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Dielectric Properties of an Ultra-Low-Temperature Cofiring Bi$_2$Mo$_2$O$_9$ Multilayer

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A Bi$_2$Mo$_2$O$_9$ multilayer ceramic capacitor structure was fabricated in a thick-film process involving tape casting and screen-printing forming techniques. A novel base metal, Al, was used as the internal electrode, and these dielectrics were co-sintered at 645°C in air. Scanning electron microscopy and energy dispersive spectroscopy (EDS) were used to investigate the local chemical compatibility between the electrode layer and ceramic layer, and no reaction or interdiffusion was found. Dielectric properties of electroded monolithic ceramic, multilayer, and monolayer samples at 100 Hz–10 MHz in a temperature range of −55°–+175°C were measured; values of the dielectric properties were similar to bulk measurements consistent with the absence of any interfacial reaction. Collectively, the data show that it is possible to use the low-temperature firing Bi$_2$Mo$_2$O$_9$ ceramic and Al internal electrode for an ultra-low-temperature cofired ceramic technology.

I. Introduction

To meet the requirement of miniaturization and integration, low-temperature cofired ceramic technology (LTCC) has played an important role in integrating the passive components within a monolithic bulk module with IC chips mounted on its surface. Dielectric layers with different function can be stacked into multilayer and cofired with internal electrodes, such as Ag, Cu, Au, their alloys, etc., by LTCC technology. LTCC packaging enables the front end receiver of modern low-profile cellular phones, such as the iPhone, to be realized.[1,2]

To cofire with internal electrodes, the dielectrics should have a lower sintering temperature than the melting temperature of electrodes and also be chemically compatible with electrodes. Recently, a series of TeO$_2$-rich compounds have been found to possess an ultra-low sintering temperature and good microwave dielectric properties.[3–10] Among them, BaTe$_4$O$_9$ has the lowest sintering temperature of 550°C, and it can be cofired with Al electrodes.[9] However, the expensive price and toxicity of TeO$_2$ limit its application. Recently, a promising replacement of TeO$_2$ system has been explored in the Bi$_2$O$_3$–MoO$_3$ binary system.[11,12] The Bi$_2$Mo$_2$O$_9$ ceramic, sintered at around 620°C, was found to have a permittivity of ~38, a *Qf* value of ~12 500 GHz, and a temperature coefficient of resonant frequency (TCF) of ~+31 ppm/°C.[11,12]

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To explore its application in passive component devices, it is necessary to study its dielectric properties in the MLCC form. In this study, a conventional tape-casting method is used to prepare a green tape of Bi$_2$Mo$_2$O$_9$. Al thick-film paste was chosen as the internal electrode and screen-printed on the Bi$_2$Mo$_2$O$_9$ tape. Warm isostatic pressing was applied to laminate the green tape into multilayer capacitors. Frequency dependence, temperature dependence, and higher field polarization-field behavior of the monolithic, multilayer, and monolayer samples were investigated.

II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of Bi$_2$O$_3$ (99.9%, MCP Inc., Lübeck, Germany) and MoO$_3$ (99.5%, Alfa Aesar, Ward Hill, MA) were prepared according to the stoichiometric formulation Bi$_2$Mo$_2$O$_9$. Powders were mixed and ball-milled with stabilized zirconia media (TOSOH Ceramics, Tosoh USA Inc., Grove City, OH) for 24 h. The powder mixture was then calcined at 600°C for 4 h. The calcined powders were vibratory milled for 24 h to obtain fine powders for tape-casting use. To obtain a fine slurry, the milled Bi$_2$Mo$_2$O$_9$ powders (56wt%) were added into a solution of methyl ethyl ketone (19wt%), ethanol (19wt%), and Polyvinyl Butyral (PVB, 6wt%) mixture and ball-milled for 24 h. Tape casting was performed on a laboratory-type tape-casting machine with a doctor blade casting head, using 75-μm-thick silicone-coated mylar (polyethylene terephthalate) as a carrier film. The casting speed was set as 420 cm/min. The cast slurries were dried at room temperature without additional air flow. The green tapes were cut into square samples of 1-inch in length. The basic multilayer cofired capacitor (MLCC) fabrication process is shown in Fig. 1. Three layers of Bi$_2$Mo$_2$O$_9$ green tapes were stacked and laminated using a uniaxial hot press at 60°C to achieve a single thick dielectric layer. A commercial aluminum ink (#2591-E, ESL Inc., ESL ElectroScience, King of Prussia, PA), which has been designed for the back surface of silicon solar cells, was screen printed on the top of the dielectric layer with a thickness of
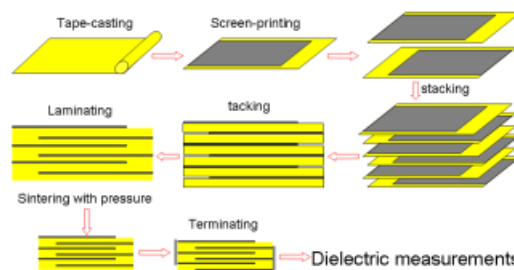

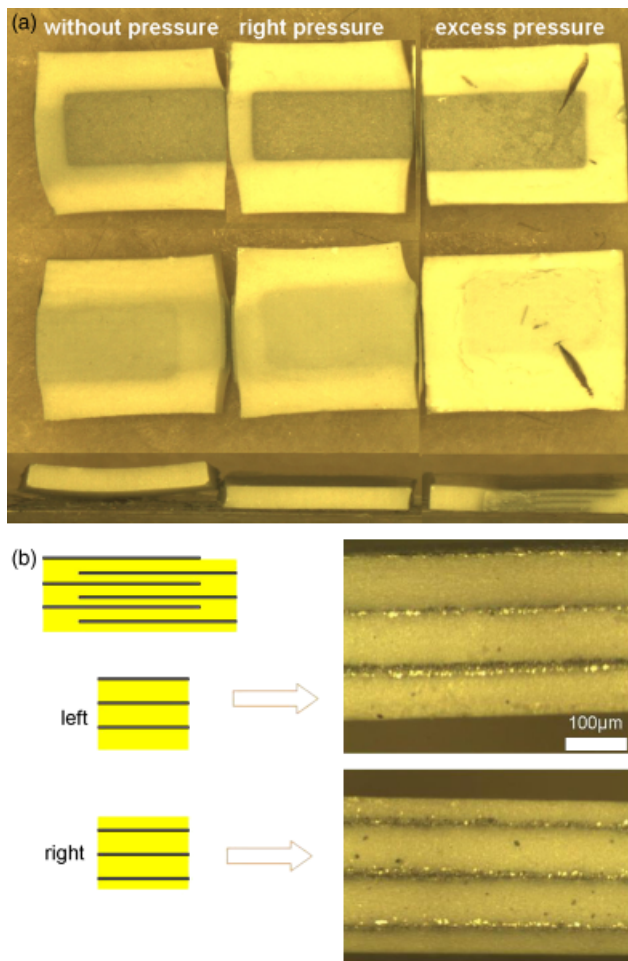**Fig. 1.** Flow chart of the preparation of Bi$_2$Mo$_2$O$_9$ MLCC samples.

Fig. 2. Photos of MLCC sample sintered without pressure, with a proper pressure, and with an excess pressure (a), and optical photos of termination profiles of MLCC sample (b).

around 15 μm. Six screen-printed layers were stacked and laminated to form MLCCs. The multilayer capacitors were sintered at a very low temperature of 640°–645°C, with proper pressure on the top to prevent warpage. Then, the sintered MLCC and monolayer samples were terminated using air-dry silver ink. The monolayer samples were prepared by the same method, with a green tape thickness of about 60 μm. Besides the active layer, one top and bottom cover layer were added to provide sufficient thickness for electrode termination and measurement. The monolithic bulk sample was formed with a dry pressing of the powder, and after sintering in the same conditions as the MLCC's, was polished to 0.4 mm and sputtered Pt on the surface to provide a simple, parallel plate capacitor structure.

The room-temperature dielectric constant and dielectric loss of the MLCC and monolithic $Bi_2Mo_2O_9$ samples were measured using an HP 4294 (Hewlett-Packard, Palo Alto, CA) in the frequency range 40 Hz–10 MHz. The temperature dependence of the dielectric permittivity and the loss of the monolithic and monolayer $Bi_2Mo_2O_9$ samples were determined at the frequency of 1 MHz, using an HP 4284 LCR meter (Hewlett-Packard) with a programmable 9023 Delta Design oven (Delta Design, San Diego, CA) in the temperature range of −55°–175°C. The high-field polarization–electric field loops were recorded with a modified Sawyer–Tower circuit. All samples were subjected to two successive triangle waves, with a frequency of 20 Hz.

III. Results and Discussions

Optical microscope photomicrographs of MLCC samples sintered with different pressures are shown in Fig. 2. As the aluminum ink used in this experiment was designed for a postfiring process on silicon wafers for solar cells, the shrinkage of the ink during the firing was much smaller than that of the $Bi_2Mo_2O_9$ ceramic tape. As seen in Fig. 2(a), although there is no delamination observed, warping is very serious in MLCC samples sintered without the application of pressure. To minimize the warpage of the $Bi_2Mo_2O_9$–Aluminum MLCCs in this study, an external force was applied during the sintering course. When the internal pressure within the MLCC was too large, the local compressive stresses in the samples caused cracks during the sintering course, as shown for the right sample in Fig. 2(a). Only when the proper pressure was applied could the warpage be successfully limited, as shown in the middle sample in Fig. 2. The optical photos of cross sections of MLCC sample sintered at 645°C for 10 min are shown in Fig. 2(b). After sintering, the thickness of the $Bi_2Mo_2O_9$ tape and aluminum electrode layer shrank from 120 and 15 μm to around 90 and 12 μm, respectively.

The scanning electron microscopic micrographs of the cross sections and the characteristic X-ray chemical energy dispersive
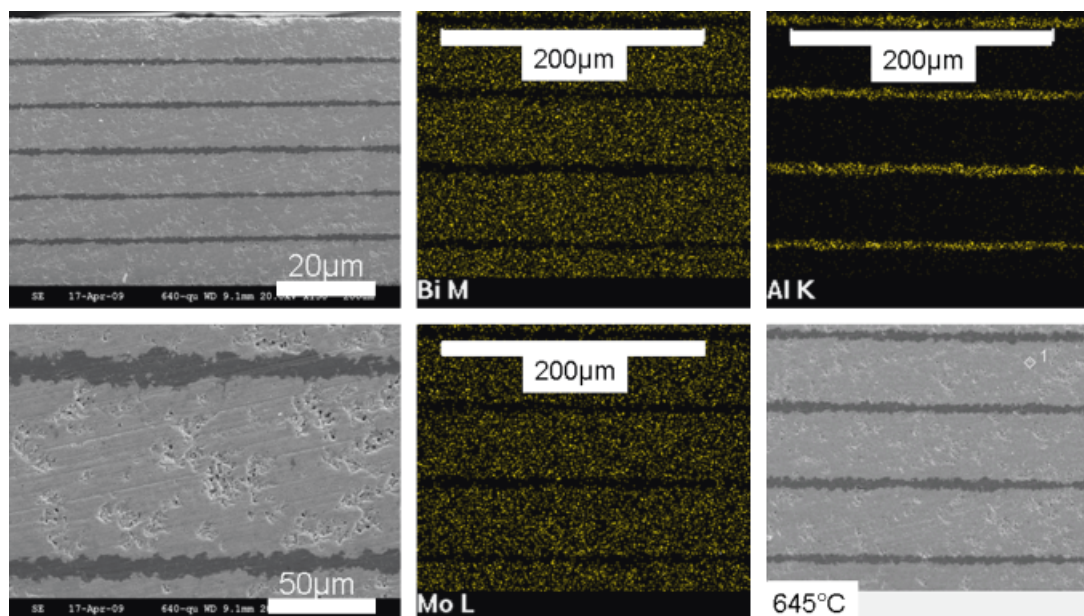

Fig. 3. Scanning electron microscopic photos and the X-ray maps of the polished surface of $Bi_2Mo_2O_9$ MLCC samples sintered at 645°C for 10 min.
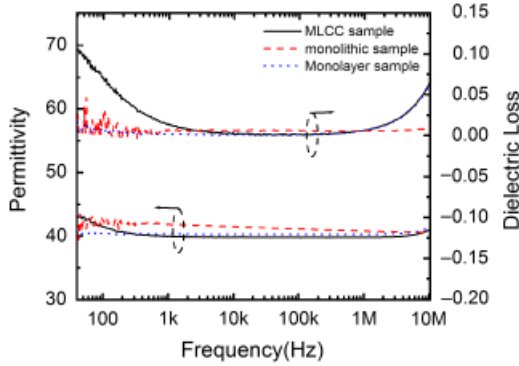
Fig. 4. Comparison of dielectric spectroscopy of MLCC, monolithic, and monolayer Bi$_2$Mo$_2$O$_9$ samples.

Fig. 5. Dielectric constant and dielectric loss of monolithic Bi$_2$Mo$_2$O$_9$ sample (a) and monolayer Bi$_2$Mo$_2$O$_9$ sample (b) as a function of temperature.

spectroscopy (EDS) maps of the polished surfaces of Bi$_2$Mo$_2$O$_9$ MLCC samples sintered at 645°C for 10 min are shown in Fig. 3. A dense and homogeneous microstructure was observed. As reported in our previous study, aluminum powder does not react with Bi$_2$Mo$_2$O$_9$ ceramic at around 645°C. From the results of our previous work[12] and the conductivity measurement of surface Al electrode, we found that the Al electrode was not oxidized to Al$_2$O$_3$. With energy-dispersive X-ray analysis (EDS) of the ceramic/metal interface, no reaction boundary layer was detected in between Bi$_2$Mo$_2$O$_9$ and the aluminum electrode. There is also no interdiffusion from the ceramic to the electrode, or from the electrode to the ceramic, observed in the EDS results. This result confirms the chemical compatibility between Bi$_2$Mo$_2$O$_9$ and the aluminum electrode in the MLCCs. In a previous work, the Bi$_2$Mo$_2$O$_9$ ceramic could be sintered well at around 630°C for 2 h. In contrast, the thick-film form of Bi$_2$Mo$_2$O$_9$ could be well densified at 645°C for 10 min with minimal pores.

To compare the dielectric properties of the cofired MLCC and monolayer samples with monolithic ceramic samples sputtered with platinum electrodes, samples were measured in the frequency range of 40 Hz–10 MHz using HP 4294, as shown in Fig. 4. The permittivities of these three different kinds of samples all stabilize at around 39, and the dielectric losses are near 0.001 below 1 MHz. The temperature dependence of the dielectric properties of monolithic ceramic samples and cofired monolayer samples in the temperature range of −55°–175°C are shown in Fig. 5. At 100 Hz, 1, and 10 kHz, both the relative permittivity and dielectric loss increase sharply when the temperature is above 100°C. At 100 kHz and 1 MHz, the temperature dependence of dielectric properties becomes more stable. This indicates that there are more dielectric polarizations that could be activated by the high temperature at a low frequency in Bi$_2$Mo$_2$O$_9$ sample than at a high frequency. The temperature coefficient of relative permittivity is defined as follows:

$$\text{TCC}(\tau_\varepsilon) = \frac{\varepsilon_r(+155°\text{C}) - \varepsilon_r(-55°\text{C})}{\varepsilon_r(-55°\text{C})(155 + 55)} 10^{-6} \text{ppm}/°\text{C} \qquad (1)$$

For the monolithic samples, the TCC value is −84.1 ppm/°C at 100 kHz and 1 MHz. The temperature coefficient of resonant frequency (TCF, 25°–125°C) is +31 ppm/°C at 6 GHz. The TCC and TCF values approximately follow the minus two times rule. The P–E loops of monolithic and monolayer Bi$_2$Mo$_2$O$_9$ samples measured at 20 Hz are shown in Fig. 6. For the monolithic samples, the P–E loop is almost linear. The thickness of the monolithic sample was 0.4 mm, and it was electrically broken down at 16 kV/mm. The thickness of the monolayer sample is 46 μm, and it was electrically broken down at 67 kV/mm. The energy density is defined as following:

$$\text{Energy density} = \tfrac{1}{2}\varepsilon_0\varepsilon_r E^2 \qquad (2)$$

The energy density at room temperature for the monolayer sample is about 0.75 J/cm^3 at 67 kV/mm, which is comparable
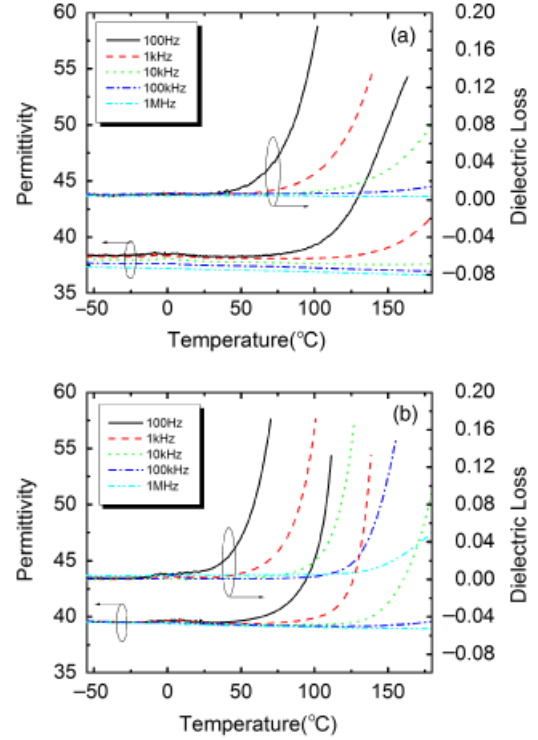
with COG capacitors with similar thicknesses. It is interesting that, although these dielectrics are low melting, they can withstand high fields without significant increase in dielectric loss.

IV. Conclusions

Multilayer Bi$_2$Mo$_2$O$_9$ cofired with Al internal electrodes were prepared by the conventional thick-film methods. Multilayer (three active layers) and monolayer samples sintered at 645°C have dense microstructure and thicknesses of 90 and 46 μm, respectively. There is no observation of reaction or interdiffusion between electrode layer and ceramic layers. The relative permittivities of multilayer, monolayer, and monolithic Bi$_2$Mo$_2$O$_9$ samples all stabilize at around 39, and the dielectric losses are near 0.001 at 1 MHz. Temperature dependence is similar for both monolayer and monolithic Bi$_2$Mo$_2$O$_9$ samples. Energy density of the monolayer Bi$_2$Mo$_2$O$_9$ sample reaches 0.75 J/cm^3 at 67 kV/mm with a thickness of 46 μm. This study extends the

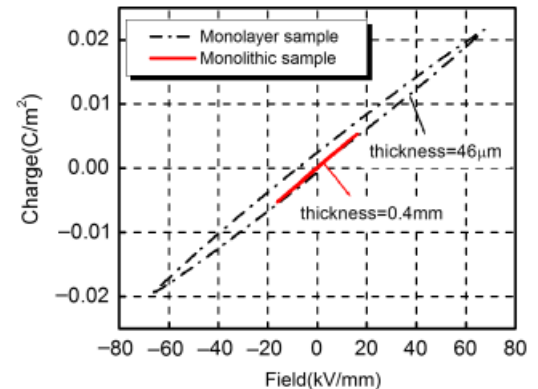**Fig. 6.** The P–E loops of monolithic and monolayer Bi$_2$Mo$_2$O$_9$ sample.

application of the ultra-low-temperature firing $Bi_2Mo_2O_9$ with Al electrodes.

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