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Temperature-stable $Li_4Ti_3O_8$ composite microwave dielectric ceramic and its applications in dielectric resonator antennas

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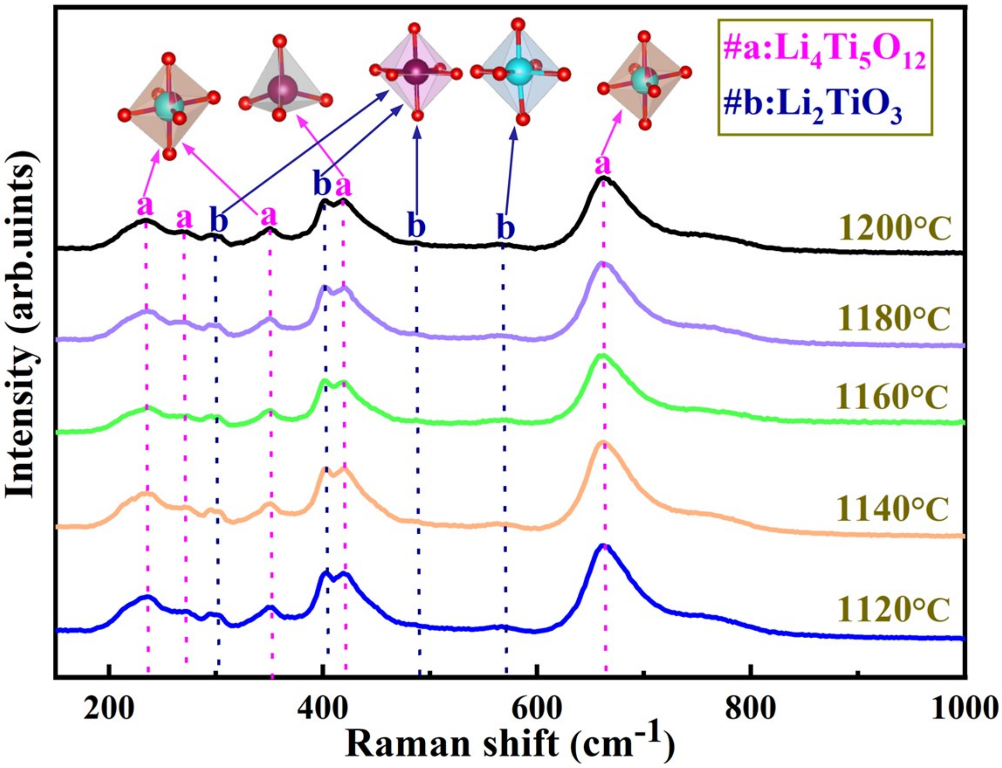

Fig. S1 Shows raman spectra in the range of 1120 − 1200 °C.

Table S1 The Rietveld refinement parameters of $Li_4Ti_3O_8$ ceramics.

formula	S.T. (°C)	Lattice parameter				R_{wp}	R_p	χ^2
		a(Å)	b(Å)	c(Å)	V_{cell}(Å^3)			
$Li_4Ti_5O_{12}$	1120	8.3554	8.3554	8.3554	583.329	11.36	8.7	1.67
Li_2TiO_3		5.0628	8.7743	9.7679	427.031			
$Li_4Ti_5O_{12}$	1140	8.3551	8.3551	8.3551	583.253	10.84	8.25	1.56
Li_2TiO_3		5.0635	8.7836	9.7521	426.902			
$Li_4Ti_5O_{12}$	1160	8.3554	8.3554	8.3554	583.312	7.82	5.81	1.053
Li_2TiO_3		5.0734	8.7978	9.7996	430.402			
$Li_4Ti_5O_{12}$	1180	8.3535	8.3535	8.3535	582.915	6.41	0.9467	0.95
Li_2TiO_3		5.0644	8.7884	9.7968	429.119			
$Li_4Ti_5O_{12}$	1200	8.3535	8.3535	8.3535	582.909	6.52	0.9852	0.98
Li_2TiO_3		5.0701	8.7945	9.7962	429.839			

Table S2 Testing parameters for Retvield refinement XRD .

parameters	
Start	5.0000°
Stop	110.0000°
Step	0.0100°
Speed	10.0°/min

Table S3 Microwave dielectric properties of ceramics at different sintering temperatures.

S.T. (°C)	ε_r	$Q\times f$ (GHz)	τ_f (ppm/°C)
1120	26.11	44811	-8.3
1140	26.43	59326	-6.4
1160	26.72	66020	-3.3
1180	26.55	56492	-6.7
1200	26.49	53706	-7.2

Table S4 Sintering shrinkage of the developed samples.

S.T. (°C)	Original diameter size (mm)	Sintering diameter size (mm)	Shrinkage (100%)
1120	12	10.33	13.9167
1140	12	10.36	13.6667
1160	12	10.30	14.1667
1180	12	10.29	14.25
1200	12	10.27	14.4167

1. Calculate the relative density of composite ceramics

The theoretical density of $Li_4Ti_3O_8$ ceramic material can be calculated using equation 6:[S8]

$$\rho_{th} = \frac{W_1 + W_2}{W_1 \ / \rho_1 + W_2 / \rho_2} \tag{S1}$$

where W represents weight fractions and ρ_{th} signifies theoretical density. ρ_1 and ρ_2 denote the theoretical densities of of $Li_4Ti_5O_{12}$ and Li_2TiO_3, respectively. The mass fraction of the two phases is provided in Table S5. The theoretical density of the ceramic is calculated using equation S1.

Table S5 The density of ceramics at different sintering temperatures.

S.T. (°C)	W_1(%)	W_2(%)	$\rho_{1theory}$ (g/cm^3)	$\rho_{2theory}$ (g/cm^3)	ρ_{bulk} (g/cm^3)	ρ_{theory} (%)	$\rho_{relative}$ (%)
1120	58.996	41.004	3.486	3.415	3.212	3.4565	92.92
1140	58.201	41.799	3.487	3.416	3.277	3.4569	94.79
1160	58.442	41.558	3.486	3.388	3.29	3.4445	95.51
1180	58.309	41.691	3.489	3.398	3.253	3.4505	94.27
1200	57.095	42.905	3.489	3.393	3.241	3.447	94.02

W_1 (%): The mass fraction of $Li_4Ti_5O_{12}$. W_2 (%): The mass fraction of Li_2TiO_3.

$\rho_{1theory}$: Theoretical density of $Li_4Ti_5O_{12}$. $\rho_{2theory}$: Theoretical density of Li_2TiO_3.

ρ_{bulk} ：Volume density of $Li_4Ti_3O_8$ (Measured by Archimedes drainage method).

ρ_{theory} ：Calculate the theoretical density of $Li_4Ti_3O_8$ according to equation S1.

$\rho_{relative}$ ：Relative density of $Li_4Ti_3O_8$ ($\rho_{bulk}/\rho_{theory}$).

2. Predicting the dielectric constant of composite ceramics

The molar fractions of $Li_4Ti_5O_{12}$ and Li_2TiO_3 can be calculated according to the following equation:

$$m_x = \frac{W_x / M_{r_x}}{\sum W_x / M_{r_x}} \quad \text{(S2)}$$

The phases $Li_4Ti_5O_{12}$ and Li_2TiO_3 are denoted as x. The mole fraction, mass fraction, and relative molecular mass are denoted as m_x, W_x, and M_{rx}, respectively. The molar fractions of the ceramics are shown in Table S6.

Table S6 The density of ceramics at different sintering temperatures.

S.T. (°C)	W_1(%)	W_2(%)	M_{r1}	M_{r2}	m_1	m_2
1120	58.996	41.004	459.0918	109.7472	0.2559	0.7441
1140	58.201	41.799	459.0918	109.7472	0.2497	0.7503
1160	58.442	41.558	459.0918	109.7472	0.2516	0.7484
1180	58.309	41.691	459.0918	109.7472	0.2506	0.7494
1200	57.095	42.905	459.0918	109.7472	0.2413	0.7587

W_1 (%): The mass fraction of $Li_4Ti_5O_{12}$. W_2 (%): The mass fraction of Li_2TiO_3.
M_{r1}: Relative molecular mass of $Li_4Ti_5O_{12}$. M_{r2}: Relative molecular mass of Li_2TiO_3.
m_1: The mole fraction of $Li_4Ti_5O_{12}$. m_2: The mole fraction of Li_2TiO_3.

The volume fraction of ceramics can be calculated using equation S3.[S9]

$$V_x = \frac{m_x M_{rx} / \rho_x}{\sum m_x M_{rx} / \rho_x} \quad \text{(S3)}$$

The mole fraction, relative molecular mass, density, and volume fraction are represented by m_x, M_{rx}, ρ_x and V_x, respectively. The volume fractions of ceramics are shown in Table S7.

Table S7 The density of ceramics at different sintering temperatures.

S.T. (°C)	m_1	m_2	M_{r1}	M_{r2}	$\rho_{1theory}$ (g/cm^3)	$\rho_{2theory}$ (g/cm^3)	V_1	V_2
1120	0.2559	0.7441	459.0918	109.7472	3.486	3.415	0.585	0.415
1140	0.2497	0.7503	459.0918	109.7472	3.487	3.416	0.577	0.423
1160	0.2516	0.7484	459.0918	109.7472	3.486	3.388	0.577	0.423
1180	0.2506	0.7494	459.0918	109.7472	3.489	3.398	0.577	0.423
1200	0.2413	0.7587	459.0918	109.7472	3.489	3.393	0.564	0.436

m_1: The mole fraction of $Li_4Ti_5O_{12}$. m_2: The mole fraction of Li_2TiO_3.

M_{r1}:Relative molecular mass of $Li_4Ti_5O_{12}$. M_{r2}: Relative molecular mass of Li_2TiO_3.

V_1: Volume fraction of $Li_4Ti_5O_{12}$. V_2: Volume fraction of Li_2TiO_3.

$\rho_{1theory}$: Theoretical density of $Li_4Ti_5O_{12}$. $\rho_{2theory}$: Theoretical density of Li_2TiO_3.

XRD analysis shows that $Li_4Ti_5O_{12}$ and Li_2TiO_3 can coexist with each other. The ε_r of multiphase composite ceramics can be approximated using mixing rules. The ε_r of $Li_4Ti_3O_8$ ceramics is predicted according to the following three equation:[S10]

$$\text{parallel mixing law: } \varepsilon = V_1\varepsilon_1 + V_2\varepsilon_2 \quad \text{(S4)}$$

$$\text{series mixing law: } 1/\varepsilon = V_1/\varepsilon_1 + V_2/\varepsilon_2 \quad \text{(S5)}$$

$$\text{logarithmic mixing law: } \ln\varepsilon_{\log} = V_1\ln\varepsilon_1 + V_2\ln\varepsilon_2 \quad \text{(S6)}$$

The volume fraction and relative permittivity of $Li_4Ti_5O_{12}$ are represented by V_1 and ε_1, respectively. V_2 and ε_2 denote the volume fraction and relative permittivity of Li_2TiO_3. The volume fractions of $Li_4Ti_5O_{12}$ and Li_2TiO_3 are calculated as 0.5774 and 0.4426, respectively (ceramics were sintered at 1160 °C). The calculated values of ε_r are 26.67, 26.04, and 26.36 using equations S4, S5, and S6, respectively.

Table S8 The density of ceramics at different sintering temperatures.

S.T. (°C)	V_1	V_2	ε_{r1}	ε_{r2}	Eq.S4.	Eq.S5	Eq.S6
1120	0.585	0.415	30.1	22	26.74	26.11	26.43
1140	0.577	0.423	30.1	22	26.67	26.04	26.36
1160	0.577	0.423	30.1	22	26.67	26.04	26.36
1180	0.577	0.423	30.1	22	26.67	26.04	26.36
1200	0.564	0.436	30.1	22	26.57	25.94	26.25

V_1: Volume fraction of $Li_4Ti_5O_{12}$. V_2: Volume fraction of Li_2TiO_3.

ε_{r1}: Relative permittivity of $Li_4Ti_5O_{12}$. ε_{r2}: Relative permittivity of Li_2TiO_3.

Eq.S4： The result is calculated according to equation S4.

Eq.S5： The result is calculated according to equation S5.

Eq.S6： The result is calculated according to equations S6.

3. Predicting the dielectric loss of composite ceramics

There are relatively fewer theoretical models available for predicting dielectric loss due to its complexity. The dielectric loss of composite ceramics can be predicted by equation S7.[S11]

$$(\tan\delta_c)^\alpha = \sum V_i (\tan\delta_i)^\alpha \qquad \text{(S7)}$$

where $\tan\delta_c$ and $\tan\delta_i$ represents the dielectric loss of composite materials and type i materials, respectively. V_i is the molar fraction of the i-th material. $\tan\delta$ and Q have a reciprocal relationship ($\tan\delta=1/Q$), where Q is the quality factor. The $Li_4Ti_3O_8$ composite ceramic is composed of two phases, and equation S7 can be written in the following form:

$$(1/Q)^\alpha = V_1(1/Q_1)^\alpha + V_2(1/Q_2)^\alpha \qquad \text{(S8)}$$

where Q is the quality factor of $Li_4Ti_3O_8$ composite ceramics, and Q_1 and Q_2 are the quality factors of $Li_4Ti_5O_{12}$ and Li_2TiO_3, respectively. The constant α is related to the mixing state of the material, where $\alpha = -1$ represents for serial mixing and $\alpha = 1$ represents for parallel mixing. According to Table S9, it can be seen that the $Q\times f$ value obtained from parallel mixing is the highest, and there is still a significant deviation from the measured $Q\times f$ value. The research has shown that the dielectric loss of composite ceramics is related to external factors such as the defects, interface, and preparation process of ceramics.

Table S9 The density of ceramics at different sintering temperatures.

S.T. (°C)	V_1	V_2	Q_1	Q_2	f (GHz)	$Q\times f$ (a = -1)(GHz)	$Q\times f$ (a = 1)(GHz)
1120	0.585	0.415	4218.57	7383.72	7.07	36279	39112
1140	0.577	0.423	4218.57	7383.72	7.01	36122	38957
1160	0.577	0.423	4218.57	7383.72	7.06	36379	39235
1180	0.577	0.423	4218.57	7383.72	7.03	36225	39068
1200	0.564	0.436	4218.57	7383.72	7.02	36421	39301

V_1: Volume fraction of $Li_4Ti_5O_{12}$. V_2: Volume fraction of Li_2TiO_3.

Q_1: Quality factor of $Li_4Ti_5O_{12}$. Q_2: Quality factor of Li_2TiO_3.

f (GHz): Resonance frequency of $Li_4Ti_3O_8$ composite ceramics.

4. Predicting the τ_f of composite ceramics

According to the Lichtenecker logarithmic rule, the value of mixed τ_f can be obtained using the following equation:[S12]

$$\tau_f = V_1\tau_{f1} + V_2\tau_{f1} \tag{S9}$$

where τ_{f1} and τ_{f2} are the τ_f values of $Li_4Ti_5O_{12}$ and Li_2TiO_3, respectively. The measured τ_f(−3.3 ppm/°C) and the calculated τ_f(−0.08 ppm/°C) are close because the negative τ_f of $Li_4Ti_5O_{12}$ (−15 ppm/°C) can compensate for the positive τ_f of Li_2TiO_3 (+20.3 ppm/°C).

Table S10 The density of ceramics at different sintering temperatures.

S.T. (°C)	V_1	V_2	τ_{f1}	τ_{f2}	τ_f
1120	0.585	0.415	-15	+20.3	-0.3505
1140	0.577	0.423	-15	+20.3	-0.0681
1160	0.577	0.423	-15	+20.3	-0.0681
1180	0.577	0.423	-15	+20.3	-0.0681
1200	0.564	0.436	-15	+20.3	0.3908

V_1: Volume fraction of $Li_4Ti_5O_{12}$. V_2: Volume fraction of Li_2TiO_3.

τ_{f1}: τ_f of $Li_4Ti_5O_{12}$. τ_{f2}: τ_f of Li_2TiO_3.

τ_f: τ_f of $Li_4Ti_3O_8$.

Table S11 The phonon parameters of $Li_4Ti_3O_8$ ceramics.

Mode	ω_{oj}	ω_{pj}	γ_j	$\Delta\varepsilon_j$	$\Delta\varepsilon_j/\varepsilon_j$(%)	tan $\delta_j \times 10^7$
1	95.318	32.945	4.888	0.1195	0.568	4.8177
2	218.813	475.459	30.181	4.7215	22.453	223.098
3	241.159	425.828	29.454	3.1178	14.826	118.366
4	268.166	391.948	30.028	2.1362	10.158	66.866
5	297.879	285.438	26.792	0.9182	4.366	20.782
6	330.676	716.498	34.178	4.6948	22.327	110.001
7	369.927	339.844	35.922	0.8439	4.013	16.606
8	405.893	404.055	61.655	0.9909	4.712	27.7996
9	448.439	269.752	26.528	0.3618	1.72	3.5781
10	482.127	792.496	169.095	2.7019	12.848	147.336
11	575.179	155.489	47.668	0.0730	0.347	0.7893
12	632.083	373.761	84.212	0.3496	1.662	5.5245
$\varepsilon_\infty = 5.16$			$\varepsilon(w) = 26.19$		tan $\delta = 7.455 \times 10^{-5}$	

References

S1 H. F. Zhou, J. Z. Gong, N. Wang and X. L. Chen, *Ceram. Int.*, 2016, **42**, 8822-8825.

S2 W, Li, L. Fang, Y. Tang, Y. H. Sun and C. C. Li, *J. Alloys Compd.*, 2017, **701**, 295-300.

S3 J. J. Bian and Y. F. Dong, *Mater. Sci. Eng. B*, 2011, **176**, 147-151.

S4 J. Zhang, R. Z. Zuo, Y. Wang and S. S. Qi, *Mater. Lett.*, 2016, **164**, 353-355.

S5 L. L. Yuan and J. J. Bian, *Ferroelectrics.*, 2009, **387**, 123-129.

S6 D. Zhou, H. Wang, L. X. Pang, X. Yao and X. G. Wu, *J. Am. Ceram. Soc.*, 2008, **91**, 4115-4117.

S7 Y. N. Wang, Y. C. Chen and R. Y. Syu, *J. Mater. Sci. Mater. Electron.*, 2015, **26**, 1494-1499.

S8 L. Z. Ma, P. C. Zhang, S. C. Liu, Q. Z. Wen, Q. B. Du and H. Li, *Ceram. Int.*, 2023, **49**, 28615-28620.

S9 S. Z. Hao, D. Zhou, C. Du, L. X. Pang, C. J. Sing, S. Trukhanov, A. Trukhanov, A. S. B. Sombra, J. Varghese, Q. Li and X. Q. Zhang, *ACS Appl. Electron. Mater.*, 2021, **3**, 2286-2296.

S10 Y. P. Ji, K. X. Song, S. Y. Zhang, Z. L. Lu, G. Wang, L. H. Li, D. Zhou, D.W.

Wang, I. M. Reaney, *J. Eur. Ceram. Soc*., 2021, **41**, 424-429.
S11 K. Wakino, T. Okada, N. Yoshida and K. Tomono, *J. Am. Ceram. Soc*., 1993, **76**, 2588.
S12 H. Zhou, D. W. Wang, H. O. Zhu, W. J. Bian, H. D. Gu, H. K. Zhu, L. X. Wang, Q. T. Zhang and S. W. Ta, *Ceram. Int*., 2022, **48**, 6998-7004.