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A new temperature stable microwave dielectric with low-firing temperature in Bi_2MoO_6–TiO_2 system

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ABSTRACT

A new temperature stable microwave dielectric with low-firing temperature in xBi_2MoO_6–$(1-x)TiO_2$ system was prepared by conventional solid state reaction method. The crystalline phases, sintering behavior, microwave dielectric properties of xBi_2MoO_6–$(1-x)TiO_2$ ceramics were studied. All the xBi_2MoO_6–$(1-x)TiO_2$ ceramics could be well sintered at 850 °C for 3 h. X-ray diffraction analysis showed that tetragonal rutile phase and monoclinic Bi_2MoO_6 phase coexisted in the ceramic. The permittivity ε_r changed from 77.5 to 33.5 and the temperature coefficient of resonant frequency τ_f value shifted from +348.1 to −37.8 ppm/°C as the x value increased from 0.06 to 0.65. The temperature stable microwave dielectric ceramic was obtained when $x = 0.57$ in the xBi_2MoO_6–$(1-x)TiO_2$ system, and it showed excellent dielectric properties of $\varepsilon_r = 36.7$, Qf = 16,800 GHz and $\tau_f = 0$ ppm/°C.

1. Introduction

With the rapid development of mobile communication and satellite communication, microwave electronic devices are required to be developed and fabricated for miniaturization and integration. The low temperature co-fired ceramic technology (LTCC) becomes an important fabricating technology that can integrate the passive components within a monolithic bulk module with IC chips mounted on its surface. As microwave dielectric, high quality factor (Qf), near zero temperature coefficient of resonant frequency (τ_f), and low-firing temperature (<961 °C, the melting temperature of Ag electrode) are essential for practical application. In addition, high relative permittivity ($\varepsilon_r > 20$) is preferred for miniaturization [1–3]. Up to now, large numbers of materials have been developed with excellent microwave dielectric properties, while most of them possess high sintering temperatures (≥1000 °C). Recently, a number of material researchers have focused their research on lowering the sintering temperatures of microwave dielectric ceramics to meet the LTCC requirements. Three approaches are usually used to develop low-firing microwave dielectric ceramics: (a) addition of oxides or glass with low melting temperature [4–11], such as V_2O_5, CuO, LiF, and B_2O_3; (b) utilization of ultra-fine particles for raw materials [12,13]; (c) development of novel glass-free low-firing dielectric ceramics, including Bi_2O_3–TeO_2, TiO_2–TeO_2, CaO–TeO_2, BaO–TeO_2, ZnO–TeO_2 binary systems, BaO–TiO_2–TeO_2 ternary system, and $Bi_2W_2O_9$ systems [14–21]. Our recent research [22] showed that Bi_2O_3–MoO_3 binary system is a new ultra-low-firing microwave dielectric material. $Bi_2Mo_3O_{12}$, $Bi_2Mo_2O_9$, and Bi_2MoO_6 are the single phases in the Bi_2O_3–MoO_3 system and all of them show excellent microwave dielectric properties. Rutile TiO_2 is a good high K (permittivity) microwave dielectric with dielectric constant (105), high quality factor (9200 at 5 GHz), and large positive τ_f value (+465 ppm/°C) [23]. In this work, rutile TiO_2 was chosen to compensate [20,21,24,25] the negative τ_f value of Bi_2MoO_6 which possess high permittivity (31), high Qf value (16,700 GHz), and negative τ_f value (−114 ppm/°C) [22]. The compounds xBi_2MoO_6–$(1-x)TiO_2$ ($x = 0.06, 0.125, 0.21, 0.33, 0.50, 0.57, 0.65$) were prepared by conventional solid state reaction method. The chemical compatibility, sintering behavior, and microwave dielectric properties were studied.

2. Experimental

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., Chengdu, China), MoO_3 (>99%, Fuchen Chemical Reagents, Tianjin, China) and rutile TiO_2 (>99%, Linghua Co. Ltd., Zhaoqing, China) were prepared by mixed-oxide method according to the stoichiometrics xBi_2MoO_6–$(1-x)TiO_2$ ($x = 0.06, 0.125, 0.21, 0.33, 0.50, 0.57, 0.65$). The final powders were calcined at a temperature between 700 and 800 °C for 5 h and the cylinder specimens (10 mm in diameter and 5 mm in height) were sintered in air at temperatures between 800 and 900 °C for 3 h.

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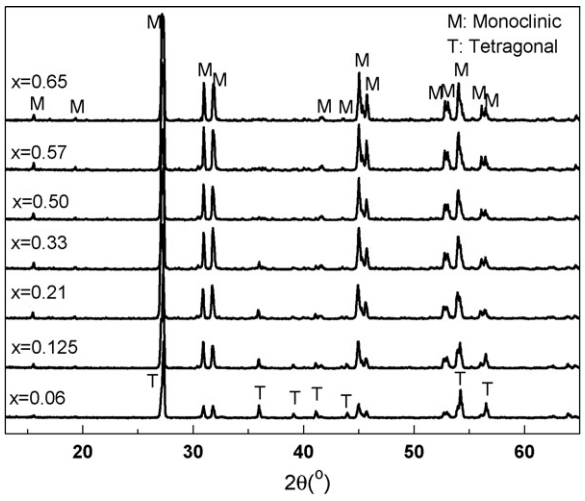

Fig. 1. X-ray diffraction patterns of $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ compounds sintered at 850 °C for 3 h. (T: Tetragonal rutile phase; O: Monoclinic Bi_2MoO_6 phase).

The crystalline phases were investigated using X-ray diffraction (XRD) with Cu Kα radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). The microstructures were observed on the fracture surfaces with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan) coupled with energy-dispersive X-ray spectroscopy (EDS). The apparent densities were measured by Archimedes' method. The dielectric properties were measured at microwave frequency by 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). The τ_f value was calculated by the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25}(85-25)} 10^6 \,(\mathrm{ppm/^\circ C}) \quad (1)$$

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

3. Results and discussion

The X-ray diffraction patterns of $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ compounds sintered at 850 °C are shown in Fig. 1. Diffraction peaks of both tetragonal rutile phase and monoclinic Bi_2MoO_6 phase present in the $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ specimens, which means that the Bi_2MoO_6 phase could coexist with rutile TiO_2 phase. With the content of Bi_2MoO_6 increasing in the compound, the intensities of the diffraction peaks of Bi_2MoO_6 phase increased greatly. When x value increased to 0.5, the diffraction peaks of rutile TiO_2 phase could barely be detected because of the low volume fraction of TiO_2 phase.

To investigate the microstructures of the sintered $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ ceramics and to obtain the volume fractions of the Bi_2MoO_6 phase in the compounds, the backscattered electron images of the fractured surfaces of $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ ceramics are shown in Fig. 2. There were two kinds of grains in the ceramic matrixes, the dark ones with smaller grain size and the light ones with bigger grain size. EDS patterns in Fig. 2(h) showed that the dark grains were Ti-rich and in the light grains the amount of Bi was nearly two times of Mo. Associating with the XRD analysis in Fig. 1, it can be concluded that the dark and the light grains were the tetragonal rutile and the monoclinic Bi_2MoO_6 grains, respectively. Because of the great difference in the sintering temperature between pure rutile TiO_2 ceramic [23] and Bi_2MoO_6 ceramic [22], the rutile grains were smaller and with regular shape, and the Bi_2MoO_6 grains were bigger and showed irregular shape. The amount of Bi_2MoO_6 phase increased greatly as the x value increased from 0.06 to 0.500. The volume fractions of Bi_2MoO_6 phase in the ceramic matrixes were obtained from the backscattered electron images in Fig. 2. The measured and the theoretical volume fractions of Bi_2MoO_6 phase are shown in Fig. 3. It shows that the measured volume fractions of Bi_2MoO_6 phase were a little higher than the theoretical values when the content of Bi_2MoO_6 was as high as $x = 0.21$ in the compounds. Combining with the EDS analysis in Fig. 2(h), it is concluded that the Ti element infiltrated slightly into the Bi_2MoO_6 grains and a solid solution with Bi_2MoO_6 phase formed in the compound.

Fig. 4 presents the bulk densities, theoretical densities and relative densities of the $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ composite ceramics sintered at 850 °C for 3 h. The relative densities of all the specimens were above 95%, suggesting that dense ceramics were obtained after sintering at 850 °C.

Table 1 shows the theoretical and the measured microwave dielectric properties of the $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ composite ceramics. The theoretical permittivity (ε_r) of the composite ceramic was obtained from the well-known Lichtenecker empirical logarithmic rule [26],

$$lg\varepsilon = y_1\, lg\varepsilon_1 + y_2\, lg\varepsilon_2 \quad (2)$$

where y_1 and y_2 are the volume fractions; ε_1 and ε_2 are the permittivities of the Bi_2MoO_6 ceramic and the rutile TiO_2 ceramic respectively. It is seen from Table 1 that the measured permittivity of the $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ composite ceramic agreed well with the theoretical value. It decreased linearly from 77.5 to 35.5 as the x value increased from 0.06 to 0.65. The Qf values of the $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ compounds were in the range between 14,500 and 16,800 GHz. As well known, microwave dielectric loss includes two parts: intrinsic loss and extrinsic loss. Intrinsic losses were caused by absorptions of phonon oscillation and extrinsic losses were caused by lattice defects (impurity, cavity, substitution, grain boundaries, size and shapes of grains, second phase, pores, etc.) [27,28]. In the $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ composite ceramics, the influence from the intrinsic factors might be shielded by the extrinsic ones. As a result it shows no direct relation between the Qf value and the composition.

Table 1
Microwave dielectric properties of $x$$Bi_2MoO_6$–$(1-x)$$TiO_2$ composite ceramics.

Compounds	ε_r (theo.)	ε_r (meas.)	Qf (GHz)	τ_f (theo.) (ppm/°C)	τ_f (meas.) (ppm/°C)
$x = 0.0$ *[20]*		105	46,000	–	+465
$x = 0.06$	81.8	78 ± 1.0	15,000 ± 500	+347.5	+348.1 ± 7.0
$x = 0.125$	65.6	65.0 ± 0.7	16,818 ± 100	+243.9	+314.5 ± 6.0
$x = 0.21$	53.9	54.5 ± 0.5	16,350 ± 100	+151.7	+207.3 ± 4.5
$x = 0.33$	45.2	46.2 ± 0.6	14,500 ± 300	+69.2	+87.8 ± 3.0
$x = 0.50$	38.6	38.5 ± 0.9	15,020 ± 100	−5.1	+47.5 ± 2.5
$x = 0.57$	36.7	36.7 ± 0.9	16,800 ± 200	−28.3	−0.0 ± 1.0
$x = 0.65$	35.0	35.5 ± 0.5	15,034 ± 300	−50.7	−37.8 ± 1.5
$x = 1.0$ *[19]*		31	1,6700	–	−114

ε_r (theo.): theoretical permittivity; ε_r (meas.): measured permittivity.
τ_f (theo.): theoretical τ_f value; τ_f (meas.): measured τ_f value.

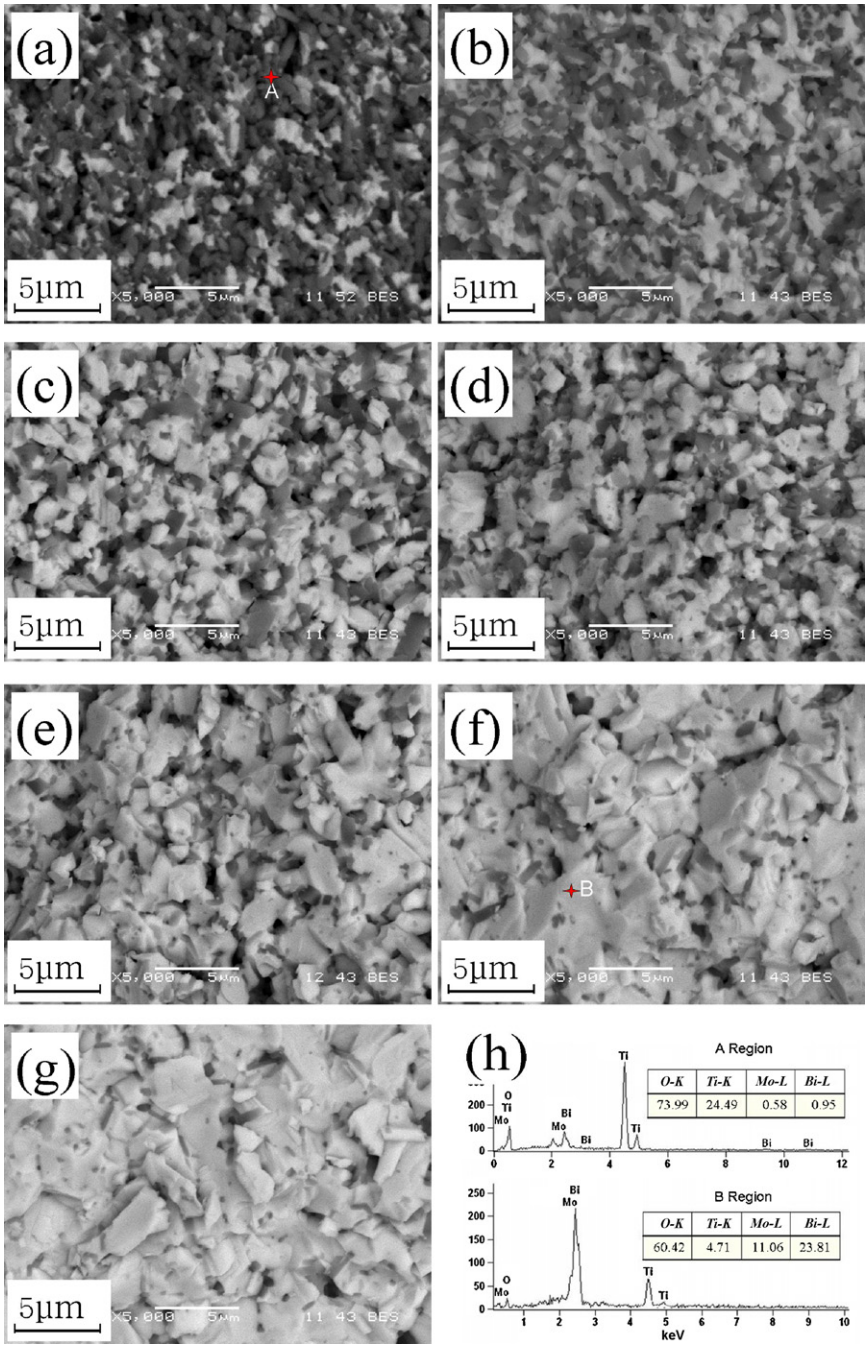

Fig. 2. Backscattered electron images and EDS analysis of the fracture surfaces of xBi$_2$MoO$_6$–$(1-x)$TiO$_2$ ceramics sintered at 850 °C for 3 h: (a) $x = 0.06$, (b) $x = 0.125$, (c) $x = 0.21$, (d) $x = 0.33$, (e) $x = 0.50$, (f) $x = 0.57$, (g) $x = 0.65$, (h) EDS pattern.

The mixing rule of τ_f value could be obtained from the Lichtenecker empirical logarithmic rule of function (2). As being well known, the relationship between temperature coefficient of permittivity (τ_ε) and τ_f is,

$$\tau_f = -\left(\frac{1}{2}\tau_\varepsilon + \alpha_L\right) \quad (3)$$

where α_L is the linear thermal-expansion coefficient. The τ_ε is defined as the following:

$$\tau_\varepsilon = \frac{1}{\varepsilon_r}\frac{d\varepsilon_r}{dT} = \frac{d(lg\varepsilon_r)}{dT} = y_1\frac{1}{\varepsilon_1}\frac{d\varepsilon_1}{dT} + y_2\frac{1}{\varepsilon_2}\frac{d\varepsilon_2}{dT} = y_1\tau_{\varepsilon 1} + y_2\tau_{\varepsilon 2} \quad (4)$$

where $\tau_{\varepsilon 1}$ and $\tau_{\varepsilon 2}$ are the τ_ε values of the Bi$_2$MoO$_6$ phase and the rutile TiO$_2$ phase, respectively. Thus, the mixing rule of τ_f value could be described like this:

$$\tau_f = y_1\tau_{f1} + y_2\tau_{f2} \quad (5)$$

where τ_{f1} and τ_{f2} are the τ_f values of the Bi$_2$MoO$_6$ phase and the rutile TiO$_2$ phase, respectively. The theoretical τ_f values of the xBi$_2$MoO$_6$–$(1-x)$TiO$_2$ composite ceramics were calculated using the function (5) and the results were listed in Table 1. Comparing the measured τ_f with the theoretical value, it is seen that the measured τ_f was a little more positive, which might result from the element diffusion in the xBi$_2$MoO$_6$–$(1-x)$TiO$_2$ compounds. The τ_f value of the composite ceramic was tailored to near zero when $x = 0.57$.

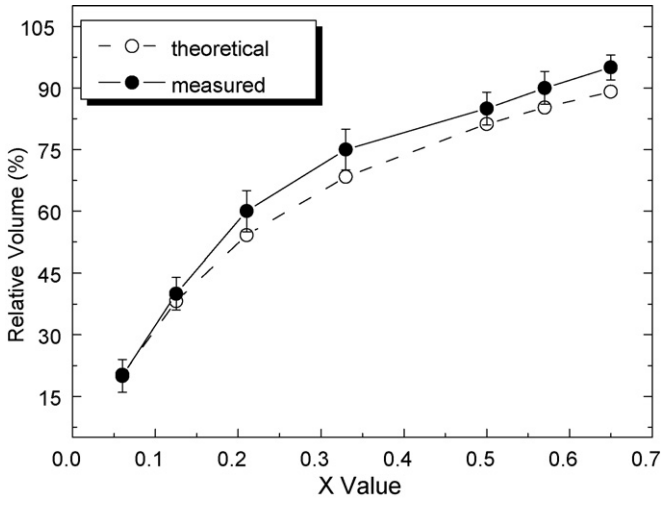

Fig. 3. Theoretical and measured volume fractions of Bi_2MoO_6 phase in the ceramic matrix vs x value.

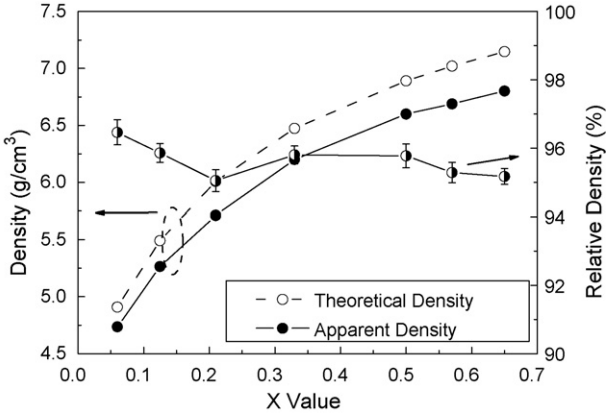

Fig. 4. Densities of xBi_2MoO_6–$(1-x)TiO_2$ composite ceramics sintered at 850 °C for 3 h

4. Conclusions

The xBi_2MoO_6–$(1-x)TiO_2$ composite ceramics were prepared by conventional solid state reaction method. All the ceramics could be well sintered at 850 °C for 3 h. Tetragonal rutile phase and monoclinic Bi_2MoO_6 phase coexisted in the ceramics in the range from 0.06 to 0.65. In the Bi_2MoO_6-rich side of the compounds, Ti element diffused slightly into the Bi_2MoO_6 grains and a solid solution with Bi_2MoO_6 phase was formed in the compound. As the x value increased from 0.06 to 0.65, the permittivity changed from 77.5 to 33.5 and the τ_f value shifted from +348.1 to −37.8 ppm/°C. The temperature stable microwave dielectric ceramic was obtained when $x = 0.57$ in the xBi_2MoO_6–$(1-x)TiO_2$ system, and it showed excellent dielectric properties of $\varepsilon_r = 36.7$, Qf = 16,800 GHz and $\tau_f = 0$ ppm/°C.

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