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Low-temperature sintering and microwave dielectric properties of $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$–$CaTiO_3$ ceramics

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Abstract

New $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.5 \geqslant x \geqslant 0$) solid solutions with the addition of B_2O_3 were prepared by a conventional oxide mixture method to develop a microwave resonator with a low sintering temperature. It was shown that $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics did not occur as a single phase but rather as a mixture of a perovskite-type phase with a minor amount of Li_3TaO_4. The perovskite phase exhibited 1:2 ordering of Li and Ta on the B-sites. The substitution of Ti^{4+} for Li^{1+} and Ta^{5+} stabilized the perovskite phase, destabilized 1:2 ordering, and improved the grain growth of $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($x=0.2$, 0.3) ceramics. As the x composition increased from 0 to 0.5, the dielectric constant, ε, increased from 24 to 48, the quality factor, $Q\times f$, decreased from 42,000 to 11,000 GHz, and the temperature coefficient of resonator frequency, τ_f, increased from a negative value to a positive one. A new microwave dielectric material with $\varepsilon=35$, $Q\times f=22{,}800$ GHz, and $\tau_f=-4.1$ ppm/°C was obtained in the $Ca[(Li_{1/3}Ta_{2/3})_{0.7}Ti_{0.3}]O_{3-\delta}$ ceramics doped with B_2O_3 sintered at a temperature as low as 1050 °C.

Keywords: Dielectric properties; Perovskites; Powders-solid state reaction; Sintering; Ca(Li,Ta)O_3

1. Introduction

The rapid growth of the wireless communication industry has created a high demand for the development of ceramic microwave components. These materials are required to have a high dielectric constant, ε, low dielectric loss (high quality factor, $Q\times f$ value), and zero temperature coefficient of resonant frequency, $\tau_f=0$ ppm/°C, but in addition, low cost and minimization of components are two crucial requirements in commercial applications. For these devices, one of the major topics is developing dielectric materials suitable for co-firing with internal conductors such as Ag (960 °C) or Cu (1050 °C).[1] Because contemporary commercial resonator materials had the sintering temperatures higher than 1300 °C,[2] there is a considerable interest in the developments of new materials with low sintering temperatures. One favored approach has involved the investigation of the eutectic or glass-forming additives on the properties of the established microwave dielectric materials. Another approach involved the study of new materials with low melting points. The later method has led to research ceramics such as $BiNb(Ta)O_4$, TiO_2–TeO_2, and $ZnTiO_3$.[3–5] Recently, the Li-based $Li_{1+x+y}M_{1-x\text{-}3y}Ti_{x+4y}O_3$ ($M=$ Nb, Ta) and $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics received much attention because of their good dielectric properties and low sintering temperatures, $\leqslant 1150$ °C.[6,7] Our recent work showed that with the addition of B_2O_3, the sintering temperature of $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics could be reduced to 1000 °C without degrading the microwave dielectric properties.[8] In the $Ca[(Li_{1/3}Nb_{2/3}),Ti]O_{3-\delta}$ system, with a combination of B_2O_3 and Bi_2O_3, a high-quality microwave dielectric material with $\varepsilon=43.1$, $Q\times f=10600$ GHz, and $\tau_f=10.7$ ppm/°C was obtained at a temperature as low as 920 °C.[9] Because the valences and chemical characteristics of the Ta are very similar to those of Nb, the $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0 \leqslant x \leqslant 0.5$) solid solutions were investigated. At the same time, B_2O_3 powders were added to improve the sinterability of the ceramics. The interrelationships among the phase stability, microstructure, and microwave dielectric properties were investigated in this study.

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2. Experimental procedure

High purity (⩾99.9%) oxide powders of $CaCO_3$, Li_2CO_3, TiO_2, Ta_2O_5 were used as the starting powders. The powders were weighed according to the compositions of $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ $(0.5 \geqslant x \geqslant 0)$ ceramics, and then milled with ZrO_2 balls for 24 hrs in ethanol. The mixtures were dried and calcined at 900 °C for 2 h. The calcined powders were remilled for 24 h again with the additions of B_2O_3 (1.0–6.0 wt.%) powders, and then the powders were pressed into pellets with 10 mm in diameter and 5 mm in thickness under 1500 kg/cm^2 isostatic pressure. These pellets were subsequently sintered from 1000 to 1200 °C for 4 h in a closed platinum (Pt) box or air. The crystalline phases were analyzed by X-ray powder diffraction (XRPD) using Cu-K_α radiation of 2θ from 10 to 70°. The microstructure of the sintered specimens was observed using scanning electron microscope (SEM). The sintered density of the specimens was measured by the Archimede's method and the measurement of dielectric constant (ε) and unloaded quality factor (Q) of the ceramics were performed on TE_{011} mode at the resonant frequency from 8 to 12 GHz by using the Hakki–Coleman's dielectric resonator method. The temperature coefficient of resonator frequency (τ_f) was calculated at temperatures ranging from 20 to 80 °C.

3. Results and discussion

XRD spectra for the $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics with B_2O_3 (1.0–6.0 wt.%) sintered at 1050 °C are shown in Fig. 1. The XRD spectra of $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics can be indexed as a $CaTiO_3$-type phase. The peaks marked with an asterisk "*" shown in Fig. 1(a) and (b) for the specimens with 1.0 and 3.0 wt.%B_2O_3, respectively, were attributed to the superlattice reflections of 1:2 ordering of Li^{1+} and Ta^{5+} on B site in $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ compound. In addition, Li_3TaO_4 phase marked by "+" (JCPDS number: 180749) was detected in these compositions. When B_2O_3 content increased up to 6.0 wt.%, as shown in the insert of Fig. 1, the XRD peak positions (2θ) of the orthorhombic phase shifted toward higher angles, indicating a decrease of the unit cell volume. For this composition, the 1:2 ordering was disappeared, and the B-enriched phase was appeared. This change in crystal structure and phase relationships could be explained by a vaporization Li from non-stoichiometric $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ matrix, resulting in B site compositional modification to the stoichiometric $Ca(Li_{1/4}Ta_{3/4})O_3$ phase.[8] This compositional modification process was occurred at the existence of extra liquid phase B_2O_3, which could combined with Li_2O and formed a secondary phase $Li_2B_4O_7$.[8] Since the ionic radii of Li^{1+} (coordination number CN = 6, 0.076 nm) is larger than that of Ta^{5+} (CN = 6, 0.064 nm),[10] the unit cell volume of $Ca(Li_{1/4}Ta_{3/4})O_3$ phase should be smaller than that of Li-enriched $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ phase.

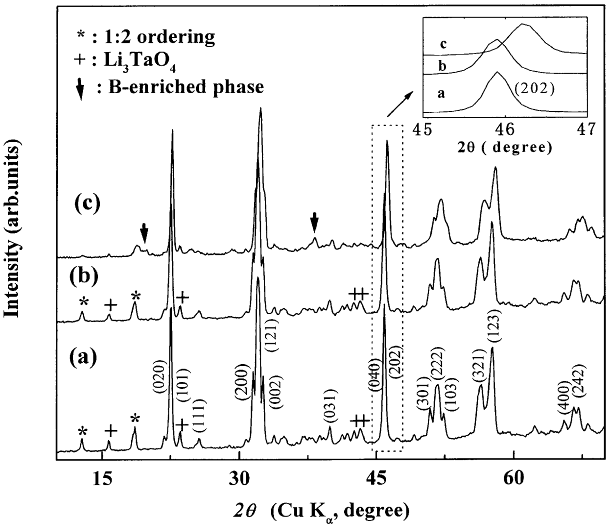


Fig. 1. XRD spectra for $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics with the addition of B_2O_3: (a) 1.0 wt.%, (b) 3.0 wt.%, (c) 6.0 wt.% sintered at 1050 °C, 4 h.

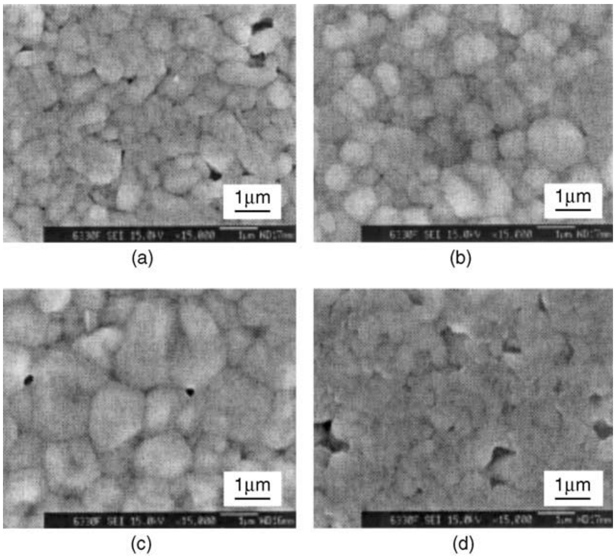
Table 1 gives the microwave dielectric properties of $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics sintered at 1175 and 1200 °C in a closed platinum (*Pt)* box as well as those with B_2O_3 (1.0–6.0 wt.%) sintered at 1050 and 1100 °C in air, respectively. The $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics sintered at 1200 °C in a platinum box have the optimum properties: $\varepsilon = 24$, $Q \times f = 42000$, and $\tau_f = -40$ ppm/°C. It was worth noting that with the addition of B_2O_3 (1.0–3.0 wt.%), the dielectric properties of the ceramics sintered at lower temperatures 1050 and 1100 °C are comparable to the undoped $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics sintered at 1200 °C in a platinum box. These beneficial effects of B_2O_3 (1.0–3.0 wt.%) on the sinterability and dielectric properties of $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics are related to the enhancement of the density at the low temperatures by a liquid sintering process. However, 6.0 wt.%B_2O_3 leads to an obvious decrease of the $Q \times f$

Table 1
The microwave dielectric properties of $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics doped with B_2O_3 (0–6.0 wt.%) sintered at the different conditions

B_2O_3 (wt.%)	T (°C)	ε	$Q \times f$ (GHz)	f_0 (GHz)
0	1175 in a Pt box	23.92	37,500	10.87
	1200 in a Pt box	24	42,300	10.82
1	1050 in air	23.9	32,000	10.628
	1100 in air	24.1	38,900	10.804
3	1050 in air	23.41	33,300	10.911
	1100 in air	24	40,300	10.861
6	1050 in air	23.4	27,500	11.281
	1100 in air	23.33	27,900	10.989

value, due to the disappearance of 1:2 ordering and the formation of the secondary phase shown in Fig. 1(c). These results agree with our previous work on the B_2O_3-doped $Ca(Li_{1/3}Nb_{2/3})O_{3-\delta}$ ceramics.[8]

Since $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics has a large negative τ_f value ($\tau_f = -40$ ppm/°C) which is undesirable in practical applications new ceramics $(1-x)Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$–$xCaTiO_3$, i.e., $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.5 \geqslant x \geqslant 0.05$) solid solutions were prepared because the τ_f of $CaTiO_3$ is a large positive value ($\tau_f = +800$ ppm/°C). In this research, it was found that the $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.5 \geqslant x \geqslant 0.05$) ceramics cannot be sintered in air up to 1200 °C due to a volatility of Li_2O. With the addition of 3.0 wt.% B_2O_3, the densification of $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics can be easily obtained at temperatures ranging from 1050 to 1100 °C in air for 4 h. As shown in Fig. 2, the $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics with 3.0 wt.% B_2O_3 sintered at 1100 °C showed a dense microstructure with small grain size (0.1–1 um). The ceramics with $x = 0.2$ and 0.3 sintered at 1050 °C had a larger grain size than that of $x = 0$. This implies that the substitution of $CaTiO_3$ for $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ improves the sinterability of $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ and enhances the grain growth. However, because of the higher sintering temperature of $CaTiO_3$, the substitution of $CaTiO_3$ up to $x = 0.5$ reduces the sinterability and suppresses the grain growth (Fig. 2(d)).



(a) (b)

(c) (d)

Fig. 2. SEM micrographs for $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics doped with 3.0 wt.% B_2O_3: (a) $x = 0.0$, sintered at 1100 °C, 4 h, (b) $x = 0.2$, (c) 0.3, (d) 0.5, sintered at 1050 °C, 4 h.

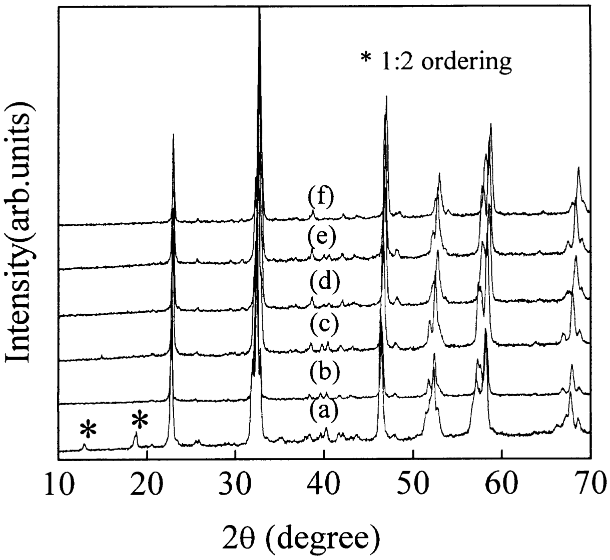


Fig. 3. XRD spectra for $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics doped with 3.0 wt.% B_2O_3 sintered at 1050 °C, 4 h: (a) $x = 0.05$, (b) 0.1, (c) 0.15, (d) 0.2, (e) 0.3, (f) 0.5.

The XRD spectra for the as sintered $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.05 \leqslant x \leqslant 0.5$) ceramics (Fig. 3) can be identified as a $CaTiO_3$-type crystal structure. The systematic peak shifts of 2θ from a low angle to a high angle with increasing x composition indicate a decrease of lattice volume due to the substitution of a smaller ion Ti^{4+} (0.0605 nm, coordination number CN = 6) for Ta^{5+} (CN = 6, 0.064 nm) and Li^{1+} (CN = 6, 0.076 nm).[10] Therefore, the $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.0 \leqslant x \leqslant 0.5$) ceramics are complete solid solutions over the entire x composition range. In addition, introducing of $CaTiO_3$ leads to stabilization of the perovsikite structure due to a larger tolerance factor and a higher electron negativity

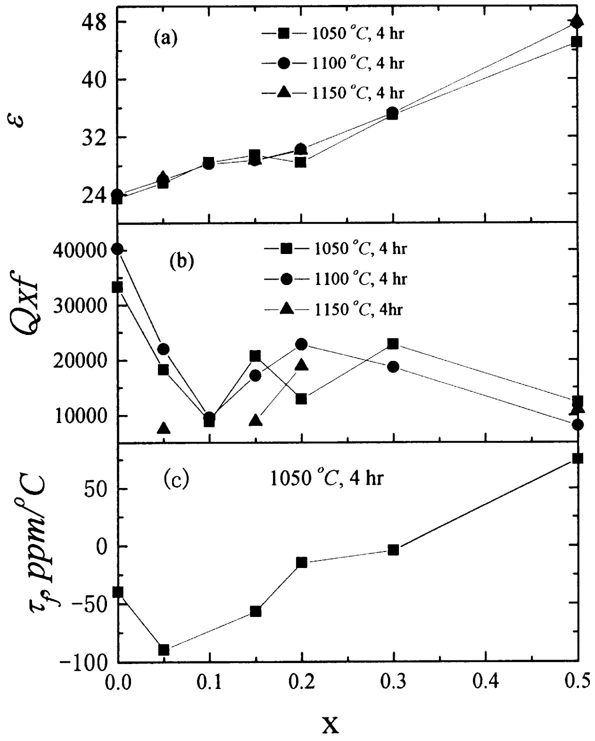


Fig. 4. The dielectric constant, ε: (a), quality factor, $Q \times f$ (b), and, the temperature coefficient of the resonant frequency, τ_f (c) as a function of x for $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics doped with 3.0 wt.% B_2O_3.

difference. As shown in Fig. 3, the secondary phase Li_3TaO_4 observed in the undoped $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ did not form in the Ti-bearing ceramics. Moreover, the disappearance of 1:2 ordering for the specimens $x \geqslant 0.1$ [Fig. 2(b)–(f)] indicates that $CaTiO_3$ destabilizes the 1:2 ordering structure, which agrees with our previous work in $Ca[(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-\delta}$ system.[9]

The apparent density (ρ) and the microwave dielectric properties of $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics with 3.0 wt.% B_2O_3 sintered at temperatures ranging from 1000 to 1150 °C are shown in Fig. 4, and Table 2, respectively. From Fig. 4, as the x composition increases from 0 to 0.5, the dielectric constant, ε, increases linearly from 24 to 48, however, the $Q\times f$ value depends not only on the chemical composition x but also on the sintering temperatures. For each composition x, there is an optimum sintering temperature to obtain the highest $Q\times f$ value. Above the optimum sintering temperature, $Q\times f$ value decreased due to a volatility of Li, the formations of extra pores, and a pyrochore phase $Ca_2Ta_2O_7$ identified with JCPDS number of 44-1008. The $Q\times f$ value of the $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics decreased extremely at composition around $x=0.1$, where the 1:2 ordering was disappeared (Fig. 3(b)). In Fig. 4(b), the $Q\times f$ value increased again with the x composition at $0.15 \leqslant x \leqslant 0.3$. This enhancement in the $Q\times f$ value may be related to the grain growth of those compositions [Fig. 2(b) and (c)]. As shown in Fig. 4(c), the temperature coefficient of resonant frequency, τ_f, of the $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ solid solutions could be improved by the composition x, and the τ_f value at $x=0.3$ is −4.1 ppm/°C. From a practical point of view, the best material is the $Ca[(Li_{1/3}Ta_{2/3})_{0.7}\,Ti_{0.3}]O_{3-\delta}$ solid solution, which has the dielectric properties: $\varepsilon=35$, $Q\times f=22800$ GHz, and $\tau_f=-4.1$ ppm/°C. Compared to the developed materials such as $(Zr,Ti)SnO_4$ and $Ba_2Ti_9O_{20}$,[2] this material has the adequate dielectric properties and a low sintering temperature (1050 °C) for the microwave applications.

Table 2
The apparent density (ρ) and microwave dielectric properties of $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.05 \leqslant x$ 0.5) ceramics doped with 3.0 wt.% B_2O_3 sintered at temperatures ranging from 1000 to 1150 °C for 4 h

x	T (°C)	ρ (g/cm^3)	f_0 (GHz)	ε	$Q\times f$ (GHz)	τ_f (ppm/°C)
0.05	1000	5.692	10.277	25.6	18,300	
	1050	5.721	10.853	26.1	22,000	−97
	1100		11.120	26.3	7500	
0.1	1000	5.673	10.217	27.6	9800	
	1050	5.744	10.636	28.4	8900	
	1100	5.78	10.480	28.3	7600	
0.15	1050	5.59	10.471	29.45	20,700	−57.2
	1100	5.33	10.336	28.71	17,200	
	1150		9.898	28.7	8900	
0.2	1050	5.445	9.902	28.4	12,900	−14.67
	1100	5.436	9.388	30.2	22,800	
	1150		9.667	30.1	18,800	
0.3	1050	5.241	9.45	35	22,800	−4.1
	1100	5.287	9.807	35.3	18,600	
0.5	1050	4.535	8.038	45.03	12,300	75
	1100	4.815	8.395	47.6	8100	
	1150		8.202	48	21,000	

4. Conclusions

The new $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.5 \geqslant x \geqslant 0$) solid solutions with the addition of B_2O_3 were prepared by a conventional oxide mixture method. The main crystalline phase of $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics is the orthorhombic perovskite structure with 1:2 ordering of Li and Ta on the B-sites. The $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics sintered at 1200 °C in a closed platinum box had the dielectric constant, $\varepsilon=24$, the quality factor, $Q\times f=42{,}000$ GHz, and the temperature coefficient of the resonant frequency, $\tau_f=-40$ ppm/°C. With the additions of B_2O_3 (1.0–3.0 wt.%), the $Ca(Li_{1/3}Ta_{2/3})O_{3-\delta}$ ceramics can be well sintered at 1100 °C in air without a degradation of the microwave dielectric properties. The $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($0.0 \leqslant x \leqslant 0.5$) ceramics are complete solid solutions with an orthorhombic perovskite structure. The substitution of Ti^{4+} for Li^{1+} and Ta^{5+} stabilized the perovskite phase, destabilized 1:2 ordered structure, and improved the grain growth of the $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ($x=0.2$ and 0.3) ceramics. As the x composition increased from 0 to 0.5, ε increased linearly from 24 to 48 and t_f of the $Ca[(Li_{1/3}Ta_{2/3})_{1-x}Ti_x]O_{3-\delta}$ ceramics increased from a negative value to a positive one. At an x composition of 0.3, the $Ca[(Li_{1/3}Ta_{2/3})_{0.7}Ti_{0.3}]O_{3-\delta}$ ceramics with $\varepsilon=35$, $Q\times f=22{,}800$ GHz, and $\tau_f=-4.1$ ppm/°C were obtained at a temperature as low as 1050 °C.

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