



This is a repository copy of *Novel scheelite-type [Ca_{0.55}(Nd_{1-x}Bix)_{0.3}]MoO₄ (0.2 ≤ x ≤ 0.95) microwave dielectric ceramics with low sintering temperature.*

White Rose Research Online URL for this paper:
<http://eprints.whiterose.ac.uk/164859/>

Version: Published Version

Article:

Hao, S., Zhou, D., Hussain, F. et al. (5 more authors) (2020) Novel scheelite-type [Ca_{0.55}(Nd_{1-x}Bix)_{0.3}]MoO₄ (0.2 ≤ x ≤ 0.95) microwave dielectric ceramics with low sintering temperature. *Journal of the American Ceramic Society*. ISSN 0002-7820

<https://doi.org/10.1111/jace.17378>

Reuse

This article is distributed under the terms of the Creative Commons Attribution (CC BY) licence. This licence allows you to distribute, remix, tweak, and build upon the work, even commercially, as long as you credit the authors for the original work. More information and the full terms of the licence here:
<https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.



eprints@whiterose.ac.uk
<https://eprints.whiterose.ac.uk/>

Novel scheelite-type $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($0.2 \leq x \leq 0.95$) microwave dielectric ceramics with low sintering temperature

Shu-Zhao Hao¹ | Di Zhou¹  | Fayaz Hussain² | Jin-Zhan Su³ | Wen-Feng Liu⁴ | Da-Wei Wang⁵  | Qiu-Ping Wang⁶ | Ze-Ming Qi⁷

¹Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an, China

²Department of Materials Engineering, NED University of Engineering & Technology, Karachi, Pakistan

³International Research Centre for Renewable Energy, State Key Laboratory of Multiphase Flow in Power Engineering, Xi'an Jiaotong University, Xi'an, China

⁴State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an, China

⁵Department of Materials Science and Engineering, University of Sheffield, Sheffield, UK

⁶School of Science, Xi'an Polytechnic University, Xi'an, China

⁷National Synchrotron Radiation Laboratory, University of Science and Technology of China, Hefei, China

Correspondence

Di Zhou, Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, School of Electronic and Information Engineering, Xi'an Jiaotong University, Xi'an 710049, China
Email: zhoudi1220@gmail.com

Funding information

National Key Research and Development Program of China, Grant/Award Number: 2017YFB0406301; National Natural Science Foundation of China, Grant/Award Number: U1632146; State Key Laboratory of Electrical Insulation and Power Equipment, Grant/Award Number: EIPE19210; Higher Education Discipline Innovation Project, Grant/Award Number: B14040; Fundamental Research Funds for the Central University

Abstract

Novel scheelite-type $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($0.2 \leq x \leq 0.95$) ceramics were prepared using the solid-state reaction method. According to the X-ray diffraction data, a solid solution was formed in $0.2 \leq x \leq 0.95$ and all the samples belong to pure scheelite phase with the tetragonal structure. As revealed by Raman spectroscopy, the number of vibrational modes decreased with the increase in x value, which further indicated that Bi^{3+} ions occupied A-site of scheelite structure. As the x value increased, the sintering temperature decreased from 740°C to 660°C; the permittivity increased from 12.6 to 20.3; the Qf value first decreased slightly and gradually remained stable. Based on the infrared reflectivity spectrum analysis, the calculated permittivity derived from the fitted data shared the same trend with the measured value. The $[\text{Ca}_{0.55}(\text{Nd}_{0.05}\text{Bi}_{0.95})_{0.3}]\text{MoO}_4$ ceramic sintered at 660 °C attained a near-zero value temperature coefficient $-\tau_f$ (-7.1 ppm/°C) and showed excellent microwave dielectric properties with a $\epsilon_r \sim 20.3$ and a Qf $\sim 33\,860$ GHz, making this system a promising candidate in the ultralow temperature cofired ceramic (ULTCC) technology.

KEYWORDS

infrared spectra, low-sintering, LTCC, Raman spectra

1 | INTRODUCTION

Microwave device is an important part of the modern wireless communication system, with the 5th generation wireless

systems coming. The investigation of microwave ceramic is drawing more and more attention.¹ Meanwhile, a series of new materials manufacturing process, such as the low-temperature cofired ceramic (LTCC) technology and

This is an open access article under the terms of the Creative Commons Attribution License, which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

© 2020 The Authors. *Journal of the American Ceramic Society* published by Wiley Periodicals LLC on behalf of American Ceramic Society (ACERS)

the ultralow-temperature co-fired ceramic (ULTCC) technology,² provide technical support for the fabrications of the miniaturized and integrated microwave devices. Hence, there is an urgent need to develop microwave ceramics suitable for LTCC/ULTCC technology. Microwave dielectric ceramics used in LTCC/ULTCC technology must meet several basic requirements. First, the microwave ceramics should have lower sintering temperatures than the melting points (MP) of metal electrodes, such as Ag with a MP ~961 °C and Al with a MP ~660 °C. Second, the dielectric loss should be very low (high-quality factor Q) to reduce the power consumption of microwave devices. Third, the temperature coefficient of resonant frequency τ_f values of the microwave ceramics should approach the zero to improve the temperature independence of microwave devices. Finally, the raw materials of the microwave ceramics should be nontoxic for the environment.³⁻¹⁰

Recently, the $A^{2+}B^{6+}O_4$ ($A^{2+} = \text{Mg, Mn, Ca, Zn, Cd, and } B^{6+} = \text{Mo, W}$) oxides with scheelite structure have been widely investigated on their microwave dielectric properties.^{11,12} Due to the low sintering temperature and the adaptive crystal structure providing the potential for the various substitutions at A- or B-site, these compositions have received extensive attentions in LTCC technology. In the previous report, Choi et al found that the CaMoO_4 possessed a high Qf value (~89 700 GHz) and a low sintering temperature (~1100 °C).¹³ Rama et al used the Cd^{2+} ion to substitute for the Ca^{2+} ion and gained good microwave dielectric properties ($\epsilon_r = 8-10$, Qf = 46 000-53 000 GHz, $\tau_f = -22$ – -57 ppm/°C) in $\text{Ca}_{1-x}\text{Cd}_x\text{MoO}_4$ ceramics at low temperature (900-1075 °C).¹⁴ Zhou et al changed the elements at A-site and gained the temperature stable $[(\text{Li}_{0.5}\text{Ln}_{0.5})_{0.2}\text{Ca}_{0.8}]\text{MoO}_4$ ceramics with excellent microwave dielectric properties ($\epsilon_r = 10.6-11$, Qf = 18 400-24 500 GHz, $\tau_f = -7.1 \sim +6.9$ ppm/°C) and low sintering temperatures (S.T = 800-900 °C).^{15,16} According to the literatures' reports,^{17,18} the CaMoO_4 ceramic has a negative τ_f value, and the Bi-doping could adjust the τ_f to near-zero and even positive value. The bismuth oxide was reported to have intrinsic low-melting temperature and might help reduce the sintering temperature of scheelite oxides. In addition, the rare-earth oxide, such as Nd_2O_3 , etc, was found to improve the dielectric property in many microwave dielectric ceramics.¹⁹ The microwave dielectric properties are closely related to the microstructures of ceramics. Choi et al ever used the Clausius-Mosotti relation to calculate the polarizability of Mo in AMoO_4 ($A = \text{Mg, Zn, Sr, Ca and Ba}$) compounds.¹³ Kim et al used the packing fraction to correlate the quality factor of scheelite $A^{2+}B^{6+}O_4$ oxides.²⁰ Furthermore, many researchers used the Raman spectroscopy to obtain the information of the vibrations and rotations.^{21,22} Some researchers used the infrared spectroscopy to reveal the complex dielectric response in ceramics.^{23,24} Based on the fitting data from the infrared spectroscopy, the permittivity and intrinsic dielectric losses could be calculated. Hence, in this work, the $(\text{Nd}_{1-x}\text{Bi}_x)^{3+}$ complex ions were used at A-site of scheelite structure to adjust the microwave dielectric

properties and the sintering temperature of CaMoO_4 ceramic. The microcharacteristics and microwave dielectric properties of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($0.2 \leq x \leq 0.95$) ceramics were studied. The relationship between the properties and vibrational modes were investigated in detail.

2 | EXPERIMENTAL SECTION

High-purity oxide powders of Bi_2O_3 (>99%), MoO_3 (>99.95%), Nd_2O_3 (>99%) and the carbonate powder of CaCO_3 (>99%) were mixed proportionally for the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($0.2 \leq x \leq 0.95$) ceramics. First, the raw materials were put into the nylon jars with zirconia balls and prepared by the method of high-energy milling. Second, the milled powders were calcined at 600 °C for 4 hours. Then, the calcined powders were ground for the second time. After the milled powders were dried, the PVA binder can be used to mix the powders and make the powders granulated. Finally, the mixed powders were pressed into pillars under a pressure of 160 MPa using the uniaxial hydraulic press. All the green bodies were put into the muffle and sintered at the temperature from 660 °C to 740 °C, the holding time is 2 hours.

Phase identifications of the samples were obtained by the powder diffraction data using the X-ray diffractometer with $\text{Cu K}\alpha$ source, operated at 40 kV and 30 mA, all the data were gathered in the range of 10-70° with a scan step of 0.02. The topography of the crystal grain of the ceramics was surveyed using the scanning electron microscopy (SEM). The IR spectra measurement of the ceramics used a Bruker Optik IFS 66v FTIR spectrometer on an infrared source base station (U4) at the National Synchrotron Radiation Lab (NSRL), China. The measurement of the Raman vibration modes of the ceramics used a Raman spectrometer, which was stimulated using an Ar^+ laser (532 nm). The quality factor was measured with a microwave network analyzer and the dielectric constant was calculated with the TE_{018} shielded cavity method, meanwhile, the τ_f value was measured in a thermal cycling chamber, the calculated value could be obtained using the following formula:

$$\tau_f = \frac{f_h - f_l}{f_l (h - l)} \text{ppm}/^\circ\text{C} \quad (1)$$

where the h and l were the values of high temperature and low temperature, respectively. The f_h was the TE_{018} resonant frequencies at high temperature, and the f_l was the TE_{018} resonant frequencies at low temperature.

3 | RESULTS AND DISCUSSIONS

In Figure 1A, the room temperature XRD patterns and the crystal structure (Inset) of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$

FIGURE 1 A, The XRD patterns of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics at room temperature and the crystal structure of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($x = 0.2-0.95$) ceramics (Inset). B, Lattice parameters of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics

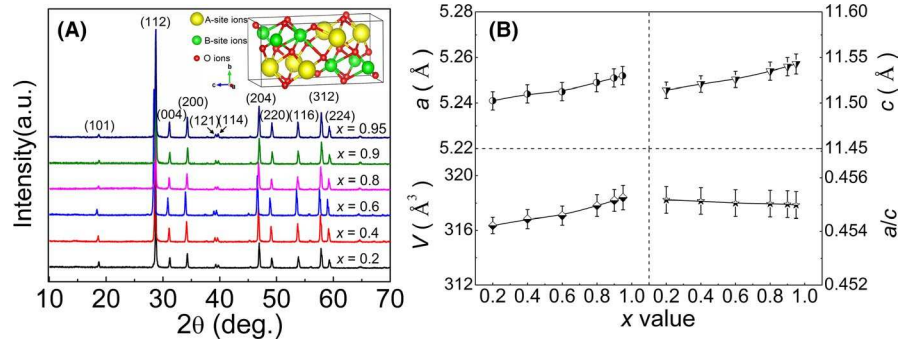
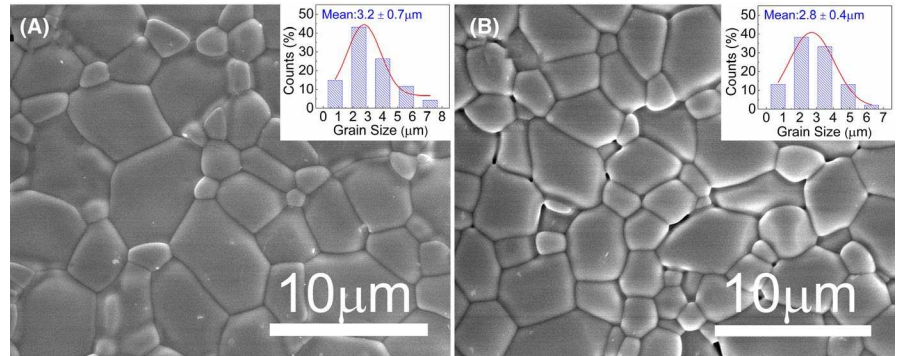


FIGURE 2 A, The SEM images of $[\text{Ca}_{0.55}(\text{Nd}_{0.8}\text{Bi}_{0.2})_{0.3}]\text{MoO}_4$ ceramic sintered at 740°C and the statistic of particle distribution (inset). B, The SEM images of $[\text{Ca}_{0.55}(\text{Nd}_{0.05}\text{Bi}_{0.95})_{0.3}]\text{MoO}_4$ ceramic sintered at 660°C and the statistic of particle distribution (inset)



ceramics are clearly observed. All the diffraction peaks are indexed as a tetragonal scheelite structure without any secondary phase.²⁵ Therefore, the complete solid solution is obtained in the whole compositions. With the increase in x value, the corresponding peaks moved to lower 2θ angles direction, which indicates an increase in the unit cell volume. According to the ionic radius reported by Shannon,²⁶ the ionic radius of Bi^{3+} (1.17\AA) is larger than that of Nd^{3+} (1.109\AA) and introduction of Bi^{3+} expanded the volume of the unit cell. Meanwhile, the intensity of (101) peak gradually decreases, indicating that the increase in content of Bi^{3+} ions enhanced the disordering at A-site.²⁷ The lattice parameters calculated from the measured XRD data are shown in Figure 1B. When the x value increases, the lattice parameters a , c and the unit cell volume V all increase, which are consistent with the peaks shifts in XRD patterns. Meanwhile, a slight decrease in a/c could be observed as shown in Figure 1B.

SEM images of the $[\text{Ca}_{0.55}(\text{Nd}_{0.8}\text{Bi}_{0.2})_{0.3}]\text{MoO}_4$ ceramic sintered at 740°C are shown in Figure 2A. The sample has dense microstructure and no pores could be revealed in this composition. The grain size distribution of the $[\text{Ca}_{0.55}(\text{Nd}_{0.8}\text{Bi}_{0.2})_{0.3}]\text{MoO}_4$ ceramic is presented in inset of Figure 2A, the average grain size is about $3.16\ \mu\text{m}$. As shown in Figure 2B, the homogeneous microstructure of $[\text{Ca}_{0.55}(\text{Nd}_{0.05}\text{Bi}_{0.95})_{0.3}]\text{MoO}_4$ ceramic sintered at 660°C can be observed. As shown in inset of Figure 2B, the mean grain size is about $2.78\ \mu\text{m}$, which is smaller than the grain size of $[\text{Ca}_{0.55}(\text{Nd}_{0.8}\text{Bi}_{0.2})_{0.3}]\text{MoO}_4$ ceramic. This result indicates that the increasing concentration of Bi^{3+} ion reduced both the sintering temperature and grains size.

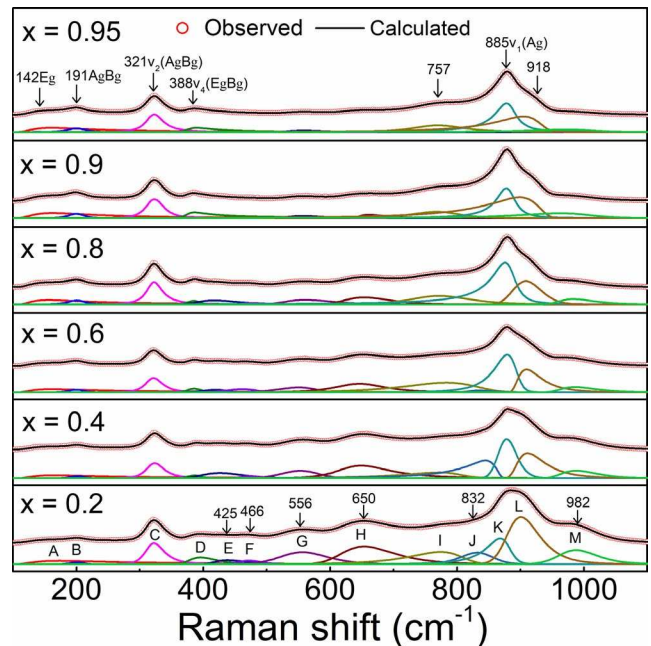


FIGURE 3 The observed and calculated Raman spectroscopy of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($x = 0.2-0.95$) ceramics

Raman spectrum is a very important tool to investigate the influence of the ionic substitution at A-site in inorganic compounds. The $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics belong to the tetragonal scheelite structure with $I4_{1/a}$ space group. According to the group theory, there may be 26 modes in the components, the calculated results show as follows:

$$\Gamma = 3A_g + 5B_g + 5E_g + 5A_u + 5E_u + 3B_u \quad (2)$$

In the scheelite primitive cell, the A_g , B_g , and E_g vibrations are Raman active vibrations, the A_u and E_u belong to the infrared active vibrations and the B_u is the inactive vibrations. Furthermore, as the literature reported,²⁸ the lattice vibrations are divided into two parts in the tetragonal scheelite structured materials. The first one is external mode, which corresponds to the movements of A-site cations and rigid Mo-O tetrahedra, the measured data below 350 cm^{-1} all belong to the external modes. The second one is internal mode, which derives from the vibrations inside the Mo-O tetrahedra, the measured data above 350 cm^{-1} all belong to the internal modes.

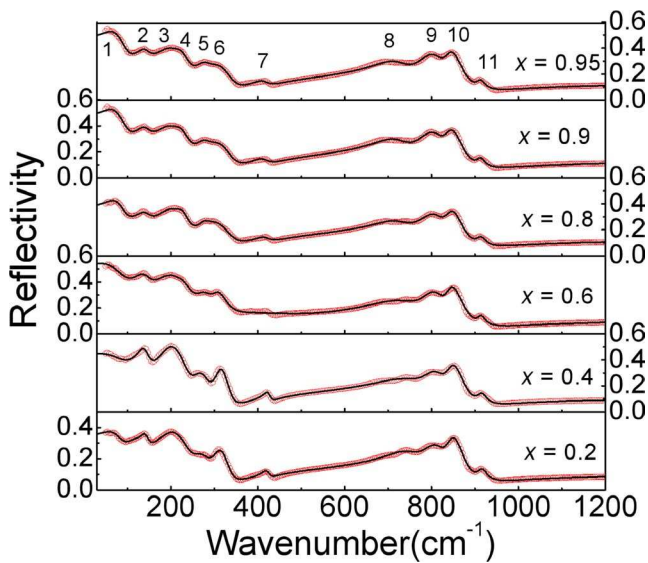


FIGURE 4 The fitted (black line) and measured (red circles) IR spectra of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($x = 0.2-0.95$) ceramics

In this study, Raman spectra of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics are demonstrated in Figure 3 in range 100 cm^{-1} – 1100 cm^{-1} . The Raman spectra were fitted using the Lorenz and Gaussian functions. The measured and fitted values match well with each other. At x value ~ 0.2 , 13 vibrational modes are clearly observed in the ceramic. With the increase in x , the number of the vibrational modes decreases and it should be attributed to the distortions of MoO_4 tetrahedra. As shown in Figure 3, the A peak located at 141 cm^{-1} corresponds to the translational movement of cation at A-site, and the B peak located at 191 cm^{-1} belongs to the rotation mode between the ion bonds. These spectrum data are in good agreement with that of Porto's report.²¹ The D-F peaks located at $388, 425, 466\text{ cm}^{-1}$, respectively, represent the bending movements of Mo-O, and the I-M peaks located at $757, 832, 885, 918, 982\text{ cm}^{-1}$ derive from the stretching movements of Mo-O. When the x value rises to 0.95, the intensities of peaks located at $918, 982\text{ cm}^{-1}$ gradually weaken and the peaks located at $556, 650\text{ cm}^{-1}$ slowly disappear. The peaks located at $321, 885\text{ cm}^{-1}$ become narrow and these results may indicate that the introduction of $(\text{Nd}_{1-x}\text{Bi}_x)^{3+}$ ions made the MoO_4 tetrahedron become distorted, which possibly affect the position of peaks and lead to the decrease in Raman vibrational modes.

IR patterns of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics are shown in Figure 4. It is clearly observed that the measured and fitted IR spectra match well with each other. According to the Equation (2), there should be 10 IR active vibrational modes in the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics. However, due to the $(\text{Nd}_{1-x}\text{Bi}_x)^{3+}$ substitutions, the number of the IR vibrational modes changes and several new vibration modes are observed in this work. As shown in Figure 4, with the increase in x value, the Mode-3 peak splits into two new peaks at 0.6 composition, and the Mode-1 peak appears at 0.8 composition. These results are closely related to the translational vibrations of Bi-O (T_{Bi}). Meanwhile, the intensity of Mode-6 observably decreases, the locations of Mode-7 and Mode-8

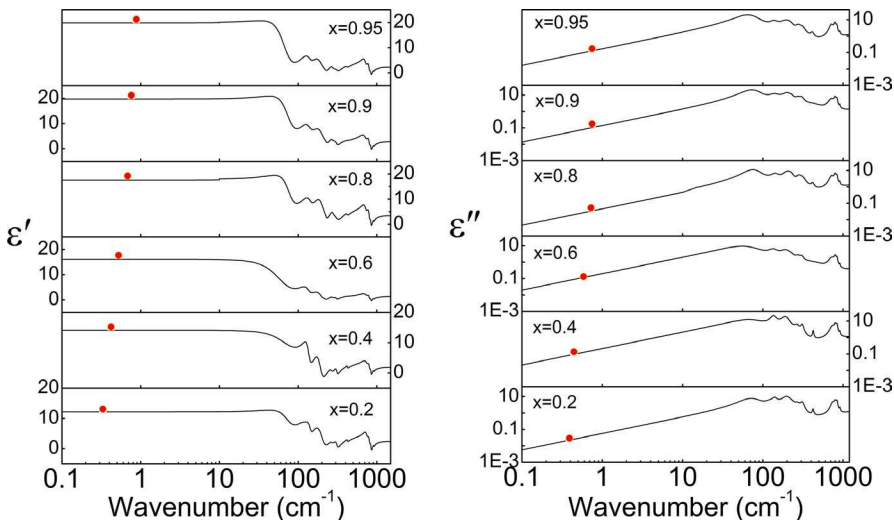


FIGURE 5 A, The real dielectric response, (B) the imaginary dielectric response of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($x = 0.2-0.95$) ceramics, the measured data marked as red circles, the fitted data marked as Solid lines

are shifted by a small amount. These phenomena indicate the increasing disordering in the MoO_4 tetrahedral with the introduction of $(\text{Nd}_{1-x}\text{Bi}_x)^{3+}$. When the x value increases to 0.95, there are two more vibrational modes (1, 4) observed.

The infrared spectra can be analyzed using the Fresnel formula (3) and the Lorentz formula (4) in the typical one-dimensional harmonic oscillator model. Furthermore, these methods are effective to analyze the complex dielectric response of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics.

$$R(\omega) = \frac{1 - \sqrt{\epsilon'(\omega)^2}}{1 + \sqrt{\epsilon'(\omega)^2}} \quad (3)$$

TABLE 1 Values of parameters derived from the fitting of the IR spectra of $[\text{Ca}_{0.55}(\text{Nd}_{0.05}\text{Bi}_{0.95})_{0.3}]\text{MoO}_4$

Mode	ω_{oj}	ω_{pj}	γ_j	$\Delta\epsilon_j$
1	79.94	298.07	55.55	18.2
2	139.59	161.79	39.25	1.7
3	172.8	137.17	32.89	0.708
4	264.95	144.05	41.27	0.681
5	308.36	158.37	65.56	0.302
6	413.13	234.2	71.27	0.306
7	684.13	378.06	91.94	0.355
8	794.55	548.92	60.63	0.477
9	838.12	299.34	33.53	0.128
10	911.01	123.33	21.02	0.018
$\epsilon_\infty = 2.11$			$\epsilon_0 = 19.79$	

where the IR reflectance denoted as $R(\omega)$; the dielectric function of $R(\omega)$ denoted as $\epsilon'(\omega)$; the high-frequency dielectric constant attributed to the electronic polarization denoted as ϵ_∞ ; the plasma and transverse frequency denoted as ω_{pj} and ω_{oj} , respectively, γ_j and n represent the damping factor and the phonon mode number, respectively.

In Figure 5, the fitted results of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics can be observed. According to the experimental measurement (ω data (sign as red circles in picture), all the measured permittivities are slightly larger than that of the calculated ones. These two results show the same trend with each other. When the x value is 0.95, the fitted parameters of $[\text{Ca}_{0.55}(\text{Nd}_{0.05}\text{Bi}_{0.95})_{0.3}]\text{MoO}_4$ derived from the IR spectra are listed in Table 1. It is noticed that the calculated permittivity of $[\text{Ca}_{0.55}(\text{Nd}_{0.05}\text{Bi}_{0.95})_{0.3}]\text{MoO}_4$ is 19.79, which is a little smaller than the measured one (20.3). Meanwhile, all the measured dielectric losses are similar with the calculated ones. These results indicated that the phonons in infrared regions basically dominated the dielectric polarization of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics in microwave regions.

The densities of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics were measured using Archimedes principle and the theoretical densities of these ceramics were calculated with the following formula.²⁹

$$\rho_{th} = \frac{nM}{NV} \text{g/cm}^3 \quad (5)$$

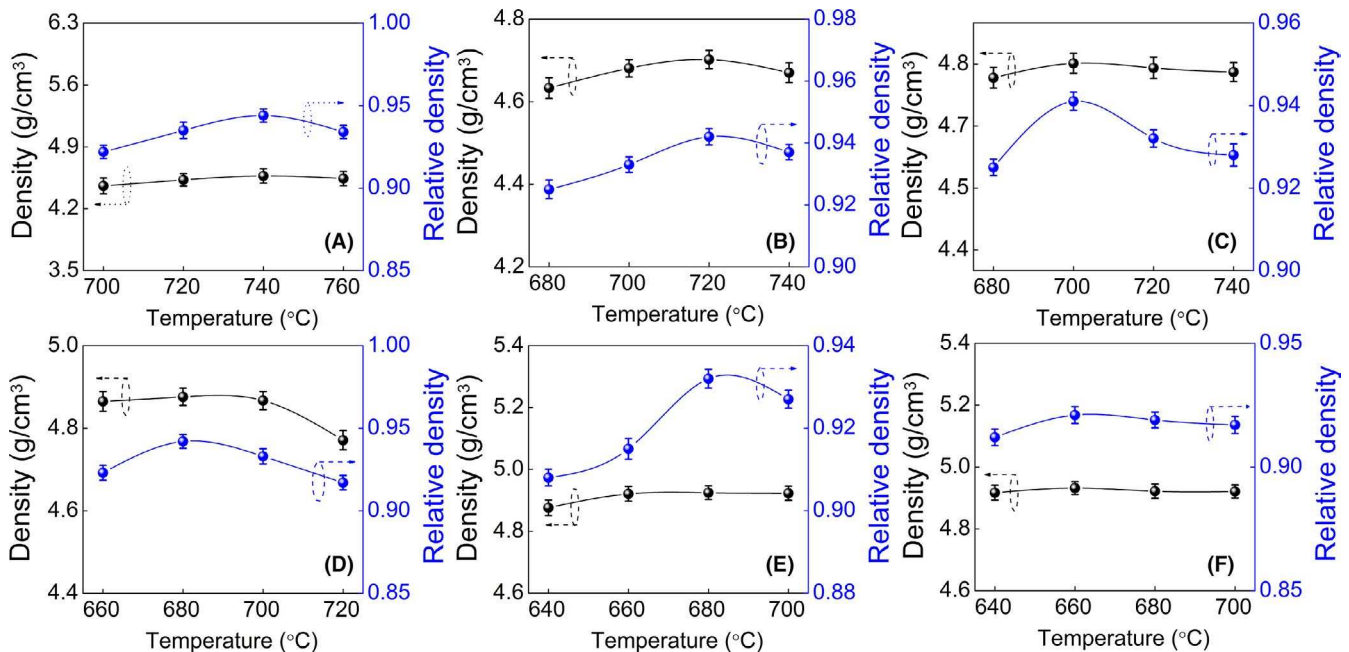


FIGURE 6 The density and relative density of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics sintered at different temperature (A) $x = 0.2$, (B) $x = 0.4$, (C) $x = 0.6$, (D) $x = 0.8$, (E) $x = 0.9$, (F) $x = 0.95$

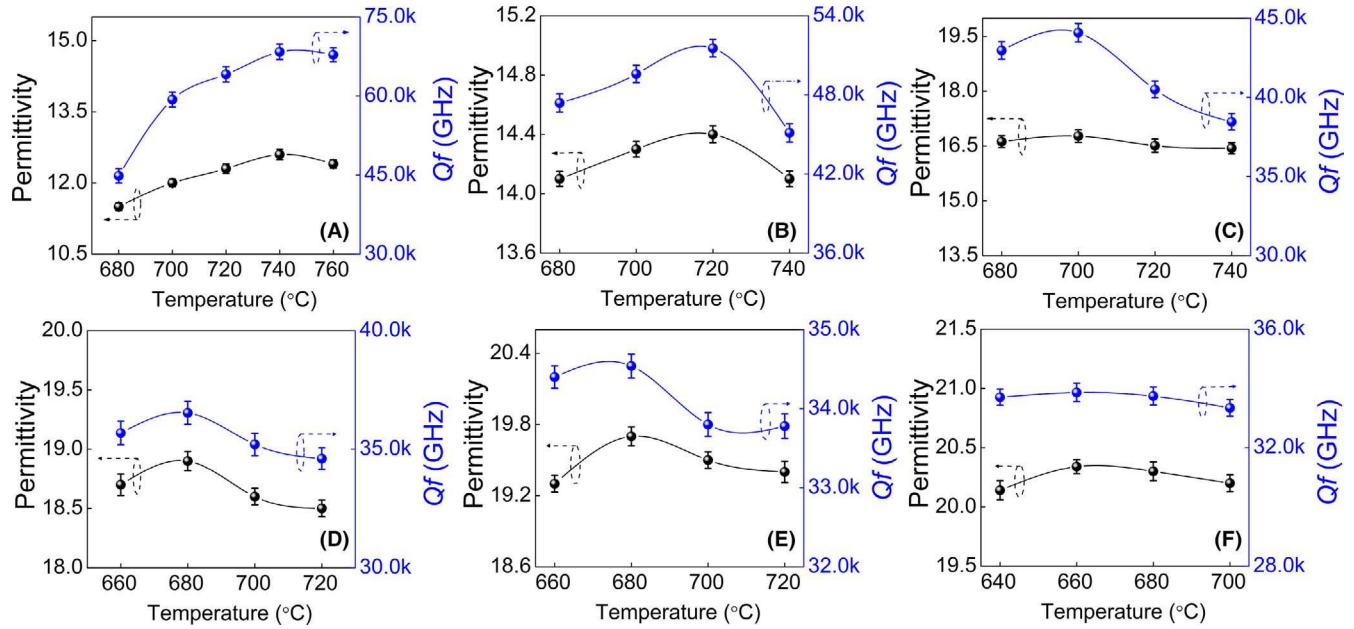


FIGURE 7 The permittivities and Qf values of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics sintered at different temperature (A) $x = 0.2$, (B) $x = 0.4$, (C) $x = 0.6$, (D) $x = 0.8$, (E) $x = 0.9$, (F) $x = 0.95$

where n is the number of per unit cell in the compounds. M and V are molecular weight; the cell volume of the ceramics, respectively, N represents the Avogadro's number ($6.022 \times 10^{23} \text{ mol}^{-1}$). Using the measured densities and the theoretical ones, the relative densities of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics could be calculated with the following equation.

$$\rho_r = \frac{\rho_m}{\rho_{th}} \times 100\% \quad (6)$$

Densities and relative densities of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics sintered at different temperature are shown in Figure 6A-F. It can be observed that all the values of density and relative density have the same variation trend. In Figure 6A, the maximal density of the $[\text{Ca}_{0.55}(\text{Nd}_{0.8}\text{Bi}_{0.2})_{0.3}]\text{MoO}_4$ ceramic is 4.51 g/cm^3 , the sintering temperature is 740°C . As we know, the bismuth oxide has a low-melting point and addition of Bi_2O_3 help reduce the sintering temperature. Therefore, with the x value increasing, the optimal sintering temperature decreases from 740°C to 660°C , and the relative density reduces from 95% to 92%. All the samples are well densified and these results are consistent with the SEM results.

Figure 7A-F shows the permittivities and Qf values of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics as a function of sintering temperature. As presented in Figure 7A, the permittivity of $[\text{Ca}_{0.55}(\text{Nd}_{0.8}\text{Bi}_{0.2})_{0.3}]\text{MoO}_4$ ceramic increase gradually and then reaches a maximum value at 740°C as the sintering temperature increases. Meanwhile, the Qf value has a quite similar trend vs sintering temperature. When the x value rises, the sintering temperature of the ceramic with best microwave

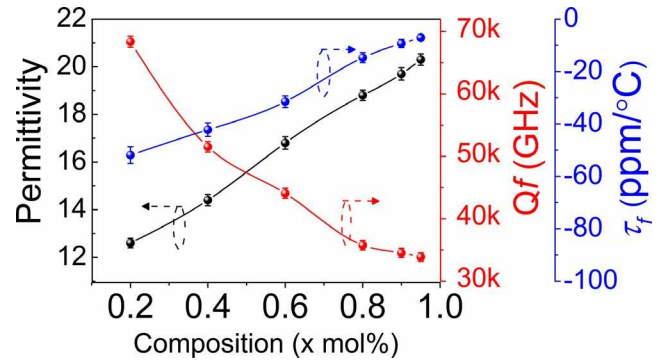


FIGURE 8 Permittivity, Qf values, and τ_f of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($x = 0.2-0.95$) ceramics with different sintering temperature

dielectric properties shifts to the low field, these results are similar to the change in the density and relative density. Then, the optimal sintering temperature of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics could be obtained.

The measured microwave dielectric properties of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics with optimal sintering temperature are shown in Figure 8. It is clearly observed that the ϵ_r value increases from 12.6 to 20.3. According to the Clausius-Mosotti equation, the dielectric constant depends on the polarizability. When the ionic substitution happens, the total ionic polarizability will increase, resulting in an increase in ϵ_r value. The molecular polarizability of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics could be estimated by the Shannon's additive rule as follows.³⁰

$$\alpha_{[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4} = 0.55\alpha_{\text{Ca}^{2+}} + 0.3(1-x)\alpha_{\text{Nd}^{3+}} + 0.3x\alpha_{\text{Bi}^{3+}} + \alpha_{\text{Mo}^{6+}} + 4\alpha_{\text{O}^{2-}} \quad (7)$$

TABLE 2 Microwave dielectric properties of the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics at different sintering temperature as a function of x value (mol%)

Compound	ST (°C)	ϵ_r	Qf (GHz)	τ_f (ppm/°C)
$[\text{Ca}_{0.55}(\text{Nd}_{0.8}\text{Bi}_{0.2})_{0.3}]\text{MoO}_4$	740°C/2 h	12.6	68 380	-52.3
$[\text{Ca}_{0.55}(\text{Nd}_{0.6}\text{Bi}_{0.4})_{0.3}]\text{MoO}_4$	720°C/2 h	14.4	51 530	-45.2
$[\text{Ca}_{0.55}(\text{Nd}_{0.4}\text{Bi}_{0.6})_{0.3}]\text{MoO}_4$	700°C/2 h	16.8	44 080	-37.5
$[\text{Ca}_{0.55}(\text{Nd}_{0.2}\text{Bi}_{0.8})_{0.3}]\text{MoO}_4$	680°C/2 h	18.8	35 750	-19.7
$[\text{Ca}_{0.55}(\text{Nd}_{0.1}\text{Bi}_{0.9})_{0.3}]\text{MoO}_4$	680°C/2 h	19.7	34 540	-11.3
$[\text{Ca}_{0.55}(\text{Nd}_{0.05}\text{Bi}_{0.95})_{0.3}]\text{MoO}_4$	660°C/2 h	20.3	33 860	-7.1

the polarizability of Bi^{3+} and Nd^{3+} ions are 6.12 \AA^3 and 5.01 \AA^3 , respectively. The molecular polarizability increases from 14.63 \AA^3 to 14.88 \AA^3 as the x value increases, indicating that the increasing ϵ_r value mainly derives from the enhanced cationic polarizability. In this work, the change in relative permittivity is consistent with the Shannon's theory. Generally, the Qf value is inversely proportional to the intrinsic dielectric losses. When the x value increases, the expanding unit cell volume and the enhancing disorder lead to the increase in dielectric loss, then the Qf value has a decreasing trend range from 68 380 to 33 860 GHz. The near-zero τ_f value is a significant factor for the microwave ceramic, when x value increases, the τ_f value shifts from $-52.3 \text{ ppm/}^\circ\text{C}$ to $-7.1 \text{ ppm/}^\circ\text{C}$. The optimal microwave dielectric properties of $[\text{Ca}_{0.55}(\text{Nd}_{0.05}\text{Bi}_{0.95})_{0.3}]\text{MoO}_4$ ceramics are obtained at 660°C with a relative permittivity of 20.3, a Qf value of 33 860 GHz (at 7.86 GHz), and a τ_f value of $-7.1 \text{ ppm/}^\circ\text{C}$, this ceramic can be potentially applied in the ULTCC technology. Furthermore, the formulas, the calcinate temperatures and microwave dielectric properties of $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics are listed in Table 2. As shown in Table 2, the ceramics (eg, $x = 0.8, 0.9$) sintered at low temperature with excellent microwave dielectric properties can be potentially applied in LTCC technology.

4 | CONCLUSION

A series of scheelite-type $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ($0.2 \leq x \leq 0.95$) ceramics are successfully prepared by solid-state reaction method. According to the XRD data, the solid solution was formed and the pure tetragonal phases are clearly observed in the $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramics. When the x value increases, the sintering temperature of the sample gradually decreases from 740°C to 660°C , and the average grain size of the sample also decreases from $3.16 \mu\text{m}$ to $2.78 \mu\text{m}$. These results indicate that the Bi^{3+} ion derived from Bi_2O_3 could effectively lower the sintering temperature and refine grains. Meanwhile, the permittivity is found to increase from 12.6 to 20.3 with increasing x , which is due to the enhancement of polarizability derived from Bi^{3+} . The Qf value decreased and gradually remained stable, which is closely related to the rare earth element Nd^{3+} . The Raman spectroscopy

showed that the internal modes gradually disappear with increasing x value, this phenomenon is due to the distorting MoO_4 tetrahedra, which is also related to the introduction of the $(\text{Nd}_{1-x}\text{Bi}_x)^{3+}$ ions. The far infrared frequency is close to the microwave frequency, the measured dielectric response from IR spectra can extrapolate to the microwave region. With the fitting data of the IR spectra, the calculated permittivity has the same trend with the measured one, this result indicates that the A-site cations mainly dominate the variation of dielectric response at microwave frequency. The $[\text{Ca}_{0.55}(\text{Nd}_{0.05}\text{Bi}_{0.95})_{0.3}]\text{MoO}_4$ ceramic sintered at low temperature (660°C) possesses optimal microwave dielectric properties with a relative permittivity of 20.3, a Qf value of 33 860 GHz and a approach zero τ_f value ($-7.1 \text{ ppm/}^\circ\text{C}$). The $[\text{Ca}_{0.55}(\text{Nd}_{1-x}\text{Bi}_x)_{0.3}]\text{MoO}_4$ ceramic system with excellent microwave dielectric properties can be potentially used in LTCC or ULTCC technologies.

ACKNOWLEDGMENTS

This work was supported by the National Key Research and Development Program of China (2017YFB0406301), the State Key Laboratory of Electrical Insulation and Power Equipment (Grant EIP19210), the 111 Project of China (B14040) and the Fundamental Research Funds for the Central University. The authors thank the administrators in IR beamline workstation (BL01B) of National Synchrotron Radiation Laboratory (NSRL) for their help in the IR measurement and fitting. The SEM work was done at International Center for Dielectric Research (ICDR), Xi'an Jiaotong University, Xi'an, China and the authors thank Ms Yan-Zhu Dai for her help in using SEM.

ORCID

Di Zhou  <https://orcid.org/0000-0001-7411-4658>

Da-Wei Wang  <https://orcid.org/0000-0001-6957-2494>

REFERENCE

- Hill MD, Cruickshank DB. Ceramic materials for 5G wireless communication systems 5G technologies will soon reach the market. Ceramic materials will play an important role in realizing the technology. *J Am Ceram Soc B*. 2019;98:20–5.
- Zhou D, Randall CA, Pang LX, Wang H, Guo J, Zhang GQ, et al. Microwave dielectric properties of Li_2WO_4 ceramic with ultra-low sintering temperature. *J Am Ceram Soc*. 2011;94: 348–50.

3. Sebastian MT, Jantunen H. High temperature cofired ceramic (HTCC), low temperature cofired ceramic (LTCC), and ultralow temperature cofired ceramic (ULTCC) materials. *J Micro Mater and Appl 2V Set*. 2017;355–425.
4. Narang SB, Bahel S. Low loss dielectric ceramics for microwave applications: a review. *J Ceram Process Res*. 2010;11:316–21.
5. Guo HH, Zhou D, Pang LX, Qi ZM. Microwave dielectric properties of low firing temperature stable scheelite structured (Ca, Bi) (Mo, V)O₄ solid solution ceramics for LTCC applications. *J Eur Ceram Soc*. 2019;39:2365–73.
6. Guo HH, Zhou D, Liu WF, Pang LX, Wang DW, Su JZ, et al. Microwave dielectric properties of temperature-stable zircon-type (Bi, Ce)VO₄ solid solution ceramics. *J Am Ceram Soc*. 2020;103:423–31.
7. Pang LX, Zhou D. Modification of NdNbO₄ microwave dielectric ceramic by Bi substitutions. *J Am Ceram Soc*. 2019;102:2278–82.
8. Chen GH, Di JC, Xu HR, Jiang MH, Yuan CL. Microwave dielectric properties of Ca₄La₂Ti_{5-x}(Mg_{1/3}Nb_{2/3})_xO₁₇ ceramics. *J Am Ceram Soc*. 2012;95:1394–7.
9. Lei W, Zou ZY, Chen ZH, Ullah B, Zeb A, Lan XK, et al. Controllable τ_f value of barium silicate microwave dielectric ceramics with different Ba/Si ratios. *J Am Ceram Soc*. 2018;101:25–30.
10. Fang L, Li CC, Peng XY, Hu CZ, Wu BL, Zhou HF. Ba₄LiNb_{3-x}Ta_xO₁₂ (x = 0–3): a series of high-Q microwave dielectrics from the twinned 8H hexagonal perovskites. *J Am Ceram Soc*. 2010;93:1229–31.
11. Daturi M, Busca G, Borel MM, Leclaire A, Piaggio P. Vibrational and XRD study of the system CdWO₄-CdMoO₄. *J Phys Chem B*. 1997;101:4358–69.
12. Kim ES, Jeon CJ, Clem PG. Effects of crystal structure on the microwave dielectric properties of ABO₄ (A = Ni, Mg, Zn and B = Mo, W) ceramics. *J Am Ceram Soc*. 2012;95:2934–8.
13. Choi GK, Kim JR, Yoon SH, Hong KS. Microwave dielectric properties of scheelite (A=Ca, Sr, Ba) and wolframite (A=Mg, Zn, Mn) AMoO₄ compounds. *J Eur Ceram Soc*. 2007;27:3063–7.
14. Rama Rao SD, Roopas Kiran S, Murthy VRK. Correlation between structural characteristics and microwave dielectric properties of scheelite Ca_{1-x}Cd_xMoO₄ solid solution. *J Am Ceram Soc*. 2012;95:3532–7.
15. Xi HH, Zhou D, Xie HD, He B, Wang QP. Raman spectra, infrared spectra, and microwave dielectric properties of low-temperature firing [(Li_{0.5}Ln_{0.5})_{1-x}Ca_x]MoO₄ (Ln = Sm and Nd) solid solution ceramics with scheelite structure. *J Am Ceram Soc*. 2015;98:587–93.
16. Zhou D, Randall CA, Pang LX, Wang H, Guo J, Zhang GQ, et al. Microwave dielectric properties of (ABi)_{1/2}MoO₄ (A = Li, Na, K, Rb, Ag) type ceramics with ultra-low firing temperatures. *J Mater Chem and Phys*. 2011;129:688–92.
17. Guo J, Randall CA, Zhang GQ, Zhou D, Chen YY, Wang H. Synthesis, structure, and characterization of new low-firing microwave dielectric ceramics: (Ca_{1-3x}Bi_{2x}Φ_x)MoO₄. *J Mater Chem C*. 2014;2:7364–72.
18. Ha JY, Choi JW, Yoon SJ, Choi DJ, Yoon KH, Kim HJ. Microwave dielectric properties of Bi₂O₃-doped Ca [(Li_{1/3}Nb_{2/3})_{1-x}Ti_x]O_{3-δ} ceramics. *J Eur Ceram Soc*. 2003;23:2413–6.
19. Ding JY, Xiao Y, Han PD, Zhang QT. Effects of rare earth oxides on dielectric properties of Y₂Ti₂O₇ series ceramics. *J Rare Earth*. 2010;28:765–8.
20. Kim ES, Kim SH. Effects of structural characteristics on microwave dielectric properties of (1-x)CaWO₄-xLaNbO₄ ceramics. *J Elect Ceram*. 2006;17:471–7.
21. Porto SPS, Scott JF. Raman spectra of CaWO₄, SrWO₄, CaMoO₄, and SrMoO₄. *J Phys Rev*. 1967;157:716.
22. Zheng H, de Györgyfalva GDCC, Quimby R, Bagshaw H, Ubcir R, Reaney IM, et al. Raman spectroscopy of B-site order-disorder in CaTiO₃-based microwave ceramics. *J Eur Ceram Soc*. 2003;23:2653–9.
23. Barker Jr, AS. Infrared lattice vibrations in calcium tungstate and calcium molybdate. *J Phys Rev*. 1964;135:A742.
24. Fukuda K, Kitoh R, Awai I. Far-infrared reflection spectra of dielectric ceramics for microwave applications. *J Am Ceram Soc*. 1994;77:149–54.
25. Kato H, Matsudo N, Kudo A. Photophysical and photocatalytic properties of molybdates and tungstates with a scheelite structure. *Chem Lett*. 2004;33:1216–7.
26. Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. *Acta Cryst*. 1976;32:751–67.
27. Hao SZ, Zhou D, Pang LX. The spectra analysis and microwave dielectric properties of [Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO₄ ceramics. *J Am Ceram Soc*. 2019;102:3103–9.
28. Hanuza J, Maczka M, Macalik L, Van der Maas J. Polarized raman spectra of NaBi(MoO₄)₂ crystal and order-disorder effect in solid scheelites. *J Moler Struc*. 1994;325:119–24.
29. Shannon RD. Dielectric polarizabilities of ions in oxides and fluorides. *J Appl Phys*. 1993;73:348–66.
30. Liao QW, Li LX, Ren X, Ding X. New low-loss microwave dielectric material ZnTiNbTaO₈. *J Am Ceram Soc*. 2011;94:3237–40.

How to cite this article: Hao S-Z, Zhou D, Hussain F, et al. Novel scheelite-type [Ca_{0.55}(Nd_{1-x}Bi_x)_{0.3}]MoO₄ (0.2 ≤ x ≤ 0.95) microwave dielectric ceramics with low sintering temperature. *J Am Ceram Soc*. 2020;00:1–8. <https://doi.org/10.1111/jace.17378>