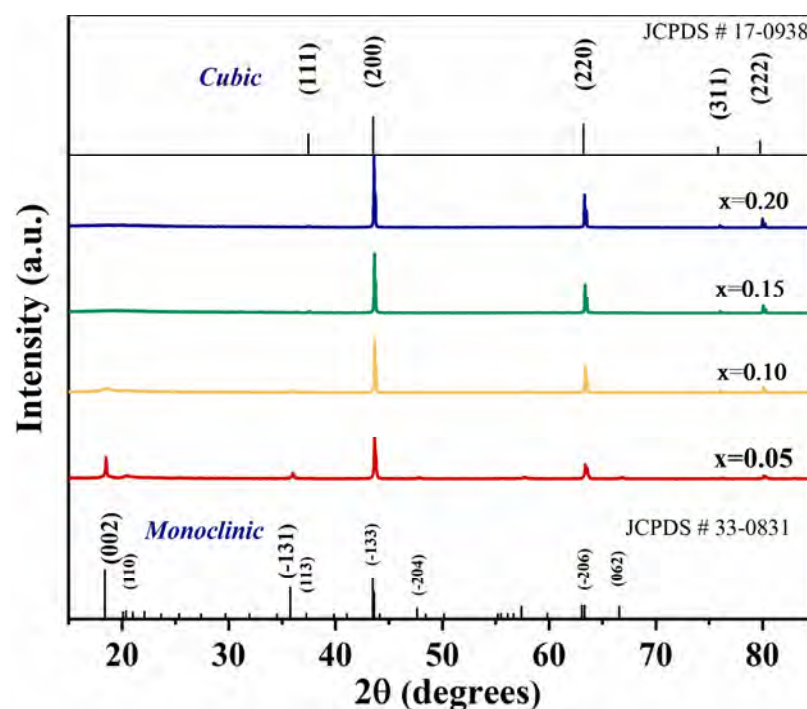


Figure 1. XRD patterns of $(1-x)\text{Li}_2\text{TiO}_3-x\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at $1050\text{ }^\circ\text{C}$ for 2 h.

Table 1. Refinement parameters of $(1-x)\text{Li}_2\text{TiO}_3-x\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at $1050\text{ }^\circ\text{C}$ for 2 h.

$(1-x)\text{Li}_2\text{TiO}_3-x\text{Li}_4\text{NbO}_4\text{F}$	Phase	a (Å)	a (Å)	a (Å)	α ($^\circ\text{C}$)	β ($^\circ\text{C}$)	γ ($^\circ\text{C}$)	V ($\text{\AA}^3$)	wt%	Rwp
x = 0.05	monoclinic	5.07065	8.77898	9.76376	90	100.0477	90	427.969	39.06	9.16
	cubic	4.14846	4.14846	4.14846	90	90	90	71.394	60.94	
x = 0.10	monoclinic	5.08391	8.88845	9.73513	90	100.8609	90	432.032	27.00	10.5
	cubic	4.14991	4.14991	4.14991	90	90	90	71.468	73.00	
x = 0.15	monoclinic	4.15168	4.15168	4.15168	90	90	90	71.560	100.00	6.96
	cubic	4.15168	4.15168	4.15168	90	90	90	71.560	100.00	
x = 0.20	monoclinic	4.15476	4.15476	4.15476	90	90	90	71.720	100.00	6.18
	cubic	4.15476	4.15476	4.15476	90	90	90	71.720	100.00	

To further demonstrate the phase transformation process, the XRD pattern was refined using the Fullprof software. The refinement results of the $x = 0.10$ sample are shown in Figure 2, and the lattice constants, R factors, and percentages of the phase for all the studied compositions are listed in Table 1. It was clear that the Li_2TiO_3 structure transformed from the ordered monoclinic phase to the disordered cubic phase with the increase of x . The ceramic unit cell volume with the cubic phase steadily increased from $71.394\text{ }\text{\AA}^3$ to $71.720\text{ }\text{\AA}^3$.

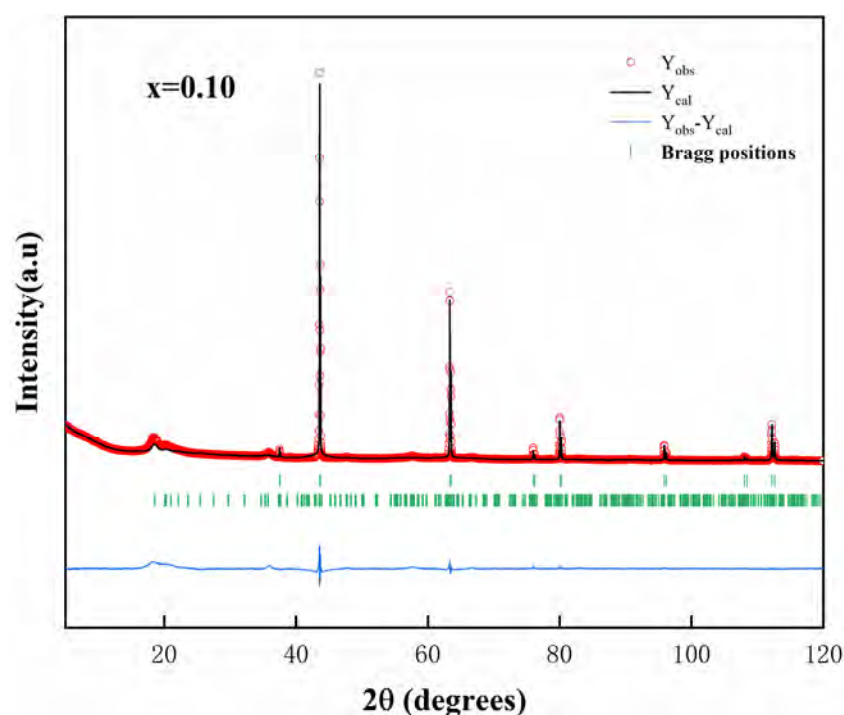


Figure 2. Refined XRD pattern of 0.90Li₂TiO₃-0.10Li₄NbO₄F ceramics sintered at 1050 °C for 2 h.

The SEM images of the (1-x)Li₂TiO₃-xLi₄NbO₄F ceramics sintered at 1050 °C are shown in Figure 3. All samples displayed porous microstructures, which were mainly attributed to the evaporation of lithium [23]. The porous microstructures were similar to those in pure Li₂TiO₃ ceramics, which indicated that it was difficult to improve the densification behavior of Li₂TiO₃ ceramics by adding Li₄NbO₄F [24]. Relatively small grains were observed for the compositions with $x = 0.15$ and 0.2 , as shown in Figure 3c,d, which were likely due to the cubic phase grain, in agreement with the phase structure as shown in Figure 1 and Table 1.

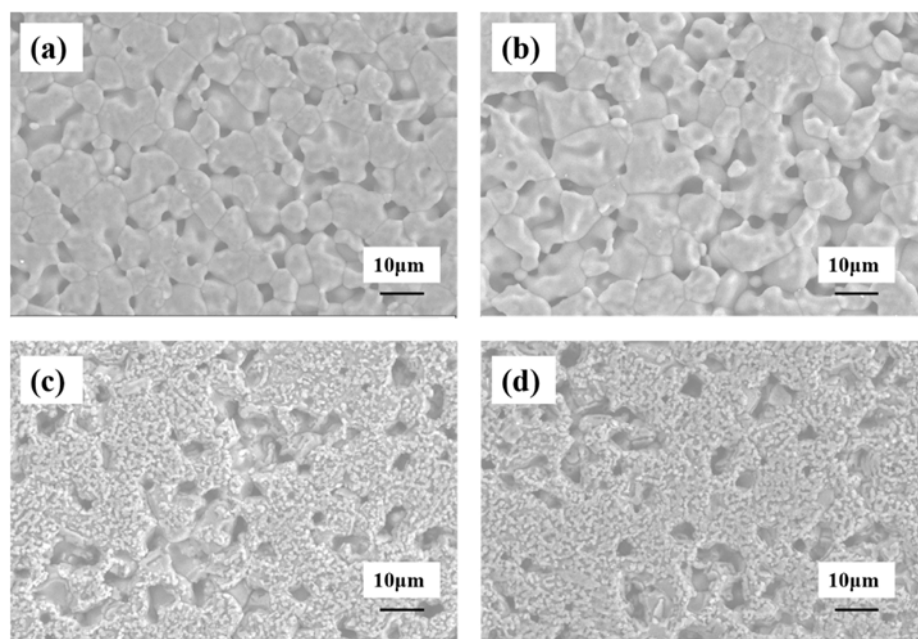


Figure 3. SEM micrographs of (1-x)Li₂TiO₃-xLi₄NbO₄F ceramics sintered at 1050 °C. (a) $x = 0.05$; (b) $x = 0.10$; (c) $x = 0.15$; (d) $x = 0.20$.

The EDS elemental mapping analysis of $x = 0.05$ and $x = 0.20$ for the ceramics sintered at $1050\text{ }^{\circ}\text{C}$ for 2 h is given in Figures 4 and 5, respectively. It was obvious that F and Nb elements were heterogeneous in samples of $x = 0.05$, while elements were distributed homogeneously in samples of $x = 0.20$, which indicated that there were two phases of monoclinic and cubic phase coexistence in the sample of $x = 0.05$, whereas there was a one-phase solid solution in the sample of $x = 0.20$.

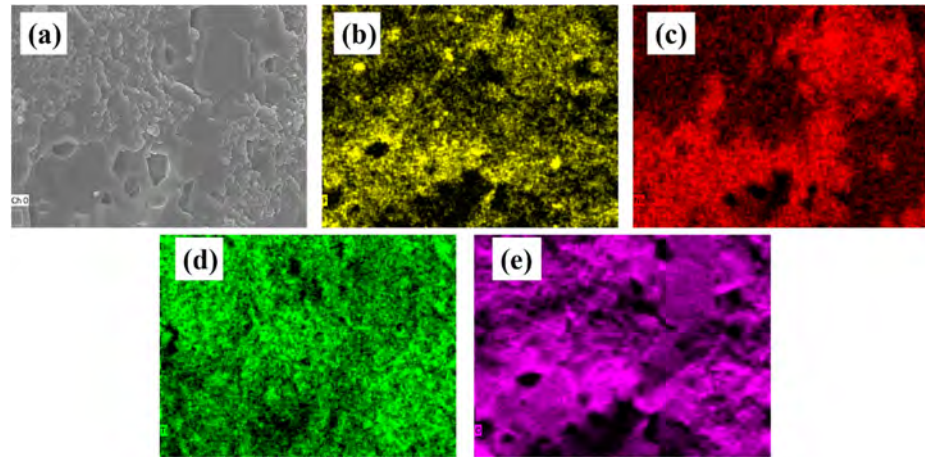


Figure 4. SEM micrographs (a) of $0.95\text{Li}_2\text{TiO}_3\text{-}0.05\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at $1050\text{ }^{\circ}\text{C}$ for 2 h and corresponding EDS analysis surface scanning of (b) F element, (c) Nb element, (d) Ti element, and (e) O element.

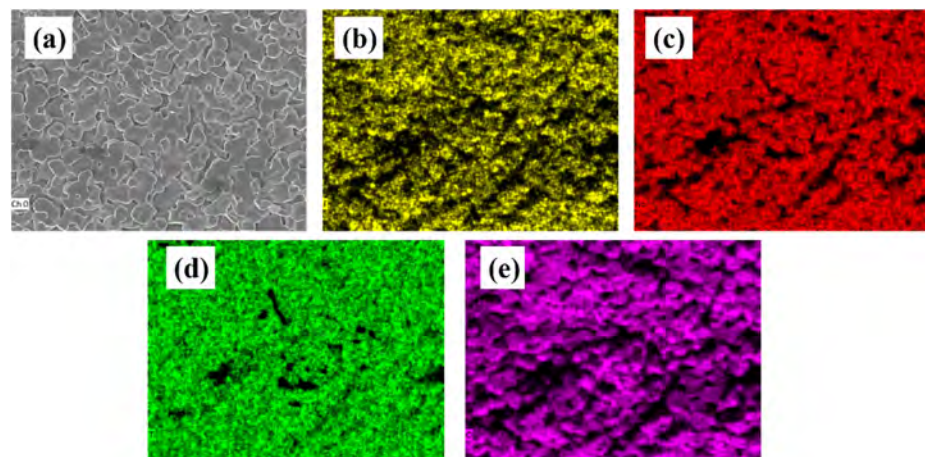


Figure 5. SEM micrographs (a) of $0.80\text{Li}_2\text{TiO}_3\text{-}0.20\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at $1050\text{ }^{\circ}\text{C}$ for 2 h and corresponding EDS analysis surface scanning of (b) F element, (c) Nb element, (d) Ti element, and (e) O element.

The bulk densities of ceramics with different $\text{Li}_4\text{NbO}_4\text{F}$ content as a function of sintering temperature are presented in Figure 6. In the range of $x \leq 0.15$, with the increase of the sintering temperature, the bulk densities originally increased slightly but later obviously decreased at $1100\text{ }^{\circ}\text{C}$, which revealed that the ceramics had overburnt behavior when sintered at $1100\text{ }^{\circ}\text{C}$. These results agreed with more and more pores observed in Figure 3, but the bulk density of the ceramics at $x = 0.20$ increased with the increase of sintering temperature. On the other hand, as the x content increased, the density decreased.

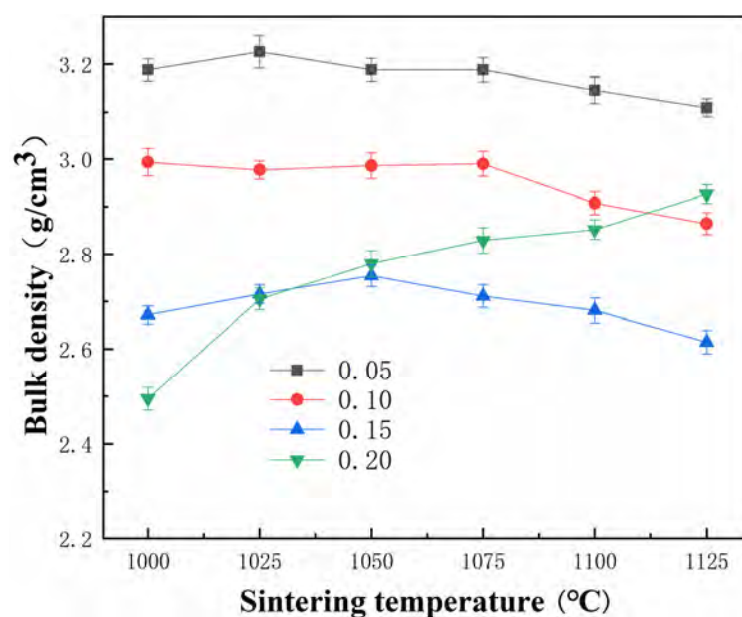


Figure 6. Variation of bulk density of $(1-x)\text{Li}_2\text{TiO}_3-x\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at 1000–1125 °C for 2 h.

Figure 7 displays the dielectric constant of samples sintered at various temperatures as a function of $\text{Li}_4\text{NbO}_4\text{F}$ additions. With the increase of the sintering temperatures and $\text{Li}_4\text{NbO}_4\text{F}$ content, the variations of ϵ_r coincided with bulk density, which suggested that the density was the main external factor that affected ϵ_r in the $\text{Li}_2\text{TiO}_3\text{--Li}_4\text{NbO}_4\text{F}$ ceramics. It is well known that the ϵ_r of ceramics is mainly determined by the dipoles in the unit cell volume and the dielectric polarizabilities of ions [25]. A higher density means that there are more dipoles in a unit volume. As shown in Figure 3, more and more pores were observed in the range of $x \leq 0.15$, which lowered the density and further influenced ϵ_r . In this case, with the exception of the composition, the ϵ_r of the $\text{Li}_2\text{TiO}_3\text{--Li}_4\text{NbO}_4\text{F}$ samples was decided by bulk density, and the ϵ_r of the $0.90\text{Li}_2\text{TiO}_3\text{--}0.10\text{Li}_4\text{NbO}_4\text{F}$ ceramics was 18.7 with a near-zero τ_f value, which was suitable for the application of the integrated circuit.

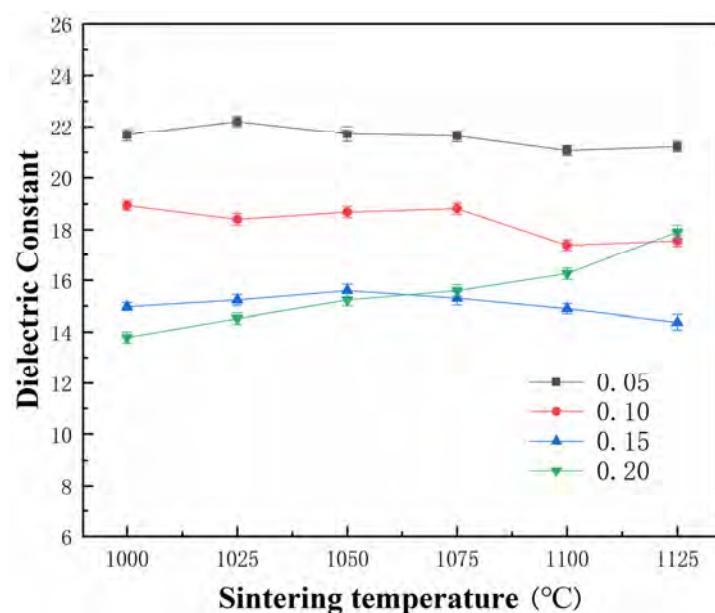


Figure 7. Dielectric constant of $(1-x)\text{Li}_2\text{TiO}_3-x\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at 1000–1125 °C for 2 h.

The variation of the Q_f value of the $(1-x)\text{Li}_2\text{TiO}_3-x\text{Li}_4\text{NbO}_4\text{F}$ ceramics with different sintering temperatures is plotted in Figure 8. The Q_f values decreased with the increase of

$\text{Li}_4\text{NbO}_4\text{F}$ content. The maximum Qf value of 76,202 GHz was achieved for the $0.95\text{Li}_2\text{TiO}_3$ - $0.05\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at 1100°C . The desired ceramics with a near-zero τ_f and high Qf value of 61,388 GHz were acquired for the $0.90\text{Li}_2\text{TiO}_3$ - $0.10\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at 1050°C , which was near to that of the pure Li_2TiO_3 (63,500 GHz). Compared with nonlithium-based ceramics, the Li_2TiO_3 - $\text{Li}_4\text{NbO}_4\text{F}$ ceramics and other lithium-based ceramics exhibited a relatively high Qf and low ϵ_r , as shown in Table 2. At $x = 0.15$ and $x = 0.20$, the Qf value increased linearly with the increase of the sintering temperature without the downward trend because the ceramics with the cubic phase need a higher sintering temperature than the ceramics with the monoclinic phase [26]. Microstructural defects, grain boundaries, porosity, and microcracks usually play important roles in dielectric loss [27]. As mentioned in Figure 3, more pores were observed in the $0.90\text{Li}_2\text{TiO}_3$ - $0.10\text{Li}_4\text{NbO}_4\text{F}$ ceramics than in the $0.95\text{Li}_2\text{TiO}_3$ - $0.05\text{Li}_4\text{NbO}_4\text{F}$ ceramics, which was consistent with the decrease of Qf .

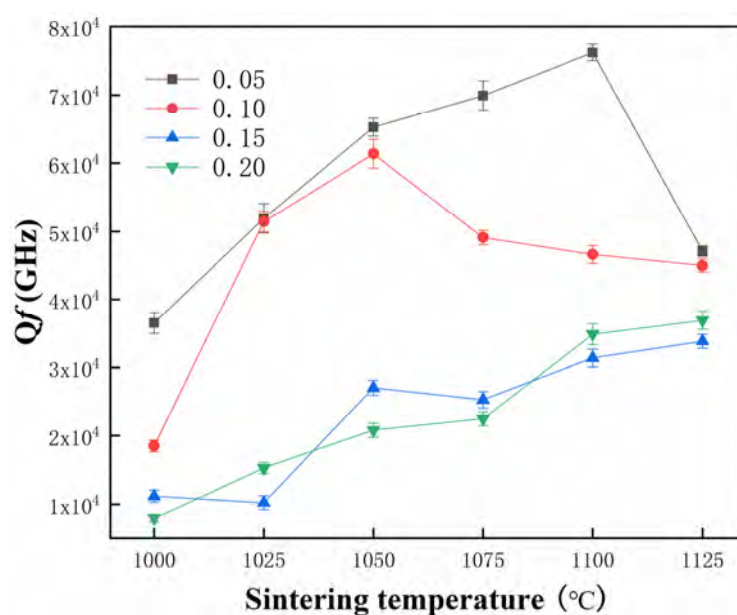


Figure 8. Quality factor of $(1-x)\text{Li}_2\text{TiO}_3$ - $x\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at 1000 – 1125°C for 2 h.

Table 2. Microwave dielectric properties of nonlithium and lithium-based microwave dielectric ceramics.

Material	ϵ_r	Qf (GHz)	τ_f (ppm/ $^\circ\text{C}$)	Sintering Temperature ($^\circ\text{C}$)	Reference
$\text{Ba}_{1.85}\text{Ca}_{0.15}\text{MgTi}_5\text{O}_{13}$	29.3	30,870	+2.1	1160	[28]
$\text{NiZrNb}_2\text{O}_8$	23.77	40,280	−27.5	1200	[29]
$\text{Ca}_3\text{Sn}_{0.95}\text{Ti}_{0.05}\text{Si}_2\text{O}_9$	11.07	42,400	−5.1	1325	[30]
$\text{ZnTiNb}_2\text{O}_8$	35.5	52,500	−60	1050	[31]
$0.9\text{Li}_2\text{TiO}_3$ - $0.1\text{Li}_4\text{NbO}_4\text{F}$	18.7	61,388	+0.9	1050	this work
$\text{Li}_2\text{TiGeO}_5$	9.43	65,300	+24.1	1140	[32]
$\text{Li}_3\text{Mg}_2\text{SbO}_6$	10.5	84,600	−9.0	1300	[33]
$\text{Li}_2\text{Mg}_{2.88}\text{Ca}_{0.12}\text{TiO}_6$	17.8	102,246	−0.7	1280	[34]

Figure 9 shows the variation of the τ_f value of the $(1-x)\text{Li}_2\text{TiO}_3$ - $x\text{Li}_4\text{NbO}_4\text{F}$ ceramics. τ_f was well known to be influenced by the composition, additive, and second phase of the materials [35]. With the increase of x , τ_f showed a negative trend. At $x = 0.10$, the $0.9\text{Li}_2\text{TiO}_3$ - $0.1\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at 1050°C for 2 h achieved a τ_f of 0.9 ppm/ $^\circ\text{C}$, which is very important for applications.

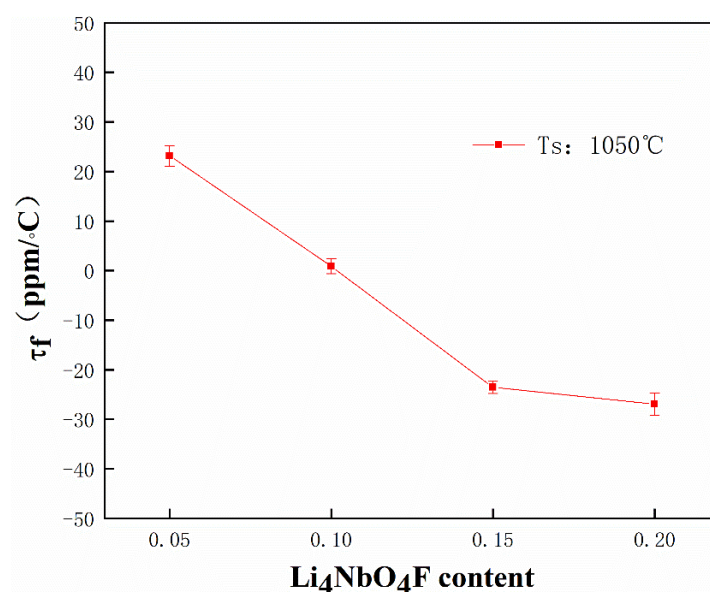


Figure 9. Temperature coefficient of resonant frequency of $(1-x)\text{Li}_2\text{TiO}_3-x\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at 1050 °C for 2 h.

4. Conclusions

In this work, the structural evolution, microstructure, surface analysis, and microwave dielectric properties of $(1-x)\text{Li}_2\text{TiO}_3-x\text{Li}_4\text{NbO}_4\text{F}$ ($x = 0.05, 0.10, 0.15, 0.20$) ceramics have been investigated. Continuous solid solutions between Li_2TiO_3 and $\text{Li}_4\text{NbO}_4\text{F}$ were formed across the entire compositional range, with the phase structure transforming from the monoclinic phase to cubic phase. With the increase of $\text{Li}_4\text{NbO}_4\text{F}$, the τ_f value of Li_2TiO_3 -based ceramics was close to zero, and the sintering temperature of the ceramics was reduced. The Q_f value of the $\text{Li}_2\text{TiO}_3-x\text{Li}_4\text{NbO}_4\text{F}$ ceramics was conspicuously enhanced compared with that of the $\text{Li}_2\text{TiO}_3\text{-Li}_3\text{NbO}_4$ ceramics doped with B_2O_3 . Excellent microwave dielectric properties of $\epsilon_r = 18.7$, $Q_f = 61,388\text{GHz}$, and $\tau_f = 0.9\text{ ppm/}^\circ\text{C}$ were obtained for the $0.90\text{Li}_2\text{TiO}_3\text{-}0.10\text{Li}_4\text{NbO}_4\text{F}$ ceramics sintered at 1050 °C. The samples with a near-zero τ_f and high Q_f were suitable for practical applications in the field of satellite communications and global positioning system antennas.

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