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Aliovalent ion engineering of $LiMg_{0.5}Ti_{0.5}O_2$ ceramics for enhanced microwave dielectric performance

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3. Results and discussion

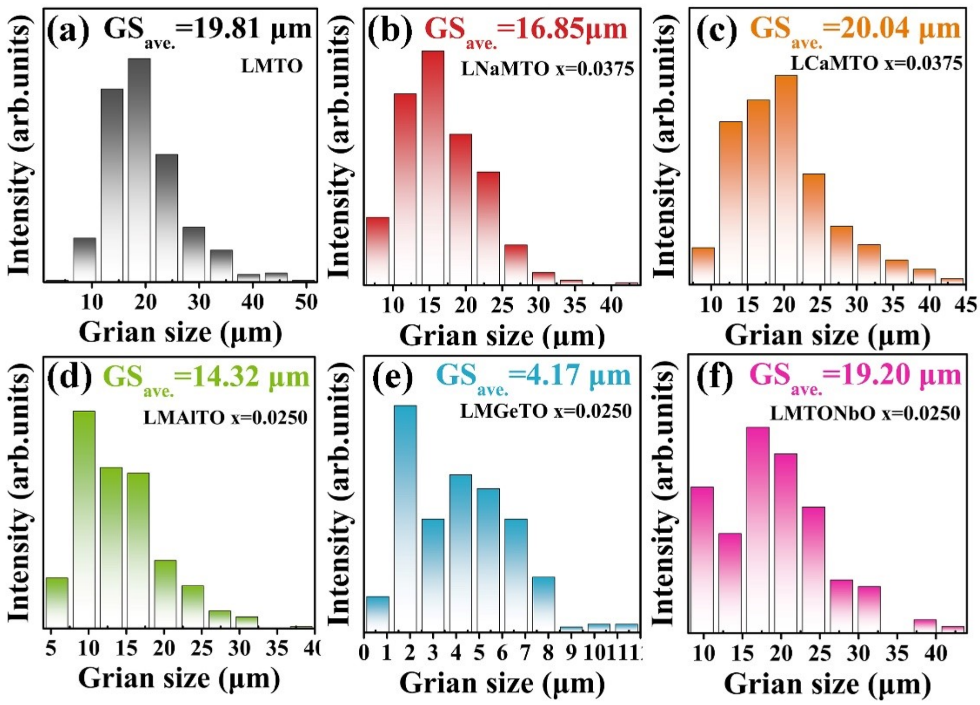

Fig. S1. (a)-(f) Grain size distribution statistics of LMTO, LNaMTO (x = 0.0375), LMCaTO (x = 0.0375), LMAlTO (x = 0.0250), LMGeTO (x = 0.0250), and LMTNbO (x = 0.0250) ceramics.

For complex chemical bond theory calculations, the intricate crystal structure of LMTO-based ceramics must be deconvoluted into a set of binary bond units. The resulting binary bond subsystems are represented by Formula (1):

$$LiMg_{0.5}Ti_{0.5}O_2 = LiO_{2/3} + Mg_{1/2}O_{2/3} + Ti_{1/2}O_{2/3} \tag{1}$$

Bond ionicity is calculated as follows:

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

$$C^\mu = 14.4 b^\mu e^{(-k_s^\mu r_o^\mu)} [\frac{(Z_A^\mu)^*}{r_o^\mu} - \frac{n}{m}\frac{(Z_B^\mu)^*}{r_o^\mu}] \quad (n > m) \tag{3}$$

$$C^\mu = 14.4 b^\mu e^{(-k_s^\mu r_o^\mu)} [\frac{n}{m}\frac{(Z_A^\mu)^*}{r_o^\mu} - \frac{(Z_B^\mu)^*}{r_o^\mu}] \quad (m > n) \tag{4}$$

$$(E_g^\mu)^2 = (\frac{39.74}{(d^\mu)^{2.48}})^2 + (C^\mu)^2 \tag{5}$$

$$b^\mu = 0.089 (N_c^\mu)^2 \tag{6}$$

$$N_c^\mu = \frac{m}{m+n} N_{CA}^\mu + \frac{n}{m+n} N_{CB}^\mu \tag{7}$$

$$k_s^\mu = (\frac{4k_F^\mu}{\pi \alpha_B})^2 \tag{8}$$

$$k_F^\mu = [3\pi^2 (N_e^\mu)^*]^{\frac{1}{3}} \tag{9}$$

$$r_o^\mu = \frac{d^\mu}{2} \tag{10}$$

$$(N_e^\mu)^* = \frac{(n_e^\mu)^*}{v_b^\mu} \tag{11}$$

$$(n_e^\mu)^* = \frac{(Z_A^\mu)^*}{(N_{CA}^\mu)^*} + \frac{(Z_B^\mu)^*}{(N_{CB}^\mu)^*} \tag{12}$$

$$v_b^\mu = \frac{(d^\mu)^3}{\sum_v (d^v)^3 N_b^v} \tag{13}$$

$$\varepsilon = \sum_\mu (4\pi \chi_b^\mu + 1) \tag{14}$$

$$\chi_b^\mu = \frac{(\hbar \Omega_p)^2}{4\pi (E_g)^2} \tag{15}$$

$$(\Omega_p)^2 = \frac{4\pi(N_e^\mu)e^2 D_\mu A_\mu}{m} \tag{16}$$

$$A_\mu = 1 - \frac{E_g^\mu}{4E_F^\mu} + \frac{1}{3}\frac{(E_g^\mu)^2}{(4E_F^\mu)^2} \tag{17}$$

$$D_\mu = \Delta_\mu^A \Delta_\mu^B - (\delta_\mu^A \delta_\mu^B - 1)[(Z_A^\mu)^* - (Z_B^\mu)^*]^2 \tag{18}$$

$$E_F^\mu = \frac{(\hbar k_F^\mu)^2}{2m} \tag{19}$$

$$k_F^\mu = [3\pi^2 (N_e^\mu)^*]^{1/3} \tag{20}$$

The variables in the theoretical framework are defined as follows: d^μ and b^μ correspond to chemical bond length and its empirical correction factor. The Thomas-Fermi screening is expressed through the term $e^{(-k_s^\mu r_o^\mu)}$, while $(Z_A^\mu)^*$ and $(Z_B^\mu)^*$ represent effective valence electron numbers. The average valence electron density is denoted by n_e^μ and v_b^μ describes the bond volume. Fundamental constants include the Bohr radius α = 0.5292 Å, Planck's constant $\hbar$ = 4.13566 × 10^{-15} eV•s, and elementary constants $e = 4.8\times10^{-10}$ esu and $m = 9.1\times10^{-28}$ g. Structural parameters include coordination numbers N_{CA}^μ and N_{CB}^μ for cations and anions, with D_μ accounting for d-electron corrections and A_μ representing the Penn dielectric correction. Electronic structure parameters comprise Fermi energy E_F^μ and Fermi wavevector k_F^μ, with Δ_μ^A, Δ_μ^B, δ_μ^A, and δ_μ^B as system-specific coefficients.

The lattice energy is calculated as follows:

$$U_{cal} = \sum_\mu (U_{bc}^\mu + U_{bi}^\mu) \tag{21}$$

$$U_{bc}^\mu = 2100m\frac{(Z_+^\mu)^{1.64}}{(d^\mu)^{0.75}} f_c^\mu \tag{22}$$

$$U_{bi}^\mu = 1270\frac{(m+n)Z_+^\mu Z_-^\mu}{d^\mu}\left(1 - \frac{0.4}{d^\mu}\right) f_i^\mu \tag{23}$$

U_{bc}^μ and U_{bi}^μ represent the lattice energy contributions from ions and covalent bonds, respectively, while Z_+^μ and Z_-^μ denote the valences of the cations and anions involved in the chemical bonding.

The bond energy is calculated as follows:

$$E_b^\mu = t_c E_c^\mu + t_i E_i^\mu \tag{24}$$

$$E_i^\mu = \frac{33200}{d^\mu} \tag{25}$$

$$E_c^\mu = \frac{(r_{CA} + r_{CB})}{d^\mu}(E_{A-A}E_{B-B})^{1/2} \tag{26}$$

$$t_i + t_c = 1 \tag{27}$$

$$t_i = \left|\frac{S_A - S_B}{6}\right| \tag{28}$$

where *S* and *r* are the electronegativity and covalent radius respectively, and $E_{A\text{-}A}$ and $E_{B\text{-}B}$ are the homonuclear bond energies.