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Short Communication

Microwave dielectric properties of Pb_2MoO_5 ceramic with ultra-low sintering temperature

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Abstract

Ultra-low firing microwave dielectric ceramic Pb_2MoO_5 with monoclinic structure was prepared via a conventional solid state reaction method. The sintering temperature ranged from 530 °C to 650 °C. The relative densities of the ceramic samples were about 97% when the sintering temperature was greater than 570 °C. The best microwave dielectric properties were obtained in the ceramic sintered at 610 °C for 2 h with a permittivity ∼19.1, a $Q \times f$ value about 21,960 GHz (at 7.461 GHz) and a temperature coefficient value of −60 ppm/°C. From the X-ray diffraction, backscattered electron image results of the co-fired samples with 30 wt% silver and aluminum additive, the Pb_2MoO_5 ceramics were found not to react with Ag and Al at 610 °C for 4 h. The microwave dielectric properties and ultra-low sintering temperature of Pb_2MoO_5 ceramic make it a promising candidate for low temperature co-fired ceramic applications.

Keywords: Double lead molybdate; Scanning electron microscopy; Microwave dielectric properties; Sintering behavior

1. Introduction

With the rapid development of wireless communications and satellite communication industry, the low temperature co-fired ceramic (LTCC) technology has become an important fabrication method due to its simplicity and advantage in minimizing and integrating electronic components.[1–3] LTCCs are widely used in microwave devices such as resonators, filters, oscillators, dielectric waveguides, microstripline substrates, and all dielectric metamaterials.[4] For LTCC applications, dielectric ceramics need to fulfill the requirements of a low sintering temperature (below melting points of Ag, Al, Cu, Au etc.), a range of high dielectric permittivities (ε_r), a high quality factor ($Q \times f$) (f = resonant frequency, Q = 1/dielectric loss at f), a near-zero temperature coefficient of resonant frequency ($\tau_f \approx 0$ ppm/°C), and chemical compatibility with metal electrodes.[5] In most cases MoO_3 and TeO_2 rich ceramics have interesting low sintering temperatures because of the low melting temperatures of TeO_2 (733 °C), MoO_3 (795 °C).[6] Kwon et al.[7] reported the microwave dielectric properties of $BaTe_4O_9$ with the lowest sintering temperature of 550 °C. Choi et al.[8] reported the microwave dielectric properties of $AMoO_4$ (A = Ba, Mg, Mn, Zn, Ca, Sr) ceramics. All these reported $AMoO_4$ ceramics possess high $Q \times f$ values (37,000–90,000 GHz), however the permittivities are low (7–11), the τ_f values are negative (−57 to −87 ppm/ °C), and the sintering temperatures are higher than the melting point of aluminum (660 °C).

Double lead molybdate (Pb_2MoO_5) crystallizes in the monoclinic system. This material is an optically anisotropic double axis crystal that is promising for the application in the modern acousto-optic devices such as modulators, deflectors and filters operating in the visible light and also in the middle infrared region of spectrum. The biaxial crystals possess unique geometries of light and sound interaction, which cannot be observed in uniaxial crystals.[9–11] The phase diagram of the PbO–MoO_3 system was reported by Jaeger et al. in 1921,[12] which showed

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Pb_2MoO_5 was a congruently melting compound with a melting point of 950 °C.[13] Single crystal growth of Pb_2MoO_5 from a melt has been reported by many researchers.[14–16] Unfortunately, up to date there are few reports on the microwave dielectric properties of Pb_2MoO_5 with regard to the LTCC application. Since the melting point of Pb_2MoO_5 is not very high, it is suggested that Pb_2MoO_5 ceramic might have an ultra-low sintering temperature. In our previous work,[17,18] several molybdates with ultra-low sintering temperature were reported. In this present work, the Pb_2MoO_5 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.

2. Experimental

2.1. Preparation of the ceramics

Stoichiometric reagent-grade raw materials of PbO (>99%, Sinopham 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 the zirconia balls (2 mm in diameter) used as milling media and then calcined at 500 °C for 4 h. Subsequently the samples were crushed and re-milled for 5 h to increase reactivity and homogeneity. The re-milled powders were dried, mixed with PVA binder, granulated, and pressed into cylinders (12 mm in diameter and 4–6 mm in height) in a steel die under a uniaxial pressure of 150 MPa. Finally the cylinders were sintered in the temperature range from 530 °C to 650 °C for 2 h. To investigate the chemical compatibility of Pb_2MoO_5 compound with Ag and Al powders, 30 wt% Ag and 30 wt% Al were mixed with the compound and co-fired at 610 °C for 4 h.

2.2. Characterization

Powder X-ray diffraction (XRD) patterns were taken at room temperature by using an X-ray diffractometer with Cu Kα radiation (Rigaku D/MAX-2400, Tokyo, Japan). Microstructures of ceramic cross-sections after thermal etching and fractured surfaces were observed with a scanning electron microscopy (SEM) (JSM-6460, JEOL, Tokyo, Japan) operated at an accelerating voltage of 10 kV. The apparent densities of sintered ceramics were measured by Archimedes' method. The relative densities were calculated to be the ratio of the apparent densities and the theoretical densities. Microwave dielectric behaviors were measured with 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) in the temperature range from 25 °C to 85 °C at 7.41–7.46 GHz. The temperature coefficient of resonant frequency (TCF or τ_f value) was calculated with the following formula:

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

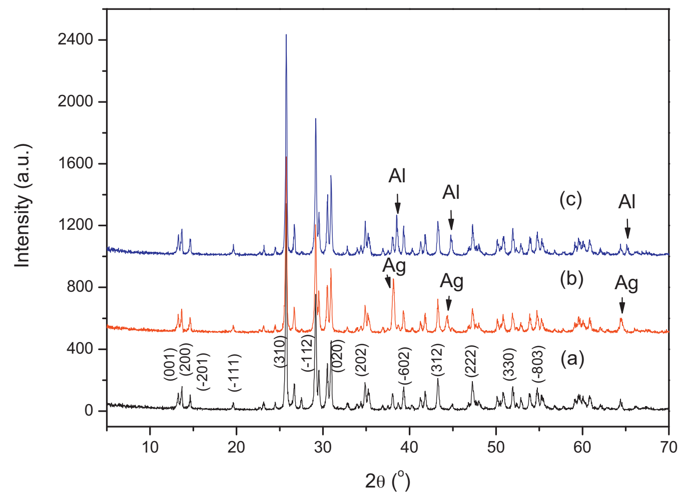

Fig. 1. X-ray diffraction patterns of (a) Pb_2MoO_5 ceramics sintered at 610 °C for 2 h and co-fired ceramics with (b) 30 wt% Ag; (c) 30 wt% Al at 610 °C for 4 h.

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

3. Results and discussion

3.1. XRD patterns

XRD patterns of the as-fired and the co-fired ceramics under different sintered conditions were shown in Fig. 1. As can be seen, the intensity of the as-prepared samples was strong which meant high crystallinity. The diffraction peaks in the XRD patterns can be indexed to monoclinic Pb_2MoO_5 by JCPDS No. 24-0579. No additional peaks in Fig. 1a were found in the patterns, indicating that there were no other impurity phases in the ceramics. For the co-fired ceramic samples (Fig. 1b and c), only the peaks of Pb_2MoO_5 and the respective metals were observed and there were no additional peaks in the XRD patterns to reflect a secondary phase formed, indicating that Pb_2MoO_5 coexisted with either silver or aluminum at the sintering temperature of 610 °C for 4 h.

3.2. SEM results

Fig. 2 showed the secondary electron images of the as-polished and fractured surfaces of the Pb_2MoO_5 ceramics sintered at different temperatures for 2 h. As can be seen in Fig. 2a and b, heterogeneous microstructures with some pores for the Pb_2MoO_5 ceramic sintered at 530 °C and 570 °C were revealed, the grain size of which was less than 1.0 μm. At 610 °C, the samples showed a densified compact structure with a grain size of 0.25–1.0 μm, as shown in Fig. 2c. When the temperature was increased to 650 °C, the grain size became larger, which ranged from 1.0 to 5.0 μm. The SEM results indicated that a sintering temperature of 610 °C was needed for the well densified ceramics of Pb_2MoO_5.

Fig. 3 showed the backscattered electron images (BSE) of co-fired ceramics with 30 wt% silver and aluminum powders.

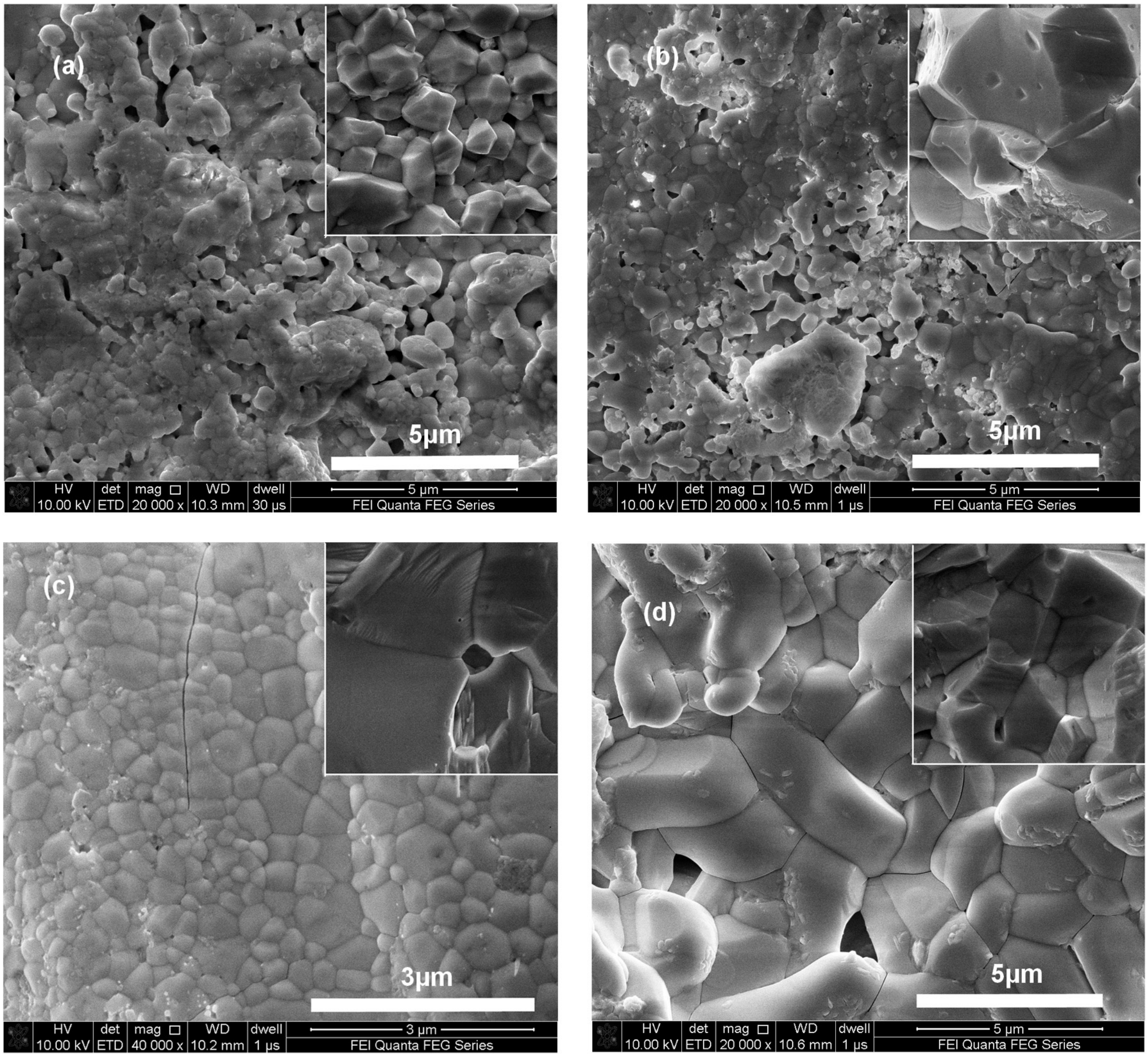

Fig. 2. Secondary electron images of the as-polished and fractured surfaces sintered at different temperatures for 2 h. (a) 530 °C; (b) 570 °C; (c) 610 °C; (d) 650 °C. The upper right corner in (a–d) are fractured surfaces.

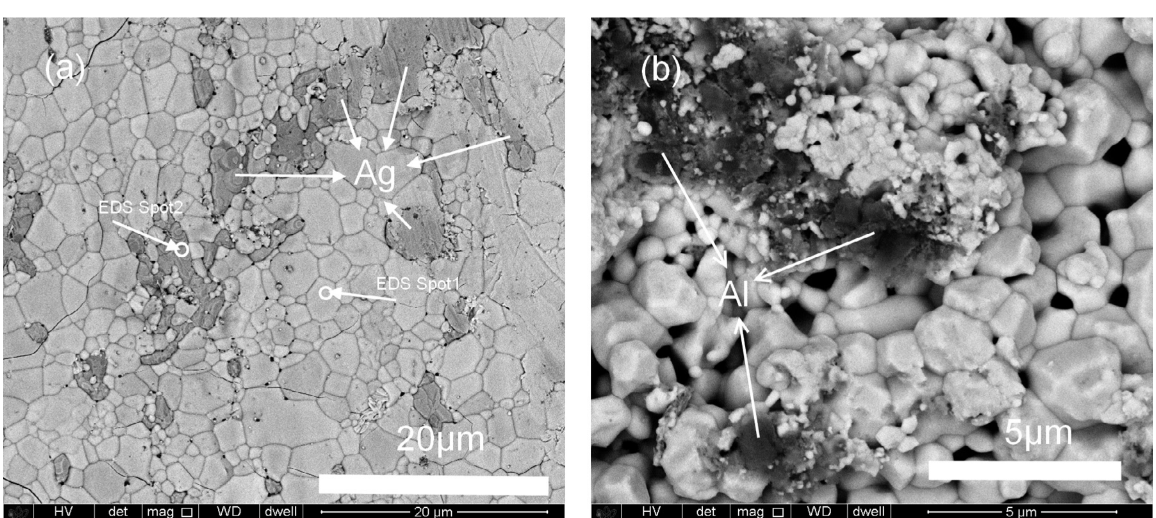

Fig. 3. BSE micrographs of co-fired samples sintered at 610 °C for 4 h. (a) With 30 wt% silver; (b) with 30 wt% aluminum.

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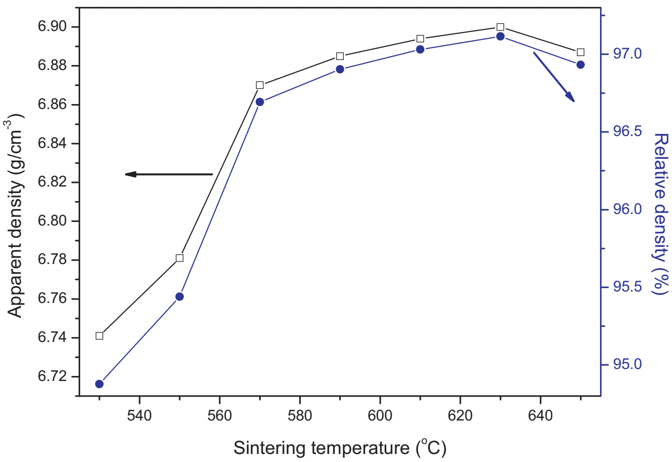

Fig. 4. Apparent and relative densities of Pb_2MoO_5 ceramics as a function of sintering temperatures.

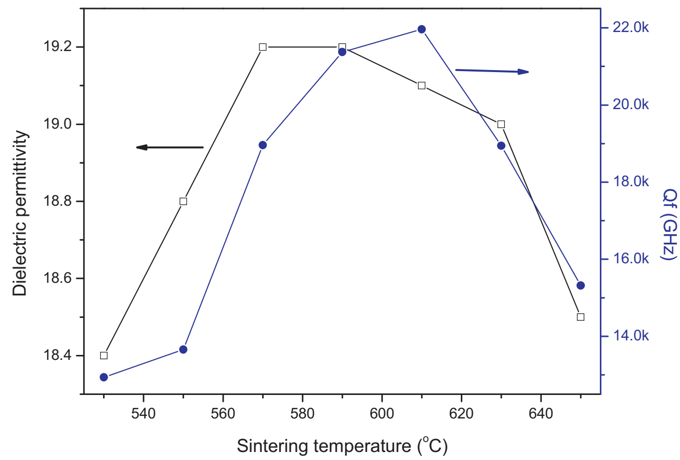

Fig. 5. Microwave dielectric properties (permittivity, $Q \times f$ value) of Pb_2MoO_5 ceramics as a function of sintering temperatures.

Energy dispersive spectrometer (EDS) results confirmed many grains in Fig. 3a with a gray color (spot 1) belonged to the Pb_2MoO_5 phase and a few dark grains (spot 2) were found to be pure silver. The EDS analysis of spot 1 gave an atomic ratio of 2.1:1.0:6.5 for Pb:Mo:O, which was close to the ideal value of 2:1:5 for Pb_2MoO_5. The EDS analysis of spot 2 gave an atomic ratio of 4.7:0.0:1.0:4.0 for Ag:Mo:Pb:O, which confirmed the phase of Ag. Similarly, the grains with dark color belonged to the pure aluminum and the major grains with light color belonged to the Pb_2MoO_5 phase, as shown in Fig. 3b. From BSE results of the co-fired ceramics combined with the XRD results, it can be concluded that the Pb_2MoO_5 phase did not react with both Ag and Al powders and no secondary phases were formed when co-fired at 610 °C for 4 h. This sintering temperature was lower than the melting points of both silver (960 °C) and aluminum (660 °C), indicating that Pb_2MoO_5 might be used as a new ultra-low temperature co-fired ceramic.

3.3. Dielectric properties

Fig. 4 showed the apparent and relative densities of Pb_2MoO_5 ceramics as a function of sintering temperature. It is seen that as sintering temperature increased from 530 °C to 650 °C, the bulk density of Pb_2MoO_5 ceramics increased from 6.741 g/cm^3 to about 6.900 g/cm^3 and reached maximum at around 630 °C. The relative density reached about 97% when the sintering temperature was above 570 °C, which meant that the Pb_2MoO_5 ceramics were well densified at a relative low temperature of about 570 °C. Fig. 5 showed the microwave dielectric relative permittivity and $Q \times f$ values of Pb_2MoO_5 ceramics as a function of sintering temperature. With the increase of the sintering temperature, microwave dielectric permittivity increased first and then reached a maximum value at sintering temperature of 580 °C. With further increase of the sintering temperature, the permittivity slightly decreased, which might be due to the secondary grain growth, grain deterioration of the dielectric constant. The $Q \times f$ value of microwave also increased with the sintering temperature up to 610 °C and thereafter decreased. Therefore the best microwave dielectric properties were obtained in Pb_2MoO_5 ceramic sample sintered at 610 °C for 2 h with a permittivity ~19.1, a $Q \times f$ value of 21,960 GHz and a temperature coefficient of −60 ppm/ °C calculated from Eq. (1).

4. Conclusions

Single phase of Pb_2MoO_5 ceramics was synthesized by a conventional solid state reaction method. The Pb_2MoO_5 ceramic can be well densified when the sintering temperature was greater than 570 °C and reached a high relative density about 97%. High performance of microwave dielectric properties can be obtained in the ceramic sample sintered at 610 °C for 2 h with microwave permittivity ~19.1, $Q \times f$ ~ 21,960 GHz and temperature coefficient ~−60 ppm/°C. The ultra-low sintering temperature and chemical compatibility with Ag and Al of the Pb_2MoO_5 ceramics indicated that Pb_2MoO_5 might be a promising candidate for the ultra-low temperature co-fired ceramic technology and dielectric resonator applications.

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