Effects of \((\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}\) substitution on the structure and microwave dielectric properties of 
\(\text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9\) ceramics

Xu ZHOU\(^a,b\), Lintao LIU\(^a\), Jiajia SUN\(^b\), Ningkang ZHANG\(^b\), Huazhang SUN\(^b\), Haitao WU\(^a\)*, Wenhong TAO\(^b\)*

\(^a\) School of Environmental and Material Engineering, Yantai University, Yantai, 264005, Shandong, China
\(^b\) School of Materials Science and Engineering, University of Jinan, Jinan, 250022, Shandong, China

Abstract

\(\text{Ce}_2[\text{Zr}_{1-x}(\text{Mg}_{1/3}\text{Sb}_{2/3})_x]_3(\text{MoO}_4)_9\) \((0.02 \leq x \leq 0.10)\) ceramics were prepared by the traditional solid-state method. A single phase, belonging to the space group of \(R\bar{3}c\), was detected by using X-ray diffraction at sintering temperatures ranging from 700 °C to 850 °C. The microstructures of samples were examined by applying scanning electron microscopy. The crystal structure refinement of these samples was investigated in detail by performing the Rietveld refinement method. The intrinsic properties were calculated and explored via Far-infrared reflectivity spectroscopy. The correlations between the chemical bonds parameters and microwave dielectric properties were calculated and analyzed by P-V-L theory. \(\text{Ce}_2[\text{Zr}_{0.94}(\text{Mg}_{1/3}\text{Sb}_{2/3})_{0.06}]_3(\text{MoO}_4)_9\) ceramics with excellent dielectric properties: \(\varepsilon_r = 10.37, Q\times f = 71748\) GHz and \(\tau_f = -13.6 \text{ ppm/}°\text{C}\) sintered at 725 °C for 6 hours.

Keywords: structure; P-V-L theory; microwave dielectric property; \((\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}\) doping

1. Introduction

It is well-known that dielectric materials have developed rapidly in the past decades. Microwave dielectric ceramics have sprung up in the communication industry and received widely attentions. It is required to have a high quality factor \((Q\times f)\), a moderate dielectric constant \((\varepsilon_r)\) and a near-zero temperature coefficient of resonant frequency \((\tau_f)\) to meet the demands of application \([1,2]\). Recently, researchers focused on novel microwave dielectric ceramics. At the same time, some researchers have been widely investigated the substitution of cationic and composite ceramics to improve the dielectric properties of microwave dielectric materials \([3-5]\). In addition, high cost limits the application of these ceramics, and consequently it is required to reduce their sintering temperature. The low temperature co-fired ceramic (LTCC) \([6-8]\) technology has became a common method due to its simplicity and high efficiency. Hence, LTCC technology is becoming more and more important in practical application.
In recent years, Mo-based microwave dielectric ceramics have been studied in depth as shown in Table 1 [9-13]. Many microwave dielectric ceramic systems have been developed, but their properties are not optimistic. The performance \((Q\times f = 19062 \text{ GHz})\) of Ce₂Zr₃(MoO₄)₉ ceramic was investigated [12]. In order to improve \(Q\times f\) of Ce₂Zr₃(MoO₄)₉ ceramics, doping \((\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}\) at Zr-sites was reported in this work. The crystal structure and sintering behavior of samples were discussed in detail. Also, relationship between the dielectric properties and structure of samples was explored scientifically by far infrared (IR) reflectivity spectrum and the P-V-L theory.

2. Experimental procedure

Highly pure powders of CeO₂, ZrO₂, MoO₃, MgO and Sb₂O₅ were weighed accurately based on the stoichiometric composition of Ce₂[Zr₁₋ₓ(Mg₁/₃Sb₂/₃)ₓ]₃(MoO₄)₉ \((0.02\leq x\leq0.10)\). The mixed powders were continuously rotated for 24 h with ethanol media and ZrO₂ balls. Mixtures were oven-dried at 80 °C and pre-sintered at 700 °C for 2 h. After that, ball milled and dried again under the same condition as above. Subsequently, the combination of powders and 10 wt% paraffin passed through a 60 mesh, and a certain size of the cylinders (length ~ 6 mm, diameter ~ 10 mm) was pressed at 200 MPa. Those pressed cylinders were sintered from 700 to 850 °C for 6 h.

Phase identification of sintered pellets were analyzed using X-ray diffraction (D8 Advance, Bruker Co., Germany) with Cu Kα radiation and refined lattice parameters were obtained using FULLPROF program to explore structure. The surface microstructures of specimens were observed by using QUANTA 250FEG type Scanning electron microscopy (SEM: FEI Co., United States), equipped with EDS. The apparent densities of specimens were analyzed using Archimedes method. The infrared reflectivity spectrum was recorded by a Bruker IFS66v FTIR spectrometer at National Synchrotron Radiation Laboratory (NRSL, BL01B infrared beamline station, University of Science and Technology of China). In addition, dielectric behaviors were surveyed by employing the TE₀₁δ cavity method with a network analyzer (N5234A, Agilent Co., USA) and the Hakki-Coleman dielectric resonator method. The \(\tau_f\) value was acquired by formula (1):

\[
\tau_f = \frac{f_T - f_0}{60 \times f_0} \times 10^6 \text{ (ppm/°C)}
\]

where, \(f_T\) and \(f_0\) represent resonant frequencies at 85 °C and 25 °C, respectively.
Relative density ($\rho_{relative}$) was applied via the following formula (2)-(3):

$$\rho_{theory} = \frac{ZA}{V_cN_A}(g/cm^3)$$

(2)

$$\rho_{relative} = \frac{\rho_{apparent}}{\rho_{theory}} \times 100\%$$

(3)

where $Z$ is the number of molecules, $N_A$ refer to Avogadro constant, $V_c$ represent unit cell volume.

3. Results and discussion

As shown in Fig. 1, the X-ray diffraction patterns of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ (0.02≤x≤0.10) ceramics sintered under different temperatures for 6 h. A single phase was detected in all samples. The peaks of sintered ceramics assigned to the standard data for Pr$_2$Zr$_3$(MoO$_4$)$_9$ (JCPDS No. 52-0688), which indicated that the Pr$_2$Zr$_3$(MoO$_4$)$_9$-like crystal structure with a $R\overline{3}c$ space group was obtained. According to the result, the composition of the crystal phase is not changed by the content of (Mg$_{1/3}$Sb$_{2/3}$)$^{4+}$ions substitution [14]. In order to meet the needs of calculating density and complex chemical bonds to further analyze its structure, included lattice parameters, bond length and unit cell volumes were obtained by Rietveld refinement [15]. Nd$_2$Zr$_3$(MoO$_4$)$_9$ was chosen as the original model via FULLPROF program. Refinement plot of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ (0.02≤x≤0.10) ceramics were displayed in Fig. 2, in which the observed values were expressed by red points, the calculated values were expressed by the black line, and the difference value between the observed and the calculated data expressed by the blue curve. Obviously, excellent agreement is shown between the fitted values and the measured values. In addition, the refined discrepancy factors ($R_{wp}$, $R_p$, and $\chi^2$), cell volume and lattice parameters of all specimens were listed in Table 2. The $R_{wp}$, $R_p$, and $\chi^2$ values were obtained in the range of 9.6-11.1%, 6.6-8.6%, and 1.70-2.23, respectively, indicating all the refinement results are acceptable and accurate.
With the amount of \((\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}\) increasing, the linear variation in lattice parameters \((a, b \text{ and } c)\) and unit cell volume \((V_m)\) were presented in Fig. 3. The lattice parameter \(c\) was linearly increased while \(a, b\) and \(V_m\) linearly decreased correspondingly along with the augment of \((\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}\) because the ionic radius of \(\text{Zr}^{4+}\) (0.72 Å) is bigger than that of \((\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}\) (0.64 Å) [16,17]. The schematic illustration (in Fig. 4) and the refined atomic positions (in Table 3) of \(\text{Ce}_2[\text{Zr}_{1-x}(\text{Mg}_{1/3}\text{Sb}_{2/3})_x]\text{MoO}_4\) samples were exhibited clearly. The crystal structure of ceramics is composed of \(\text{CeO}_9, \text{Zr/Mg/SbO}_6\) and \(\text{MoO}_4\)
polyhedra with common vertex angle.

The apparent densities of the Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ (0.02≤x≤0.10) ceramics as a function of sintering temperature were illustrated in Fig. 5. As the temperature increases, the apparent densities of each composition increases at first and then decreased slightly. For example, the apparent density of Ce$_2$[Zr$_{0.94}$(Mg$_{1/3}$Sb$_{2/3}$)$_{0.06}$]$_3$(MoO$_4$)$_9$ ceramics increases from 3.71g/cm$^3$ to 3.83g/cm$^3$, then the apparent density drops to 3.81g/cm$^3$ at 800°C. In general, an appropriate sintering temperature plays a vital role in the densification of the sample. Higher sintering temperature will accelerate the growth of crystal grains, and the pores will not be discharged in time, resulting in a poor densification sample. Relative density of each composition at a high relative density was embedded in Fig. 5. The apparent densities of the major sample was an approximate value of 3.80 g/cm$^3$ and relative density also has reached more than 95%. It is noticeable that the good degree of densification was in accord with the SEM results. Fig. 6(a-e) depicts the SEM microphotographs of the specimens at their optimal temperatures. It is quite clear that the dense micro-structure and unambiguous grain boundary of the specimens can be observed. As provided in Fig. 6(f), EDS of Ce$_2$[Zr$_{0.94}$(Mg$_{1/3}$Sb$_{2/3}$)$_{0.06}$]$_3$(MoO$_4$)$_9$ ceramics was gained at 725°C for 6 h. Atom ratio of O, Mo, Zr, Ce, Sb and Mg were 73.56%, 16.91%, 5.93%, 3.48%, 0.07% and 0.05 %, respectively, which is
The $\varepsilon_r$ of ceramics with different $(\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}$ contents ($x=0.02, 0.04, 0.06, 0.08, 0.1$) as a function of sintering temperature were revealed in Fig. 7(a). The factors that affect the $\varepsilon_r$ are mainly divided into external parameters and intrinsic factors. Intrinsic factors include lattice structure and ionic polarizabilities, while external parameters include impurities, density, and second phase [18]. No secondary phase was detected in Fig. 1 and the lattice structure had no change. Thus, the dielectric constant of $\text{Ce}_2[\text{Zr}_{1-x}(\text{Mg}_{1/3}\text{Sb}_{2/3})_x]_3(\text{MoO}_4)_9$ ($0.02 \leq x \leq 0.10$) ceramics was determined mainly by apparent
density. Fig. 5 shown that the apparent densities of sample increased and then decreased slightly as the temperature increases. It was easy to notice that the $\varepsilon_r$ existed almost similar trend with apparent density, which indicated that the main contribution of the dielectric constant was apparent density.

The $Q\times f$ of Ce$_2[Zr_{1-x}(Mg_{1/3}Sb_{2/3})_x]_3(MoO_4)_9$ (0.02≤x≤0.10) ceramics sintered at 700 °C-850 °C for 6 h was plotted in Fig. 7(b). The quality factor depends on the presence of intrinsic and extrinsic dielectric losses at microwave frequency. The extrinsic losses are dominated by porosity, secondary phase and lattice defects, while the intrinsic loss is mainly contributed by lattice vibrational modes [19]. It was obvious that the $Q\times f$ of each composition existed similar trend, which increased firstly and then decreased. The optimal points of $Q\times f$ were presented at 800 °C, 800 °C, 725 °C, 725 °C, 725 °C and 775 °C, respectively. In this study, the excellent properties of Ce$_2[Zr_{0.94}(Mg_{1/3}Sb_{2/3})_{0.06}]_3(MoO_4)_9$ ceramics ($\varepsilon_r = 10.37$, $Q\times f = 71748$ GHz and $\tau_f = −13.6$ ppm/°C) were obtained at 725°C for 6 hours. At optimal sintering temperature, the quality factor of Ce$_2[Zr_{0.94}(Mg_{1/3}Sb_{2/3})_{0.06}]_3(MoO_4)_9$ ceramics has been greatly improved compared to previous reports, owing to the partial replacement of Zr$^{4+}$ by (Mg$_{1/3}$Sb$_{2/3}$)$^{4+}$ ions.

As we know, chemical bonds theory of complex crystals used to characterize the intrinsic relationships between chemical bond and crystal structure. Zhang [15] successfully generalized Phillips-Van Vechten-Levine (PVL) theory suggest that the crystalline structure parameters could be calculated by chemical bond. Any complex crystal can be decomposed into multiple binary crystals. The bond equation of Ce$_2[Zr_{1-x}(Mg_{1/3}Sb_{2/3})_x]_3(MoO_4)_9$ (0.02≤x≤0.10) ceramics was shown in formula (4). In this work, there are three types of bonds which were Ce-O, Zr(Mg/Sb)-O, and Mo-O, respectively. The
The bond ionicity $f_i$ could usually be evaluated by using Eq. (5)–(9) [15,20,21]:

$$\varepsilon = \frac{n^2 - 1}{1 - f_i} + 1$$  \hspace{1cm} (5)

$$f^\mu_i = \frac{(C^\mu)^2}{(E^\mu_s)^2}$$  \hspace{1cm} (6)

$$(E^\mu_s)^2 = (E^\mu_h)^2 + (C^\mu)^2$$  \hspace{1cm} (7)

$$(E^\mu_h)^2 = \frac{39.74}{(d^\mu)^4}$$  \hspace{1cm} (8)

$$C^\mu = 14.4b^\mu \exp(-k^\mu/mr_0^\mu)[(Z^\mu_s)^* - n_m (Z^\mu_h)^*] / r_0^\mu$$  \hspace{1cm} (9)

where $E^\mu_s$ represent the average energy gap, $E^\mu_h$ represent the homopolar part, $f^\mu_i$ is the bond ionicity of an individual bond $\mu$, $C^\mu$ represent the heteropolar part and $\exp(-k^\mu/mr_0^\mu)$ is Thomas-Fermi screening factor [22].

The bond ionicity $f_i$ were explored quantitatively as shown in Table 4. In addition, $\varepsilon_r$ and an individual bond ionicity $f_i(Mo1-O(2))$ as a function of the content of $(Mg_{1/3}Sb_{2/3})^{4+}$ substitution were shown in Fig. 8. The $\varepsilon_r$ values display a decreasing tendency from 10.47 to 10.03 along with the augment of $(Mg_{1/3}Sb_{2/3})^{4+}$. The positive correlation between relative permittivity and $f_i$ was described in formula (5). As increasing of $(Mg_{1/3}Sb_{2/3})^{4+}$ contents, $f_i(Mo1-O(2))$ and $\varepsilon_r$ values show the same tendency which indicated the $\varepsilon_r$ values were strongly dependent on $f_i(Mo1-O(2))$. 

The bond ionicity of cations were $P_{Ce}=3$, $P_{Zr/(Mg/Sb)}=4$ and $P_{Mo}=6$, while the valence of the oxygen ion follows formula 4, and the effective valences in the Ce-O bond, Zr(Mg/Sb)-O bond, and Mo-O bond are $PO_{Ce}=-2/3$, $PO_{Zr/(Mg/Sb)}=-4/3$, and $PO_{Mo}=-3$, respectively.
Lattice energy can be used to predict and explain many physical and chemical properties of ionic crystals, so larger lattice energy, the more stable structure. The lattice energy \( U \) (in Table 5) of specimen could be evaluated according to the following formulas (10)-(13) [15,20,21]. Fig. 9 presented \( U(\text{Zr}(\text{Mg/Sb})_1\text{O}(4)) \) values and the quality factor \( Q\times f \) as a variation of \((\text{Mg}_{1/3}\text{Sb}_{2/3})^{4+}\) substitution. The \( Q\times f \) values were increased from 49033 GHz to 64012 GHz, and then decreased to 48690 GHz. They all show the same trend of increasing first and then decreasing, indicating that \( Q\times f \) is mainly affected by \( U(\text{Zr}(\text{Mg/Sb})_1\text{O}(4)) \).

\[
U_{\text{cal}} = \sum_{\mu} U_{\mu}^b
\]

\[
U_{\mu}^b = U_{bc}^\mu + U_{bi}^\mu
\]

\[
U_{bc}^\mu = 2100m \left( \frac{Z_A^{\mu}}{Z_B^{\mu}} \right)^{1.64} \frac{f_C^\mu}{(d^{\mu})^{0.77}}
\]

\[
U_{bi}^\mu = 1270(m + n)Z_A^{\mu}Z_B^{\mu} \frac{1 - 0.4}{d^{\mu}} f_i^\mu
\]

Where \( U_{bi}^\mu \) and \( U_{bi}^\mu \) represent ionic energy part and covalent energy part, \( f_C^\mu \) is the bond ionicity of an individual bond \( \mu \), \( Z_A^{\mu} \) and \( Z_B^{\mu} \) are the valence states of cation and anion which constituted the \( \mu \) bond.
Zhang [23,24] had reported a strong relationship between bond energy \( E \) and \( \tau_f \), which the larger bond energy, the closer to zero the \( \tau_f \) value. The \( E \) value of an individual bond \( \mu \) could be calculated by Eq. (14)-(18) [25-27]:

\[
E^\mu = t_c E_c^\mu + t_i E_i^\mu
\]  
(14)

\[
E_c^\mu = \frac{(r_{cA} + r_{cB})}{d^\mu} \left( E_{A-A} E_{B-B} \right)^{1/2} \text{(KJ/mol)}
\]  
(15)

\[
E_i^\mu = \frac{1389.088}{d^\mu} \text{(KJ/mol)}
\]  
(16)

\[
t_i = \left| \frac{(S_A - S_B)}{6} \right|
\]  
(17)

\[
t_c + t_i = 1
\]  
(18)

where \( S \) represent the electronegativity of ions, \( t_i \) and \( t_c \) are are covalent and ionic blending coefficient, respectively, \( r_{cA} \) and \( r_{cB} \) are the covalent radii, \( E_{A-A} \) and \( E_{B-B} \) are homonuclear bond energy [28].

The \( \tau_f \) and an individual bond ionicity \( E_{(Mo1-O(1))} \) as a function of the content of \((Mg_{1/3} Sb_{2/3})^{4+}\) substitution were illustrated in Fig. 10. In addition, the calculated bond energy \( E \) are shown in Table 6. The \( \tau_f \) values of ceramics fluctuated slightly between \(-8.59 \text{ ppm/°C} \) and \(-13.69 \text{ ppm/°C} \) with \((Mg_{1/3} Sb_{2/3})^{4+}\) increasing in our experiments. The bond energy \( E_{(Mo1-O(1))} \) and \( \tau_f \) have the same trend, indicating that \( \tau_f \) is mainly influenced by \( E_{(Mo1-O(1))} \).
The $\tau_f$ is obtained by Eq. (19) and the $\alpha$ is described via Eq. (20)-(23):

$$
\tau_f = \left(\frac{\tau_c}{2} + \alpha\right) \tag{19}
$$

$$
\alpha = \sum_{\mu} F_{\mu}^\alpha \alpha_{\mu}^\alpha \tag{20}
$$

$$
\alpha_{\mu}^\alpha = -3.1685 + 0.8376 \gamma_{\mu} \tag{21}
$$

$$
\gamma_{\mu} = \frac{k Z_{A}^{\mu} N_C^\mu}{U_{\beta}^{\mu} \Delta_{\lambda}} \beta_{\mu} \tag{22}
$$

$$
\beta_{\mu} = \frac{m(m+n)}{2n} \tag{23}
$$

Where $k$ is Boltzmann constant, $N_C^\mu$ represent the coordination number of cation, $\tau_c$ is temperature coefficient of the dielectric constant, $F_{\mu}^\alpha$ represent the proportion of $\mu$ bond. Calculated $\alpha$ values were shown in Table 7. Obviously, the value of $\alpha_{Zr(Mg/Sb) - O}$ and $\alpha_{Ce-O}$ were positive. The value of $\alpha_{Mo-O}$ had a positive influence on $\tau_f$ because of $\alpha_{Mo-O} < 0$.

As is known, it is difficult to detect the intrinsic loss and extrinsic loss of microwave dielectric ceramics by conventional testing methods. Far-infrared spectral analysis can reflect the intrinsic loss to a certain extent. These spectra were analyzed by using the classical harmonic oscillator model that was applied to study infrared spectroscopy. It relies on two formulas: the standard Lorentzian formula (Eq. (24)) and the Fresnel formula (Eq. (25)) [29,30]. The dielectric loss tangent $\tan\delta$ is evaluated by Eq. (26).

$$
\varepsilon^* (\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\alpha_{pj}^2}{\omega_{pq}^2 - \omega^2 + j \omega \gamma_j} \tag{24}
$$
\[
R = \left| \frac{1 - \sqrt{\varepsilon'^*(\omega)}}{1 + \sqrt{\varepsilon'^*(\omega)}} \right|^2
\]  

(25)

\[
\tan \delta = \frac{\varepsilon''}{\varepsilon'} = \frac{\sum_{j=1}^{n} \Delta \varepsilon_j (\gamma_j \omega)}{\varepsilon_c + \sum_{j=1}^{n} \Delta \varepsilon_j}
\]  

(26)

where \(\gamma_j\) is damping factor, \(\varepsilon_c\) is dielectric constant, \(\omega_{pj}\) is plasma frequency, \(\varepsilon^*(\omega)\) is a complex dielectric function, \(\omega_{ej}\) is the eigen frequency, \(n\) is the number of transverse phonon modes, \(R\) is the IR reflectivity.

As shown in Fig. 11(a), the fitted infrared spectra of the \(\text{Ce}_2[\text{Zr}_{0.94}(\text{Mg}_{1/3}\text{Sb}_{2/3})_{0.06}]_3(\text{MoO}_4)_9\) sample is depicted. The fitted infrared reflectivity spectrum were in good agreement with measured part. In addition, real and imaginary parts of the permittivity were given in Fig. 11(b). Table 8 lists the fitted phonon parameters, indicating it was fitted with sixteen modes. As compared with the measured permittivity, the calculated one was slightly big. The measured value (1.35×10^{-4}) and calculated value (2.68×10^{-4}) of the dielectric loss remained in the same order of magnitude. Both the fitted and measured values correspond well, which indicated that in the microwave frequencies, the dielectric polarization mainly caused by absorption of phonons in the infrared region [31-33].

4. Conclusion

\(\text{Ce}_2[\text{Zr}_{1-x}(\text{Mg}_{1/3}\text{Sb}_{2/3})_x]_3(\text{MoO}_4)_9\) (\(x=0.02, 0.04, 0.06, 0.08\) and \(0.10\)) ceramics were fabricated well via the traditional solid-state method. The pure-phase with space group of \(R\overline{3}c\) was detected for all specimens. The dense micro-structure and clear grain boundary of the specimens can be observed in SEM photos. The crystal structure was investigated deeply by the Rietveld refinement method. The \(\varepsilon_r, Q\times f\) and
$\tau_f$ values of these samples were strongly dependent on chemical bonds such as $f_{\text{Mo1-O(2)}}$, $U_{\text{(Zr(Mg/Sb)1-O(4))}}$ and $E_{\text{Mo1-O(1)}}$, respectively. The infrared reflectivity spectrum were in good agreement with the dielectric properties of samples. Meanwhile, Ce$_2$[Zr$_{0.94}$(Mg$_{1/3}$Sb$_{2/3}$)$_{0.06}$]$_3$(MoO$_4$)$_9$ ceramic with $\varepsilon_r = 10.37$, $Q\times f = 71748$ GHz and $\tau_f = -13.6$ ppm/°C, were obtained at 725°C for 6 hours.

Acknowledgments

This work was supported by the National Natural Science Foundation (No. 51972143). The authors would like to thank the administrators in IR beamline workstation of National Synchrotron Radiation Laboratory (NSRL) for the help in IR measurement.
References

[1] Guo HH, Zhou D, Liu WF, et al. Microwave dielectric properties of temperature-stable zircon-type \( (\text{Bi, Ce})\text{VO}_4 \) solid solution ceramics. \textit{J Am Ceram Soc} 2020, \textbf{103}: 423-431.

[2] Zheng JJ, Yang YK, Wu HT, et al. Structure, infrared spectra and microwave dielectric properties of the novel \( \text{Eu}_2\text{TiO}_5 \) ceramics. \textit{J Am Ceram Soc} 2020, \textbf{103}: 4333-4341.

[3] Li CC, Yin CZ, Deng M, \textit{et al}. Tunable microwave dielectric properties in \( \text{SrO-V}_2\text{O}_5 \) system through compositional modulation. \textit{J Am Ceram Soc} 2020, \textbf{103}: 2315-2321.

[4] Bi JX, Xing CF, Yang CH, \textit{et al}. Phase composition, microstructure and microwave dielectric properties of rock salt structured \( \text{Li}_2\text{ZrO}_3\)-\( \text{MgO} \) ceramics. \textit{J Eur Ceram Soc} 2018, \textbf{38}: 3840-3846.

[5] Pang LX, Zhou D. Modification of \( \text{NdNbO}_4 \) microwave dielectric ceramic by Bi substitutions. \textit{J Am Ceram Soc} 2019, \textbf{102}: 2278-2282.

[6] Yin CZ, Li CC, Yang GJ, \textit{et al}. \( \text{NaCa}_4\text{V}_5\text{O}_{17} \): A low-firing microwave dielectric ceramic with low permittivity and chemical compatibility with silver for LTCC applications. \textit{J Eur Ceram Soc} 2019, \textbf{40}: 386-390.

[7] Tao BJ, Wang WF, Liu HY, \textit{et al}. Low-temperature sintering \( \text{LiF-doped Li}_4\text{Mg}_3[\text{Ti}_{0.6}(\text{Mg}_{1/3}\text{Nb}_{2/3})_{0.4}]\text{O}_9 \) microwave dielectric ceramics for LTCC applications. \textit{Ceram Int} 2021, \textbf{47}: 2584-2590.

[8] Guo HH, Zhou D, Pang LX, \textit{et al}. Microwave dielectric properties of low firing temperature stable scheelite structured \( (\text{Ca, Bi})(\text{Mo, V})\text{O}_4 \) solid solution ceramics for LTCC applications. \textit{J Eur Ceram Soc} 2019, \textbf{39}: 2365-2373.

[9] Liu W, Zuo R. Low temperature fired \( \text{Ln}_2\text{Zr}_3(\text{MoO}_4)_9 \) (\( \text{Ln} = \text{Sm, Nd} \)) microwave dielectric ceramics. \textit{Ceram Int} 2017, \textbf{43}: 17229-17232.

[10] Zhang YH, Sun JJ, Dai N, \textit{et al}. Crystal structure, infrared spectra and microwave dielectric properties of novel extra low-temperature fired \( \text{Eu}_2\text{Zr}_3(\text{MoO}_4)_9 \) ceramics. \textit{J Eur Ceram Soc} 2019, \textbf{39}: 1127-1131.

[11] Zhang YH, Wu HT. Crystal structure and microwave dielectric properties of \( \text{La}_2(\text{Zr}_{1-x}\text{Ti}_x)_3(\text{MoO}_4)_9 \) (\( 0 \leq x \leq 0.1 \)) ceramics. \textit{J Am Ceram Soc} 2019, \textbf{102}: 4092-4102.

[12] Tao BJ, Xing CF, Wang WF, \textit{et al}. A novel \( \text{Ce}_2\text{Zr}_3(\text{MoO}_4)_9 \) microwave dielectric ceramic with ultra-low firing temperature. \textit{Ceram Int} 2019, \textbf{45}: 24675-24683.
[13] Zheng JJ, Liu YH, Tao BJ, et al. Crystal structure and optimised microwave dielectric properties of Ce$_2$(Zr$_{1-x}$Ti$_x$)$_3$(MoO$_4$)$_9$ solid solutions. *Ceram Int* 2021, 47: 5624-5630.

[14] Xiao M, He SS, Meng J, et al. Bond ionicity, lattice energy, bond energy and the microwave dielectric properties of non-stoichiometric MgZrNb$_{2+x}$O$_{8+2.5x}$ ceramics. *Mater Chem Phys* 2020, 242: 122412.

[15] Wu ZJ, Meng QB, Zhang SY. Semiempirical study on the valences of Cu and bond covalency in Y$_{1-x}$Ca$_x$Ba$_2$Cu$_3$O$_{6-y}$. *Phys Rev B* 1998, 58: 958-962.

[16] Kim SH, Kim ES. Intrinsic factors affecting the microwave dielectric properties of Mg$_2$Ti$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$O$_4$ ceramics. *Ceram Int* 2016, 42: 15035-15040.

[17] Pei CJ, Tan JJ, Li Y, et al. Effect of Sb-site nonstoichiometry on the structure and microwave dielectric properties of Li$_3$Mg$_2$Sb$_{1-x}$O$_6$ ceramics. *J Adv Ceram* 2020, 9: 588-594.

[18] Xia WS, Zhang LY, Wang Y, et al. Extrinsic effects on microwave dielectric properties of high-Q MgZrTa$_2$O$_8$ ceramics. *J Mater Sci:Mater Electron* 2016, 27: 11325-11330.

[19] Silverman BD. Microwave Absorption in Cubic Strontium Titanate. *Phys Rev* 1962, 125: 1921-1930.

[20] Xue DF, Zhang SY. Calculation of the nonlinear optical coefficient of the NdAl$_3$(BO$_3$)$_4$ crystal. *J Phys Condens Matter* 1996, 8: 1949-1956.

[21] Berkov DV. Evaluation of the energy barrier distribution in many-particle systems using the path integral approach. *J Phys Condens Matter* 1998, 10: L89-L95.

[22] Levine BF. Bond susceptibilities and ionicities in complex crystal structures. *J Chem Phys* 1973, 59: 1463-1486.

[23] Zhang P, Zhao YG, Wang XY. The correlations between electronic polarizability, packing fraction, bond energy and microwave dielectric properties of Nd(Nb$_{1-x}$Sb$_x$)O$_4$ ceramics. *J Alloy Compd* 2015, 644: 621-625.

[24] Zhang P, Zhao YG. Effects of structural characteristics on microwave dielectric properties of Li$_2$Mg(Ti$_{1-x}$Mn$_x$)$_3$O$_8$ ceramics. *J Alloy Compd* 2015, 647: 386-391.

[25] Sanderson RT. Multiple and single bond energies in inorganic molecules. *J Inorg Nucl Chem* 1968, 30: 375-393.

[26] Sanderson RT. Chemical bonds, bond energy. New York(US): Academic press, 1971.
[27] Sanderson RT. Electronegativity and bond energy. *J Am Ceram Soc* 1983, **105**: 2259-2261.
[28] Luo YR. Comprehensive handbook of chemical bond energies. Boca Raton(US): CRC press, 2007.
[29] Chen Z, Jia H, Sharafudeen K, *et al*. Up-conversion luminescence from single vanadate through blackbody radiation harvesting broadband near-infrared photons for photovoltaic cells. *J Alloy Compd* 2016, **663**: 204-210.
[30] Guo J, Zhou D, Wang L, *et al*. Infrared spectra, Raman spectra, microwave dielectric properties and simulation for effective permittivity of temperature stable ceramics AMoO$_4$–TiO$_2$ (A=Ca, Sr). *Dalton Trans* 2013, **42**: 1483-1491.
[31] Pang LX, Zhou D, Qi ZM, *et al*. Structure-property relationships of low sintering temperature scheelite-structured (1−x)BiVO$_4$–xLaNbO$_4$ microwave dielectric ceramics. *J Mater Chem C* 2017, **5**: 2695-2701.
[32] Liu LT, Chen YG, Feng ZB, *et al*. Crystal structure, infrared spectra, and microwave dielectric properties of the EuNbO$_4$ ceramic. *Ceram Int* 2021, **47**: 4321-4326.
[33] Li JM, Zhang CM, Liu H, *et al*. Structure, morphology, and microwave dielectric properties of SmAlO$_3$ synthesized by stearic acid route. *J Adv Ceram* 2020, **9**: 558-566.
Figure captions

Fig. 1. XRD patterns of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ($x = 0.02, 0.04, 0.06, 0.08$ and $0.1$) ceramics sintered at densification temperature for 6 h.

Fig. 2. Refinement results of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ceramics calcined under various conditions as indicated: (a) $x = 0.02$, (b) $x = 0.04$, (c) $x = 0.06$, (d) $x = 0.08$, (e) $x = 0.10$.

Fig. 3. The lattice parameters $(a, b$ and $c)$ and unit cell volume $(V_m)$ of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ceramics as a function of the substitution amount of (Mg$_{1/3}$Sb$_{2/3}$)$_{4+}$.

Fig. 4. The schematic illustration of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ceramics.

Fig. 5. Apparent densities of the Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ceramics as a function of the sintering temperature.

Fig. 6. SEM microphotographs of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ceramics at densification temperature for 6 h: (a) $x = 0.02$, (b) $x = 0.04$, (c) $x = 0.06$, (d) $x = 0.08$, (e) $x = 0.10$; (f) EDS analysis of Ce$_2$[Zr$_{0.94}$(Mg$_{1/3}$Sb$_{2/3}$)$_{0.06}$]$_3$(MoO$_4$)$_9$ ceramics sintered at $725°C$ for 6 h.

Fig. 7. $Q\times f$ and $\varepsilon_r$ values of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ceramics sintered at 700-800 °C: (a) $\varepsilon_r$, (b) $Q\times f$.

Fig. 8. $\varepsilon_r$ and the Mo1-O(2) bond ionicity of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ceramics as a function of the content of (Mg$_{1/3}$Sb$_{2/3}$)$_{4+}$ substitution.

Fig. 9. $Q\times f$ and the Zr(Mg/Sb)1-O(4) lattice energy of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ceramics as a function of the content of (Mg$_{1/3}$Sb$_{2/3}$)$_{4+}$ substitution.

Fig. 10. $\tau_f$ and the Mo1-O(1) bond energy of Ce$_2$[Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$]$_3$(MoO$_4$)$_9$ ceramics as a function of the content of (Mg$_{1/3}$Sb$_{2/3}$)$_{4+}$ substitution.

Fig. 11(a). Measured (black line) and fitted (red line) infrared reflectivity spectrum, and (b) real and imaginary parts of the complex permittivity for Ce$_2$[Zr$_{0.94}$(Mg$_{1/3}$Sb$_{2/3}$)$_{0.06}$]$_3$(MoO$_4$)$_9$ ceramic sintered at $725°C$ for 6 h.
Table captions

Table 1 Summarized microwave dielectric properties of Mo-based microwave dielectric ceramics.

Table 2 The refinement parameters of Ce₂[Zr₁₋ₓ(Mg₁/₃Sb₂/₃)ₓ]₃(MoO₄)₉ ceramics sintered at optimized sintering temperature.

Table 3 The refined atomic positions of Ce₂[Zr₁₋ₓ(Mg₁/₃Sb₂/₃)ₓ]₃(MoO₄)₉ samples.

Table 4 The bond iconicity fᵢ of Ce₂[Zr₁₋ₓ(Mg₁/₃Sb₂/₃)ₓ]₃(MoO₄)₉ (x=0.02-0.10) ceramics sintered at densification temperature for 6 h.

Table 5 The lattice energy U of Ce₂[Zr₁₋ₓ(Mg₁/₃Sb₂/₃)ₓ]₃(MoO₄)₉ (x=0.02-0.10) ceramics sintered at densification temperature for 6 h.

Table 6 The bond energy E of Ce₂[Zr₁₋ₓ(Mg₁/₃Sb₂/₃)ₓ]₃(MoO₄)₉ (x=0.02-0.10) ceramics sintered at densification temperature for 6 h.

Table 7 The coefficient of thermal expansion α of Ce₂[Zr₁₋ₓ(Mg₁/₃Sb₂/₃)ₓ]₃(MoO₄)₉ (x=0.02-0.10) ceramics sintered at densification temperature for 6 h.

Table 8 The phonon parameters after fitting of the Ce₂[Zr₀.₉₄(Mg₁/₃Sb₂/₃)₀.₀₆]₃(MoO₄)₉ sample sintered at 725 °C for 6 h.
### Table 1

| Materials                          | Sintering temperatures (°C) | ε₀ | Q·f (GHz) | τ f (ppm/°C) | References |
|-----------------------------------|-----------------------------|----|-----------|--------------|------------|
| Sm₂Zr₃(MoO₄)₉                  | 875                         | 11.0 | 74,012     | -45.3       | [9]        |
| Nd₂Zr₃(MoO₄)₉                    | 850                         | 10.8 | 58,942     | -40.9       | [9]        |
| Eu₂Zr₃(MoO₄)₉                    | 600                         | 10.75 | 74,900     | -8.88       | [10]       |
| La₂Zr₃(MoO₄)₉                    | 650                         | 10.8 | 61,790     | -29.1       | [11]       |
| La₃(Zr₀.92Ti₀.08)₃(MoO₄)₉          | 750                         | 10.33 | 80,658     | 3.48        | [11]       |
| Ce₂Zr₃(MoO₄)₉                    | 575                         | 10.69 | 19,062     | -1.29       | [12]       |
| Ce₃(Zr₀.90Ti₀.08)₃(MoO₄)₉          | 775                         | 11.28 | 84,200     | -7.86       | [13]       |
| Ce₃[Zr₁₋ₓ(1/₃Mg₂/₃Sb₁/₃)x](MoO₄)₉ | 725                         | 10.37 | 71,748     | -13.6       | This work |

### Table 2

| Structural parameters | Ce₃[Zr₁₋ₓ(1/₃Mg₂/₃Sb₁/₃)x](MoO₄)₉ |
|-----------------------|--------------------------------------|
|                       | X=0.02 | X=0.04 | X=0.06 | X=0.08 | X=0.10 |
| a=b (Å)               | 9.8344(1) | 9.8333(0) | 9.8310(9) | 9.8288(2) | 9.8254(1) |
| c (Å)                 | 58.8580(5) | 58.8603(6) | 58.8723(1) | 58.8835(0) | 58.8729(0) |
| α=β (°)               | 90     | 90     | 90     | 90     | 90     |
| γ (°)                 | 120    | 120    | 120    | 120    | 120    |
| Vm (Å³)               | 4929.84(0) | 4928.92(1) | 4928.30(5) | 4926.38(1) | 4922.07(5) |
| Rp (%)                | 8.33   | 8.52   | 6.60   | 7.62   | 7.46   |
| Rwp (%)               | 10.60  | 11.10  | 10.50  | 9.60   | 9.51   |
| χ²                    | 2.04   | 2.23   | 1.90   | 1.70   | 1.71   |
| Atom | Wyckoff position | Site | x   | y   | z   | Occupancy |
|------|------------------|------|-----|-----|-----|-----------|
| Ce   | 12c              | 3    | 0.6667 | 0.3333 | 0.0297 | 0.3333 |
| Zr1  | 6b               | -3   | 0.0000 | 0.0000 | 0.0000 | 0.1667 |
| Zr2  | 12c              | 3    | 0.3333 | 0.6667 | 0.0712 | 0.3333 |
| Mo1  | 36f              | 1    | 0.0982 | 0.7275 | 0.0250 | 1.0000 |
| Mo2  | 18e              | 2    | 0.2834 | 0.2834 | 0.2500 | 0.5000 |
| O1   | 36f              | 1    | -0.0959 | 0.5941 | 0.0308 | 1.0000 |
| O2   | 36f              | 1    | 0.1628 | 0.6664 | 0.0027 | 1.0000 |
| O3   | 36f              | 1    | 0.2061 | 0.7312 | 0.0500 | 1.0000 |
| O4   | 36f              | 1    | 0.1192 | 0.9207 | 0.0201 | 1.0000 |
| O5   | 36f              | 1    | 0.2879 | 0.4692 | 0.2456 | 1.0000 |
| O6   | 36f              | 1    | 0.1708 | 0.1902 | 0.2729 | 1.0000 |
|                  | Bond ionicity $f_i$ (%) | x=0.02 | x=0.04 | x=0.06 | x=0.08 | x=0.1 |
|------------------|-------------------------|--------|--------|--------|--------|--------|
| Ce-O(1)$^1$      | 0.8484                  | 0.8518 | 0.8467 | 0.8488 | 0.8491 |
| Ce-O(1)$^2$      | 0.8484                  | 0.8518 | 0.8467 | 0.8489 | 0.8491 |
| Ce-O(1)$^3$      | 0.8485                  | 0.8518 | 0.8467 | 0.8489 | 0.8491 |
| Ce-O(2)$^1$      | 0.8527                  | 0.8527 | 0.8553 | 0.8561 | 0.8558 |
| Ce-O(2)$^2$      | 0.8527                  | 0.8527 | 0.8553 | 0.8561 | 0.8558 |
| Ce-O(2)$^3$      | 0.8527                  | 0.8527 | 0.8553 | 0.8561 | 0.8558 |
| Ce-O(6)$^1$      | 0.8523                  | 0.8540 | 0.8524 | 0.8544 | 0.8521 |
| Ce-O(6)$^2$      | 0.8523                  | 0.8540 | 0.8524 | 0.8544 | 0.8521 |
| Ce-O(6)$^3$      | 0.8523                  | 0.8540 | 0.8524 | 0.8545 | 0.8521 |
| Zr(Mg/Sb)1-O(4)x6| 0.7964                  | 0.7868 | 0.7851 | 0.7873 | 0.7880 |
| Zr(Mg/Sb)2-O(3)$^1$ | 0.7912                  | 0.7757 | 0.8014 | 0.7895 | 0.7978 |
| Zr(Mg/Sb)2-O(3)$^2$ | 0.7912                  | 0.7758 | 0.8015 | 0.7895 | 0.7978 |
| Zr(Mg/Sb)2-O(3)$^3$ | 0.7913                  | 0.7758 | 0.8015 | 0.7895 | 0.7979 |
| Zr(Mg/Sb)2-O(5)$^1$ | 0.7849                  | 0.7824 | 0.7920 | 0.7884 | 0.7891 |
| Zr(Mg/Sb)2-O(5)$^2$ | 0.7850                  | 0.7824 | 0.7920 | 0.7884 | 0.7891 |
| Zr(Mg/Sb)2-O(5)$^3$ | 0.7850                  | 0.7825 | 0.7920 | 0.7885 | 0.7892 |
| Mo1-O(1)         | 0.7237                  | 0.7167 | 0.7298 | 0.7194 | 0.7251 |
| Mo1-O(2)         | 0.7237                  | 0.7068 | 0.7193 | 0.7113 | 0.7113 |
| Mo1-O(3)         | 0.7315                  | 0.7344 | 0.7248 | 0.7348 | 0.7237 |
| Mo1-O(4)         | 0.7369                  | 0.7269 | 0.7474 | 0.7377 | 0.7363 |
| Mo2-O(5)$^x2$    | 0.7248                  | 0.7344 | 0.7338 | 0.7381 | 0.7288 |
| Mo2-O(6)$^x2$    | 0.7276                  | 0.7064 | 0.7268 | 0.7183 | 0.7258 |
Table 5

| Ce$_2$Zr$_{1-x}$(Mg$_{1/3}$Sb$_{2/3}$)$_x$(MoO$_4$)$_9$ | Lattice energy $U$ (eV) |
|-----------------------------------------------|-------------------------|
| x=0.02                                        | x=0.04                  | x=0.06 | x=0.08 | x=0.1 |
| Ce-O(1)$_1$                                   | 3364                    | 3208   | 3413   | 3352   | 3354   |
| Ce-O(1)$_2$                                   | 3364                    | 3207   | 3412   | 3351   | 3352   |
| Ce-O(1)$_3$                                   | 3364                    | 3207   | 3412   | 3351   | 3352   |
| Ce-O(2)$_1$                                   | 3276                    | 3188   | 3235   | 3200   | 3212   |
| Ce-O(2)$_2$                                   | 3276                    | 3188   | 3234   | 3199   | 3212   |
| Ce-O(2)$_3$                                   | 3276                    | 3188   | 3234   | 3199   | 3211   |
| Ce-O(6)$_1$                                   | 3284                    | 3160   | 3296   | 3236   | 3291   |
| Ce-O(6)$_2$                                   | 3284                    | 3160   | 3295   | 3235   | 3291   |
| Zr(Mg/Sb)$_{1-0}(4x6)$                        | 10580                   | 10780  | 11189  | 11023  | 11007  |
| Zr(Mg/Sb)$_{2-0}(3x3)$                        | 10844                   | 11319  | 10360  | 10916  | 10512  |
| Zr(Mg/Sb)$_{2-0}(3x3)$                        | 10842                   | 11317  | 10358  | 10914  | 10510  |
| Zr(Mg/Sb)$_{2-0}(3x3)$                        | 10842                   | 11315  | 10358  | 10913  | 10509  |
| Zr(Mg/Sb)$_{2-0}(5x3)$                        | 11152                   | 10998  | 10850  | 10968  | 10955  |
| Zr(Mg/Sb)$_{2-0}(5x3)$                        | 11151                   | 10997  | 10849  | 10967  | 10954  |
| Zr(Mg/Sb)$_{2-0}(5x3)$                        | 11149                   | 10995  | 10847  | 10965  | 10951  |
| Mo1-O(1)                                      | 43980                   | 43859  | 43164  | 44597  | 43763  |
| Mo1-O(2)                                      | 43964                   | 45433  | 44862  | 45862  | 45940  |
| Mo1-O(3)                                      | 42658                   | 40742  | 43989  | 42023  | 43995  |
| Mo1-O(4)                                      | 41707                   | 42121  | 39969  | 41489  | 41852  |
| Mo2-O(5)×2                                    | 43793                   | 40747  | 42479  | 41418  | 43146  |
| Mo2-O(6)×2                                    | 43329                   | 45493  | 43655  | 44782  | 43658  |
### Table 6

| Bond energy $E$ (kJ/mol) | $x=0.02$ | $x=0.04$ | $x=0.06$ | $x=0.08$ | $x=0.1$ |
|--------------------------|-----------|-----------|-----------|-----------|----------|
| **Ce-**$\text{O}(1)^i$  | 420.9821  | 397.1351  | 428.3333  | 419.0938  | 419.3161 |
| **Ce-**$\text{O}(1)^2$  | 420.8959  | 397.0431  | 428.2441  | 418.9913  | 419.2306 |
| **Ce-**$\text{O}(1)^3$  | 420.8097  | 396.9971  | 428.1549  | 418.9230  | 419.1622 |
| **Ce-**$\text{O}(2)^i$  | 407.8353  | 394.2862  | 401.9027  | 396.5835  | 398.4747 |
| **Ce-**$\text{O}(2)^2$  | 407.7868  | 394.2408  | 401.8555  | 396.5376  | 398.4283 |
| **Ce-**$\text{O}(2)^3$  | 407.7382  | 394.1954  | 401.8084  | 396.4917  | 398.3820 |
| **Ce-**$\text{O}(6)^i$  | 409.1178  | 390.1848  | 410.8842  | 401.8398  | 410.1627 |
| **Ce-**$\text{O}(6)^2$  | 409.0527  | 390.1552  | 410.8513  | 401.7927  | 410.1136 |
| **Ce-**$\text{O}(6)^3$  | 409.0038  | 390.0811  | 410.7692  | 401.7299  | 410.0482 |
| **Zr(Mg/Sb)-**$\text{O}(4)\times6$ | 483.6989  | 494.9655  | 519.9098  | 509.8280  | 508.8463 |
| **Zr(Mg/Sb)-**$\text{O}(3)^i$ | 499.2091  | 527.2509  | 470.9886  | 503.4523  | 479.7139 |
| **Zr(Mg/Sb)-**$\text{O}(3)^2$ | 499.0641  | 527.0891  | 470.8595  | 503.3048  | 479.5799 |
| **Zr(Mg/Sb)-**$\text{O}(3)^3$ | 499.0158  | 527.0352  | 470.8380  | 503.2557  | 479.5353 |
| **Zr(Mg/Sb)-**$\text{O}(5)^i$ | 517.6120  | 507.9184  | 499.6205  | 506.5205  | 505.7748 |
| **Zr(Mg/Sb)-**$\text{O}(5)^2$ | 517.5340  | 507.8684  | 499.5479  | 506.4707  | 505.7003 |
| **Zr(Mg/Sb)-**$\text{O}(5)^3$ | 517.3781  | 507.7182  | 499.4268  | 506.3214  | 505.5515 |
| **Mo1-**$\text{O}(1)$    | 597.0129  | 595.5327  | 580.8629  | 609.3766  | 592.6962 |
| **Mo1-**$\text{O}(2)$    | 596.7025  | 627.2896  | 614.5251  | 635.2764  | 636.8040 |
| **Mo1-**$\text{O}(3)$    | 571.2568  | 536.2299  | 597.0474  | 559.2248  | 597.2891 |
| **Mo1-**$\text{O}(4)$    | 553.2635  | 561.9021  | 521.2639  | 549.2328  | 555.9438 |
| **Mo2-**$\text{O}(5)\times2$ | 593.3090  | 536.3134  | 567.7086  | 547.9217  | 580.6343 |
| **Mo2-**$\text{O}(6)\times2$ | 584.2142  | 628.5494  | 590.4598  | 613.1024  | 590.6287 |
Table 7

|                  | Thermal expansion coefficient $\alpha$ (10^{-6}/K) |
|------------------|---------------------------------------------------|
|                  | x=0.02    | x=0.04    | x=0.06    | x=0.08    | x=0.1     |
| Ce-O(1)$^1$      | 9.9082    | 10.5441   | 9.7205    | 9.9551    | 9.9472    |
| Ce-O(1)$^2$      | 9.9082    | 10.5484   | 9.7243    | 9.9590    | 9.9551    |
| Ce-O(1)$^3$      | 9.9082    | 10.5484   | 9.7243    | 9.9590    | 9.9551    |
| Ce-O(2)$^1$      | 10.2595   | 10.6302   | 10.4297   | 10.5784   | 10.5271   |
| Ce-O(2)$^2$      | 10.2595   | 10.6302   | 10.4339   | 10.5827   | 10.5271   |
| Ce-O(2)$^3$      | 10.2595   | 10.6302   | 10.4339   | 10.5827   | 10.5313   |
| Ce-O(6)$^1$      | 10.2227   | 10.7524   | 10.1780   | 10.4255   | 10.1983   |
| Ce-O(6)$^2$      | 10.2268   | 10.7524   | 10.1821   | 10.4297   | 10.1983   |
| Ce-O(6)$^3$      | 10.2268   | 10.7568   | 10.1821   | 10.4339   | 10.1983   |
| Zr(Mg/Sb)1-O(4)x6| 3.5771    | 3.4520    | 3.2100    | 3.3060    | 3.3154    |
| Zr(Mg/Sb)2-O(3)$^1$| 3.4129    | 3.1367    | 3.7204    | 3.3695    | 3.6208    |
| Zr(Mg/Sb)2-O(3)$^2$| 3.4141    | 3.1378    | 3.7217    | 3.3707    | 3.6220    |
| Zr(Mg/Sb)2-O(3)$^3$| 3.4141    | 3.1389    | 3.7217    | 3.3713    | 3.6227    |
| Zr(Mg/Sb)2-O(5)$^1$| 3.2311    | 3.3207    | 3.4093    | 3.3385    | 3.3462    |
| Zr(Mg/Sb)2-O(5)$^2$| 3.2317    | 3.3213    | 3.4099    | 3.3391    | 3.3468    |
| Zr(Mg/Sb)2-O(5)$^3$| 3.2329    | 3.3225    | 3.4111    | 3.3403    | 3.3486    |
| Mo1-O(1)         | -0.4301   | -0.4225   | -0.3783   | -0.4680   | -0.4165   |
| Mo1-O(2)         | -0.4291   | -0.5177   | -0.4839   | -0.5425   | -0.5469   |
| Mo1-O(3)         | -0.3452   | -0.2125   | -0.4307   | -0.3026   | -0.4310   |
| Mo1-O(4)         | -0.2809   | -0.3092   | -0.1553   | -0.2657   | -0.2909   |
| Mo2-O(5)x2       | -0.4184   | -0.2128   | -0.3333   | -0.2607   | -0.3772   |
| Mo2-O(6)x2       | -0.3890   | -0.5212   | -0.4097   | -0.4791   | -0.4099   |
Table 8

| Mode | $\omega_{ij}$ | $\omega_{ip}$ | $\gamma_j$ | $\Delta\varepsilon_j$ |
|------|---------------|---------------|-----------|---------------------|
| 1    | 118.72        | 225.22        | 35.46     | 3.60                |
| 2    | 150.75        | 341.96        | 12.89     | 5.15                |
| 3    | 202.86        | 162.23        | 31.95     | 0.64                |
| 4    | 270.42        | 386.82        | 31.62     | 2.05                |
| 5    | 333.43        | 104.55        | 6.68      | 0.10                |
| 6    | 350.41        | 60.52         | 5.92      | 0.03                |
| 7    | 398.23        | 259.20        | 34.10     | 0.42                |
| 8    | 422.68        | 169.58        | 22.11     | 0.16                |
| 9    | 602.91        | 412.83        | 155.98    | 0.47                |
| 10   | 695.94        | 338.65        | 22.47     | 0.24                |
| 11   | 736.26        | 462.78        | 17.08     | 0.40                |
| 12   | 774.75        | 178.17        | 15.75     | 0.05                |
| 13   | 811.10        | 228.68        | 18.10     | 0.08                |
| 14   | 888.05        | 388.88        | 7.79      | 0.19                |
| 15   | 898.43        | 238.71        | 12.23     | 0.07                |
| 16   | 957.54        | 192.66        | 9.89      | 0.04                |