Inorganic Chemistry
Article
pubs.acs.org/IC

Structure, Phase Evolution, and Microwave Dielectric Properties of $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ Ceramic with Ultralow Sintering Temperature

Di Zhou,*[†] Wen-Bo Li,[†] Jing Guo,[†] Li-Xia Pang,[‡] Ze-Ming Qi,[§] Tao Shao,[§] Hui-Dong Xie,[∥] Zhen-Xing Yue,[⊥] and Xi Yao[†]

[†]Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education & International Center for Dielectric Research, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, People's Republic of China

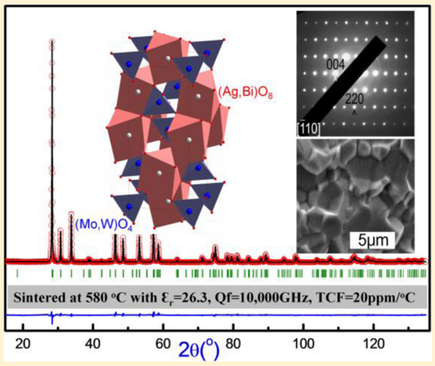
[‡]Micro-optoelectronic Systems Laboratories, Xi'an Technological University, Xi'an 710032, Shaanxi, People's Republic of China

[§]National Synchrotron Radiation Laboratory, University of Science and Technology of China, Anhui 230029, Hefei, People's Republic of China

[∥]School of Science, Xi'an University of Architecture & Technology, Xi'an 710055, Shaanxi People's Republic of China

[⊥]State Key Laboratory of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, People's Republic of China

ABSTRACT: In the present work, the microwave dielectric ceramic $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ was prepared by using the solid-state reaction method. $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ was found to crystallize in the scheelite structure, in which Ag^+ and Bi^{3+} occupy the A site randomly with 8-coordination while Mo^{6+} and W^{6+} occupy the B site with 4-coordination, at a sintering temperature above 500 °C, with lattice parameters $a = b = 5.29469(2)$ Å and $c = 11.62114(0)$ Å, space group $I4_1/a$ (No. 88), and acceptable $R_p = 9.38$, $R_{wp} = 11.2$, and $R_{exp} = 5.86$. High-performance microwave dielectric properties, with permittivity ~26.3, Q_f value ~10000 GHz, and temperature coefficient ~+20 ppm/°C, were obtained in the sample sintered at 580 °C. Its chemical compatibility with aluminum at its sintering temperature was revealed and confirmed by both X-ray and energy dispersive spectrometer analysis. This ceramic could be a good candidate for ultralow-temperature cofired ceramics.



■ INTRODUCTION

Low-temperature cofired ceramics (LTCC) technology has played a more and more important role in fabricating highly integrated microwave devices. In addition to the traditional way of lowering the sintering temperatures of microwave dielectric ceramics by adding sintering aids, there is an increasing need to search for new microwave dielectric ceramics with intrinsic low sintering temperatures.[1−3]

With the exploration of TeO_2-rich and MoO_3-rich systems,[4−6] LTCC technology has been developed into a new level, ultralow-temperature cofired ceramic (ULTCC) technology, in which the ceramic matrix and inter metal electrode can be cofired at a temperature below 700 °C. Generally, a sintering temperature lower than the melting points of metal electrodes, chemical compatibility, high quality factor (Q_f), and near-zero temperature coefficient of resonant frequency (TCF) are all critical factors for ULTCC technology. It was reported in our previous work[7] that the scheelite structure $(Ag_{0.5}Bi_{0.5})MoO_4$ could be sintered at 690 °C with good microwave dielectric properties, permittivity ~30.4, Q_f value ~12600 GHz, and TCF value +57 ppm/°C. Although it has the same electrovalence and similar ionic radius and polarization, when W^{6+} fully held the B site, $(Ag_{0.5}Bi_{0.5})WO_4$ was found to crystallize in a wolframite structure with microwave permittivity ~35.9, $Q_f \approx 13000$ GHz, temperature coefficient ~−69 ppm/°C, and sintering temperature 580 °C.[8] It is noted that the scheelite structure $(Ag_{0.5}Bi_{0.5})MoO_4$ and wolframite structure $(Ag_{0.5}Bi_{0.5})WO_4$ ceramics possess opposite TCF values. Considering the successful achievement of temperature-stable microwave dielectric ceramics of $(Li_{0.5}Bi_{0.5})(W_{0.6}Mo_{0.4})O_4$ by mixing the scheelite and wolframite phases, $((Li_{0.5}Bi_{0.5})(W_{0.6}Mo_{0.4})O_4$ ceramic sintered at 620 °C with a relative permittivity of 31.5, a Q_f value of 8500 GHz (at 8.2 GHz), and a TCF value of +20 ppm/°C),[9] in the present work W^{6+} was chosen to substitute for Mo^{6+} in $(Ag_{0.5}Bi_{0.5})MoO_4$. The sintering behavior, microstructure, microwave dielectric properties, and chemical compatibility with both silver and aluminum were investigated in detail.

■ EXPERIMENTAL SECTION

Proportionate amounts of reagent-grade starting materials, Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., Chengdu, People's Republic of China), Ag_2CO_3 (>99%, Sinopharm Chemical Reagent Co., Ltd., Shanghai, People's Republic of China), WO_3, and MoO_3 (>99%,

Received: February 28, 2014
Published: May 21, 2014

© 2014 American Chemical Society

Fuchen Chemical Reagents, Tianjin, People's Republic of China), were measured according to the stoichiometric formulation $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$. Powders were mixed and milled for 4 h by using a planetary mill (Nanjing Machine Factory, Nanjing, People's Republic of China) at 150 rpm with zirconia balls (2 mm in diameter) as milling media. The powder mixture was then dried and calcined at 400 and 500 °C for 4 h, respectively. The calcined powders were ball-milled for 5 h at 200 rpm to obtain fine powders. Then, the powders were pressed into cylinders (10 mm in diameter and 4−5 mm in height) in a steel die with 5 wt % PVA binder at a uniaxial pressure of 150 MPa. Samples were sintered in the temperature range from 520 to 600 °C for 2 h. Room-temperature X-ray diffraction (XRD) was performed by using an XRD instrument with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Prior to examination, all sintered pellets were crushed in a mortar and pestle to give a powder. The diffraction pattern was obtained over 10−80° at a step of 0.02°. The results were analyzed by using the Rietveld profile refinement method, with the FULLPROF program. The specimens for transmission electron microscopy were prepared from the sintered pellets and examined by using a JEOL 2100 TEM microscope operated at 200 kV. To examine the grain morphology, the as-fired and fractured surfaces were examined by using scanning electron microscopy (SEM; JSM-6460, JEOL, Tokyo, Japan). Room-temperature infrared reflectivity spectra were measured by using a Bruker IFS 66v FTIR spectrometer on Infrared beamline station U4 at the National Synchrotron Radiation Laboratory (NSRL), People's Republic of China. Dielectric properties at microwave frequencies were measured with the $TE_{01\delta}$ dielectric resonator method with a network analyzer (HP 8720 Network Analyzer, Hewlett-Packard) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency TCF (τ_f) was calculated with the formula

$$\mathrm{TCF}\ (\tau_f) = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 \qquad (1)$$

where f_T and f_{T_0} are the $TE_{01\delta}$ resonant frequencies at temperatures T and T_0, respectively.

■ RESULTS AND DISCUSSION

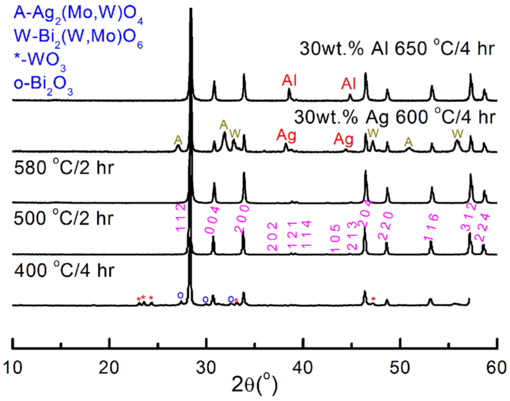


Figure 1. XRD patterns of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ sample calcined at 400 °C/4 h, and 500 °C/4 h and sintered at 580 °C/2 h and its cofired samples with 30 wt % Ag and Al powders.

Figure 1 presents XRD patterns of pure $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ samples calcined at 400 °C/4 h and 500 °C/4 h and sintered at 580 °C/2 h and its cofired samples with 30 wt % Ag and Al powders. Refined atomic fractional coordinates are given in Table 1. It is seen that, after calcination at 400 °C for 4 h, most of the initial materials reacted and the main phase with a scheelite tetragonal structure was formed. In addition, the remnant WO_3 and Bi_2O_3 phases could also be revealed. When the calcination temperature was increased to 500 °C, only the single scheelite tetragonal phase was observed, which means that the following reaction was finished at this temperature:

$$Ag_2CO_3 + Bi_2O_3 + 2MoO_3 + 2WO_3 \xrightarrow{500\ °C} 4(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4 + CO_2\uparrow \qquad (2)$$

For the cofired sample with 30 wt % Al powders, only the peaks of the scheelite phase and aluminum were observed, which means that the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ sample is chemically compatible with Al at the sintering temperature. However, the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ sample seems to react seriously with silver powders. Traces of $Ag_2(Mo,W)O_4$ and $Bi_2(W,Mo)O_6$ phased were revealed in addition to the scheelite and Ag phases, which means that the following possible reaction took place:

$$(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4 + Ag \xrightarrow{600\ °C} Ag_2(Mo,W)O_4 + Bi_2(Mo,W)O_6 \qquad (3)$$

This result implies that, when the ratio of Ag to Bi is larger than 1:1, the silver-rich compound $Ag_2(Mo,W)O_4$ can be formed prior to the formation of the scheelite phase.

To study the crystal structure, refinements were carried out using Fullprof software on the basis of the fine XRD data. The observed and calculated XRD patterns are shown in Figure 2. The refined values of lattice parameters are $a = b = 5.29469(2)$ Å and $c = 11.62114(0)$ Å with a space group $I4_1/a$ (No. 88) and acceptable $R_p = 9.38$, $R_{wp} = 11.2$, and $R_{exp} = 5.86$ using the data (ICSD #67491) reported by Teller as the starting model.[10] The cell parameters of $(Ag_{0.5}Bi_{0.5})MoO_4$ are $a = b = 5.285$ Å and $c = 11.63$ Å as reported by Perepelitsa et al.[11] In the scheelite structure, Mo^{6+} is four-coordinated and its ionic radius is 0.41 Å, while the ionic radius of W^{6+} is 0.60 Å.[12] Hence, it is understandable that the cell volume was increased from 324.84 to 325.78 Å^3 when half of Mo^{6+} was replaced by W^{6+}. It must be noted that only the parameters a and b increased and the parameter c decreased, which is similar to the situation in $(Li_{0.5x}Bi_{1-0.5x})(Mo_xV_{1-x})O_4$ and $Bi(Fe_{x/3}Mo_{2x/3}V_{1-x})O_4$. This implies that the a/c value in scheelite structure increases with the radius of B site ions. Two transmission electron diffraction patterns of selected area of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ sample are shown in the inset of Figure 2. All patterns were indexed according to a scheelite tetragonal unit cell with lattice parameters $a = b = 5.29$ Å and $c = 11.62$ Å, which is in a good agreement with the XRD results.

Figure 3 presents SEM images of the natural surface and fractured surfaces of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic sintered at 580 °C/2 h. It can be seen that a dense and homogeneous microstructure without pores was observed from both the natural and fractured surfaces, which means that the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic could be well densified at 580 °C. The grain size was found to be 1−4 μm. The sintering temperature of pure $(Ag_{0.5}Bi_{0.5})MoO_4$ was about 690 °C,[7] and the formation of the solid solution effectively lowered the sintering temperature. As seen from the BSE image of the cofired sample with 30 wt % Ag (Figure 3c), there are at least three different types of grains, flakes with light color, matrix grains, and a precipitate of the liquid phase, which are consistent with the XRD results above.

Table 1. Refined Atomic Fractional Coordinates from XRD Data for the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ Sample[a]

atom	site	occ	x	y	z	B_{iso}
Ag	4b	0.125	0.000 00	0.250 00	0.625 00	0.76147
Bi	4b	0.125	0.000 00	0.250 00	0.625 00	0.76147
Mo	4a	0.125	0.000 00	0.250 00	0.125 00	0.87329
W	4a	0.175	0.000 00	0.250 00	0.125 00	0.87329
O	16f	1.000	0.1537(1)	0.0079(1)	0.2062(0)	1.87934

[a] The lattice parameters at room temperature are $a = b = 5.29469(2)$ Å and $c = 11.62114(0)$ Å. The space group is $I4_1/a$ (No. 88).

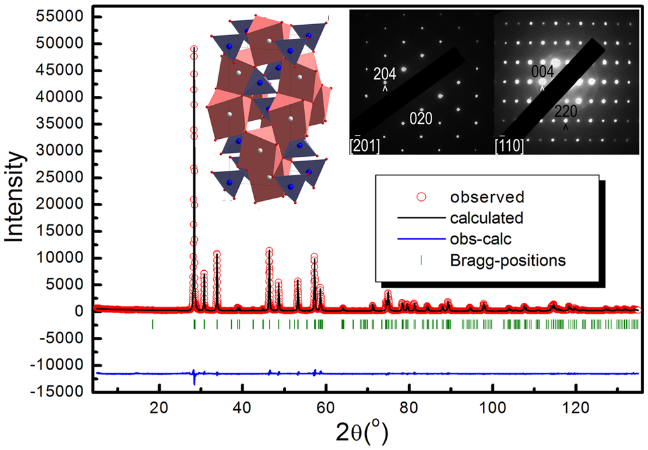


Figure 2. Experimental (circles) and calculated (line) XRD profiles for the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ sample at room temperature ($R_p = 9.38$, $R_{wp} = 11.2$, and $R_{exp} = 5.86$. The short vertical lines below the patterns mark the positions of Bragg reflections. The bottom continuous line is the difference between the observed and the calculated intensity. Insets give the schematic structure of ABO_4 and transmission electron diffraction patterns of selected areas.

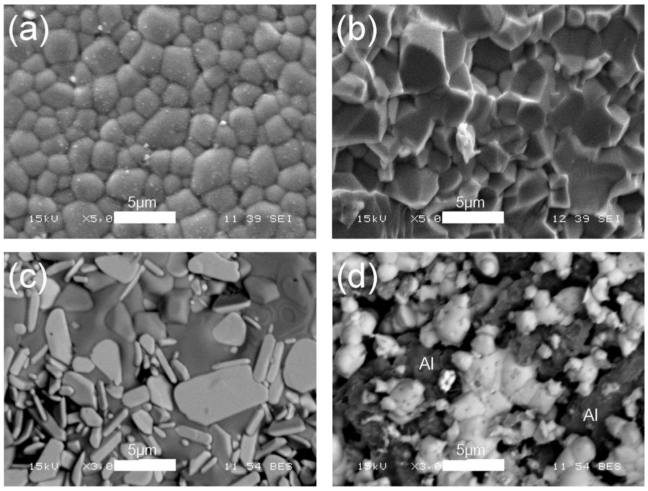


Figure 3. SEM images of the natural surface (a) and fractured surface (b) of $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic sintered at 580 °C/2 h and BSE photos of the cofired sample (c) with 30 wt % Ag at 600 °C/4 h and (d) with 30 wt % Al at 650 °C/4 h.

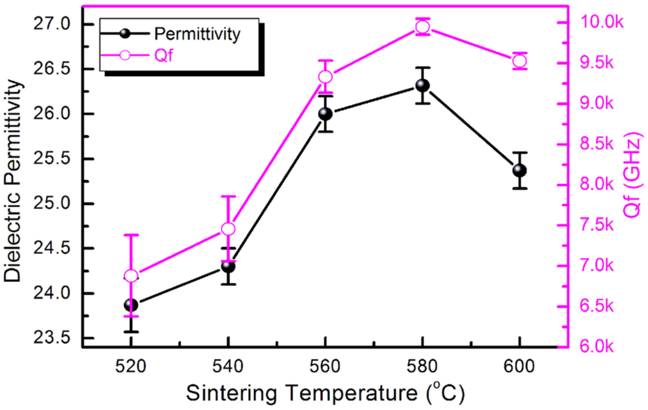


Figure 4. Microwave dielectric permittivities and Q_f values of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic as a function of sintering temperature.

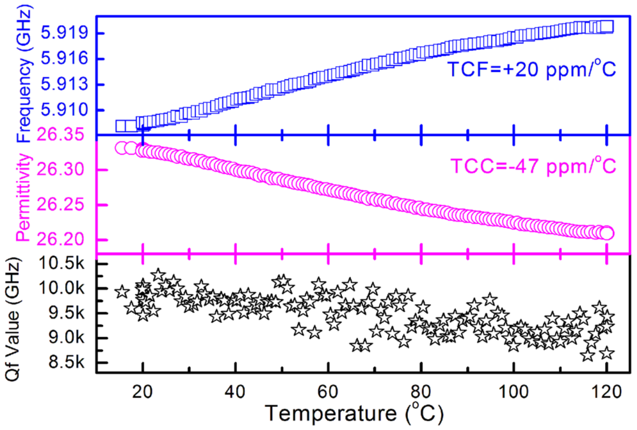


Figure 5. Resonant frequencies, dielectric permittivities, and Q_f values of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic sintered at 580 °C for 2 h over 20−120 °C.

The microwave dielectric permittivity and Q_f value of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic as a function of sintering temperature are presented in Figure 4. As the sintering temperature was increased from 520 to 580 °C, the microwave dielectric permittivity increased from 23.9 to 26.3 and the Q_f value also reached a maximum value of 10000 GHz at 580 °C. With a further increase in sintering temperature, both the microwave dielectric permittivity and Q_f value decreased due to the secondary grain growth. The temperature dependences of resonant frequency, microwave dielectric permittivity, and Q_f value in the temperature range 20−120 °C are shown in Figure 5. It is seen that the resonant frequency increased almost linearly with temperature, having a temperature coefficient (TCF) of about +20 ppm/°C. Meanwhile, the permittivity decreased linearly with temperature, with a temperature coefficient (TCC) of −47 ppm/°C. The TCF and TCC values follow the simple proportional rule

$$\mathrm{TCF} = -\alpha_l - 0.5\mathrm{TCC} \qquad (4)$$

where α_l is the linear thermal expansion coefficient. The Q_f value decreased slightly from 10000 to 9000 GHz as the temperature was increased from 20 to 120 °C. The microwave dielectric properties of pure $(Ag_{0.5}Bi_{0.5})MoO_4$ ceramic are permittivity ~30.4, Q_f value ~12600 GHz, and TCF value +57 ppm/°C.[7] The polarizabilities of W^{6+} and Mo^{6+} calculated by Yoon et al. and Choi et al. are 3.2 and 3.28 Å^3, respectively.[13,14] This could explain the smaller permittivity of $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ in comparison to that of $(Ag_{0.5}Bi_{0.5})MoO_4$. The TCF value is determined by the TCC value. Usually, the absolute TCC value depends on the dielectric permittivity, which means that the TCC increases with permittivity. In the scheelite solid solution $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$, the decrease in TCF value results from a decrease of the permittivity value.

To better understand the microwave dielectric behavior of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic, IR reflectivity spectra was analyzed by using a classical harmonic oscillator model:

$$\varepsilon^*(\omega) = \varepsilon_\infty + \sum_{j=1}^{n} \frac{\omega_{pj}^2}{\omega_{oj}^2 - \omega^2 - j\gamma_j\omega} \tag{5}$$

where $\varepsilon^*(\omega)$ is the complex dielectric function, ε_∞ is the dielectric constant caused by the electronic polarization at high frequencies, γ_j, ω_{oj}, and ω_{pj} are the damping factor, the transverse frequency, and plasma frequency of the jth Lorentz oscillator, respectively, and n is the number of transverse phonon modes. The complex reflectivity $R(\omega)$ can be written as

$$R(\omega) = \left| \frac{1 - \sqrt{\varepsilon^*(\omega)}}{1 + \sqrt{\varepsilon^*(\omega)}} \right|^2 \tag{6}$$

The fitted IR reflectivity values and complex permittivities of $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic are shown in Figure 6. The phonon parameters obtained from the fitting of the infrared reflectivity spectra of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic are shown in Table 2. Its dielectric permittivity at optical frequency was 4.36, and the extrapolated value in the microwave region was 24.85, which is in reasonable agreement with the measured value of 26.3. The dielectric polarization contribution from the first four modes (63.91, 93.81, 125.42, and 244.60 cm^{-1}) is about 17.94, which is 68% of the total value, meaning that the IR phonon oscillations that are close to the microwave region dominate the microwave dielectric permittivity. The calculated dielectric loss is almost the same as the measured value, which means that the extrinsic dielectric loss caused by the defects in the ceramic sample is not too much in comparison with the intrinsic value. Hence, it can be concluded that the polarization of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic in the microwave region is due to the absorptions of phonon oscillations in the infrared region.

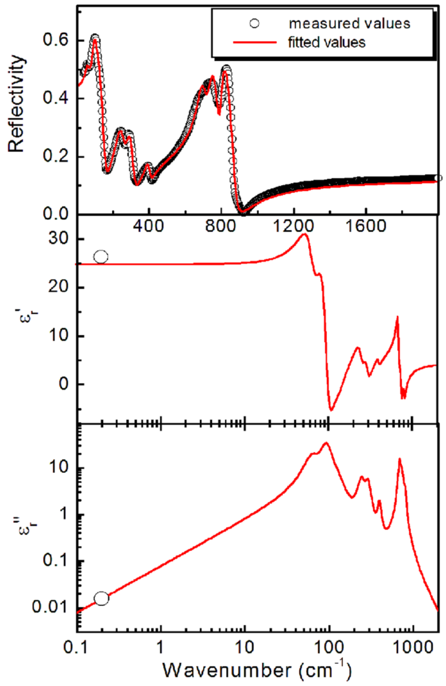


Figure 6. Fitted and measured infrared reflectivity values and complex permittivities of pure $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic sintered at 580 °C.

Table 2. Phonon Parameters Obtained from the Fitting of Infrared Reflectivity Spectra of the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ Ceramic[a]

mode	ω_{oj}	ω_{pj}	γ_j	$\Delta\varepsilon_j$
1	63.91	151.79	27.47	5.64
2	93.81	293.55	30.46	9.79
3	125.42	151.65	52.23	1.46
4	244.60	250.72	49.87	1.05
5	291.27	238.84	43.70	0.67
6	397.49	148.71	30.31	0.14
7	689.76	679.21	50.75	0.97
8	736.76	576.71	53.97	0.61
9	799.14	319.01	33.54	0.16

[a] $\varepsilon_\infty = 4.36$ and $\varepsilon_0 = 24.85$.

■ CONCLUSIONS

The single phase $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ with scheelite structure could be formed at a calcination temperature of 500 °C, and a well-densified ceramic sample could be obtained at a sintering temperature of about 580 °C, with good microwave dielectric properties: microwave permittivity ~26.3, Q_f value ~10000 GHz, and temperature coefficient ~+20 ppm/°C. An infrared reflectivity study confirmed that the phonon oscillations in the infrared region dominated the microwave dielectric performance in the microwave region. Although the $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ ceramic reacted with silver at its sintering temperature, it was proved to be chemically compatible with aluminum. The scheelite structure $(Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O_4$ could be a promising candidate for ultralow-temperature cofired ceramics.

■ AUTHOR INFORMATION

Corresponding Author

*D.Z.: tel (fax), +86-29-82668679; e-mail, zhoudi1220@gmail.com.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the National Science Foundation of China (51202182, 51202178), the Fundamental Research Funds for the Central University, the international cooperation project of Shaanxi Province (2013KW12-04), the State Key Laboratory of New Ceramic and Fine Processing Tsinghua University, and the 111 Project of China (B14040). The authors thank the administrators of the IR beamline workstation of the National Synchrotron Radiation Laboratory

(NSRL) for their help with IR measurements. The TEM and SEM experiment was partially done at the International Center for Dielectric Research (ICDR), Xi'an Jiaotong University, Xi'an, People's Republic of China, and the authors thank Ms. Lu Lu and Ms. Yan-Zhu Dai for their help in using TEM and SEM instruments.

■ REFERENCES

(1) Sebastian, M. T.; Jantunen, H. *Int. Mater. Rev.* **2008**, *53*, 57−90.
(2) Zhou, D.; Pang, L. X.; Guo, J.; Qi, Z. M.; Shao, T.; Wang, Q. P.; Xie, H. D.; Yao, X.; Randall, C. A. *Inorg. Chem.* **2014**, *53*, 1048−55.
(3) Pang, L. X.; Zhou, D. *J. Am. Ceram. Soc.* **2010**, *93*, 3614−7.
(4) Kwon, D. K.; Lanagan, M. T.; Shrout, T. R. *J. Am. Ceram. Soc.* **2005**, *88*, 3419−22.
(5) Udovic, M.; Valant, M.; Suvorov, D. *J. Am. Ceram. Soc.* **2004**, *87*, 591−7.
(6) Zhou, D.; Wang, H.; Pang, L. X.; Randall, C. A.; Yao, X. *J. Am. Ceram. Soc.* **2009**, *92*, 2242−6.
(7) Zhou, D.; Randall, C. A.; Pang, L. X.; Wang, H.; Guo, J.; Zhang, G. Q.; Wu, Y.; Guo, K. T.; Shui, L.; Yao, X. *Mater. Chem. Phys.* **2011**, *129*, 688−92.
(8) Zhou, D.; Pang, L. X.; Xie, H. D.; Guo, J.; He, B.; Qi, Z. M.; Shao, T.; Yao, X.; Randall, C. A. *Eur. J. Inorg. Chem.* **2014**, *2*, 296−301.
(9) Zhou, D.; Guo, J.; Yao, X.; Pang, L. X.; Shao, T.; Qi, Z. M. *Funct. Mater. Lett.* **2012**, *5*, 1250042.
(10) Teller, R. G. *Acta Crystallogr., Sect. C* **1992**, *48*, 2101−4.
(11) Perepelitsa, A. *Russ. J. Inorg. Chem. (Engl. Transl.)* **1977**, *2*, 549.
(12) Shannon, R. D. *J. Appl. Phys.* **1993**, *73*, 348−66.
(13) Choi, G. K.; Kim, J. R.; Yoon, S. H.; Hong, K. S. *J. Eur. Ceram. Soc.* **2007**, *27*, 3063−7.
(14) Yoon, S. H.; Kim, D. W.; Cho, S. Y.; Hong, K. S. *J. Eur. Ceram. Soc.* **2006**, *26*, 2051−4.