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Microwave Dielectric Properties of Low Temperature Firing $Bi_2Mo_2O_9$ Ceramic

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Preparation, phase stability, sintering behavior, microwave dielectric properties of single-phase $Bi_2Mo_2O_9$ ceramic and its chemical compatibility with Ag have been investigated. The single-phase $Bi_2Mo_2O_9$ ceramic can be well densified in the temperature range from 620° to 645°C with relative density about 96%. X-ray diffraction data show that $Bi_2Mo_2O_9$ has a monoclinic structure ($P2_1/n$), with lattice parameters $a = 11.9664$ Å, $b = 10.8089$ Å, and $c = 11.8871$ Å. When sintering temperature $\geq 650°C$, $Bi_2Mo_3O_{12}$ appears as a secondary phase. Pure monoclinic $Bi_2Mo_2O_9$ ceramic sintered at 620°C for 2 h exhibits good microwave dielectric properties with permittivity about 38, Q_f value about 12 500 GHz and temperature coefficient of resonant frequency about +31ppm/°C. The permittivity of single-phase $Bi_2Mo_2O_9$ corrected for porosity is about 40.17. However, the reaction between $Bi_2Mo_2O_9$ and Ag will affect its further application in low-temperature cofired ceramic.

I. Introduction

Rapid development in wireless communication systems has increased demand for the miniaturization of components such as band pass filters and local oscillators. Low-temperature cofired ceramic (LTCC) technology offers significant benefits over other established packaging technologies for high density, high RF, and fast digital applications requiring hermetical packaging and good thermal management.[1,2] Microwave dielectric materials with low sintering temperature, high dielectric constant ε_r, low dielectric loss, and near-zero temperature coefficient of resonant frequency TCF are needed to cofire with low loss, low-melting-point conductors such as Ag, Cu, Au, or Al.

Many materials with good microwave dielectric properties have high sintering temperature (above 1000°C) such as $ZnO–Nb_2O_5$ system,[3,4] $Bi(Nb,Ta,Sb)O_4$,[5–7] $BaO–TiO_2–Nb_2O_5$ system,[8,9] $Li_2O–Nb_2O_5–TiO_2$ system,[10,11] $(Zr,Sn)TiO_4$,[12,13] and $(A_1A_2)(B_1B_2)O_3$ complex perovskite system.[14–16] To lower the sintering temperature, addition or substitution of some sintering aids, such as V_2O_5, CuO, Bi_2O_3, and B_2O_3, are a often used method. Another approach has been devoted to the use of glass–ceramic composites. However, most glasses are known to exhibit low permittivity, which makes them parasitic phases in high-permittivity ceramics. Recently, much attention has been attracted by a third method, which is based on many low-temperature firing ceramic compounds such as the $Bi_2O_3–TeO_2$, $TiO_2–TeO_2$, $CaO–TeO_2$, $BaO–TeO_2$ binary systems, $BaO–TiO_2–TeO_2$ ternary system and $Bi_2W_2O_9$ systems.[17–23] TeO_2-rich compounds show relatively low sintering temperatures between 500° and 800°C. However, they react with Ag electrode. This problem was recently overcome for $BaTe_4O_9$ through the use of Al electrodes.[22] However, TeO_2 is rather expensive and it is poisonous. Recently Feteira and Sinclair[23] had found that a single phase of $Bi_2W_2O_9$, which could be formed and sintered below 885°C without any sintering aid addition, exhibited good microwave dielectric properties with dielectric constant ε_r lying between 28 and 41, $Q \times f$ between 3900 and 8000 GHz and temperature coefficient TCF between −42 to −63 ppm/°C. The chemical compatibility of $Bi_2W_2O_9$ with Au made it possible for application in LTCC technology.[23,24]

The phase diagram and compounds of the $Bi_2O_3–MoO_3$ system have been studied by many researchers. Belyaev and Bleijenberg *et al.*[25,26] reported two congruently melting compounds, $Bi_2O_3–3MoO_3(\alpha)$ and $Bi_2O_3–MoO_3(\gamma)$, in the region 0–50 mol% Bi_2O_3. Erman *et al.*[27–29] found some other compounds, $Bi_2O_3–2MoO_3(\beta)$ (not a congruently melting compound) and (ε) phase having solid solubility with a composition of $xBi_2O_3–MoO_3$ ($1.3 < \times < 1.4$). $7Bi_2O_3–MoO_3$, $3Bi_2O_3–MoO_3$, low and high temperature forms of $3Bi_2O_3–2MoO_3$ were also identified by X-ray diffraction (XRD) results as reported by Egashira *et al.*[29] in Bi_2O_3-rich region. The MoO_3 rich region in $Bi_2O_3–MoO_3$ system showed very low reaction temperature and low melting temperature below 700°C. This system constitutes some potential compounds for LTCC applications. However, the microwave dielectric properties of this system have not been reported.

Monoclinic phase of $Bi_2Mo_2O_9$, which belongs to space group $P2_1/n$,[30] attracts our attention because of its easy preparation and empty report of dielectric characterization. In the present work the synthesis, phase evolution, microstructure and microwave dielectric properties of $Bi_2Mo_2O_9$ ceramic have been investigated. The chemical compatibility of $Bi_2Mo_2O_9$ with Ag has also been discussed.

II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., Chengdu, China) and MoO_3 (>99%, Fuchen Chemical Reagents, Tianjin, China) were prepared according to $Bi_2Mo_2O_9$ 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 zirconia balls (2 mm in diameter) as milling media. Differential scanning calorimetry (DSC) and thermogravimetry analysis of mixed powders were carried out using a thermoanalyzer system (Netzsch STA-449C, Netzsch, Selb, Germany) with heating rate of 10°C/min. The other mixed oxides were calcined at 600°C for 4 h. After being crushed and remilled for 5 h using ZrO_2 balls and deionized water, powders were pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die under uniaxial pressure of 20 kN/cm^2 with 5 wt% PVA solution binder addition, amount of

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which was about 8 wt% and burnt out at 500°C for 4 h. Green samples were sintered at temperature range from 600° to 655°C for 2 h. To investigate the chemical compatibility of $Bi_2Mo_2O_9$ with Ag, 20 wt% Ag was mixed with $Bi_2Mo_2O_9$ and calcined at 620°C for 4 h.

The crystalline structures of samples were investigated using XRD with Cu$K\alpha$ radiation (Rigaku D/MAX-2400 X-ray diffractometry, Tokyo, Japan). Microstructures of sintered ceramic were observed on the as-fired surface and fractured surface respectively with scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan) The apparent densities of sintered ceramics were measured by Archimedes' method. Dielectric behaviors at microwave frequency were measured 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 (TCF) (τ_f) was calculated by the following formula:

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

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

III. Results and Discussions

The room temperature XRD patterns for $Bi_2Mo_2O_9$ ceramics sintered in temperature range from 635° to 655°C are shown in Fig. 1. When sintering temperature is below 645°C, all peaks can be indexed as a single-phase monoclinic structure ($P2_1/n$). The lattice parameters were calculated as $a = 11.9664$ Å, $b = 10.8089$ Å, and $c = 11.8871$ Å, which agreed well with the results reported by Chen, van den Elzen and *et al.*[30,31] The theoretical density of $Bi_2Mo_2O_9$ ceramics calculated from XRD data was about 6.5 g/cm^3. When sintering temperature increases further, $Bi_2Mo_3O_{12}$ and Bi_2MoO_6 phases appear as the secondary phase in ceramics sintered at temperatures $\geq$ 650°C. Egashira *et al.*[29] also gave the result that after DTA measurement (up to 800°C) pure $Bi_2Mo_2O_9$ would partially decompose to Bi_2MoO_6 and $Bi_2Mo_3O_{12}$ phase. These conclusions are also supported by DSC results as shown in Fig. 2. There is one exothermic peak at about 297°C and three endothermic peaks at 604°, 656° and 692°C in the DSC curve respectively. The first endothermic peaks at 604°C indicates the formation monoclinic $Bi_2Mo_2O_9$ and the one at 656°C indicates the appearance of $Bi_2Mo_3O_{12}$ phase. The last endothermic peaks at 692°C corresponds to the melting of the compound, which is similar to that reported by Chen and Sleight.[28,30]

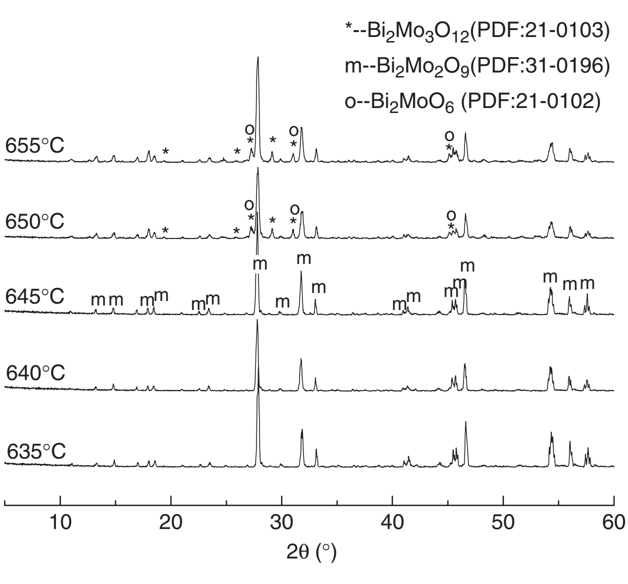

Fig. 1. X-ray diffraction patterns of $Bi_2Mo_2O_9$ ceramics sintered at different temperatures for 2 h (m—monoclinic phase of $Bi_2Mo_2O_9$, *—phase of $Bi_2Mo_3O_{12}$, o—phase of Bi_2MoO_6).

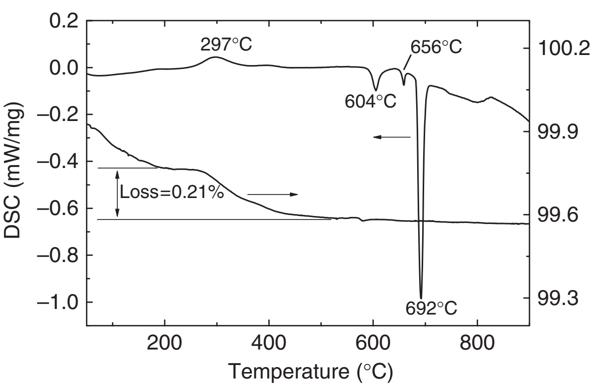

Fig. 2. Differential scanning calorimetry (DSC) and thermogravimetry (TG) analysis of mixed Bi_2O_3–$2MoO_3$ powders.

The apparent density and relative density of $Bi_2Mo_2O_9$ ceramics sintered at different temperatures are shown in Fig. 3. When sintering temperature is above 620°C, ceramics reach a bulk density of about 6.25 g/cm^3, which is equivalent to a relative density of about 96% of the theoretical density. The maximum density is reached at 630°C, and above this temperature a slight decrease is observed, which should be attributed to the Bi volatilization and phase decomposition. The SEM micrographs of the as-fired surface and fractured surface of $Bi_2Mo_2O_9$ ceramics are shown in Fig. 4. Homogeneously fine microstructures with a little pores existing can be revealed for $Bi_2Mo_2O_9$ ceramics sintered at 630°C for 2 h. Grain sizes lie between 2 and 8 μm and no abnormal grains are observed.

Microwave dielectric properties of $Bi_2Mo_2O_9$ ceramics as a function of sintering temperature are shown in Fig. 5. Microwave permittivity increases from about 25 to about 38 as sintering temperature increases from 600° to 620°C. Then permittivity reaches saturated and maintains stable, which does not change as temperature increases. To eliminate the influence of pores on the permittivity of ceramics, the following equation is used:

$$\varepsilon_r = \varepsilon^{meas} \times (1 + 1.5P) \quad (2)$$

where P is porosity.[32] The calculated permittivity eliminating influence of pores is about 40.17. $Q \times f$ value has the similar trend with permittivity. When sintering temperature increases to 620°C, $Q \times f$ value gets a stable maximum about 12 500 GHz. TCF value of $Bi_2Mo_2O_9$ ceramics is also not sensitive to sintering temperature and stabilizes about +31ppm/°C as shown in Fig. 5. In conclusion, $Bi_2Mo_2O_9$ ceramic sintered at 620°C for

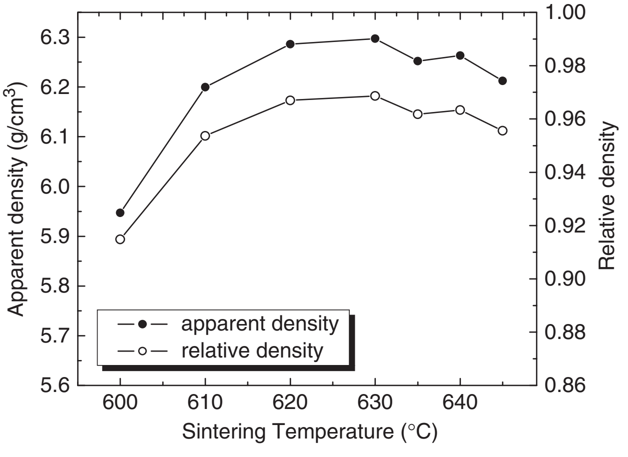

Fig. 3. Apparent density and relative density of $Bi_2Mo_2O_9$ ceramics sintered at different temperatures.

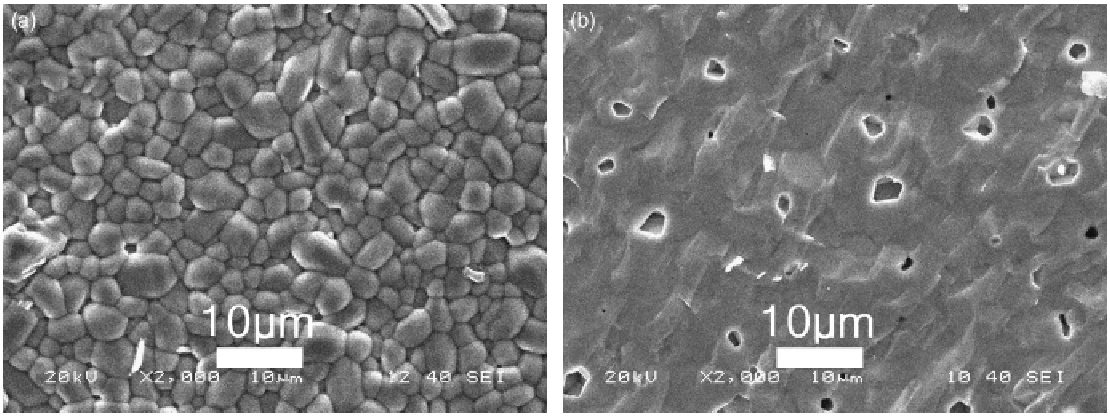

Fig. 4. Scanning electron microscopy micrographs of as-fired surface (a) and fractured surface (b) of $Bi_2Mo_2O_9$ ceramics sintered at 630°C for 2 h.

2 h exhibits good microwave dielectric properties with permittivity about 38, $Q \times f$ value about 12 500 GHz and TCF about +31ppm/°C. The possible application of $Bi_2Mo_2O_9$ ceramics in microwave circuit is worth of consideration due to its low sintering temperature (about 620°C) and attractive dielectric properties. Nevertheless, to apply $Bi_2Mo_2O_9$ ceramics in LTCC technology, it must have chemical compatibility with some metal electrodes, such as Ag, Cu, Au, and Al etc. In present work we find that $Bi_2Mo_2O_9$ are easy to react with Ag to form a new phase of $AgBi(MoO_4)_2$ and other phases containing Ag and Mo. This will limit the further application of $Bi_2Mo_2O_9$ ceramics. The several systems of microwave dielectric ceramics with low sintering temperature, such as Bi_2O_3–TeO_2, TiO_2–TeO_2, CaO–TeO_2, BaO–TeO_2 and etc TeO_2-based ceramics, all seem to be easy to react with Ag[17–23] because of the easy formation of Ag_6TeO_6, Ag_2TeO_3, and $Ag_3Te_2O_7$ phases.[33] Because of the limitation of our laboratory, the experiments on the chemical compatibility of $Bi_2Mo_2O_9$ ceramics with Cu, Au, and Al have not been carried out.

IV. Conclusions

Dense ceramics of single monoclinic phase of $Bi_2Mo_2O_9$ can be well sintered in the temperature range from 620° to 645°C with relative density about 96%. A secondary phase of $Bi_2Mo_3O_{12}$ will appear in ceramics when sintering temperature $\geq$ 650°C. Pure monoclinic $Bi_2Mo_2O_9$ ceramic sintered at 620°C for 2 h exhibits good microwave dielectric properties with permittivity about 38, $Q \times f$ value about 12 500 GHz and TCF about +31ppm/°C. The permittivity of single-phase $Bi_2Mo_2O_9$ corrected for porosity is about 40.17. Although $Bi_2Mo_2O_9$ ceramic has good microwave dielectric properties and very low firing temperature, the reactive between it and Ag will affect its commercial application in LTCC.

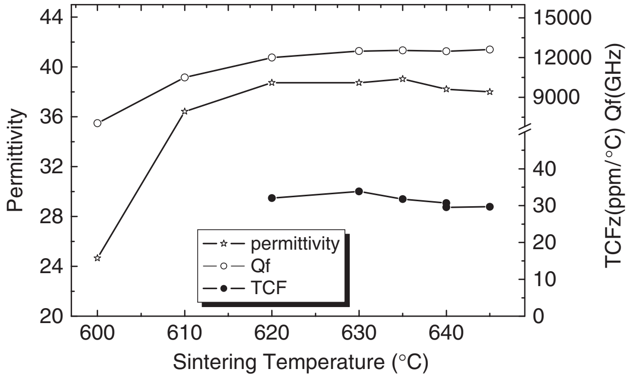

Fig. 5. Microwave dielectric constant, $Q \times f$ values and temperature coefficient of resonant frequency of $Bi_2Mo_2O_9$ ceramic as a function of sintering temperature.

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