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Short communication

Microwave dielectric properties of scheelite structured low temperature fired $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic

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Abstract

A $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic was prepared via the solid state reaction method. The pure monoclinic phase was formed at around 650 °C. Ceramic samples with relative densities above 97% were obtained when sintering temperature was around 840 °C. The best microwave dielectric properties were achieved in the $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic sintered at 840 °C for 2 h with permittivity ~25.2, Qf of 40,000 GHz and temperature coefficient of resonance frequency ~−65 ppm/°C at 8.2 GHz. The temperature dependence of microwave dielectric properties was also studied in a wide temperature range from −250 °C to +120 °C. The Qf value increased with the decrease of temperature and reached a maximum of 150,000 GHz at −250 °C.

Keywords: Electronic materials; Low temperature co-fired ceramic; Microwave dielectric property

1. Introduction

Microwave dielectric ceramics have been studied for decades and the exploration for new microwave dielectric materials will continue due to requirements for low cost and series dielectric permittivity [1,2]. The low temperature co-fired ceramics (LTCC) technology has become an important fabrication method to achieve miniaturization and integration. Hence, the low temperature (below melting points of Ag, Cu, etc.) fired ceramics with high performance of microwave dielectric properties have attracted much attention in recent years [3,4].

Since the $BaTe_4O_9$ ceramic with a sintering temperature around 550 °C, dielectric permittivity ~17.5, and Qf about 54,700 GHz was reported by Kwon et al. [5,6]; many Te-rich ceramics with ultra-low sintering temperature have been explored, such as TiO_2–TeO_2, CaO–TeO_2, BaO–TeO_2, ZrO_2–TeO_2, MgO–TeO_2 and BaO–TiO_2–TeO_2 [5–10]. In our previous studies, the Bi-rich and Mo-rich systems were found to possess intrinsic low sintering temperatures, such as the Bi_2O_3–MoO_3 binary system [11], Li_2O–Bi_2O_3–MoO_3 ternary system [12] and Li_2O–Bi_2O_3–MoO_3–V_2O_5 quaternary system [13]. The low melting points of Bi_2O_3 (817 °C) and MoO_3 (795 °C) determine that the compounds that are rich in both of them might have low sintering temperatures. The monoclinic scheelite structured $Bi(Fe_{1/3}Mo_{2/3})O_4$ ceramic, in which the FeO_4 and MoO_4 tetrahedra take on an ordered arrangement, was found to be well densified at around 830 °C and displayed high performance of microwave dielectric properties with permittivity ~27.2, Qf ~14,500 GHz and temperature coefficient ~−80 ppm/°C [14]. A similar ordered scheelite structure can also be formed in $Bi(Ga_{1/3}Mo_{2/3})O_4$, $Bi(In_{1/3}Mo_{2/3})O_4$ and $Bi(Sc_{1/3}Mo_{2/3})O_4$, while an analogous phase cannot be formed in the situation of Al and Cr holding the B site [15–17]. In this present work, the $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic was prepared via the solid state reaction method. The phase evolution, microstructure and microwave dielectric properties were studied in detail.

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2. Experimental procedure

Proportionate amounts of reagent-grade starting materials of Bi_2O_3, In_2O_3 (> 99%, Guo-Yao Co., Ltd., Shanghai, China) and MoO_3 (> 99%, Fuchen Chemical Reagents, Tianjin, China) were weighed according to the stoichiometric formulation of $Bi(In_{1/3}Mo_{2/3})O_4$ composition. Powders were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with the Yttria Stabilized Zirconia (2 mm in diameter) milling media. The mixed oxides were then calcined at 650 °C for 4 h. After being crushed and re-milled for 5 h using the ZrO_2 milling media and deionized water, powders were pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die with 5 wt% PVA binder addition under a uniaxial pressure of 200 MPa. Samples were sintered in the temperature range from 780 to 880 °C for 2 h.

The crystalline structures of samples were investigated using X-ray diffraction with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of sintered ceramics were observed on the as-fired surfaces with scanning electron microscopy (SEM; JSM-6460, JEOL, Tokyo, Japan). The apparent densities of sintered ceramics were measured by Archimedes' method. The infrared reflectivity spectra were measured on the fine polished surface of ceramic sample using a Bruker IFS66v FTIR spectrometer on the infrared beamline station (U4) at National Synchrotron Radiation Laboratories. (NSRL), China. Dielectric behaviors at microwave frequency were measured with the $TE_{01\delta}$ shielded cavity method [18] with a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonance frequency τ_f (TCF) was calculated with the following formula:

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

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

3. Results and discussions

The X-ray diffraction patterns of the calcined and sintered samples are shown in Fig. 1. It is seen that the pure monoclinic phase with a space group C2/c (15) can be formed at 650 °C. Even when the sintering temperature increased to 880 °C, there is no trace of decomposition or second phases observed, which means that the pure monoclinic $Bi(In_{1/3}Mo_{2/3})O_4$ phase remained stable in a wide temperature range 650–880 °C. The cell parameters were calculated as $a = 16.988$ Å, $b = 11.619$ Å, $c = 5.344$ Å and $\beta = 105.18°$ and the theoretical density was 7.344 g/cm^3. All the results agree well with those reported by Mokhosoev [16], as shown in ICCD-PDF card 40-0413 in Fig. 1.

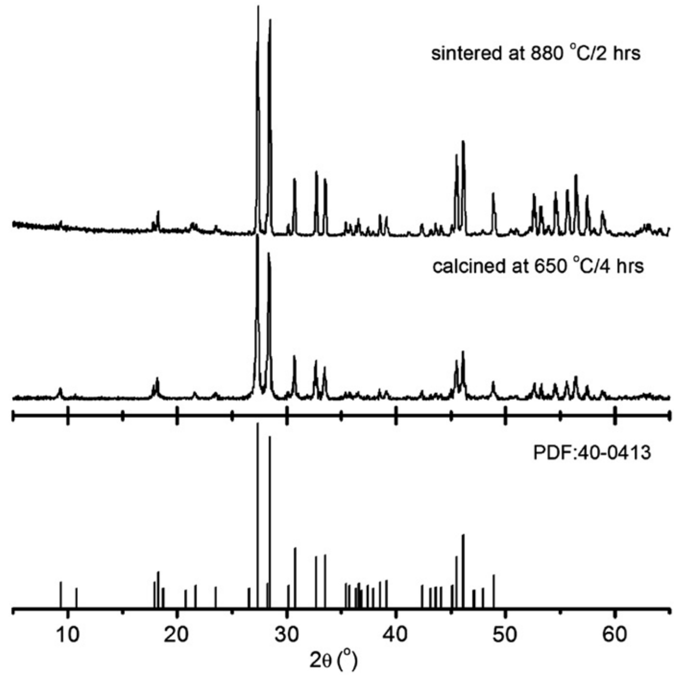

Fig. 1. X-ray diffraction patterns of calcined and sintered samples of $Bi(In_{1/3}Mo_{2/3})O_4$ and the comparison with PDF card: 40-0413.

The SEM micrographs of as-fired surfaces of the $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic sintered at different temperatures are shown in Fig. 2. It is seen that many pores can be observed from the SEM photo of the ceramic sintered at 800 °C for 2 h and the grain size is smaller than 1 μm. When the sintering temperature increased to 840 °C, dense and homogeneous microstructure with almost no pores could be observed and the grain size increased to 1–2 μm as shown in Fig. 2(b).

Fig. 3 shows the apparent density, microwave dielectric permittivity and Qf value of $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic as a function of sintering temperature. It is seen that the apparent density of ceramics increased from 6.80 g/cm^3 to around 7.18 g/cm^3 as the sintering temperature increased from 780 to 840 °C and then reached a saturated value due to the elimination of pores during the sintering process. The dense ceramic sample has a relative density above 97%. The dielectric permittivity at microwave frequency was influenced seriously by the pores due to its low permittivity value (about ~1). Hence, the change trend of microwave dielectric permittivity as a function of sintering temperature is similar to that of density. Dielectric loss in the microwave frequency region was separated into two parts: intrinsic and extrinsic dielectric losses. The intrinsic dielectric loss caused by absorptions of phonon oscillation determines the upper limit of Qf value and the Qf value can be easily deteriorated by the extrinsic dielectric loss caused by defects [19]. The total number of grain boundaries decreases with the increase of average grain size and the decrease of pores. It is expected that the optimal Qf value can be achieved in dense ceramics without pores and secondary grain growth. For the $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic, the best microwave

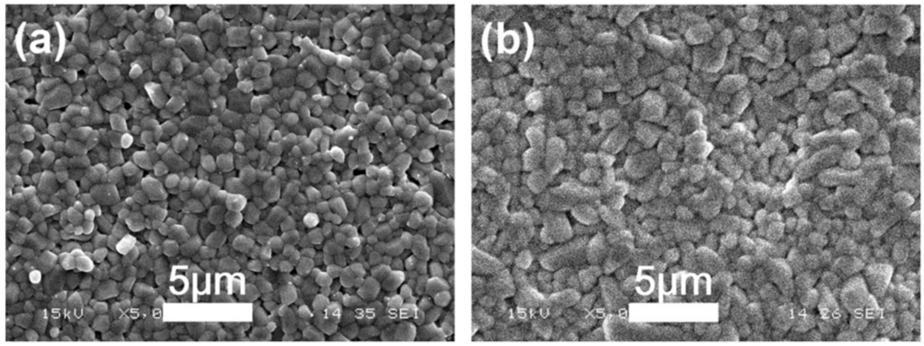

Fig. 2. SEM photo of $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic sintered at (a) 800 °C for 2 h and (b) 840 °C for 2 h.

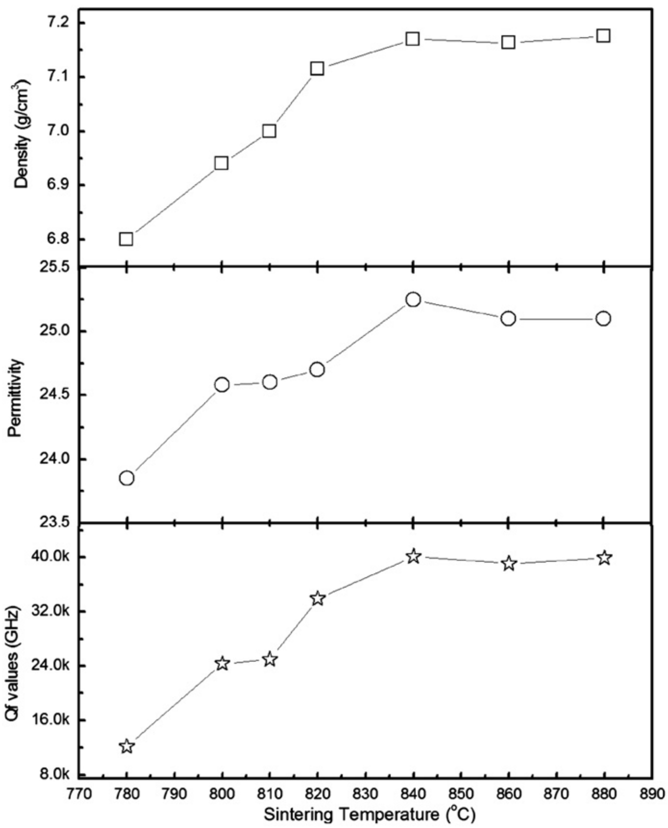

Fig. 3. Apparent density and microwave dielectric properties of $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic as a function of sintering temperature.

dielectric properties were obtained in the ceramic sintered at 840 °C for 2 h with permittivity ~25.3, and Qf about 40,000 GHz at a resonance frequency of about 8.2 GHz.

The microwave dielectric permittivity and Qf value in the temperature range from −250 °C to +120 °C of $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic sample sintered at 840 °C for 2 h are shown in Fig. 4. It is seen that the microwave dielectric permittivity increased almost linearly from 24.4 to 25.4 without any abnormity as temperature increased from −250 °C to +120 °C. The temperature coefficient of resonance frequency was found to be about −65 ppm/°C. The Qf value increased from 40,000 GHz to around 150,000 GHz as the temperature decreased from room temperature to −250 °C, which indicates that the $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic can work well as a resonator in a wide temperature range.

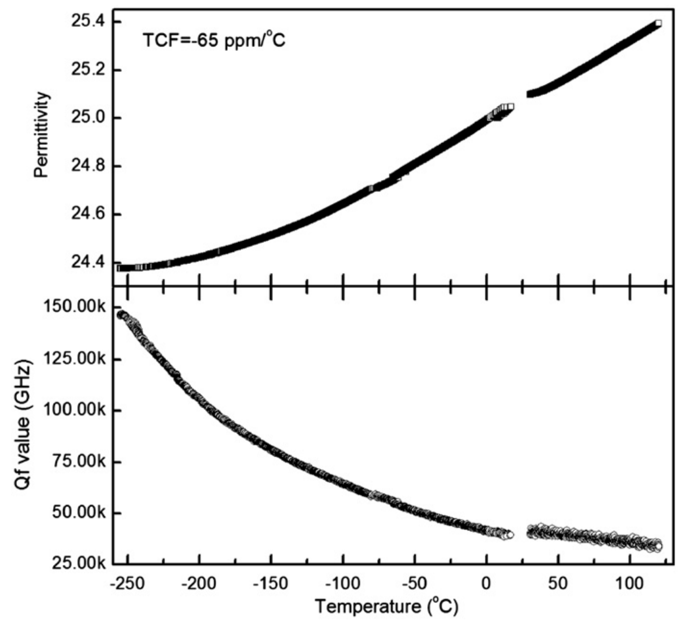

Fig. 4. Microwave dielectric permittivity and Qf value in the temperature range from −250 °C to +120 °C for $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic sintered at 840 °C for 2 h.

The IR reflectivity spectra of $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic were analyzed using a classical harmonic oscillator model as follows [20]:

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

where $\varepsilon^*(\omega)$ is the complex dielectric function and 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 [20]

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

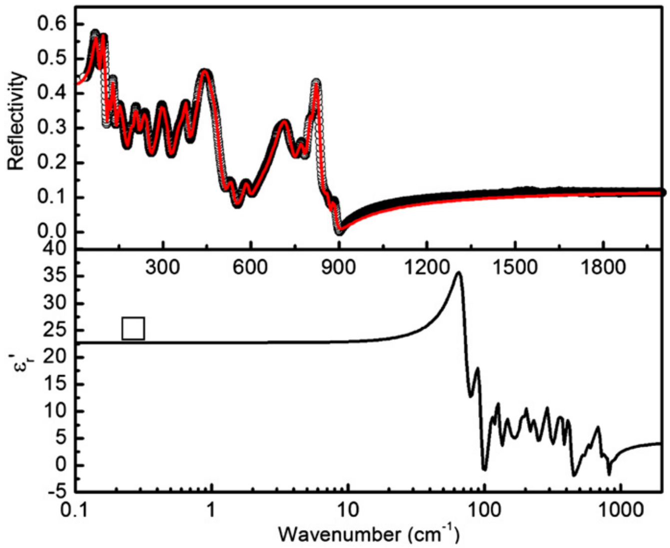

Fig. 5. Fitted (line) and measured (circle) infrared reflectivity values, and real part of dielectric permittivity of $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic sintered at 840 °C for 2 h.

The fitted IR reflectivity values and the real part of dielectric permittivity of $Bi(In_{1/3}Mo_{2/3})O_4$ ceramics are shown in Fig. 5. Twenty-four modes are chosen to fit the IR reflectivity values. The dielectric permittivity at optical frequency is 4.38 and the extrapolated value to microwave region is 22.8, which is quite close to the measured value 25.3. Hence, it can be concluded that the maximum polarization contribution for $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic in the microwave region is attributed to the absorptions of phonon oscillation in infrared region.

4. Conclusions

The $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic can be well densified when the sintering temperature is ≥ 840 °C and reached a high relative density above 97%. High performance of microwave dielectric properties can be obtained in the ceramic sample sintered at 840 °C for 2 h with microwave permittivity $\sim$25.2, Qf$\sim$40,000 GHz and temperature coefficient ~ -65 ppm/°C. The maximum polarization contribution for the $Bi(In_{1/3}Mo_{2/3})O_4$ ceramic in the microwave region was attributed to the absorptions of phonon oscillation in the infrared region. It might be promising for the low temperature co-fired ceramic technology (LTCC) and dielectric resonator applications.

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