Supplementary material

Mechanism of ionic polarizability, bond valence, and crystal structure on the microwave dielectric properties of disordered $Li_{10}MTi_{13}O_{32}$ (M = Zn, Mg) spinels

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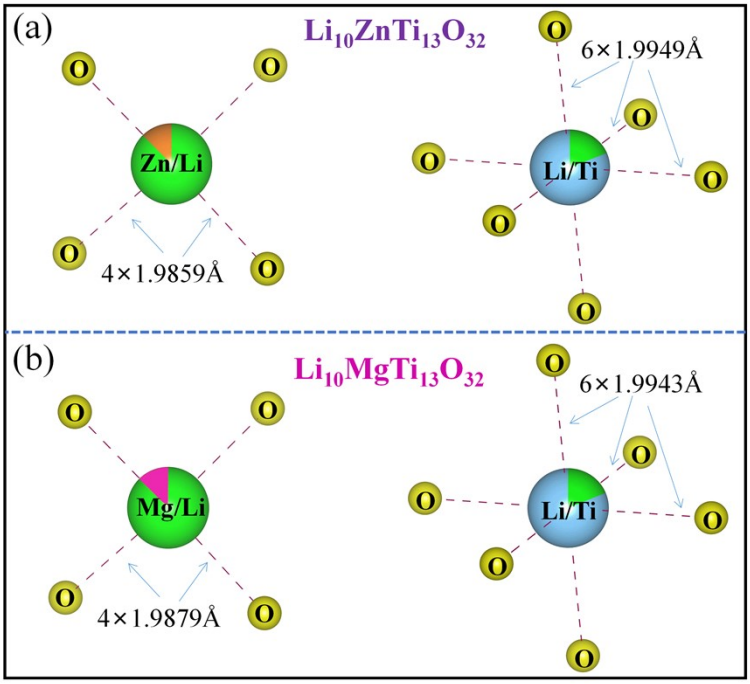

Fig. S1 Bond lengths in polyhedra of $Li_{10}MTi_{13}O_{32}$ (M = Zn, Mg) from Rietveld refinements of XRD data.

The test principle of the microwave dielectric properties:

The ε_r and dielectric loss values of all samples were measured in the TE_{011} mode which is confirmed by the software developed by Chengdu Enchi Microwave Technology Co, Ltd. The sample fixture, or resonant cavity, is designed by the instrument company.

The cylindrical disk of sample inserted between two mathematically infinite conducting plates changes the electromagnetic field of the resonant cavity. By using the scanning signal generated by the vector network analyzer, the resonant frequency and other information related to the electromagnetic field can be obtained. Based on changes in those parameters, with the diameter and height of the sample, the relative permittivity and dielectric loss can be calculated by the software. For more details about the testing, please refer to the following literatures:

[S1] L. Li, et al. IEEE Transactions on Microwave Theory and Techniques 64 (2016): 3781-3786.

[S2] D. Kajfez. IEEE transactions on microwave theory and techniques 32 (1984): 941-943.

[S3] Y. Kobayashi, et al. IEEE Transactions on Microwave Theory and Techniques 33 (1985) 1361-1366.

P-V-L theory:

According to their crystal structure and complex chemical bond theory, the composite crystal of $Li_{10}MTi_{13}O_{32}$ (M = Zn, Mg) was decomposed into the sum of binary crystals:[1,2]

$$Li_{10}MTi_{13}O_{32}\ (M = Zn, Mg) = MO + Li(1)_7O_7 + Li(2)_3O_{4.5} + Ti_{13}O_{19.5} \quad (S1)$$

Table S1. Chemical bond type, bond length, and ionic coordination number of $Li_{10}MTi_{13}O_{32}$ (M = Zn, Mg) crystals.

Compounds	Central ions and number	Ionic coordination number	Bond length	Bond type and number	Total number of central atoms for each type of chemical bond
$Li_{10}ZnTi_{13}O_{32}$= $ZnLi(1)_7Li(2)_3Ti_{13}O_{32}$	Zn×1	4	1.9859	Zn-O×(4×1)	(4×1)/4=1
	Li(1)×7	4	1.9859	Li(1)-O×(4×7)	(4×7)/4=7
	Li(2)×3	6	1.9949	Li(2)-O×(6×3)	(6×3)/6=3
	Ti×13	6	1.9949	Ti-O×(6×13)	(6×13)/6=13
	O×32	4	1.9859	O-Zn×(1×(1/8)×32)	(1×(1/8)×32)/4=1
			1.9859	O-Li(1)×(1×(7/8)×32)	(1×(7/8)×32)/4=7
			1.9949	O-Li(2)×(3×(3/16)×32)	(3×(3/16)×32)/4=4.5
			1.9949	O-Ti×(3×(13/16)×32)	(3×(13/16)×32)/4=19.5
$Li_{10}MgTi_{13}O_{32}$= $MgLi(1)_7Li(2)_3Ti_{13}O_{32}$	Zn×1	4	1.9879	Mg-O×(4×1)	(4×1)/4=1
	Li(1)×7	4	1.9879	Li(1)-O×(4×7)	(4×7)/4=7
	Li(2)×3	6	1.9943	Li(2)-O×(6×3)	(6×3)/6=3
	Ti×13	6	1.9943	Ti-O×(6×13)	(6×13)/6=13
	O×32	4	1.9879	O-Zn×(1×(1/8)×32)	(1×(1/8)×32)/4=1
			1.9879	O-Li(1)×(1×(7/8)×32)	(1×(7/8)×32)/4=7
			1.9943	O-Li(2)×(3×(3/16)×32)	(3×(3/16)×32)/4=4.5
			1.9943	O-Ti×(3×(13/16)×32)	(3×(13/16)×32)/4=19.5

The relationship between bond ionicity (f_i) and ε_r can be described by the following formula:[3]

$$\varepsilon_r = \frac{n^2 - 1}{1 - f_i} + 1 \tag{S2}$$

where n expressed the refractive index, which is about 1.718 for spinel. The f_i of μ bond is obtained by the following formula:[4]

$$f_i^{\mu} = \frac{(C^{\mu})^2}{(E_g^{\mu})^2} \tag{S3}$$

where E_g^{μ} and C^{μ} are average energy interval and heteropolar part, respectively (Table S2, ESI).

Table S2. The bond type, C^{μ}, and E_g^{μ} of $Li_{10}MTi_{13}O_{32}$ (M = Zn, Mg) ceramics.

Compounds	Bond type (μ)	C^{μ} (eV)	E_g^{μ} (eV)
$Li_{10}ZnTi_{13}O_{32}$	Li1–O	-6.323525053	9.61970447
	Zn–O	-10.05033941	12.39197592
	Li2–O	-10.2068281	12.47259352
	Ti–O	-25.85267461	26.82810157
$Li_{10}MgTi_{13}O_{32}$	Li1–O	-6.312018476	9.598520766
	Mg–O	-10.03105049	12.36575908
	Li2–O	-10.21384197	12.48140793
	Ti–O	-25.87303644	26.84915252

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1. J. Phillips, *Rev. Mod. Phys.*, 1970, **42**, 317–356.

2. J. C. Phillips, and J. A. Van Vechten, *Phys. Rev. Lett.*, 1969, **22**, 705–708.

3. S. S. Batsanov, *Russ. Chem. Rev.*, 1982, **51**, 684−697.

4. B. F. Levine, *J. Chem. Phys.*, 1973, **59**, 1463−1486.