## Supplementary information

# Tailoring Microwave Dielectric Properties through High-Entropy Strategy in Spinel-type Titanium Ceramics

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The bulk density of the high-entropy MZLCNT ceramics was measured via the Archimedes method. The theoretical density of the crystalline phase, denoted as $\rho_{theo}$, was calculated in accordance with equation (1)[1]:

$$\rho_{theo} = \frac{ZA}{V_C N_A} \tag{1}$$

Here $Z$ is the number of molecules in A unit cell, A is the molar molecular weight, $Vc$ is the volume of a unit cell, and $N_A$ is Avogadro's constant.

The relative density($\rho_{relative}$) was used to evaluate the densification of the ceramics, which can be calculated by using the following equation (2):

$$\rho_{relative} = \frac{\rho_{bulk}}{\rho_{theo}} \tag{2}$$

The $\rho_{bulk}$ and $\rho_{theo}$ represent bulk density and theoretical density respectively.

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**Table S1**. The bulk density, theoretical density, and relative density of high-entropy MZLCNT ceramics.

| $x$ value | 0.0 | 0.1 | 0.2 | 0.3 | 0.4 |
|---|---|---|---|---|---|
| $P_{bulk}$(g/cm$^3$) | 4.283 | 4.177 | 4.073 | 3.964 | 3.910 |
| $\rho_{theo}$(g/cm$^3$) | 4.398 | 4.280 | 4.161 | 4.044 | 3.985 |
| $\rho_{relative}$(%) | 97.4 | 97.6 | 97.9 | 98.0 | 98.1 |

**Table S2.** The oxygen vacancy content of high-entropy MZLCNT ceramics

| Parameter | $x$ = 0.0 | $x$ = 0.2 | $x$ = 0.4 |
|---|---|---|---|
| $Ti^{3+}$ $2p_{3/2}$ | 45448 | 41174 | 29854 |
| $Ti^{4+}$ $2p_{3/2}$ | 55983 | 62439 | 73685 |
| δ (%) | 22.4 | 19.8 | 14.4 |

The ionicity ($f_i$) of the chemical bond $\mu$ in high-entropy MZLCNT ceramics are computed by the following equation:

$$f_i^{\mu} = \frac{(C^{\mu})^2}{(E_g^{\mu})^2} \tag{3}$$

$$(E_g^{\mu})^2 = (E_h^{\mu})^2 + (C^{\mu})^2 \tag{4}$$

$$E_h^{\mu} = \frac{39.74}{(d^{\mu})^{2.48}} \tag{5}$$

$$C^{\mu} = 14.4 b^{\mu} e^{(-k_s^{\mu} r_o^{\mu})} [\frac{(Z_A^{\mu})^*}{r_o^{\mu}} - \frac{n}{m} \frac{(Z_B^{\mu})^*}{r_o^{\mu}}], n \geq m \tag{6}$$

Where $E_g^{\mu}$ represents the average energy gap between molecular orbitals and antibonding molecular orbitals, $E_h^{\mu}$ and $C^{\mu}$ are respectively the homogeneous and heteropolar components of the energy gap. $d^{\mu}$ refers to the bond length of the $\mu$ bond, and $b^{\mu}$ is the correction factor. The $e^{(-k_s^{\mu} r_o^{\mu})}$ is the Thomas Fermi shielding factor, $(Z_A^{\mu})^*$, and $(Z_B^{\mu})^*$ indicate the number of effective valence electrons of A and B.

The lattice energy of different chemical bonds in high-entropy MZLCNT ceramics, calculated using follow equation:

$$U = \sum_{\mu} (U_{bc}^{\mu} + U_{bi}^{\mu}) \tag{7}$$

$$U_{bc}^{\mu} = 2100m \frac{(Z_{+}^{\mu})^{1.64}}{(d^{\mu})^{0.75}} f_c^{\mu} \tag{8}$$

$$U_{bi}^{\mu} = 1270 \frac{(m+n) Z_{+}^{\mu} Z_{-}^{\mu}}{d^{\mu}} (1 - \frac{0.4}{d^{\mu}}) f_i^{\mu} \tag{9}$$

Where $U_{bi}^{\mu}$ and $U_{bc}^{\mu}$ represent the lattice energies contributed by ions and covalent contributions respectively. $Z_{+}^{\mu}$ and $Z_{-}^{\mu}$ indicate the bond valence of the cation and anion in the chemical bond $\mu$.

**Table. S3** The bong length, ionicity ($f_i$), covalency ($f_c$) and lattice energy of different bond in high-entropy MZLCNT ceramics.

| *x* value | Bond type | Bond length (Å) | $f_i$ (%) | $f_c$ (%) | Lattice energy (kJ/mol) |
|---|---|---|---|---|---|
| 0.0 | A(1)-O | 1.90 | 62.55 | 37.45 | 2329 |
| | A(2)-O | 2.17 | 64.76 | 35.24 | 1920 |
| | Ti-O | 2.17 | 89.14 | 10.86 | 7649 |
| 0.1 | A(1)-O | 1.84 | 60.64 | 39.36 | 2211 |
| | A(2)-O | 2.10 | 63.28 | 36.72 | 1971 |
| | Ti-O | 2.10 | 85.74 | 14.26 | 7855 |
| 0.2 | A(1)-O | 1.83 | 62.44 | 37.56 | 2204 |
| | A(2)-O | 2.09 | 65.97 | 34.03 | 1974 |
| | Ti-O | 2.09 | 85.48 | 14.52 | 7865 |
| 0.3 | A(1)-O | 1.87 | 68.44 | 31.56 | 2170 |
| | A(2)-O | 2.08 | 67.36 | 32.64 | 1989 |
| | Ti-O | 2.08 | 84.25 | 15.75 | 7925 |
| 0.4 | A(1)-O | 1.92 | 74.73 | 25.27 | 2130 |
| | A(2)-O | 2.05 | 75.52 | 24.48 | 2010 |
| | Ti-O | 2.05 | 82.57 | 17.43 | 8005 |

The lattice distortion ($\varepsilon^{W-H}$) of high-entropy MZLCNT ceramics can be calculated by the following equation:

$$\varepsilon^{W-H} = \frac{\beta_{hkl}}{4tan(\theta_{hkl})} \tag{10}$$

Where $\varepsilon^{W-H}$, $\beta_{hkl}$, and $\theta_{hkl}$ represent the lattice distortion, full width at half of the maximum and diffraction angle.

**Table S4**. The lattice distortion of high-entropy MZLCNT ceramics with $x$ =0.0-0.4.

| | | Peak position ($2\theta_{hkl}$)/ $\beta_{hkl}$ | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| *x value* | $\Delta S_{config}$ | Peak 1 | Peak 2 | Peak 3 | Peak 4 | Peak 5 | Peak 6 | Peak 7 | $\varepsilon^{W-H}$ (%) |
| 0.0 | 1.09R | 18.256/ 0.116 | 30.016/ 0.097 | 35.338/ 0.100 | 42.955/ 0.101 | 53.276/ 0.095 | 56.782/ 0.105 | 62.343/ 0.105 | 1.858 |
| 0.1 | 1.38R | 18.244/ 0.120 | 30.015/ 0.100 | 35.342/ 0.100 | 42.955/ 0.108 | 53.277/ 0.096 | 56.783/ 0.103 | 62.356/ 0.109 | 1.621 |
| 0.2 | 1.52R | 18.261/ 0.112 | 30.020/ 0.104 | 32.358/ 0.104 | 42.961/ 0.111 | 53.284/ 0.100 | 56.800/ 0.108 | 62.363/ 0.113 | 1.034 |
| 0.3 | 1.58R | 18.259/ 0.109 | 30.018/ 0.098 | 35.356/ 0.103 | 42.959/ 0.095 | 52.281/ 0.097 | 56.798/ 0.098 | 62.362/ 0.111 | 1.110 |
| 0.4 | 1.61R | 18.256/ 0.131 | 30.017/ 0.091 | 35.354/ 0.099 | 42.957/ 0.094 | 53.280/ 0.094 | 56.797/ 0.095 | 62.359/ 0.090 | 2.327 |

The bond strength of the A(1)-O bond in the high-entropy MZLCNT ceramic [$AO_4$] tetrahedron is calculated by equation (11)[2]:

$$S = S_0 \left( \frac{R_i}{R_0} \right)^{-N} \tag{11}$$

where $R_i$ is the average A-O bond length in the [$AO_4$] tetrahedra, with $N$ and $R_0$ representing empirical constants defined by the cation site and cation-anion pair.

**Reference**

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$CaSn_xSiO_{(3+2x)}$-based positive $\tau_f$ compensator, *Ceram Int* 44 (2018) 18209–18212. https://doi.org/10.1016/j.ceramint.2018.07.029.

[2] I.D. Brown, R.D. Shannon, Empirical Bond-Strength-Bond-Length Curves for Oxides, 1973.