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The Spectra analysis and Microwave Dielectric Properties of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ Ceramics

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Abstract

A series of low-temperature firing ceramics with scheelite structure, $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ (x = 0.2 ~ 0.95), were prepared via solid-state reaction. The sintering temperature ranges from 660 °C to 760°C. A standard tetragonal scheelite phase was formed without secondary phase. When the x value was 0.95, the temperature coefficient of resonant frequency (τ_f) moved to a near zero

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value (－2.1 ppm/°C) with a dielectric constant 13.7 and the quality factor (Qf) of 33,200 GHz. The Raman spectra shows that the more vibration modes appeared with x value, which is due to the increasing of Bi concentration and results in increase in permittivities and decrease in Qf values. The classical harmonic oscillator model is used in the infrared spectra and extrapolate to the microwave range. The $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics show high-performance microwave dielectric properties at low-sintering temperature.

I. Introduction

Recently, due to the progress of the material manufacturing process, the investigation of microwave materials has been in various fields. For example, the low-temperature co-fired ceramic (LTCC) technology, being used in producing minimizing and integrating electronic devices, has some requirements for the microwave materials: low sintering temperature could make the microwave ceramics use the same temperature to fire with the electrode materials, low dielectric loss could keep the materials' service life, a near zero temperature coefficient of resonant frequency could stabilize the microwave materials at different working temperature.[1] Meanwhile, the ultra-low temperature co-fired ceramic (ULTCC) technology has further requirement of sintering temperature, because much lower temperature could save energy, reduce progressing time, decrease the cost of production.[2] Hence, a category of microwave ceramic material, densifying at temperature approaching 700°C, all can be used in these two technologies.

In the previous report, the materials based on tellurates, vanadates and molybdates have inherently low sintering temperature and show good microwave dielectric properties.[3-5] However, tellurates and vanadates have inevitable defects, which are from the toxic component materials and limit the application. Molybdates have more potential in production and application of microwave materials. The scheelite type $AMoO_4$ oxides have been extensively investigated with their flexible structure and different A-site cations, as reported by Zhou et. al.,[6,7] Li_2MoO_4 and $(Li_{0.5}Ln_{0.5})MoO_4$ (Ln = Nd, Er, Gd, Y, Yb, Sm and Ce) microwave ceramics have low sintering temperatures (S.T = 540°C ~ 800°C), great microwave dielectric properties (ε_r = 5.5 ~ 20.6, Qf = 3940 ~ 46,500 GHz, τ_f = －160 ~ +235 ppm/°C). As reported by Choi et.

al.,[8] $CaMoO_4$ possesses good microwave dielectric properties (ε_r = 10.8, Qf = 89,700 GHz, τ_f = −57 ppm/°C) and sintering temperature is about 1100°C. Multiple valence states of A-site cations give the $AMoO_4$ oxides researched as microwave materials more opportunities to improve the dielectric properties.

Microwave ceramics have complex microstructures, for researching the relationship between the dielectric properties and the crystal structures, there are a lot of tools to be used in investigation. Raman spectroscopy, which could get the information of molecular vibration and rotation, is a useful tool to study the short-range character of the ceramic's microstructure.[9] Meanwhile, the infrared spectroscopy, using harmonic oscillator model, could reveal the complex dielectric response, especially, the intrinsic dielectric losses determined by polar optical phonon could be obtained.[10] Scheelite type ABO_4 molybdates show great microwave dielectric properties. It is a significant way to use the spectroscopy to understand the mechanism of the dielectric characteristics and the crystal structure in these type of materials.

In this work, a series of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ (x = 0.2, 0.4, 0.6, 0.8, 0.9, and 0.95) ceramics were prepared by the solid-state reaction method. The results of microstructure and microwave dielectric properties are discussed as a function of the composition.

II. Experimental Procedure

The starting materials of Bi_2O_3 (> 99%, Guo-Yao Co. Ltd., Shanghai, China), $CaCO_3$ (> 99%, Guo-Yao Co.Ltd., Shanghai, China), MoO_3 (> 99.95%, Zaibang Co. Ltd., Shanghai, China), Sm_2O_3 (> 99%, Guo-Yao Co. Ltd., Shanghai, China)were proportional mixed for the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ (x = 0.2, 0.4, 0.6, 0.8, 0.9, and 0.95) ceramics. The preparative powders were milled for 4 h in a planetary mill (Nanjing Machine Factory, Nanjing, China) and then calcined at 600 °C for 4 h. To increase the powders' activity, there-milled method was used for 5 h. Then dried powders were mixed with PVA binder and granulated, and then these powders were pressed into cylinders (10 mm in diameter and 3 ~ 4 mm in height) in a steel die under a uniaxial pressure of 150 MPa. Samples were sintered in the temperature from 660 °C to 760 °C for 2 h.

The X-ray diffraction (XRD) with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan) was used to research the crystal structure of the samples.The surface microstructure of the ceramic was observed with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan). The Raman spectra at room temperature were obtained on polished samples with a Raman spectrometer (in Via, Renishaw, Gloucestershire, UK) excited by an Ar^+ laser (514.5 nm). The IR reflectivity spectra were measured using a Bruker Optik IFS 66v FTIR spectrometer (IFS 66v/S Vacuum; Bruker OptikGmbh, Germany) on an infrared beamline station (U4) at the National Synchrotron Radiation Lab. (NSRL), China. Microwave dielectric behaviors were measured with the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA) in the temperature range of 25 °C – 85°C. The temperature coefficient of resonant frequency (τ_f value) was calculated with the following formula:

$$\boldsymbol{\tau_f = \frac{f_{85}-f_{25}}{f_{25}(85-25)} \times 10^6} \quad (1)$$

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85 and 25 °C, respectively.

III. Results and Discussions

The XRD patterns of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics ($0.2 \le x \le 0.95$) sintered at different temperature are shown in Figure 1. The powder diffraction patterns of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics are similar to the PDF card (No. 04-008-6634). All the peaks can be indexed as a tetragonal scheelite phase with a space group $I4_1/a$.[11] As the x value increases, no secondary phase appears and all the peaks move to the low 2θ angles direction. This phenomenon indicates that pure phase was formed in the ceramic and the unit cell volumeof the ceramic may expand with the x value increase. According to the Shannon ionic radius,[12] the ionic radius of Bi^{3+} is 1.17Å, the ionic radius of Sm^{3+} is 1.079Å. When these ions have the same coordination number, the ionic radius of Bi^{3+} is larger than that of Sm^{3+}, considering the ion of larger ionic radius replaces the small one, the volume of the unit cell may have a trend of expanding. It is observed that the intensity of (101) peak decreases with the increasing x value, this result is similar to the report about the scheelite materials doped bismuth compositions and the decreasing intensity of (101) peak may be associated with the disordering of the A-site ion.[13] The SEM micrograph of the $[Ca_{0.55}(Sm_{0.05}Bi_{0.95})_{0.3}]MoO_4$ ceramic is observed from the inset of Fig. 1 and the surface microstructure shows uniformity and densification.

The lattice parameters of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics are obtainedfrom the X-ray diffraction dates. As shown in the Figure 2. The lattice parameters (*a, c*) increase slightly and the unit cell volume also has a trend of rising with the x value increase. When the Bi^{3+} ion replaces the Sm^{3+} ion, the larger ionic radius may change the structure of unit cell, and expand the unit cell volume, the lattice parameters are consistent with the results. In addition, the value of a/c shows a decrease with the x value increase.

Raman spectroscopy is a vibrational spectra technology that is used to determine the unique structural information of inorganic compounds. The $CaMoO_4$ with the scheelite crystal structure belongs to the space group $I4_1/a$ and have two formula units in the primitive cell.[9] According to the group theory, the calculated results show that there are 26 vibrations in $CaMoO_4$ as follows:

$$\Gamma = 3A_g + 5B_g + 5E_g + 5A_u + 5E_u + 3B_u \tag{2}$$

In the scheelite primitive cell, there are 13 Raman active vibrations ($3A_g$, $5B_g$ and $5E_g$), 8 infrared active vibrations ($4A_u$ and $4E_u$) and 3 inactive vibrations ($3B_u$). From the literature's report,[14] the vibrations in the Raman spectra of $AMoO_4$ structure can be divided into two groups, internal and external. The vibrations inside $[MoO_4]^{2-}$ molecular group with an immovable mass center are internal modes, and the vibrations correspond to the motion of A^{2+} cation and the rigid molecular units are external modes.

The room-temperature Raman spectra of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics in the frequency range of 100 ~ 1100 cm^{-1} is shown in Figure 3. The modes above 300 cm^{-1} are internal modes, and the odd ones belong to the external modes. As the internal modes, the peaks located at 770, 883 cm^{-1} are associate with the stretching motions, and the peaks located at 321, 385 cm^{-1} represent the bending motions. Meanwhile, the peak located at 145 cm^{-1} is very weak, and it is the translational mode among the external mode, the 198 cm^{-1} peak is about rotation between the ion bonds. The results are good agreement with the reported in the literature.[15] As the x value rises, a new Raman peak located at 918 cm^{-1} can be observed, the peak located at 883 cm^{-1} become narrow and the 321cm^{-1} peak become weak, these phenomena may indicate that MoO_4 tetrahedra become more disorder and more Mo-O bond lengths occur. Consequently, the Raman spectra have more active modes in the internal region with the x value increasing.

The infrared reflectivity spectra of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics ($0.2 \le x \le 0.95$) is shown in Figure 4. As a function of x value, the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics have the tetragonal scheelite structure. Compared with the same structure of $CaMoO_4$ceramic, the number of the IR active vibration modes of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics increase. When two cations appear in the same position, it may cause the splitting of the phonon modes (two-mode behavior). It is supposed that the new modes of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics are related to the two-mode behavior. Seven modes (Mode-5 to Mode-11) at high frequencies correspond to internal modes, and four modes (Mode-1 to Mode-4) at low frequencies correspond to external modes. With the increase of Bi concentration, the peaks of Mode-1 appear and the intensity increases, it is related with the translational mode of Bi-O (T_{Bi}). The intensity of the peaks of internal modes all become weaker, it is inferred that the $[MoO_4]$ tetrahedral becomes more disordered and affects the position and intensity of peaks of internal modes. With the x value increase from 0.2 to 0.95, the peak of Mode-3 changes to the new ones (new Mode-3 and Mode-4), compared with the change of Mode-1, the other external modes change a little, it is inferred that the Mode-1 gradually dominates the dielectric contributions.

The classical harmonic oscillator model based on the Fresnel equation [Eq. (3)] and the Lorentz formula [Eq. (4)] can be used in analyzing the infrared spectra, meanwhile, the complex dielectric response of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics can be obtained from this method.

$$R(\omega) = \frac{\left|1-\sqrt{\varepsilon^{*}(\omega)}\right|^{2}}{\left|1+\sqrt{\varepsilon^{*}(\omega)}\right|^{2}} \qquad (3)$$

$$\varepsilon^{*}(\omega) = \varepsilon_{\infty} + \sum_{j=1}^{n} \frac{\omega_{pj}^{2}}{\omega_{oj}^{2} - \omega^{2} - i\gamma_{j}\omega} \qquad (4)$$

where $\varepsilon^*(\omega)$ is a dielectric function for the infrared reflectance $R(\omega)$; ε_∞ is the permittivity at high-frequency caused by the electronic polarization; ω_{pj}, ω_{oj}, and γ_j are the plasma frequency, the transverse frequency, and damping factor of the *j*-th Lorentz oscillator, respectively; n is the number of transverse phonon modes.

The calculated permittivity $\varepsilon'(\omega)$ and dielectric loss $\varepsilon''(\omega)$ obtained from the fits of infrared reflectivity are observed in Figure 5. Compared with the experimental microwave date, the calculated permittivity is a little smaller than the measured one at microwave frequency, the calculated dielectric loss is similar to that measured at microwave frequency. Therefore, it can be concluded that the dielectric polarization of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ceramics in microwave regions is dominated by the phonons in infrared regions.

The relative densities and the microwave dielectric properties of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ceramics ($0.2 \leq x \leq 0.95$) as a function of x value are shown in Figure 6. As the x value increases from 0.2 to 0.95, the relative densities have a trend of decreasing and the values are all above 90%, which indicates that the ceramics were well densified. The relative permittivity increases from 13.7 to 22.3. According to the Shannon theory,[16] when the ion with larger ionic polarizability replaces the small one, the relative permittivity has a trend of increasing, the polarizability of Bi^{3+} ion (6.12 $Å^3$) is larger than the Sm^{3+} ion (4.74 $Å^3$), it means that the ionic polarizability of cation become larger and the value of relative permittivity increases. In this study, the results of the relative permittivity accords with the theory. Meanwhile,the intrinsic dielectric losses impact the Qf value of microwave dielectric ceramic, the Bi^{3+} ion replaces the Sm^{3+} ion, the unit cell volume expands and the structure of crystal become abnormal, the dielectric losses increases and the Qf value decreases. In this study, the Qf value decreases from 59,300 to 33,210 GHz with the increasing x value. Meanwhile, the approaching zero temperature coefficient of resonant frequency is very important for the microwave materials to work at different working temperature, as the function of x value rising, the value of the temperature coefficient of resonant frequency shifts from －51.9 ppm/°C to －2.1 ppm/°C and reach the approaching zero value. The temperature independent microwave dielectric properties are obtained in the $[Ca_{0.55}(Sm_{0.05}Bi_{0.95})_{0.3}]MoO_4$ ceramic sintered at 660 °C with a relative permittivity of 22.3, a Qf value of 33,210 GHz (at 7.74 GHz), and a τ_f value of －2.1 ppm/°C. This ceramic have potential to be used in ultra-low temperature co-fired ceramic (ULTCC) technology. Meanwhile, the other series of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics, which have near-zero temperature coefficient of resonant frequency, have the potential to be used in the low-temperature co-fired ceramic (LTCC) technology. The compositions, the sintering temperature, microwave dielectric properties (relative permittivity, Qf value, τ_f value) of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ceramics ($0.2 \leq x \leq 0.95$) are all summarized in Table 1.

IV. Conclusion

A series of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ solid solution ceramics are well formed.The microstructures and microwave dielectric properties of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics are investigated. The vibrational properties of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics are investigated by Raman and infrared spectra as a function of x value. From the X-ray diffraction, the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics show the pure tetragonal scheelite phase. As the function of x value rising, the relative permittivity increases and the quality factor decreases, and it means that the increasing quantity of the Bi^{3+} ion make the ionic polarizability magnify and make the structure of crystal abnormal. From the Raman and infrared reflectivity spectra, more internal modes are observed with the increasing x value, which means that the MoO_4 tetrahedra become more distorted, and the disorder is one reason to decrease the Qf values of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics. A near-zero temperature coefficient value (−2.1 ppm/°C) was obtained with x=0.95 and the sintering temperature below 700 °C. This system of $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics can be used as low-sintering temperature ceramics.

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References

1. Sebastian MT,Ubic R, Jantunen H. Low loss dielectric ceramic materials and their applications. Inter Mater Rev. 2015;60:392–411.

2. Yu H, Liu J, Zhang W, Zhang S. Ultra-low sintering temperature ceramics for LTCC applications: a review. J Mater Sci: Materials in Electronics, in press. 2016.

3. Kwon DK, Lanagan MT, Shrout TR. Microwave dielectric properties of BaO-TeO_2 binary compounds. Mater letter. 2007;61:1827–31.

4. Kalathil SE, Neelakantan A, Ratheesh R. Microwave dielectric properties of ultra-low temperature cofireable $Ba_3V_4O_{13}$ ceramics. J Am Ceram Soc.2014;97:1530–3.

5. Zhou D, Wang H, Pang LX, Randall CA, Yao X. Bi_2O_3–MoO_3 binary system: an alternative ultra-low sintering temperature microwave dielectric. J Am Ceram Soc.2009;92:2242–46.

6. Pang LX, Zhou D, Guo J,Yue ZX,Yao X.Microwave Dielectric Properties of $(Li_{0.5}Ln_{0.5})MoO_4$ (Ln=Nd,Er, Gd, Y, Yb, Sm, Ce) Ceramics. J Am Ceram Soc. 2015;98:130–5.

7. Zhou D, Randall CA, Wang H, Pang LX, Yao X.Microwave dielectric ceramics in Li_2O–Bi_2O_3–MoO_3 system with ultra-low sintering temperatures. J Am Ceram Soc. 2010;93:1096–1100.

8. Choi GK, Kim JR,Yoon SH,Hong KS. Microwave Dielectric Properties of Scheelite (A = Ca, Sr, Ba)and Wolframite (A = Mg, Zn,Mn) $AMoO_4$ Compounds. J Eur Ceram Soc. 2007;27(8-9)3063–67.

9. Baddour-Hadjean R, Pereira-Ramos JP. Raman Microspectrometry Applied to the Study of Electrode Materials for Lithium Batteries. Chem Rev. 2010;110:1278–1319.

10. Chen MH, Tanner DB, Nino JC. Infrared study of the phonon modes in bismuth pyrochlores. Phys Rev B. 2005;72:054303.

11. Sleight AW, Aykan K, Rogers DB. New nonstoichiometric molybdate, tungstate, and vanadate catalysts with the scheelite-type structure.J Solid State Chem. 1975;13:231–6.

12. Shannon RD. Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides. Acta Cryst. 1976;32:751–67.

13. Zhou D,Wang H,Wang QP,Wu XG,Guo J,Zhang GQ,Shui L,Yao X,et.al. Microwave dielectric properties and ramanspectrascopy of scheelite solid slution $[(Li_{0.5}Bi_{0.5})_{1-x}Ca_x]MoO_4$ ceramics withulter-low

sintering temperatures.Funct Mater Lett. 2010;3:253–7.

14. Nicol M, Durana JF. Vibrational Raman spectra of $CaMoO_4$ and $CaWO_4$ at high pressures. J Chem Phys. 1971;54:1436–40.

15. Porto SPS, Scott JF. Raman Spectra of $CaWO_4$, $SrWO_4$, $CaMoO_4$ and $SrMoO_4$. Phys Rev.1967;157:716–9.

16. Shannon RD. Dielectric Polarizabilities of Ions in Oxides and Fluorides. J Appl Phys. 1993;73:348-66.

Table 1

Microwave dielectric properties of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics at different sintering temperature as a function of x value (mol%).

Compound	S.T(°C)	ε_r	Qf(GHz)	τ_f(ppm/°C)
$[Ca_{0.55}(Sm_{0.8}Bi_{0.2})_{0.3}]$ MoO_4	760°C/2h	13.7	59,300	− 51.9
$[Ca_{0.55}(Sm_{0.6}Bi_{0.4})_{0.3}]$ MoO_4	740°C/2h	15.1	51,305	− 42.2
$[Ca_{0.55}(Sm_{0.4}Bi_{0.6})_{0.3}]$ MoO_4	720°C/2h	16.6	44,080	− 31.5
$[Ca_{0.55}(Sm_{0.2}Bi_{0.8})_{0.3}]$ MoO_4	700°C/2h	18.8	34,805	− 9.7
$[Ca_{0.55}(Sm_{0.1}Bi_{0.9})_{0.3}]$ MoO_4	680°C/2h	20.6	33,340	− 5.3
$[Ca_{0.55}(Sm_{0.05}Bi_{0.95})_{0.3}]$ MoO_4	660°C/2h	22.3	33,210	− 2.1

Figure Captions

Figure 1.XRD patterns of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics sintered at different temperatures (x value ranges from 0.2 to 0.95).Inset the micrograph of surface of the $[Ca_{0.55}(Sm_{0.05}Bi_{0.95})_{0.3}]MoO_4$ ceramic sintered at 660 ^{o}C/2h.

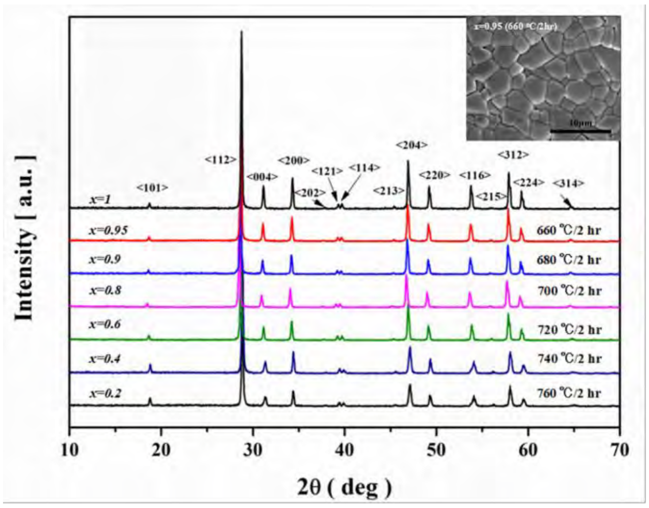
Figure 2.Cell parameters of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics as a function of the x value (x value ranges from 0.2 to 0.95).

Figure 3.Raman spectroscopy of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics (x value ranges from 0.2 to 0.95).

Figure 4.Measured (red circles) and fitted (solid line) IR spectra for the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]$ MoO_4 ceramics (x value ranges from 0.2 to 0.95).

Figure 5.The real (a) and imaginary (b) parts of the complex dielectric response of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics (x value ranges from 0.2 to 0.95). Red circles are experimental microwave date; Solid lines are the results from the fits of infrared spectra.

Figure 6.Relative densities and microwave dielectric properties (Permittivity, Qf values and TCF) of the $[Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}]MoO_4$ ceramics (x value ranges from 0.2 to 0.95) at different sintering temperature (S.T).


x=0.95 (660 °C/2hr)
10μm
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x=1
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<213>
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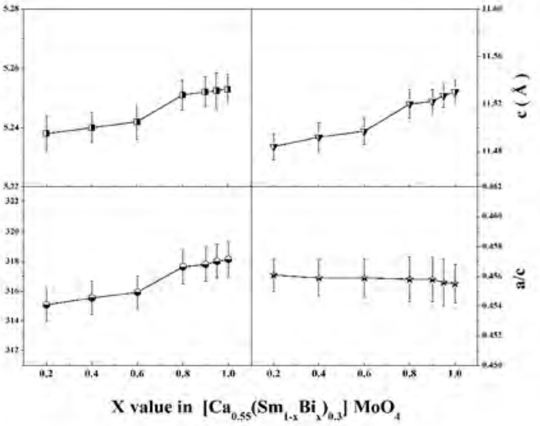
x=0.95
660 °C/2 hr
x=0.9
680 °C/2 hr
x=0.8
700 °C/2 hr
x=0.6
720 °C/2 hr
x=0.4
740 °C/2 hr
x=0.2
760 °C/2 hr
10
20
30
40
50
60
70
2θ (deg)


a (Å)
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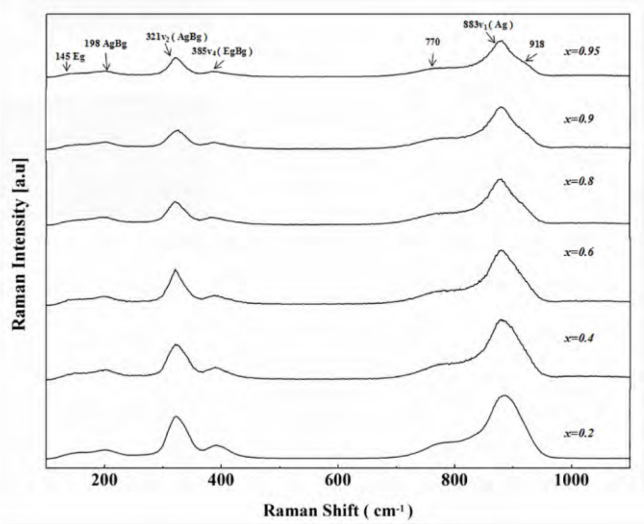
5.24
5.26
5.28
c (Å)
11.48
11.52
11.56
11.60
V (Å^3)
312
314
316
318
320
322
a/c
0.450
0.452
0.454
0.456
0.458
0.460
0.462
0,2
0,4
0,6
0,8
1,0
X value in [$Ca_{0.55}(Sm_{1-x}Bi_x)_{0.3}$] MoO_4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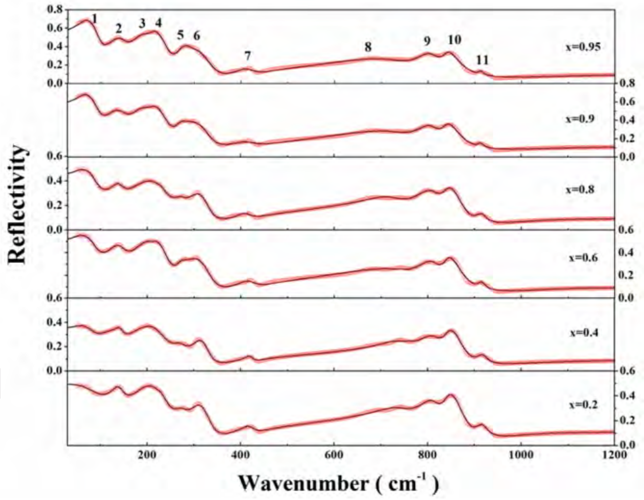
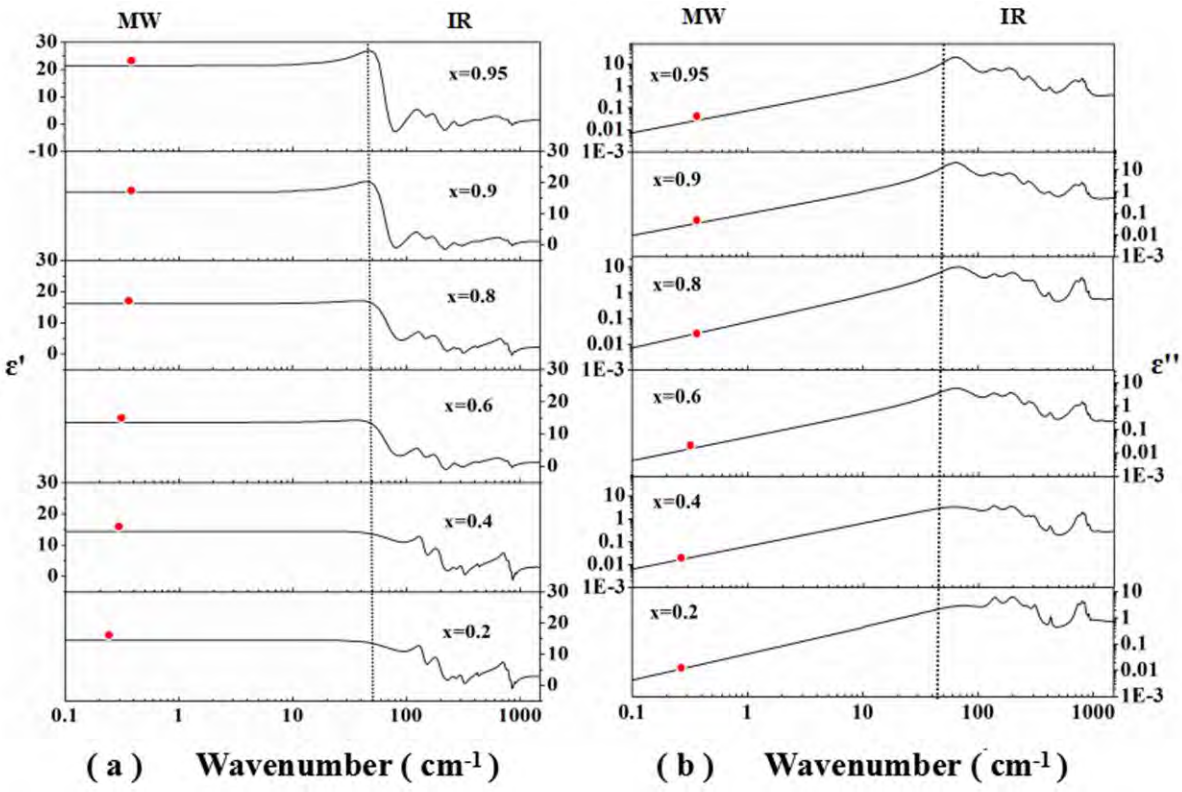
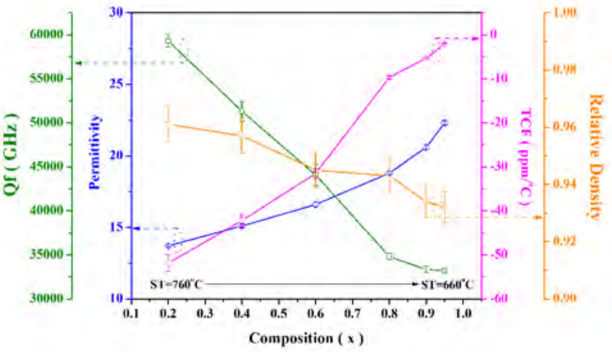
198 AgBg
321ν2 (AgBg)
385ν4 (EgBg)
770
883ν1 (Ag)
918
x=0.95
x=0.9
x=0.8
x=0.6
x=0.4
x=0.2
Raman Intensity [a.u]
200
400
600
800
1000
Raman Shift (cm-1)


1
2
3
4
5
6
7
8
9
10
11
x=0.95
x=0.9
x=0.8
x=0.6
x=0.4
x=0.2
0.0
0.2
0.4
0.6
0.8
Reflectivity
200
400
600
800
1000
1200
Wavenumber (cm-1)


MW
IR
MW
IR
ε'
ε''
x=0.95
x=0.9
x=0.8
x=0.6
x=0.4
x=0.2
30
20
10
0
-10
1E-3
0.01
0.1
1
10
0.1
1
10
100
1000
(a)
Wavenumber (cm-1)
(b)
Wavenumber (cm-1)


Qf (GHz)
30000
35000
40000
45000
50000
55000
60000
Permittivity
10
15
20
25
30
TCF (ppm/°C)
0
-10
-20
-30
-40
-50
-60
Relative Density
0.90
0.92
0.94
0.96
0.98
1.00
ST=760°C
ST=660°C
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1.0
Composition (x)