Microwave dielectric properties of low firing temperature stable scheelite structured (Ca, Bi)(Mo, V)O₄ solid solution ceramics for LTCC applications

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A R T I C L E   I N F O

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A B S T R A C T

In the present work, a systematic study on microwave properties of Ca₁₋ₓBixMo₁₋ₓVₓO₄ (0.2 ≤ x ≤ 0.5) solid solution ceramics synthesized by using the traditional solid-state reaction method was conducted. A scheelite structured solid solution was formed in the composition range 0.2 ≤ x ≤ 0.5. We successfully prepared a microwave dielectric ceramic Ca₀.₆₆B𝑖₀.₃₄M𝑜₀.₆₆V₀.₃₄O₄ with a temperature coefficient of resonant frequency (TCF) near to zero and a low sintering temperature by using (Bi, V) substituted (Ca, Mo) in CaMoO₄ to form a solid solution. The Ca₀.₆₆B𝑖₀.₃₄M𝑜₀.₆₆V₀.₃₄O₄ ceramic can be well sintered at only 870 °C and exhibits good microwave dielectric properties with a permittivity (εr) ~ 21.9, a Qf ~ 18.150 GHz (at 7.2 GHz) (Q = quality factor = 1/dielectric loss; f = resonant frequency), a TCF ~ +0.1 ppm/°C. The chemical compatibility with silver indicated that the Ca₀.₆₆B𝑖₀.₃₄M𝑜₀.₆₆V₀.₃₄O₄ ceramic might be a good candidate for the LTCC applications.

1. Introduction

The Low Temperature Co-fired Ceramic (LTCC) technology is a multilayer ceramic manufacturing technology that integrates interconnects, passive components, and packages. LTCC is a leading technology for modern electronic devices fabrication and it is widely used in aerospace, military, communications, medical, automotive electronics and other fields [1–4], with a very broad application market and development prospects. Excellent high frequency characteristics, high density integration, and high reliability make the LTCC an indispensable material for the aerospace and military industries. Furthermore, it is worth mentioning that energy saving, material saving, green, and environmental protection have become an unstoppable trend in the development of electronic components industry. The LTCC also caters to this development demand, which minimizes the environmental pollution caused by raw materials, waste materials and production processes [5–8]. Therefore, the development of microwave dielectric ceramics with excellent performance and lower sintering temperature than the melting point of Ag (961 °C) has currently become one of the most important topics in microwave dielectric materials research.

In recent years, microwave dielectric ceramics with a scheelite structure (ABO₄) have attracted much attention due to its high Qf value and low sintering temperature [9,10]. As an important member of the metal molybdate family with a scheelite crystal structure, CaMoO₄ has a wide application potential in various fields, such as solid-state scintillators [11], luminescence material [12], and microwave devices applications [13]. Choi et al. reported that CaMoO₄ can be sintered at 1100 °C and exhibits excellent microwave dielectric properties with a permittivity (εr) ~ 11.7, a Qf ~ 55,000 GHz (Q = quality factor = 1/dielectric loss; f = resonant frequency), a temperature coefficient of resonant frequency (TCF) ~ −60 ppm/°C [13]. However, temperature coefficient of resonant frequency is the key physical parameter for evaluating the temperature stability of microwave devices. In practical applications, in order to avoid a large drift of the carrier signal of the microwave device as the ambient temperature changes. Therefore, the temperature coefficient of the resonant frequency should be as close as possible to zero. Thus, the high sintering temperature and large negative TCF value limit its application in LTCC technology. Therefore, further studies to reduce its sintering temperature and adjust its TCF to near zero are of great interest. We have noticed that the BiVO₄ ceramic with the same scheelite structure have excellent microwave dielectric properties (εr = 68, Qf = 8000 GHz, and TCF = −260 ppm/°C), and it
is important to point out that its sintering temperature is only 820 °C [14,15]. In addition, the internal stress can be introduced into the monoclinic scheelite-structured BiVO₄ ceramic through ion substitution. [16–18] With the increase of ion substitution, the internal stress increases and the crystal structure gradually transforms from monoclinic to tetragonal phase and TCF will become positive. The low sintering temperature, similar ionic radius (r_Bi⁺ = 1.17 Å similar to r_Ca⁺ = 1.12 Å, r_MoO₄²⁻ = 0.355 Å similar to r_MoO₄²⁻ = 0.41 Å), [19] and the common scheelite structure, which usually has wide cation solubility make the CaMoO₄ and the BiVO₄ are very attractive constituents for the goal of developing LTCC dielectrics.

In this investigation, the Ca₁₋ₓBiₓMo₁₋ₓVₓO₄ (0.2 ≤ x ≤ 0.5) solid solution ceramics were synthesized by solid-state reaction method. The structural evolution, sintering behaviors, microstructures, microwave dielectric properties, infrared (IR) reflectivity spectra, Raman, chemical compatibility with Ag, and the relation between structure and microwave dielectric properties were investigated in detail.

2. Experimental section

Samples of the Ca₁₋ₓBiₓMo₁₋ₓVₓO₄ (0.2 ≤ x ≤ 0.5) were synthesized by using the conventional solid-state reaction method, and the raw materials were CaCO₃ (99.8%), Bi₂O₃ (99%), MoO₃ (99.95%) and V₂O₅ (99%). Then the mixed powders were ball-milled in a nylon jar with zirconia balls for 4 h using ethanol as a medium. The mixtures were calcined at 650 °C for 4 h in air. After being crushed, the calcined powders were re-milled with ethanol for 4 h using a planetary mill, dried, and the as-dried powders were ground with 5 wt.% polyvinyl alcohol (PVA) binder addition and uniaxially pressed into several pellets (10 mm in diameter and 4–5 mm in height) under a pressure of 100 MPa. Samples were sintered in the temperature range 780–880 °C for 4 h. In order to study the chemical compatibility of the scheelite solid solution compound with Ag electrode, 20 wt.% Ag powders was mixed with the temperature-stable Ca₀.₆₆Bi₀.₃₄Mo₀.₆₆V₀.₃₄O₄ ceramic powders and co-fired at 870 °C for 2 h.

The samples were investigated using room-temperature X-ray diffraction (XRD) with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). The microstructures and energy-dispersive spectroscopy (EDS) of the sintered samples was observed by electron scanning microscopy (SEM; Quanta 250, FEI). The mean grain size was calculated from each SEM image of the Ca₁₋ₓBiₓMo₁₋ₓVₓO₄ (0.2 ≤ x ≤ 0.5) sample using image analysis software (Nano Measurer 1.2) [20]. The high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) patterns measurements were conducted on a JEM-2100 at an accelerating voltage of 200 kV. The Raman spectra were performed with a Laser Raman Spectrometer. The room temperature infrared reflectivity spectra were measured using a Bruker IFS 66v FTIR spectrometer on Infrared beamline station (U4) at National Synchrotron Radiation Lab (NSRL), China. The X-ray photoelectron spectroscopy (XPS) analysis was measured for the Ca₀.₆₆Bi₀.₃₄Mo₀.₆₆V₀.₃₄O₄ by a Thermo Fisher ESCALAB Xi+ with a monochromatic Al Kα radiation source. The microwave dielectric properties were measured using a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency (TCF) was measured in the temperature range from 25 °C – 85 °C. The TCF values were calculated by the following equation:

\[ TCF(\tau_f) = \frac{f_T - f_0}{f_0 \times (T - T_0)} \times 10^6 \]  

where, \( f_T \) and \( f_0 \) represent resonant frequencies at temperatures T and \( T_0 \) respectively.

3. Results and discussion

X-ray diffraction (XRD) patterns of the Ca₁₋ₓBiₓMo₁₋ₓVₓO₄ (0.2 ≤ x ≤ 0.5) ceramics sintered at their optimal temperatures are presented in Fig. 1a. All compositions were found to crystallize in monoclinic scheeléite structure with no second phase observed from the XRD results, indicating that the tetragonal scheeléite structure (space group I₄₁/a) is stable for the Ca₁₋ₓBiₓMo₁₋ₓVₓO₄ (0.2 ≤ x ≤ 0.5). Due to the difference in ionic radius (r_Bi⁺ = 1.17 Å > r_Ca⁺ = 1.12 Å, CN = 8; r_MoO₄²⁻ = 0.355 Å < r_MoO₄²⁻ = 0.41 Å, CN = 4) [19], a slight change in lattice parameters will occur as the amount of substitution of (Bi,V) increases. The lattice parameters of the Ca₁₋ₓBiₓMo₁₋ₓVₓO₄ (0.2 ≤ x ≤ 0.5) ceramics were calculated by the least squares method using Jade software [21]. To
observe the changes in lattice parameters clearly, cell parameters of the Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ (0.2 ≤ x ≤ 0.5) ceramics as a function of x are shown in Fig. 1b. The lattice parameters a decreased from 5.308 to 5.040 Å while the lattice parameters c increased from 11.290 to 11.568 Å with the increase of x, along with a decrease in the cell volume from 318.04 to 293.89 Å$^3$. In order to show the changes of the diffraction peaks clearly, the enlarged portion of the XRD patterns from 30° to 36° are presented in Fig. 1c. With the increase of substitution content, the (004) diffraction peak shifted towards lower angle direction while the (200) diffraction peak shifted towards higher angle direction. It is commensurate with the enlargement of c axis and contraction of a axis, respectively. Because for the tetragonal system, the following equation can be derived from the Bragg’s equation (2dsinθ = λ) and d-spacings formula (1/d$^2$ = (h$^2$+k$^2$)/a$^2$ + l$^2$/c$^2$):

$$\sin^2 \theta = \frac{\lambda^2}{4a^2}(h^2 + k^2) + \frac{\lambda^2}{4c^2}l^2$$

(2)

According to the above formula, the θ of the (200) diffraction peak is inversely proportional to the lattice parameter a, and the θ of the (004) diffraction peak is inversely proportional to the lattice parameter c. Therefore, the θ of the (200) diffraction peak increased as the lattice parameter a decreased, namely, the (200) diffraction peak position shifted toward higher angle direction. The θ of the (004) diffraction peak decreased as the lattice parameter c increased, namely, the (004) diffraction peak position shifted toward lower angle direction. The regular shift of the XRD peaks in Fig. 1c and the changes of the lattice parameters in Fig. 1b further indicate the formation of solid solution in the Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ (0.2 ≤ x ≤ 0.5) ceramics. This is consistent with the observation from the back-scattered electron images (BEI) and energy dispersive spectra (EDS) analysis of as-fired surfaces of the Ca$_{0.56}$Bi$_{0.34}$Mo$_{0.66}$V$_{0.34}$O$_4$ ceramic sintered at 870°C as shown in Fig. 1d. It can be seen that there is only one kind of grain, combined with the analysis results of EDS, further indicating that a solid solution is formed in the Ca$_{0.56}$Bi$_{0.34}$Mo$_{0.66}$V$_{0.34}$O$_4$ ceramic.

The scanning electron microscopy (SEM) analysis was carried out to study the surface micro-morphology of the Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ (0.2 ≤ x ≤ 0.5) ceramics. Fig. 2a–c shows the SEM images (only focus on those that show differences) of the samples sintered at optimal conditions. It can be seen that all the ceramics exhibit dense microstructures with almost no pores and a relatively flat surface. Fig. 2d shows the mean grain size of the Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ (0.2 ≤ x ≤ 0.5) ceramics sintered at optimal temperatures as a function of x value. It can be seen that the mean grain size increased from 2.3 to 3.4 μm with increasing x value. In addition, the sintering temperatures of pure CaMoO$_4$ and BiVO$_4$ ceramics are 1100°C and 820°C, respectively [13,15]. However, optimal sintering temperatures of the Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ (0.2 ≤ x ≤ 0.5) ceramics are in range 800–880°C. The reason might be that Bi$^{3+}$ and V$^{5+}$ ions enter the lattice of CaMoO$_4$ to form a solid solution, and the difference in ionic radius (r$_{Bi^{3+}}$ = 1.17 Å > r$_{Ca^{2+}}$ = 1.12 Å, CN = 8; r$_{V^{5+}}$ = 0.355 Å < r$_{Mo^{6+}}$ = 0.41 Å, CN = 4) [19] cause a slight lattice distortion of the CaMoO$_4$ phase. These lattice defects might increase the internal energy of the crystal, activate the crystal lattice, and also accelerate the mass mobility, so that the density of defects would increase the internal energy of the crystal, activate the solid solution, and the distortion of the CaMoO$_4$ phase. These lattice parameters are shown in Fig. 3. It can be seen that the bulk density increases linearly with the increase of x. To make clear the changes of density with composition, we also calculated the theoretical density of the different compositions of the Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ (0.2 ≤ x ≤ 0.5) solid solution ceramics according to the theoretical density formula ($\rho_{th} = \frac{w}{V} = \frac{\sum n_i w_i}{\sum n_i}$), where, W is the unit cell weight of solid solution, i is the atom contained in the unit cell, n is the number of species of atoms contained in the unit cell, V is the unit cell volume of the solid solution. The calculated theoretical density as a function of x value are shown in Fig. 3a. It can be seen that the theoretical density also increases linearly with the increase of x, which could be ascribed to the theoretical density of BiVO$_4$ (6.98 g/cm$^3$) [27] is much larger than that of CaMoO$_4$ (4.25 g/cm$^3$) [28]. Therefore, the density is gradually increased as the BiVO$_4$ content increases in the Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ (0.2 ≤ x ≤ 0.5) solid solution. As shown in Fig. 3b, the $\epsilon_r$ of samples increases linearly from 15.1 to 34.5 as the x value increases from 0.2 to 0.5. The variation in polarizabilities ($\alpha_{i\omega}$) value versus x value presented similar behavior to that of permittivity, suggesting that the change of permittivity can be explained well by Shannon’s additive rule. [29] Shannon suggested that polarizabilities of oxides may be estimated by summing the polarizabilities of constituent ions [29,30].

The polarizabilities $\alpha_x$ of Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ could be calculated as follows:

$$\alpha_x = (1 - x) \times (\alpha_{Ca^{2+}} + \alpha_{Mo^{6+}}) + x \times (\alpha_{Bi^{3+}} + \alpha_{V^{5+}}) + 4\alpha_{O^{2-}}$$

(3)

where $\alpha_{Ca^{2+}}$, $\alpha_{Mo^{6+}}$, $\alpha_{Bi^{3+}}$, and $\alpha_{V^{5+}}$ are the polarizabilities of Ca$^{2+}$, Bi$^{3+}$, Mo$^{6+}$, and V$^{5+}$, respectively [13,30]. The permittivity can be calculated by the following equation:

$$\epsilon_r = \frac{3\rho_m + 8\pi\alpha_\omega}{3\rho_m - 4\pi\alpha_\omega}$$

(4)

where, $\rho_m$ is the cell volume, $\alpha$ is the sum of ionic polarizability of individual ions. With the increase of substitution content, the increase in permittivity is due to the increase of ionic polarizability coupled with the contraction of cell volume according to the Eq. (4). The $\epsilon_r$ of samples increased linearly from 12.3 to 27.9 as the x value increases from 0.2 to 0.5, which is close to the measured dielectric constant. This result indicates that the variation of the dielectric constant with solid solution composition can be well explained by the Shannon’s additive rule. Fig. 3(c) shows that the Qf values of the Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ ceramics decreased with increasing x value. At microwave region, the relationship between Qf value and relative permittivity can be obtained as following:

$$Q_f \times f \approx \frac{2\pi f (\varepsilon - 1)}{\varepsilon (\varepsilon + 1)}$$

(5)

where Q is the quality factor, f is the frequency, $\varepsilon$ is the equivalent electric charge number, $\varepsilon$ is the electric charge for an electron, m is the equivalent atom weight, V is the unit volume, $\epsilon_r$ is the permittivity, $\gamma$ is the damping parameter, $\epsilon'(\omega)$ is the complex permittivity and $\epsilon''(\omega)$ is the electronic part of the static permittivity. The above relation was successfully used to explain the reciprocal relationship between the $\epsilon_r$ and Qf in scheelite solid solutions [31]. It shows that Qf has inverse relation to $\epsilon_r$, so the Qf values decreased with the increase of the components. It is assumed that the intrinsic microwave dielectric loss is mainly dominated by low frequency modes corresponding to Ca/Bi/Mo/VO4 vibrations. Bi$^{3+}$ (6.12 Å$^3$) has a polarizability larger than Ca$^{2+}$ (3.16 Å$^3$) while V$^{5+}$ (2.92 Å$^3$) has a smaller polarizability than Mo$^{6+}$ (3.28 Å$^3$). However, considering that $\Delta \alpha_{Ca^{2+}} - \alpha_{Bi^{3+}}$ is much larger than $\Delta \alpha_{Mo^{6+}} - \alpha_{V^{5+}}$, the main contribution should come from Bi$^{3+}$ instead of Ca$^{2+}$. From $\alpha_{Bi^{3+}} > \alpha_{Ca^{2+}}$, it can be inferred that the contribution to microwave dielectric constant from Bi$^{3+}$ polarization is larger than that of Ca$^{2+}$ and the oscillation of Bi$^{3+}$ is also stronger than that of Ca$^{2+}$ in the scheelite structure. Therefore, the substitution of Bi$^{3+}$ decreases the Qf value of the Ca$_{1-x}$Bi$_x$Mo$_{1-x}$V$_x$O$_4$ ceramics. As shown in Fig. 3d, the TCF value shifts from -44.9 ppm/C to +71.6 ppm/C as x value increases from 0.2 to 0.5. In general, BiVO$_4$ material has three different structures: monoclinic scheelite, tetragonal zircon
and tetragonal scheelite. The BiVO₄ ceramics synthesized via solid-state reaction method are usually crystallized in a monoclinic scheelite structure. The TCF of BiVO₄ with monoclinic scheelite structure is −260 ppm/°C [14,15]. The monoclinic scheelite BiVO₄ is ferroelastic at room temperature and reversibly transforms to paraelastic BiVO₄ with a standard tetragonal scheelite structure (space group I₄₁/a) under high temperature (255 °C) [32]. Besides, according to Hazen et al.’s work, this phase transition can also occur through stress induction [17]. In our previous work, the (Li₁/₂Bi₁/₂)²⁺ and (Na₁/₂Bi₁/₂)²⁺ complex ions were introduced into the A site of BiVO₄ by ion substitution, and the Mo⁶⁺ ion was introduced into the B site, and a large internal stress was successfully introduced into the monoclinic scheelite structure. With the increase of the amount of ion substitution, the internal stress gradually increases, causing the lattice parameters to change, then the lattice structure gradually changes from a monoclinic phase to a tetragonal phase. Therefore, the ferroelastic–paraelastic phase transition temperature was shifted from 255 °C to near room temperature, and the TCF value becomes positive [16,18]. This is because the TCF is usually defined as follows:

$$TCF = - \left( \frac{1}{2} \tau_e + \alpha_l \right)$$

(6)

where $\tau_e$ is the temperature coefficient of dielectric constant and $\alpha_l$ is the thermal expansion coefficient. Generally, the $\alpha_l$ of microwave dielectric is relatively small (< + 20 ppm/°C). Hence, the TCF value mainly depends on $\tau_e$. According to our previous work, in the [(Liₓ₋₀.₅Biₓ₋₀.₅)ₓBi₁₋ₓ]Mo₁₋ₓVₓO₄ [16] and (Na₀.₅Bi₀.₅₋ₓₓ)(MoₓV₁₋ₓ)O₄ [18] system, When the materials belong to ferroelastic–monoclinic phase, the relative permittivity increases sharply with temperature ranging from 25 to 85 °C. This determines that it has a large positive temperature coefficient of dielectric permittivity ($\tau_e$), which means a large negative TCF value. However, when the materials belong to
paraelastic-tetragonal phase, the relative permittivity decreases sharply with temperature ranging from 25 to 85 °C. This determines that it has a large negative temperature coefficient of dielectric permittivity ($\tau_{\varepsilon}$), which means a positive TCF value. Therefore, the phase transformation from monoclinic to tetragonal structure determines the sign of the TCF value, namely, the TCF value becomes positive. In our previous work, we found that the ferroelastic-paraelastic phase transition could be exist in many systems such as $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{x}\text{Bi}_{1-x}]\text{[Mo}_x\text{V}_{1-x}]\text{O}_4$, $(\text{Na}_{0.5}x\text{Bi}_{1-0.5}x)(\text{Mo}_x\text{V}_{1-x})\text{O}_4$ and $(1-x)\text{BiVO}_4-x(\text{Ag}_{0.5}\text{Bi}_{0.5})\text{MoO}_4 \ [16,18,25]$. For $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{x}\text{Bi}_{1-x}]\text{[Mo}_x\text{V}_{1-x}]\text{O}_4$, $(\text{Na}_{0.5}x\text{Bi}_{1-0.5}x)(\text{Mo}_x\text{V}_{1-x})\text{O}_4$ and $(1-x)\text{BiVO}_4-x(\text{Ag}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$ systems, the phase transition point occurs at $x = 0.098$, $x = 0.1$, and $x = 0.1$, respectively. In addition, in this work, both end members (TCF$_{\text{CaMoO}_4} = -60 \text{ ppm/°C}$, TCF$_{\text{BiVO}_4} = -260 \text{ ppm/°C}$) in the Ca$_{1-x}$Bi$_x$Mo$_1-x$V$_x$O$_4$ system have negative TCF. However, a near-zero TCF value appears at $x = 0.34$. Therefore, it was deduced that there should be a phase transition in the range of $0.5 < x < 1$ of the Ca$_{1-x}$Bi$_x$Mo$_1-x$V$_x$O$_4$ system, leading the TCF value of BiVO$_4$ shifted from negative to positive, thereby adjusting the negative TCF value of CaMoO$_4$ to near zero. The phase transition in Ca$_{1-x}$Bi$_x$Mo$_1-x$V$_x$O$_4$ (0.5 < $x$ < 1) solid solutions will be studied in more detail in our future work. It is important to note that a temperature-stable micro-wave dielectric ceramic can be obtained at $x = 0.34$, indicating that the substitution of (Bi, V) for (Ca, Mo) in CaMoO$_4$ is an effective method to adjust TCF to near zero. High performance of microwave dielectric properties can be obtained in the Ca$_{0.66}$Bi$_{0.34}$Mo$_{0.66}$V$_{0.34}$O$_4$ ceramic sintered at 870 °C for 4 h, with a $\varepsilon_r \approx 21.9$, a $Q_f \approx 18,150$ GHz (at 7.2 GHz) and a TCF $\approx +0.1 \text{ ppm/°C}$.

In order to further understand the crystal structure of Ca$_{1-x}$Bi$_x$Mo$_1-x$V$_x$O$_4$ (0.2 $\leq x \leq$ 0.5), Raman spectroscopic investigation was also conducted. Pure CaMoO$_4$ belongs to a tetragonal crystal structure (space group: I$4_1$/a) with a point group C$_{4h}$ (4/m). The Ca ions are at S$_4$ sites, as are the Mo’s, and the oxygen ions are at C$_1$ sites. Theoretical group analysis gives an irreducible representation of the vibrational modes as follow:

$$\Gamma = 3A_g + 5A_u + 5B_g + 3B_u + 5E_g + 5E_u$$

The 3$A_g$, 5$B_g$, 5$E_g$ modes are the Raman-active optical modes, whereas the 5$A_u$, 3$B_u$, and 5$E_u$ modes are infrared-active modes. In order to observe the lattice vibrational modes, the Raman spectra of Ca$_{1-x}$Bi$_x$Mo$_1-x$V$_x$O$_4$ was fitted by the standard Gaussian-Lorentzian model, then the specific position information of the peaks can be obtained. The fitted Raman spectra are plotted in Fig. 4b as black solid lines. As seen from Fig. 4a, the peaks at 136.0 cm$^{-1}$ (E$_g$), 198.5 cm$^{-1}$ (A$_g$) and 258.2 cm$^{-1}$ (E$_g$) belong to the external modes, and peaks at

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320.6 cm\(^{-1}\) (B\(_g\)), 384.6 cm\(^{-1}\) (B\(_g\)), 395.0 cm\(^{-1}\) (E\(_g\)), 789.0 cm\(^{-1}\) (E\(_g\)),
826.7 cm\(^{-1}\) (B\(_g\)), 838.5 cm\(^{-1}\) (B\(_g\)) and 873.2 cm\(^{-1}\) (A\(_g\)) belong to the
internal modes. Each vibration mode is in good agreement with the
results reported in the literature [33]. While it is noteworthy that as the
increases of x, the intensity of peak at 826.7 cm\(^{-1}\) increases gradually,
while the intensity of peak at 873.2 cm\(^{-1}\) decreases. It is due to that the
Raman spectrum of the scheelite ABO\(_4\) structure crystals mainly re-
flect the structure of the BO\(_4\) tetrahedrons in the scheelite crystals. In the
Ca\(_{1-x}\)Bi\(_x\)Mo\(_{1-x}\)V\(_x\)O\(_4\) solid solution, peaks at 826.7 cm\(^{-1}\) and 873.2 cm\(^{-1}\)
represent the anti-symmetric \(\nu_3\) stretching mode in the [VO\(_4\)] tetra-
hedron and the \(\nu_1\) stretching mode in the [MoO\(_4\)] tetrahedron, re-
spectively. Therefore, as the amount of V substitution increases, the
peak at 826.7 cm\(^{-1}\) becomes stronger, and the peak at 873.2 cm\(^{-1}\)
becomes weaker.

Far-infrared re-
fl
ectivity is an e-
ff
ective method to analyse intrinsic
dielectric properties of microwave ceramics. As discussed above, there
are thirteen infrared-active modes including 5A\(_{\text{u}}\), 3B\(_g\) and 5E\(_g\) modes. As seen from Fig. 5a, the peaks located at 248.3 cm\(^{-1}\) (\(\nu_2\)-A\(_{\text{u}}\)),

Fig. 6. (a) The experimental (circle) and calculated (line) X-ray powder diffraction profiles for CBMV\(_{0.34}\) sample sintered at 870 °C (The short vertical lines below the
patterns mark the positions of Bragg reflections. The bottom continuous line is the difference between the observed and calculated intensity.). Insets is the schematic
crystal structure ofCBMV\(_{0.34}\) (b, c, e) HRTEM image, SAED pattern and schematic of crystal structure of CBMV\(_{0.34}\)viewed along the [111] zone axis. (d) The enlarged
part of HRTEM image.
Table 2

Refined atomic fractional coordinates from XRD data of the Ca_{0.66}Bi_{0.34}Mo_{0.66}V_{0.34}O_{4} ceramic and the cell parameters are

<table>
<thead>
<tr>
<th>Atom</th>
<th>Wyckoff position</th>
<th>x</th>
<th>y</th>
<th>z</th>
<th>Biso</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ca</td>
<td>4b</td>
<td>0.165</td>
<td>0.00000</td>
<td>0.25000</td>
<td>0.62500</td>
</tr>
<tr>
<td>Bi</td>
<td>4b</td>
<td>0.085</td>
<td>0.00000</td>
<td>0.25000</td>
<td>0.62500</td>
</tr>
<tr>
<td>V</td>
<td>4a</td>
<td>0.085</td>
<td>0.00000</td>
<td>0.25000</td>
<td>0.12500</td>
</tr>
<tr>
<td>Mo</td>
<td>4a</td>
<td>0.165</td>
<td>0.00000</td>
<td>0.25000</td>
<td>0.12500</td>
</tr>
<tr>
<td>O</td>
<td>16f</td>
<td>1.000</td>
<td>0.15419</td>
<td>-0.01452</td>
<td>0.21038</td>
</tr>
</tbody>
</table>

The fitted infrared reflectivity values and the complex permittivities are shown in Fig. 5b, and the related parameters are listed in Table 1. The calculated permittivity value of 17.3 was obtained according to the fitting result, which is a little smaller than the measured value 21.9.

The optical dielectric constants from the infrared spectra of the CBMV_{0.34} ceramic is about 1.86, which is only 10.8% of the total polarizability contribution at microwave frequencies, indicating that the main polarization contributions to permittivity of microwave dielectric ceramics come from ionic polarization rather than electronic, which is quite popular in high k microwave dielectric ceramics.

As a result, the TCF value of CaMoO_{4} can be effectively adjusted to zero by replacing (Ca, Mo) by (Bi, V), and a temperature stable microwave dielectric ceramic was obtained at x = 0.34. Therefore, it is necessary to study the CBMV_{0.34} in more detail. In order to investigate the crystal structure details of CBMV_{0.34} ceramic, refinements were performed based on XRD data recorded on the powders. The refinement confirmed that CBMV_{0.34} adopts a tetragonal structure with a space group I4_{1}/a (No. 88). Measured and calculated XRD patterns are presented in Fig. 6a. As listed in Table 2, the refined cell parameters are a = b = 5.2052 Å, c = 11.5470 Å, and α = 90° with a space group I4_{1}/a (No. 88). The goodness of fit of refinement, which is defined as the ratio of R_{wp} to R_{exp}, is 1.87. A schematic of the crystal structure is shown in Fig. 6a. To further confirm the CBMV_{0.34} structure, high-resolution transmission electron microscopy (HRTEM) and selected area electron diffraction (SAED) patterns analysis were employed. Fig. 6b, c display the HRTEM image and SAED patterns of CBMV_{0.34} ceramic recorded along the [111] zone axis. The HRTEM image shows that the characteristic spacings of the (101) and (011) lattice planes of CBMV_{0.34} ceramic are all 0.48 nm, which correspond well with XRD refinements.

Fig. 6e illustrates the CBMV_{0.34} crystal structure along the direction of the corresponding zone axes. The HRTEM image and schematic of crystal structure can be well matched, and the structural models of CBMV_{0.34} cell are superposed on the Fig. 6d (a partial enlargement of HRTEM). All these results are in good agreement, which fully demonstrates that CBMV_{0.34} belongs to the tetragonal structure with a space group I4_{1}/a (No. 88).

X-ray photoelectron spectroscopy (XPS) was performed for CBMV_{0.34} ceramic to analyze chemical composition and oxidation state of each element. Fig. 7a–f illustrates the XPS spectra of CBMV_{0.34} with

![Fig. 7. XPS spectra of CBMV_{0.34} ceramic with (a) the survey spectrum and high-resolution spectra of (b) Ca 2p, (c) Bi 4f, (d) Mo 3d, (e) V 2p and (f) O 1 s. (all peaks have been calibrated with respect to the C 1 s peak at 284.8 eV).](image-url)

2371
the survey and high-resolution spectra of all elements. As shown in Fig. 7a, the survey spectrum revealed the presence of Ca, Bi, Mo, V, and O in CBMV0.34 and C from contamination carbon as reference. The peak position also confirmed the oxidation state of each element as presented in Fig. 7b–f. The peak located at 530.0 eV is assigned to O 1s of O2− [35]. The Ca (2p1/2) peak at 346.8 eV agreed with the peak position of CaO3 in the literature [35], and Bi (4f7/2) at 159.0 eV and Mo (3d5/2) at 232.4 eV matched well with BiVO4 and CoMoO4, respectively [36,37]. XPS signals from V 2p can be found at binding energies of 516.7 eV (2p3/2) and 524.2 eV (2p1/2), with a doublet splitting of 7.5 eV, consistent with the V 2p spin-orbit, which can be matched well with V2O5 [38]. These results confirmed that the oxidation states of Ca, Bi, Mo, and V, are +2, +3, +6 and +5, respectively, which are comparable to those of CBMV0.34 for Ca, Bi, Mo and V.

The sintering temperature of CBMV0.34 (870 °C) is lower than the melting point of Ag (∼961 °C), which raises the possibility that CBMV0.34 ceramic may be suitable for LTCC technology, provided that no reaction occurs. To evaluate the chemical compatibility of CBMV0.34 ceramic with silver electrode, it was co-fired with 20 wt.% Ag powders at 870 °C for 2 h. Fig. 8a–b shows the XRD pattern and backscattered electron images (BEI) of the co-fired ceramic. From the XRD results, it is seen that only the diffraction peaks of CBMV0.34 and Ag were detected. Furthermore, we clearly observed in Fig. 8b that there are two types of grains, one with dark-color (marked as A) and the other with light-color (marked as B). EDS analysis was employed to identify the chemical compositions of two different color grains. According to the EDS analysis, the dark colored grains belong to CBMV0.34 phase while the light colored grains belong to Ag phase. These results confirmed that the chemical compatibility between CBMV0.34 ceramic and Ag electrodes, indicating that the CBMV0.34 ceramic have potential for exploitation in LTCC technology.

4. Conclusions

In the Ca1−xBiMo1−xVxO4 (0.2 ≤ x ≤ 0.5) ceramics, we found that a tetragonal scheelite structured solid solution was formed in the composition range 0.2 ≤ x ≤ 0.5. As x increased from 0.2 to 0.5, sintering temperature of the Ca1−xBiMo1−xVxO4 ceramics decreased from 880 to 800 °C, while the TCF shifted linearly from −44.9 to +71.6 ppm/°C. Optimum microwave dielectric properties can be obtained in Ca0.62Bi0.38Mo0.66V0.34O4 ceramic sintered at 870 °C for 4 h, with a εr = 21.9, a Qf ~ 18,150 GHz (at 7.2 GHz) and a TCF ~ +0.1 ppm/°C. It is demonstrated that a temperature-stable microwave dielectric ceramics can be obtained by the substitution of (Bi, V) for (Ca, Mo) in CaMoO4. Therefore, we conclude that the substitution of (Bi, V) for (Ca, Mo) is an effective way to adjust the TCF value of CaMoO4 to near zero and to decrease the sintering temperature effectively. Furthermore, we found that the Ca0.62Bi0.38Mo0.66V0.34O4 ceramic is chemically compatible with Ag powders at its sintering temperature, suggesting that this system could be good candidate for LTCC technology applications.

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