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Microwave Dielectric Properties of Scheelite Structured $PbMoO_4$ Ceramic with Ultralow Sintering Temperature

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In this work, a low-firing microwave dielectric ceramic $PbMoO_4$ with tetragonal structure was prepared via a solid-state reaction method. The sintering temperature ranges from 570°C to 670°C. Ceramic samples with relative densities above 97% were obtained when sintering temperature was around 600°C. The best microwave dielectric properties were obtained in the ceramic sintered at 650°C for 2 h with a permittivity ~26.7, a $Q \times f$ value about 42 830 GHz (at 6.2 GHz) and a temperature coefficient value of 6.2 ppm/°C. From the X-ray diffraction, backscattered electron imaging results of the cofired sample with 30 wt% silver and aluminum additive, the $PbMoO_4$ ceramic was found not to react with Ag and Al at 630°C. The microwave dielectric properties and low sintering temperature of $PbMoO_4$ ceramic make it a candidate for low-temperature cofired ceramic applications.

I. Introduction

Molybdates and tungstate-based oxides constitute an important class of materials that exhibit various functional properties, especially the metal molybdates, which have been received special attention due to their novel and interesting properties for widespread technological applications. As one member of the scheelite-type family of molybdates, tetragonal structured $PbMoO_4$ single crystal has attracted considerable attention because it was used as acousto-optic light detectors and modulators.[1–4] In addition, in recent years, $PbMoO_4$ has been found to present excellent optical and chemical properties due to its electronic structure and relatively low band gap energy as compared with the others scheelite structures. Bi *et al.* demonstrated that $PbMoO_4$ particles possess excellent photocatalytic activities for the degradation of organic compounds under UV light irradiation.[5] Unfortunately, the preparation, sintering behavior, and the microwave dielectric properties of $PbMoO_4$ ceramic were rarely reported.

To cofire with internal electrodes, such as Ag, Cu, Au, and Al, the dielectrics are required to possess lower sintering temperatures than the melting points of electrodes and also be chemically compatible with electrodes. In the past decades, hundreds of microwave dielectric materials have been reported,[6–15] but with high sintering temperatures. Hence, the decrease in sintering temperature is still a key problem in the application of low-temperature cofired ceramics (LTCC) technology. Recently, a series of Bi_2O_3-rich compounds, MoO_3-rich compounds have been found to possess ultralow sintering temperatures and good microwave dielectric properties. Among them several researchers have reported the microwave dielectric properties of AWO_4 and $AMoO_4$ (A = Ba, Mg, Mn, Zn, Ca, Sr) ceramics with high $Q \times f$ values (37 000–90 000 GHz).[16,17] However, all the $AMoO_4$ ceramics possess low permittivity,[7–11] negative TCF values (−57 to −87 ppm/°C),[18,19] and higher sintering temperatures than the melting point of aluminum (660°C). In fact, the scheelite structure with the general formula ABO_4 is quite adaptable and this provides the possibility to study the structure–property relation and design new materials with specific properties. As reported by Shannon,[20] Pb^{2+} has a larger ionic polarization (6.58 Å^3) than that of Bi^{3+} (6.12 Å^3), Meanwhile, the PbO has a lower melting point below 900°C. Hence, the Pb-rich compounds might possess both low sintering temperature and large microwave dielectric permittivity. In this work, the $PbMoO_4$ ceramic was prepared via the solid-state reaction method. The sintering behavior, microstructure, microwave dielectric properties, and chemical compatibility with Ag and Al were studied in detail.

II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of PbO (>99%; Guo-Yao Co. Ltd., Shanghai, China) and MoO_3 (>99%; Yutong Chemical Reagents, Tianjin, China) were mixed and milled for 4 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) operating at a running speed of 450 rpm with zirconia balls (2 mm in diameter) used as milling media and then calcined at 500°C for 4 h. After being crushed and remilled for 5 h to increase reactivity and better homogeneity, then dried powders were mixed with PVA binder and granulated, and then these powders were pressed into cylinders (12 mm in diameter and 4–6 mm in height) in a steel die under a uniaxial pressure of 150 MPa. Samples were sintered in the temperature ranges from 570°C to 670°C for 2 h. To investigate the chemical compatibility of $PbMoO_4$ compound with Ag and Al powders, 30 wt% Ag and 30 wt% Al were mixed with the compound and cofired at the 630°C for 4 h.

The crystalline structures of samples were investigated using X-ray diffraction (XRD) with CuK_α radiation (Rigaku D/MAX-2400 X-ray diffractometer; Tokyo, Japan). Microstructures of sintered ceramic were observed on the fracture surface with scanning electron microscopy (SEM) (JSM-6460; JEOL, Tokyo, Japan). The apparent densities of sintered ceramics were measured by Archimedes method. Microwave dielectric behaviors were measured with the $TE_{01\delta}$ shielded cavity method with a network analyzer

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(8720ES; Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023; Delta Design, Poway, CA) in the temperature range 25°C–85°C. The temperature coefficient of resonant frequency (TCF or τ_f value) was calculated with the following formula:

$$TCF = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \times 10^6 (\text{ppm}/^\circ\text{C}) \quad (1)$$

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

III. Results and Discussions

The XRD patterns of $PbMoO_4$ powder sintered at 500°C and cofired ceramic samples are shown in Fig. 1. All the X-ray diffraction peaks of sample calcined at 500°C/4 h can be indexed to a tetragonal scheelite structure. For the cofired ceramic samples, it is noted that only the peaks of $PbMoO_4$ and the respective metals were observed and there are no additional peaks in the XRD patterns to reflect a secondary phase formed, implying that $PbMoO_4$ does not react with either silver or aluminum at the sintering temperature 630°C for 4 h.

The backscattered electron image micrograph of cofired samples with 30 wt% silver and aluminum powders are shown in Fig. 2. From Fig. 2(a), it can be clearly seen that most grains with a gray color belong to the $PbMoO_4$ phase and the very few grains with a light white color are found to be pure silver. Similarly, as shown in Fig. 2(b), the grains with dark color belong to the pure aluminum and the major grains with light color belong to the $PbMoO_4$ phase. Combined with the XRD analysis, all the results indicate that the $PbMoO_4$ ceramic is chemically compatible with both Ag and Al at its sintering temperature.

The SEM micrographs of as-fired surfaces of the $PbMoO_4$ ceramic sintered at different temperatures are shown in Fig. 3. As shown in Fig. 3, heterogeneous microstructures with litter pores for the $PbMoO_4$ ceramic sintered at 570°C/4 h were revealed. As seen from Figs. 3(b)–(f), with the increase in sintering temperature, the grain size of cofired ceramics increase from 2–6 μm at 600°C to 6–12 μm at 650°C.

Figure 4 shows the apparent density and relative density of $PbMoO_4$ ceramic as a function of sintering temperature. It is seen that as sintering temperature increased from 570°C to 620°C, the bulk density of $PbMoO_4$ ceramic increased from 6.598 g/cm^3 to about 6.684 g/cm^3 and reached a maximum value at around 650°C. As seen from Fig. 4, the relative density reached about 97% when sintering temperature was above 600°C, which means that the $PbMoO_4$ ceramic can be well densified at a relative low temperature about 600°C.

Microwave dielectric relative permittivity and $Q \times f$ values of $PbMoO_4$ ceramics are shown in Fig. 5. As the sintering temperature increases, microwave dielectric permittivity increases first along with the elimination of the pores and then reaches a maximum value at sintering temperature 650°C. With the further increase in sintering temperature, the permittivity usually decreases slightly before melting due to the secondary grain growth, grain deterioration of the dielectric constant. The $Q \times f$ value of microwave dielectric ceramic is usually determined by the intrinsic and extrinsic dielectric losses. The extrinsic loss is influenced by many defects, such as grain boundaries, particle size, secondary grain, pores, etc.[21,22] Hence, for a microwave dielectric ceramic, the high $Q \times f$ values can only be achieved at a narrow sintering temperature, at which the influenced of defects is minimized. For the $PbMoO_4$ ceramic, high and stable $Q \times f$ values were obtained in ceramics sintered at 610°C–650°C. The best microwave dielectric properties was obtained in $PbMoO_4$ ceramic sample sintered at 650°C for 2 h with a permittivity~26.7, a $Q \times f$ value of 42 830 GHz and a temperature coefficient of 6.2 ppm/°C.

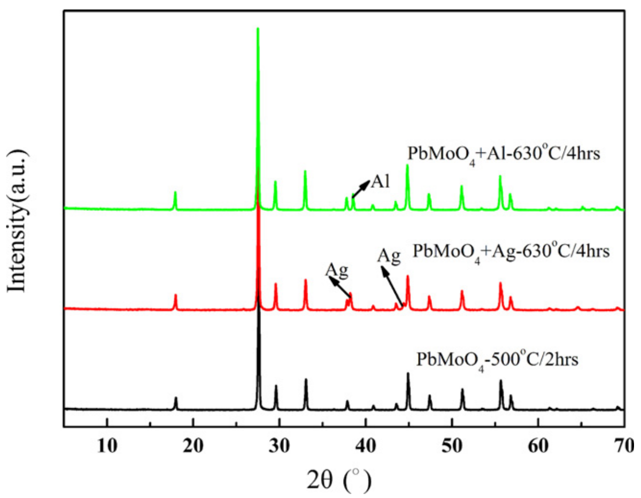

Fig. 1. X-ray diffraction patterns of $PbMoO_4$ ceramics sintered at 500°C for 2 h and cofired ceramics with 30 wt% Ag and 30 wt% Al at 630°C for 4 h.

IV. Conclusion

The $PbMoO_4$ ceramic can be well densified when the sintering temperature is above 600°C and a high relative density above 97% was obtained. From the X-ray diffraction and EDS analysis of cofired samples, the $PbMoO_4$ ceramic was found to be chemically compatible with both aluminum and silver metals. High performance of microwave dielectric properties can be obtained in the ceramic sample sintered at 650°C for 2 h with microwave permittivity ~26.7, $Q \times f$ ~42 830 GHz and temperature coefficient ~ +6.2 ppm/°C. It might be promising for the (LTCC) and dielectric resonator applications.

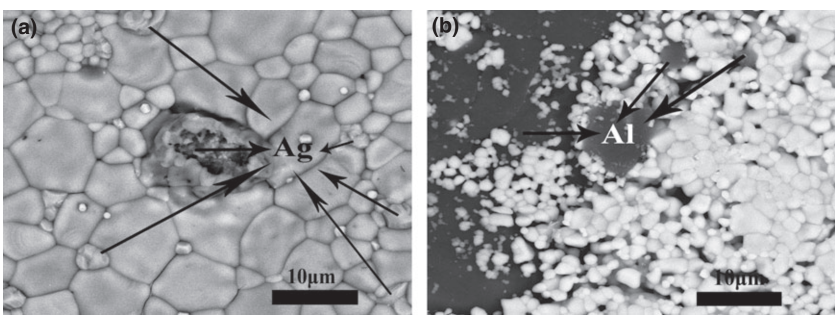

Fig. 2. Backscattered electron image micrograph of cofired samples with 30 wt% silver (a) and 30 wt% aluminum (b) sintered at 630°C/4 h.

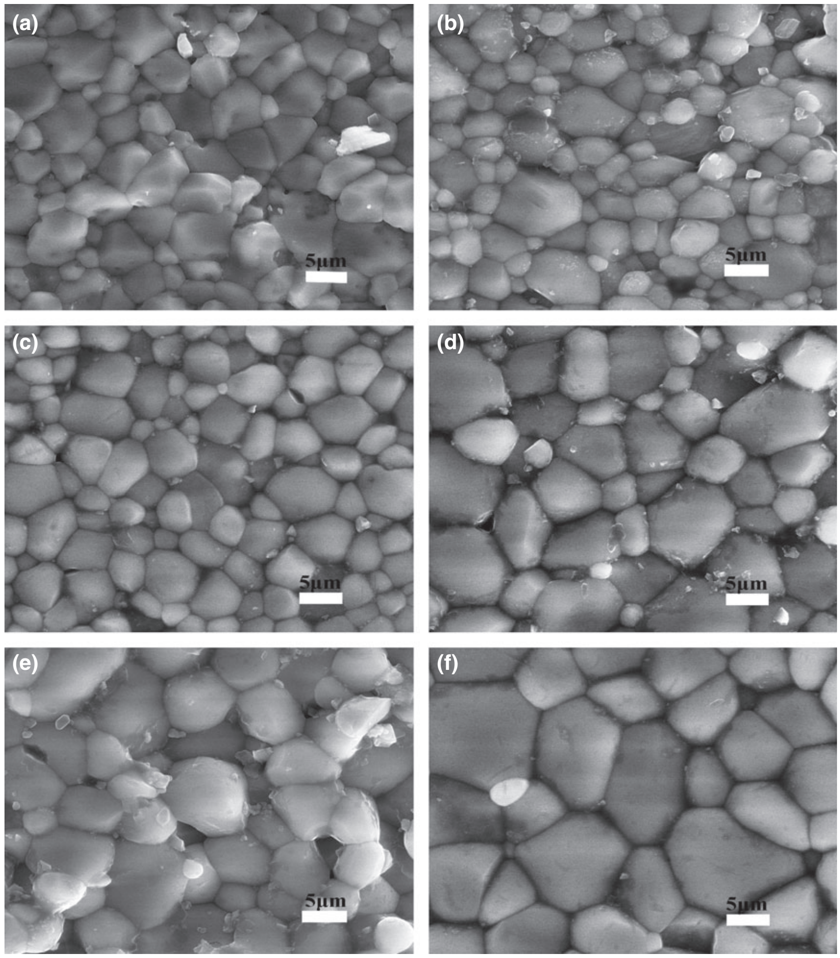

Fig. 3. SEM micrographs of $PbMoO_4$ ceramic at (a) 570°C/4 h; (b) 600°C/2 h; (c) 610°C/2 h; (d) 630°C/2 h; (e) 640°C/2 h; and (f) 650°C/2 h.

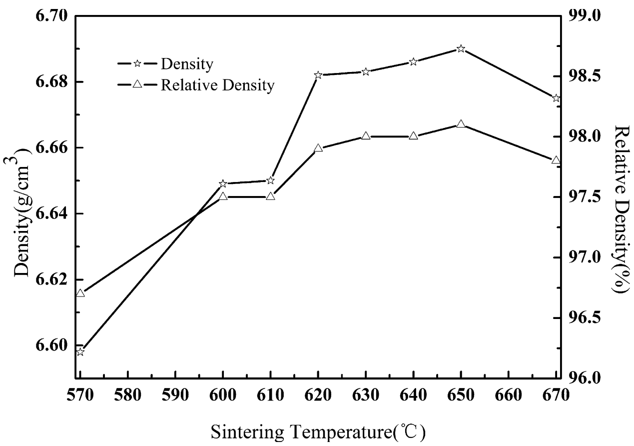

Fig. 4. Bulk densities and relative density of $PbMoO_4$ ceramics as a function of sintering temperatures.

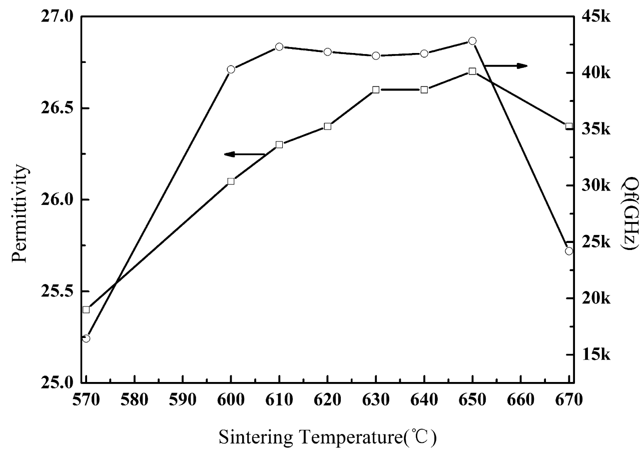

Fig. 5. Microwave dielectric properties (permittivity, $Q \times f$ value) of $PbMoO_4$ ceramics as a function of sintering temperatures.

Acknowledgments

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