Crystal structure and enhanced microwave dielectric properties of the $\text{Ce}_2[\text{Zr}_{1-x}(\text{Al}_{1/2}\text{Ta}_{1/2})_x]_3(\text{MoO}_4)_9$ ceramics at microwave frequency

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Abstract: Dense microwave dielectric ceramics of $\text{Ce}_2[\text{Zr}_{1-x}(\text{Al}_{1/2}\text{Ta}_{1/2})_x]_3(\text{MoO}_4)_9$ (CZMAT) ($x = 0.02\text{--}0.10$) were prepared by the conventional solid-state route. The effects of $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$ on their microstructures, sintering behaviors, and microwave dielectric properties were systematically investigated. On the basis of the X-ray diffraction (XRD) results, all the samples were matched well with $\text{Pr}_2\text{Zr}_3(\text{MoO}_4)_9$ structures, which belonged to the space group $R\bar{3}c$. The lattice parameters were obtained using the Rietveld refinement method. The correlations between the chemical bond parameters and microwave dielectric properties were calculated and analyzed by using the Phillips–Van Vechten–Levine (P–V–L) theory. Excellent dielectric properties of $\text{Ce}_2[\text{Zr}_{0.94}(\text{Al}_{1/2}\text{Ta}_{1/2})_{0.06}]_3(\text{MoO}_4)_9$ with a relative permittivity (ϵ_r) of 10.46, quality factor ($Q \times f$) of 83,796 GHz, and temperature coefficient of resonant frequency (τ_f) of -11.50 ppm/°C were achieved at 850 °C.

Keywords: microwave dielectric ceramics; $\text{Ce}_2[\text{Zr}_{1-x}(\text{Al}_{1/2}\text{Ta}_{1/2})_x]_3(\text{MoO}_4)_9$ (CZMAT); Phillips–Van Vechten–Levine (P–V–L) theory; low sintering temperature

1 Introduction

With the rapid growth of wireless communication industry, microwave dielectric ceramics are widely studied for their use in global positioning system (GPS) patch antennas, resonators in filters or oscillators at microwave frequencies in radar detectors, and mobile telephones [1–3]. The important characteristics required for excellent microwave dielectric ceramics are

high-quality factor ($Q \times f$) for the enhancement of frequency selectivity, low dielectric constant (ϵ_r) for fast signal speed, and near-zero temperature coefficient of resonant frequency (τ_f) to improve the stability of the frequency against temperature change [4–6]. It is difficult to balance these three parameters of microwave dielectric properties. To meet the development requirements of the communication technology, it is necessary to explore the novel microwave dielectric ceramics with excellent dielectric properties, such as Eu_2TiO_5 , $\text{Ba}_2\text{CuGe}_2\text{O}_7$, Y_2MgTiO_6 , and CaAl_2O_4 [7–10]. In addition, researchers focused on the improvement of the microwave dielectric properties through ion substitution and the use of composite ceramics [11–16].

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For instance, the crystal structure and dielectric properties of Ti^{4+} -substituted CaSnSiO_5 ceramics were investigated by Du *et al.* [11]. Yang *et al.* [12] reported the trirutile-type $\text{Co}_{0.5}\text{Ti}_{0.5}\text{TaO}_4$ ceramics with a ϵ_r of 40.69, $Q \times f$ of 17,291 GHz, and τ_f of 114.54 ppm/°C. A temperature-stable $\text{CaSnSiO}_5\text{--K}_2\text{MoO}_4$ composite microwave ceramic was prepared through the cold sintering process [13].

Rare-earth molybdate ($\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$) ceramics have attracted great attention recently due to their low dielectric loss and sintering temperature [17,18]. Tao *et al.* [19] reported that the $\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9$ ceramics with performance parameters of $Q \times f = 19,062$ GHz, $\epsilon_r = 10.69$, and $\tau_f = -1.29$ ppm/°C were attained at 575 °C. Moreover, Shi *et al.* [20] improved $Q \times f$ value by the partial replacement of Mo^{6+} by W^{6+} ions in $\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9$ ceramic. The effect of Ti^{4+} doping on $\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9$ ceramic properties was analyzed [21]. The substitution of complex ions for divalent or tetravalent ions was recently investigated as an alternative approach to increase the $Q \times f$ value of dielectric materials [22]. Improved $Q \times f$ values were obtained when $(\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}$ substituted the Zr-site of $\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9$ ceramics [23]. Hence the high $Q \times f$ values can be obtained not only by the substitution of the tetravalent cations at the Zr-sites, but also by the isovalent substitution of combinations of aliovalent cations. With reference to $\text{Ce}_2[\text{Zr}_{1-x}(\text{Mg}_{1/3}\text{Sb}_{2/3})_x]_3(\text{MoO}_4)_9$ ceramics, we wonder if the Al^{3+} can be used. Considering that Sb^{5+} (0.60 Å) and Ta^{5+} (0.64 Å) ions possess a similar ionic radius at the same coordination number (CN = 6), Ta^{5+} was introduced to form $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$ to replace Ti^{4+} .

In the present work, the effect of substituting $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$ for the Zr-sites on the microwave dielectric properties of $\text{Ce}_2[\text{Zr}_{1-x}(\text{Al}_{1/2}\text{Ta}_{1/2})_x]_3(\text{MoO}_4)_9$ (CZMAT) ceramics was investigated. Microstructure and sintering behaviors of the CZMAT ceramics were determined using the X-ray diffraction (XRD) and the scanning electron microscopy (SEM). The lattice parameters of CZMAT ceramics were obtained via the Rietveld refinement method. To investigate the relationship between the dielectric properties and chemical bond characteristics, the chemical bond theory was used to calculate the bond ionicity, bond energy, lattice energy, and coefficient of thermal expansion.

2 Experimental

High-purity powders CeO_2 (99.9%, Macklin), Al_2O_3 (99.09%, Macklin), Ta_2O_5 (99.5%, Macklin), ZrO_2 (99.99%, Aladdin), and MoO_3 (99.95%, Aladdin) were

weighted accurately based on the formula of CZMAT. The mixed powders were ball-milled with ZrO_2 balls and ethanol media for 24 h. The oven-dried slurry was pre-sintered for 2 h in a muffle furnace and ball-milled for 24 h. Afterward, the oven-dried slurry was admixed with 10 wt% paraffin, pressed into a cylindrical billet (10 mm stainless steel die, 6 MPa), and sintered at 775–875 °C for 6 h.

The crystal structures were confirmed by XRD (Model D/MAX-B, Rigaku Co.) with Cu K α radiation (working at 40 kV and 40 mA) in the 2θ range of 5°–80°. The microstructure was observed by the scanning electron microscope (FeSEM Quanta 250, FEI Co.). The apparent densities of specimens were analyzed using the Archimedes method (Mettler Toledo, XS64). To obtain the lattice parameters of the specimens, the XRD data were analyzed by FULLPROF program on the basis of Rietveld refinements. A network analyzer (Agilent Co., N5234A) was used to obtain the ϵ_r and $Q \times f$ of samples with the TE_{018} method at microwave frequency. The τ_f values are obtained by Eq. (1) as follows:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times 60} \times 10^6 \text{ (ppm/°C)} \quad (1)$$

where f_{25} and f_{85} represent resonant frequencies at 25 and 85 °C, respectively.

3 Results and discussion

The XRD patterns of the CZMAT ceramics sintered at optimal temperatures are exhibited in Fig. 1(a). All the diffraction peaks match well with the $\text{Pr}_2\text{Zr}_3(\text{MoO}_4)_9$ standard pattern (PDF# 51-1851), and no secondary phase was detected, thereby suggesting that the $\text{Pr}_2\text{Zr}_3(\text{MoO}_4)_9$ -like crystal structure with a $R\bar{3}c$ space group is formed. The crystal structure of the CZMAT ceramics does not change with increasing $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$. The magnified results in the 2θ range of 22.4°–22.8° are plotted in Fig. 1(b). The diffraction peaks (119) slightly shift to a higher angle with the augmentation of $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$, because the ionic radius of Zr^{4+} (0.72 Å) is longer than that of $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$ (0.64 Å), which corresponds with the decrease of the unit cell volume based on Bragg's diffraction law.

In addition, the FULLPROF software was used to obtain structural parameters, such as lattice parameters, bond length, and unit cell volumes. The refined results

Fig. 3 Lattice parameters (a , b , and c) and unit cell volume (V_m) of CZMAT ceramics as a function of the substitution amount of $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$.

Table 2 Refined atomic positions of CZMAT ceramics

Atom	Wyckoff position	Site	x	y	z	Occupancy
Ce	12c	3	0.6667	0.3333	0.0297	0.3333
Zr(AlTa)1	6b	−3	0.0000	0.0000	0.0000	0.1667
Zr(AlTa)2	12c	3	0.3333	0.6667	0.0712	0.3333
Mo1	36f	1	0.0958	0.7278	0.0248	1.0000
Mo2	18e	2	0.2822	0.2822	0.2500	0.5000
O1	36f	1	−0.0979	0.5964	0.0295	1.0000
O2	36f	1	0.1497	0.6566	0.0025	1.0000
O3	36f	1	0.2050	0.7336	0.0514	1.0000
O4	36f	1	0.1265	0.9374	0.0221	1.0000
O5	36f	1	0.2940	0.4767	0.2456	1.0000
O6	36f	1	0.1550	0.1949	0.2723	1.0000

Fig. 4 Schematic illustration of CZMAT ceramics.

grain boundary fraction decreases with the content of $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$ substitution. All grain boundaries are straight, and the angle of grain boundary is close to 120° , which indicates that the ceramic reaches a dense microstructure. For $x = 0.02$ – 0.10 , the grain size increases gradually, indicating that the $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$ ion can increase the grain size of CZMAT ceramics.

The diametric shrinkage ratio was used to analyze the

Fig. 5 SEM microphotographs of the CZMAT ceramics sintered at 850°C for 6 h: (a) $x = 0.02$, (b) $x = 0.04$, (c) $x = 0.06$, (d) $x = 0.08$, and (e) $x = 0.10$.

sintering behaviors of the CZMAT ceramics. Figure 6(a) shows the diametric shrinkage ratio curves of CZMAT ceramics sintered at 775 – 875°C . The diametric shrinkage ratio of CZMAT ceramic increases, reaches the maximum value at 850°C , and then decreases slightly. The increase of diametric shrinkage ratio can be attributed to the pore elimination. A higher sintering temperature will accelerate the growth of crystal grains, and the pores will not be discharged in time, thereby resulting in a sample with poor densification. The apparent density of the CZMAT ceramics is illustrated in Fig. 6(b). The apparent density of CZMAT ceramic is obtained by using the Archimedes method. The apparent density of CZMAT ceramic increases with sintering temperature and then decreases slightly; this trend is consistent with that of the diametric shrinkage ratio.

Figure 7 illustrates the ε_r and $Q \times f$ values of CZMAT ceramics as a function of sintering temperature. As shown in Fig. 7(a), the ε_r of each composition increases initially due to the disappearance of pores and then decreases slightly. For $x = 0.04, 0.06, 0.08$, and 0.10 , the ε_r values of samples reach the maximum (10.45, 10.53, 10.52, and 10.47, respectively) at 825°C . For $x = 0.02$, the maximum ε_r value (10.61) is obtained at 850°C . The variation in dielectric constant is consistent with the density, suggesting that density serves as the main extrinsic factor of ε_r . The $Q \times f$ of CZMAT ceramics as a function of the sintering temperature is displayed in

Fig. 6 (a) Diametric shrinkage ratio of CZMAT ceramics as a function of sintering temperature; (b) apparent density of CZMAT ceramics as a function of sintering temperature.

Fig. 7 (a) ϵ_r values of CZMAT ceramics as a function of sintering temperature; (b) $Q \times f$ values of CZMAT ceramics as a function of sintering temperature.

Fig. 7(b). $Q \times f$ values increase with the sintering temperature and then decrease slightly. The optimal values are obtained at 850 °C. Densification and a relatively uniform microstructure are the main reasons for optimizing the quality factor; the decline of $Q \times f$ values at a higher sintering temperature can be attributed to intrinsic loss [24,25].

In recent years, Mo-based microwave dielectric ceramics were studied in depth, as shown in Fig. 8 [10,17–21,26–32]. Most Mo-based microwave dielectric ceramics have $Q \times f$ in the range of 20,000–80,000 GHz. New double molybdates of lanthanides and transition metal zirconium ($\text{Ln}_2\text{O}_3\text{--ZrO}_2\text{--MoO}_3$ systems) have attracted great attention due to the excellent microwave dielectric properties. Several studies have focused on the microwave dielectric properties of $\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$ ($\text{Ln} = \text{La}, \text{Ce}, \text{Nd}, \text{Sm}$). Liu and Zuo [17] reported that $\text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9$ ($\text{Ln} = \text{Sm}, \text{Nd}$) ceramics exhibited properties of $\epsilon_r = 11.0$, $Q \times f = 74,012$ GHz, and $\tau_f = -45.3$ ppm/°C at sintering temperature of 875 °C for $\text{Ln} = \text{Sm}$ and $\epsilon_r = 10.8$, $Q \times f = 58,942$ GHz, and $\tau_f = -40.9$ ppm/°C at the sintering temperature of 850 °C for $\text{Ln} = \text{Nd}$. In particular, $\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9$ ceramics with $Q \times f = 19,062$ GHz were prepared by the traditional solid-state method [19]. In this study, excellent $Q \times f$ of 83,796 GHz was obtained in $\text{Ce}_2[\text{Zr}_{0.94}(\text{Al}_{1/2}\text{Ta}_{1/2})_{0.06}]_3(\text{MoO}_4)_9$ ceramic. The dielectric properties of $\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9$ ceramics can be optimized efficiently by doping $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$ at Zr-site ions. This study enriched the microwave dielectric systems. The CZMAT ceramic with low-temperature and high-quality factors is a good candidate for passive communication devices.

In general, the microwave dielectric properties are associated with the extrinsic factors. The extrinsic factors include grain boundaries, pores, abnormal grains, defect, and dislocation, which are the main

Fig. 8 $Q \times f$ with ϵ_r of Mo-salt microwave dielectric ceramics.

factors that produce the dielectric loss. The intrinsic factors need to be investigated in detail because of the dense microstructures and no secondary phases [33]. The dense microstructures of the CZMAT ceramic are observed at 850 °C. The observed ($\alpha_{\text{obs.}}$) and theoretical ($\alpha_{\text{theo.}}$) dielectric polarizability values are the microscopic parameters that can be used to evaluate the structural dependence of ϵ_r . According to the Clausiuse–Mosotti equation and the additive rule of dielectric polarizability, $\alpha_{\text{obs.}}$ and $\alpha_{\text{theo.}}$ can be evaluated by Eqs. (2) and (3):

$$\alpha_{\text{theo.}} \left(\text{Ce}_2 \left[\text{Zr}_{1-x} (\text{Al}_{1/2} \text{Ta}_{1/2})_x \right]_3 (\text{MoO}_4)_9 \right) \\ = 2\alpha(\text{Ce}^{3+}) + 3(1-x)\alpha(\text{Zr}^{4+}) + \frac{3}{2}x\alpha(\text{Al}^{3+}) \\ + \frac{3}{2}x\alpha(\text{Ta}^{5+}) + 9\alpha(\text{Mo}^{6+}) + 36\alpha(\text{O}^{2-}) \quad (2)$$

$$\alpha_{\text{obs.}} = \frac{1}{b} V_m \frac{\epsilon_r - 1}{\epsilon_r + 2} \quad (3)$$

where $\alpha(\text{Ce}^{3+})$, $\alpha(\text{Zr}^{4+})$, $\alpha(\text{Al}^{3+})$, $\alpha(\text{Ta}^{5+})$, and $\alpha(\text{O}^{2-})$ are the ion polarizability values, which were obtained by Shannon and Rossman [34]. The value of $\alpha(\text{Mo}^{6+})$ was obtained by Choi *et al.* [35]. b is $4\pi/3$, and V_m represents the unit cell volume. The values of $\alpha_{\text{theo.}}$ and $\alpha_{\text{obs.}}$ of CZMAT ceramics are shown in Fig. 9. The values of $\alpha_{\text{theo.}}$ and $\alpha_{\text{obs.}}$ decrease gradually with the increase of x . The discrepancy between $\alpha_{\text{theo.}}$ and $\alpha_{\text{obs.}}$ can be explained by the atomic vibration and polyhedral distortion.

The relationship between property and structure of dielectric materials, which are composed of complex oxide crystals, is worth analyzing and exploring. Any complex crystal can be decomposed into multiple binary crystals on the basis of the P–V–L theory. Hence, the chemical bond parameters of an individual bond can be calculated. The bond equation of CZMAT ceramics is shown in Eq. (4).

Fig. 9 ϵ_r , $\alpha_{\text{theo.}}$, and $\alpha_{\text{obs.}}$ of CZMAT ceramics as a function of x .

The effective valence electron number, which is an important intermediate parameter in the calculation of bond parameters, can be calculated by using Eqs. (5)–(9) as follows:

$$(Z_A^\mu)^* = Z_A^\mu \times (q_A^\mu)^* \quad (5)$$

$$(Z_B^\mu)^* = Z_B^\mu \times (q_B^\mu)^* \quad (6)$$

$$(q_A^\mu)^* = \frac{P_A^\mu}{Z_A^\mu} \quad (7)$$

$$(q_B^\mu)^* = \frac{P_B^\mu}{N - Z_B^\mu} \quad (8)$$

$$(n_\mu)^* = \frac{(Z_A^\mu)^*}{N_{cA}^\mu} + \frac{(Z_B^\mu)^*}{N_{cB}^\mu} = \frac{P_A^\mu}{N_{cA}^\mu} + \frac{Z_B^\mu \times P_B^\mu}{N_{cB}^\mu \times (N - Z_B^\mu)} \quad (9)$$

where A and B represent the cation and anion, respectively. $(Z_A^\mu)^*$ and $(Z_B^\mu)^*$ are the effective numbers of valence electrons of cation and anion, respectively. Z_A^μ and Z_B^μ are the valence states of cation and anion, respectively. $(q_A^\mu)^*$ and $(q_B^\mu)^*$ are the effective charge of valence electrons of cation and anion, respectively. P_A^μ and P_B^μ are the valence states of cation and anion, respectively. $(n_\mu)^*$ represents the effective number of valence electrons of an individual bond μ . N_{cA}^μ and N_{cB}^μ are the coordination numbers of cation and anion, respectively.

The coordination and charge distributions of various ions in CZMAT ceramics are illustrated in Fig. 10. The coordination numbers of Ce, Zr(AlTa), Mo, and O atoms are 9, 6, 4, and 2, respectively. The valence of cations is expressed as $P_{\text{Ce}} = +3$, $P_{\text{Zr(AlTa)}} = +4$, and $P_{\text{Mo}} = +6$, whereas the valence of the oxygen ion is expressed as Eq. (4). The valences in the Ce–O, Zr(AlTa)–O, and Mo–O bonds are $P_{\text{O–Ce}} = -2/3$, $P_{\text{O–Zr(AlTa)}} = -4/3$, and $P_{\text{O–Mo}} = -3$, respectively. On the basis of Eqs. (5) and (6), the effective valence electron number of cations

Fig. 10 Coordination and charge distribution of various ions in CZMAT ceramics.

are 3, 4, and 6, whereas the effective valence electron numbers of oxygen ion in the Ce–O, Zr(AlTa)–O, and Mo–O bonds are 2, 4, and 9, respectively. Figure 10 shows that the effective valence electron numbers in the Ce–O bond, Zr(AlTa)–O bond, and Mo–O bond are 4/3, 8/3, and 6, respectively.

According to the P–V–L theory, the ϵ_r can be predicted using bond ionicity [36]. ϵ_r and bond ionicity f_i^μ can be estimated by Eqs. (10) and (11) as follows:

$$\epsilon_r = \frac{n_0^2 - 1}{1 - f_i} + 1 \quad (10)$$

$$f_i^\mu = \frac{(C^\mu)^2}{(E_g^\mu)^2} \quad (11)$$

where C^μ represents the heteropolar part, n_0 represents the refractive index, and E_g^μ represents the average energy gap.

Table 3 lists the bond ionicity of individual bonds, and the calculation process has been described in previous works. In addition, ϵ_r and $f_{i(\text{Zr(AlTa)-O(4)})}$ as a function of the content of $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$ substitution are shown in Fig. 11. The ϵ_r values of CZMAT ceramics fluctuate slightly between 10.42 and 10.61 with the increase of $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$. The same trend is observed in $f_{i(\text{Zr(AlTa)-O(4)})}$, indicating that the Zr(AlTa)–O(4) bond ionicity is an important factor of the dielectric constant.

The physical properties are predicted by lattice energy, and the stability of materials is positively associated

Table 3 Bond ionicity f_i of CZMAT ceramics sintered at densification temperature for 6 h (Unit: %)

CZMAT	$x = 0.02$	$x = 0.04$	$x = 0.06$	$x = 0.08$	$x = 0.10$
Ce–O(1) ^a	84.5357	85.1309	84.7987	84.8688	85.1623
Ce–O(1) ^b	84.5392	85.1336	84.8020	84.8712	85.1649
Ce–O(1) ^c	84.5409	85.1358	84.8043	84.8736	85.1676
Ce–O(2) ^a	85.0511	85.2794	85.4450	84.7653	85.3967
Ce–O(2) ^b	85.0526	85.2815	85.4464	84.7668	85.3982
Ce–O(2) ^c	85.0547	85.2830	85.4484	84.7687	85.4003
Ce–O(6) ^a	85.8941	85.7706	85.2546	84.7946	85.0485
Ce–O(6) ^b	85.8949	85.7720	85.2557	84.7960	85.0501
Ce–O(6) ^c	85.8967	85.7739	85.2582	84.7980	85.0523
Zr(AlTa)1–O(4) × 6	79.0762	78.9242	79.1490	79.9002	79.0536
Zr(AlTa)2–O(3) ^a	78.1308	78.5497	78.8413	77.2802	79.3695
Zr(AlTa)2–O(3) ^b	78.1361	78.5559	78.8463	77.2856	79.3742
Zr(AlTa)2–O(3) ^c	78.1379	78.5568	78.8479	77.2865	79.3758
Zr(AlTa)2–O(5) ^a	78.7914	78.7627	78.0512	75.8209	78.8991
Zr(AlTa)2–O(5) ^b	78.7930	78.7653	78.0539	75.8231	78.9008
Zr(AlTa)2–O(5) ^c	78.7979	78.7705	78.0586	75.8296	78.9058
Mo1–O(1)	72.2742	71.7665	71.8583	68.2504	71.6738
Mo1–O(2)	71.7013	72.5478	71.7377	69.6950	72.5912
Mo1–O(3)	73.7729	74.1055	73.6013	72.3716	72.8307
Mo1–O(4)	72.6301	73.1087	74.0083	72.2410	73.1157
Mo2–O(5) × 2	72.9817	73.0468	73.5072	72.6904	73.3890
Mo2–O(6) × 2	69.8482	71.0914	71.9889	69.9255	72.3347

^{a, b, c} Three different bonds.

Fig. 11 ϵ_r and the Zr(AlTa)–O(4) bond ionicity of CZMAT ceramics as a function of x .

with lattice energy. The lattice energy U can be expressed as Eq. (12):

$$U = \sum (U_{bc}^\mu + U_{bi}^\mu) \quad (12)$$

where U_{bi}^μ and U_{bc}^μ represent ionic and covalent energy parts, respectively. The lattice energy U of CZMAT ceramics is presented in Table 4. $U_{(\text{Ce-O}(1))}$

values and $Q \times f$ as a variation of $(\text{Al}_{1/2}\text{Ta}_{1/2})^{4+}$ substitution are exhibited in Fig. 12. The variation of $Q \times f$ is consistent with that of $U_{(\text{Ce-O}(1))}$, thereby indicating that $Q \times f$ is influenced by $U_{(\text{Ce-O}(1))}$. For $x = 0.06$, superior performances are obtained ($\epsilon_r = 10.46$, $Q \times f =$

Table 4 Lattice energy U of CZMAT ceramics sintered at densification temperature for 6 h (Unit: kJ/mol)

CZMAT	$x = 0.02$	$x = 0.04$	$x = 0.06$	$x = 0.08$	$x = 0.10$
Ce–O(1) ^a	1124	1102	1116	1060	1101
Ce–O(1) ^b	1124	1102	1115	1060	1100
Ce–O(1) ^c	1124	1102	1115	1060	1100
Ce–O(2) ^a	1089	1092	1070	1068	1084
Ce–O(2) ^b	1089	1092	1070	1068	1084
Ce–O(2) ^c	1089	1092	1070	1067	1084
Ce–O(6) ^a	1028	1056	1084	1066	1108
Ce–O(6) ^b	1028	1056	1084	1066	1108
Ce–O(6) ^c	1028	1056	1084	1066	1108
Zr(AlTa)1–O(4) × 6	10,685	10,947	10,739	9801	10,890
Zr(AlTa)2–O(3) ^a	3718	3710	3631	3724	3577
Zr(AlTa)2–O(3) ^b	3717	3709	3630	3724	3576
Zr(AlTa)2–O(3) ^c	3717	3709	3630	3724	3576
Zr(AlTa)2–O(5) ^a	3610	3675	3759	3950	3655
Zr(AlTa)2–O(5) ^b	3610	3675	3759	3949	3655
Zr(AlTa)2–O(5) ^c	3608	3674	3758	3948	3655
Mo1–O(1)	43,332	44,960	44,407	47,819	45,136
Mo1–O(2)	44,274	43,705	44,600	45,712	43,668
Mo1–O(3)	40,662	40,977	41,430	41,235	43,268
Mo1–O(4)	42,726	42,762	40,673	41,477	42,783
Mo2–O(5) × 2	42,112	42,868	41,601	40,635	42,310
Mo2–O(6) × 2	47,089	45,994	44,196	45,360	44,087

^{a, b, c} Three different bonds.

Fig. 12 $Q \times f$ and the Ce–O(1) lattice energy of CZMAT ceramics as a function of the value of x .

83,796 GHz, and $\tau_f = -11.50$ ppm/°C), indicating that the $Q \times f$ of $\text{Ce}_2[\text{Zr}_{0.94}(\text{Al}_{1/2}\text{Ta}_{1/2})_{0.06}]_3(\text{MoO}_4)_9$ ceramics is greatly improved compared with that of $\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9$ ($Q \times f = 19,062$ GHz).

τ_f plays a crucial role in dielectric materials. It symbolizes the resistance of materials to temperature changes in service. In addition, it is related to structural characteristics, such as bonding types, chemical properties of ions, distance between anions, and the temperature coefficients of the relative permittivity [37–39]. The relationships among τ_f , τ_ϵ , and α are illustrated in Eq. (13). α and τ_ϵ are the coefficient of thermal expansion and the temperature coefficient of dielectric constant, respectively.

$$\tau_f = -\left(\frac{\tau_\epsilon}{2} + \alpha\right) \quad (13)$$

The α values of Ce–O, Zr/AlTa–O, and Mo–O bonds are explored quantitatively, as shown in Table 5. The calculation process used has been described in Ref. [23]. Obviously, the average α value of Mo–O bonds is negative, thereby indicating that the α value of Mo–O bonds is also an important factor of τ_f . A strong relationship was reported between bond energy E and τ_f . A smaller $|\tau_f|$ corresponded to higher bond energy values. The E values (Table 6) of an individual bond μ can be calculated by using Eqs. (14) and (15). The variation of τ_f and bond ionicity $E_{(\text{Mo-O})}$ along with x is exhibited in Fig. 13. The maximum value (-8.96 ppm/°C) of τ_f is shown at $x = 0.04$. The same trend is observed between τ_f and $E_{(\text{Mo-O})}$, indicating that $E_{(\text{Mo-O})}$ is a primary intrinsic factor of τ_f .

$$E^\mu = t_c E_c^\mu + t_i E_i^\mu \quad (14)$$

$$E_c^\mu = \frac{r_{cA} + r_{cB}}{d^\mu} (E_{A-A} E_{B-B})^{1/2} \text{ (kJ/mol)} \quad (15)$$

Fig. 13 τ_f and the Mo–O bond energy of CZMAT ceramics as a function of the value of x .

Table 5 Coefficients of thermal expansion α of CZMAT ceramics sintered at densification temperature for 6 h (Unit: 10^{-6} K^{-1})

CZMAT	$x = 0.02$	$x = 0.04$	$x = 0.06$	$x = 0.08$	$x = 0.10$
Ce–O(1) ^a	9.8772	10.1377	9.9707	10.6649	10.1497
Ce–O(1) ^b	9.8772	10.1377	9.9825	10.6649	10.1619
Ce–O(1) ^c	9.8772	10.1377	9.9825	10.6649	10.1619
Ce–O(2) ^a	10.2965	10.2595	10.5356	10.5613	10.3586
Ce–O(2) ^b	10.2965	10.2595	10.5356	10.5613	10.3586
Ce–O(2) ^c	10.2965	10.2595	10.5356	10.5741	10.3586
Ce–O(6) ^a	11.0955	10.7173	10.3586	10.5870	10.0656
Ce–O(6) ^b	11.0955	10.7173	10.3586	10.5870	10.0656
Ce–O(6) ^c	11.0955	10.7173	10.3586	10.5870	10.0656
Zr(AlTa)1–O(4) $\times$ 6	3.5173	3.3635	3.4965	4.1414	3.4168
Zr(AlTa)2–O(3) ^a	3.2361	3.2561	3.4022	3.2443	3.5143
Zr(AlTa)2–O(3) ^b	3.2379	3.2579	3.4041	3.2443	3.5162
Zr(AlTa)2–O(3) ^c	3.2379	3.2579	3.4041	3.2443	3.5162
Zr(AlTa)2–O(5) ^a	3.4277	3.3173	3.1785	2.8774	3.3717
Zr(AlTa)2–O(5) ^b	3.4277	3.3173	3.1785	2.8790	3.3717
Zr(AlTa)2–O(5) ^c	3.4314	3.3191	3.1802	2.8805	3.3717
Mo1–O(1)	–0.3892	–0.4898	–0.4564	–0.6499	–0.5002
Mo1–O(2)	–0.4483	–0.4129	–0.4682	–0.5339	–0.4105
Mo1–O(3)	–0.2067	–0.2294	–0.2616	–0.2478	–0.3850
Mo1–O(4)	–0.3497	–0.3521	–0.2075	–0.2649	–0.3535
Mo2–O(5) $\times$ 2	–0.3086	–0.3591	–0.2735	–0.2047	–0.3220
Mo2–O(6) $\times$ 2	–0.6109	–0.5500	–0.4435	–0.5134	–0.4368

^{a, b, c} Three different bonds.

Table 6 Bond energies E of CZMAT ceramics sintered at densification temperature for 6 h (Unit: kJ/mol)

CZMAT	$x = 0.02$	$x = 0.04$	$x = 0.06$	$x = 0.08$	$x = 0.1$
Ce–O(1) ^a	421.8634	412.4175	418.0710	392.4194	411.8061
Ce–O(1) ^b	421.7595	412.3348	417.9690	392.3445	411.7236
Ce–O(1) ^c	421.7076	412.2686	417.9010	392.2697	411.6412
Ce–O(2) ^a	406.1271	407.8353	398.1042	395.6522	404.5445
Ce–O(2) ^b	406.0789	407.7706	398.0580	395.6065	404.4967
Ce–O(2) ^c	406.0147	407.7220	397.9963	395.5456	404.4331
Ce–O(6) ^a	379.4668	392.4194	404.0515	394.7405	415.3005
Ce–O(6) ^b	379.4387	392.3745	404.0197	394.6950	415.2502
Ce–O(6) ^c	379.3827	392.3146	403.9403	394.6344	415.1831
Zr(AlTa)1–O(4) $\times$ 6	489.1556	504.5196	491.6626	437.0270	499.9738
Zr(AlTa)2–O(3) ^a	517.0295	515.4886	500.7861	516.3107	490.6075
Zr(AlTa)2–O(3) ^b	516.8738	515.3079	500.6398	516.1551	490.4669
Zr(AlTa)2–O(3) ^c	516.8219	515.2821	500.5911	516.1292	490.4200
Zr(AlTa)2–O(5) ^a	497.6415	509.2637	523.8240	557.6761	504.5195
Zr(AlTa)2–O(5) ^b	497.5934	509.1881	523.7439	557.6156	504.4699
Zr(AlTa)2–O(5) ^c	497.4492	509.0370	523.6106	557.4341	504.3212
Mo1–O(1)	584.8428	616.6531	605.8023	679.1822	620.2080
Mo1–O(2)	603.4309	591.5759	609.6643	634.1063	590.7976
Mo1–O(3)	534.4540	539.7044	548.3580	546.1831	582.9941
Mo1–O(4)	573.1271	573.2225	534.3987	550.6677	573.6364
Mo2–O(5) $\times$ 2	561.4135	575.2659	551.5499	535.1186	564.5744
Mo2–O(6) $\times$ 2	661.8175	637.9446	601.6032	626.7947	599.0907

^{a, b, c} Three different bonds.

where E^μ is the bond energy for the type μ bond, which is composed of nonpolar covalence energy E_c^μ and complete ionicity energy E_i^μ parts; t_c and t_i are covalent and ionic blending coefficients, respectively; r_{cA} and r_{cB} are the covalent radii; and E_{A-A} and E_{B-B} are the homonuclear bond energies.

4 Conclusions

Dense microwave dielectric ceramics of CZMAT ($x = 0.02$ – 0.10) were prepared by the conventional solid-state route. The sintered samples belong to the trigonal structure with the $R\bar{3}c$ space group identified by the XRD. According to the results of SEM, the dense ceramics were obtained at 850 °C. The lattice parameters of the samples were obtained by the Rietveld refinement method. Based on the chemical bond theory, the microwave dielectric properties were investigated. The optimum dielectric performance of $\epsilon_r = 10.46$, $Q \times f = 82,189 \text{ GHz}$, and $\tau_f = -12.74 \text{ ppm/}^\circ\text{C}$ for $\text{Ce}_2[\text{Zr}_{0.94}(\text{Al}_{1/2}\text{Ta}_{1/2})_{0.06}]_3(\text{MoO}_4)_9$ ceramic was obtained at 850 °C.

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