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Preparation of Li_2MoO_4 using aqueous solution method and microwave dielectric properties after sintering

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Abstract A novel aqueous solution method was used to prepare Li_2MoO_4 powder, which was pressed and sintered directly into ceramic pellets without any calcination or milling stage involved. Pure Li_2MoO_4 ceramic with the maximum bulk density of 2.898 g/cm^3 (95.63 % of the theoretical value) and excellent microwave dielectric properties of $\varepsilon_r = 5.58$, $Q \times f = 49{,}328$ GHz, $\tau_f = -168$ ppm/°C ($f = 10.17$ GHz) was obtained at 540 °C/2 h. The maximum $Q \times f$ value in this work is higher than that of Li_2MoO_4 ceramic prepared by the conventional solid-state reaction method. The results show that the aqueous solution method is a simple and effective method to produce Li_2MoO_4 ceramics.

1 Introduction

In recent years, with the rapid development of commercial wireless technologies and satellite communication, the low temperature co-fired ceramics (LTCC) technology has played an important role due to its simplicity and advantage in minimizing and integrating electronic components [1]. The search for new microwave dielectric ceramics with high performance, low sintering temperature, and low cost has always attracted much attention [2]. So far, there are many good examples in TeO_2-rich, Bi_2O_3-rich, and MoO_3-rich systems [3–8]. In addition to possessing a low sintering temperature (<960 °C), the microwave dielectric material for substrate application should have a low dielectric constant to avoid the signal delay, a high quality factor ($Q \times f$) value (a low dielectric loss) to ensure the frequency selectivity and reduce the insertion loss, and a near-zero temperature coefficient of resonant frequency to assure the temperature stability [9].

In the past decade, a so-called ultra-low temperature co-fired ceramic (ULTCC), which is focused on the microwave dielectric ceramic with intrinsic low sintering temperature, has started a new stage for the LTCC technology [10]. The search of novel ULTCC in the low eutectic points Mo-rich and Te-rich compounds has attracted more and more attention [11, 12]. One of the classic ULTCCs is Li_2MoO_4 ceramics [13].

Conventionally, Li_2MoO_4 ceramic is prepared by solid-state reaction method. It is synthesized from Li_2CO_3 and MoO_3 at temperature from 500 to 550 °C. Then it can be well sintered at 540 °C for 2 h to a high density of 2.895 g/cm^3 (95.5 %) with a relative permittivity of ~5.5, a $Q \times f$ value of ~46,000 GHz and a τ_f value of ~−160 ppm/°C at 13.051 GHz [13]. However, this approach has two significant disadvantages: (1) The use of mechanical milling process can not ensure microscopically complete mixing of starting materials, which may hinder the complete reaction of starting materials in the calcination stage and reduce the purity of sintered ceramic; (2) impurity may be introduced in milling process, which is deleterious to the microwave dielectric performance of ceramics.

Although Li_2MoO_4 ceramic has been studied by some researchers, the preparation of Li_2MoO_4 ceramic through the aqueous solution method has not been investigated. In this paper, we report an aqueous solution method for the synthesis of pure Li_2MoO_4 powder. The as-synthesized powder was pressed and sintered directly into ceramic pellets without any calcination or milling stage involved. The phase composition, densification, microstructure and microwave dielectric properties of the ceramics were investigated.

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2 Experimental procedure

The Li_2MoO_4 powder was prepared using the aqueous solution method. $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ (>99 %; SINOPHARM Chemical Reagent, Shanghai, China) and $LiOH{\cdot}H_2O$ (≥95.0; SINOPHARM Chemical Reagent, Shanghai, China) were weighed according to the stoichiometric compositions of Li_2MoO_4 and then dissolved into deionized water by vigorous agitation. The resulting aqueous solution in a porcelain mortar was thermally treated by a thermostatic water bath of 60 °C until the water was completely evaporated, leaving a layer of dry product on the surface of the mortar. After that, the resulting product was mixed with some absolute ethanol (about twice the weight of the product) used as dispersants, ground into fine powder, and dried. The obtained powder was granulated with 3 wt% ethanol binder and pressed into cylinders (10 mm in diameter and 5 mm in height) in a steel die under uniaxial pressure of 200 MPa. Then these samples were dried at 120 °C for 2 h and sintered at various temperatures ranging from 510 to 550 °C for 2 h under the air atmosphere at a heating rate of 3 °C/min.

The crystalline phases of the sintered samples and green samples were identified using X-ray diffraction (XRD) (Rigaku, D/MAX-2500, Tokyo, Japan) with Cu $K\alpha$ radiation. Microstructures of sintered ceramics were examined by scanning electron microscopy (SEM) (ZEISS, GeminiSEM 500, Germany). Microwave dielectric properties of sintered samples were measured on a network analyzer (Agilent 8720ES) at microwave frequency. The temperature coefficient of resonant frequency (τ_f) was obtained by measuring the $TE_{01\sigma}$ resonant frequency from 25 to 85 °C and calculated using the Eq. (1):

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \tag{1}$$

where f_1 and f_2 are the $TE_{01\sigma}$ resonant frequency of the samples at 25 and 85 °C, respectively.

The apparent densities ρ_{bulk} of the sintered ceramics were measured by Archimedes' method. The relative density was calculated by Eq. (2):

$$\rho_{relative} = \frac{\rho_{bulk}}{\rho_{theory}} \times 100\,\% \tag{2}$$

3 Results and discussion

Figure 1 shows the XRD patterns of Li_2MoO_4 powder and its sintered ceramics in the temperature range of 510–550 °C. All the peaks in the X-ray diffraction patterns can be indexed based on the PDF card 12-0763 of hexagonal Li_2MoO_4. No additional peak was found in the patterns, indicating that there was no other impurity phase in the powder or the sintered ceramics. The peaks are narrow and sharp, indicating a good crystallization. Therefore, the aqueous solution method can efficiently transform the mixture of $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$ and $LiOH{\cdot}H_2O$ into pure Li_2MoO_4. The formation process can be described by the following reactions:

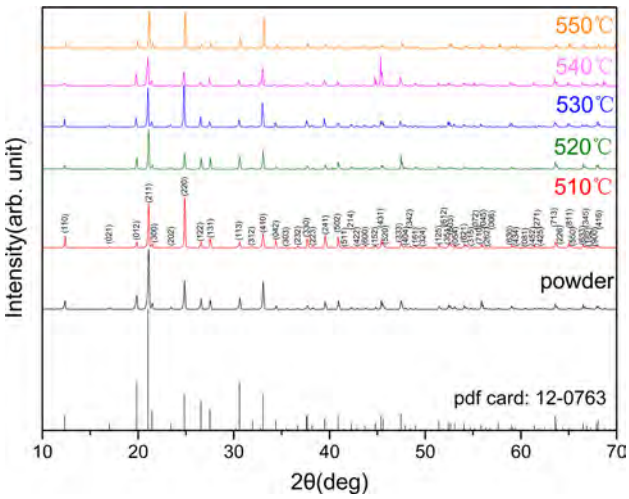

Fig. 1 The X-ray diffraction (XRD) patterns of Li_2MoO_4 powder prepared in this study and Li_2MoO_4 ceramics sintered at different temperatures for 2 h

$$Mo_7o_{24}^{6-} + 8OH^- \rightarrow 7MoO_4^{2-} + 4H_2O \tag{3}$$

$$NH_4^+ + OH^- \rightarrow NH_3 \cdot H_2O \longrightarrow \Delta NH_3 \uparrow + H_2O \tag{4}$$

$$2Li^+ + MoO_4^{2-} \overset{crystallize}{\longrightarrow} Li_2MoO_4\,(crystal) \tag{5}$$

Figure 2a–e presents the SEM photos of Li_2MoO_4 ceramics sintered at different temperatures. With the increasing of sintering temperature, the grain size has an increasing tendency. For Li_2MoO_4 sintered at 540 °C, the ceramics exhibit homogeneous structures and a grain size of 3–15 μm. There are almost no pores and the surface seems smoother than the others. However, when sintering temperature is above 540 °C, some of the grains grow rapidly with the grain size of 40 μm, indicating the grain abnormal growth, which may decrease the density and deteriorate the microwave dielectric properties of ceramics.

Figure 3 shows the relative densities of Li_2MoO_4 ceramics as a function of sintering temperature. With the rise of the sintering temperature, the relative density increases, reaches a maximum value of 95.63 % at 540 °C, and decreases thereafter. The increase of relative density with the rise of sintering temperature may be attributed to the elimination of pores and grain growth which reduces the grain boundary area. The decrease of relative density

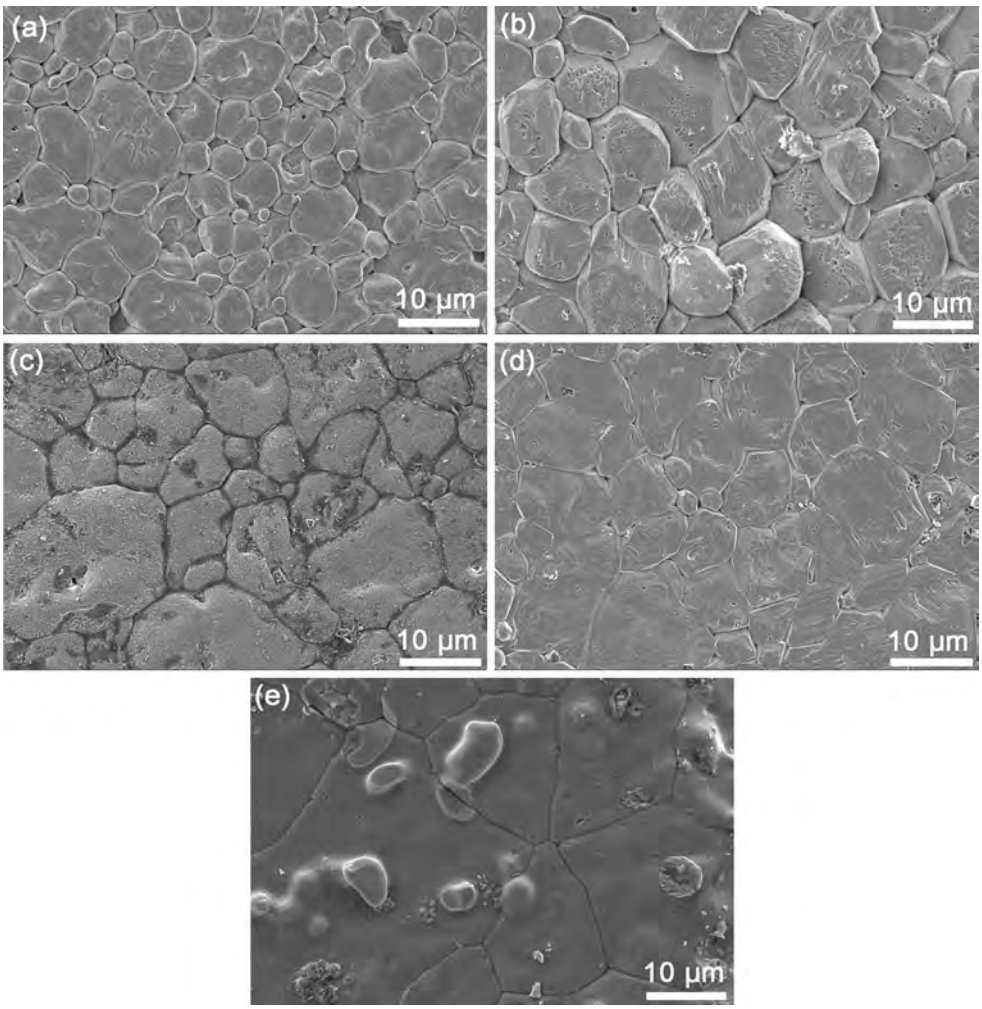

Fig. 2 The SEM images of Li_2MoO_4 ceramics sintered at **a** 510 °C, **b** 520 °C, **c** 530 °C, **d** 540 °C, **e** 550 °C for 2 h

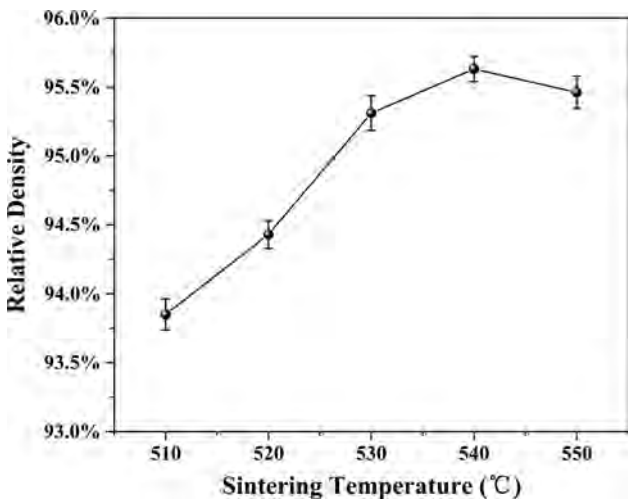

Fig. 3 The relative density of Li_2MoO_4 ceramics as a function of sintering temperature

above 540 °C may be due to the grain abnormal growth, as observed in Fig. 2e.

The relative permittivity of Li_2MoO_4 ceramics as a function of the sintering temperature are shown in Fig. 4. In general, the dielectric constant at microwave frequency is dependent on the density, second phase, and the crystal structure [14]. Comparing Fig. 3 with Fig. 4, the curve of dielectric constant shows a similar tendency with that of relative density. Owing to the elimination of the pores ($\varepsilon_r \approx 1$), microwave dielectric constant increases with the rise of the sintering temperature. After reaching the maximum value of 5.58 at 540 °C, it decreases to 5.56, which may be caused by the grain abnormal growth. Therefore, the maximum relative permittivity value obtained in this study is similar to that reported by Zhou et al. [13] for Li_2MoO_4 ceramics prepared by conventional solid-state reaction method.

Figure 5 shows the Q × f values of Li_2MoO_4 ceramics as a function of the sintering temperature. Generally, the Q × f value of microwave dielectric ceramic is determined by the intrinsic loss and extrinsic loss. The intrinsic loss is mainly caused by lattice vibration modes while the extrinsic loss is dominated by second phases, oxygen vacancies, grain sizes and densification or porosity [15]. With the increase of sintering temperature from 510 to 540 °C, the Q × f value of ceramics increases from 34,025 to 49,328 GHz. The significant increase of the Q × f value ranging from 510 to 540 °C is mainly attributed to the increase of density as well as the uniformity of grain growth, which can be seen from the microstructures in Fig. 2a–d. However, with further increase of sintering temperature, the Q × f value decreases due to the inhomogeneous grain size caused by the grain abnormal growth, as observed in Fig. 2e. The similar behavior was also reported in the other researches [16, 17]. In this work, Li_2MoO_4 ceramic sintered at 540 °C has the maximum Q × f value of 49,328 GHz, which is higher than that of 46,000 GHz reported by Zhou et al. [13] for Li_2MoO_4 ceramic prepared by conventional solid-state reaction method. It can be attribute to the significant decrease of impurity content in the Li_2MoO_4 ceramics. In the aqueous solution method, the impurities can be reduced due to elimination of the two milling steps. It was reported that minor contamination from milling media could degrade quality factor (Q) by 15–20 % [18]. Besides, with water as the reaction environment, the raw materials can fully react, which leads to purer product than that prepared by solid-state reaction method.

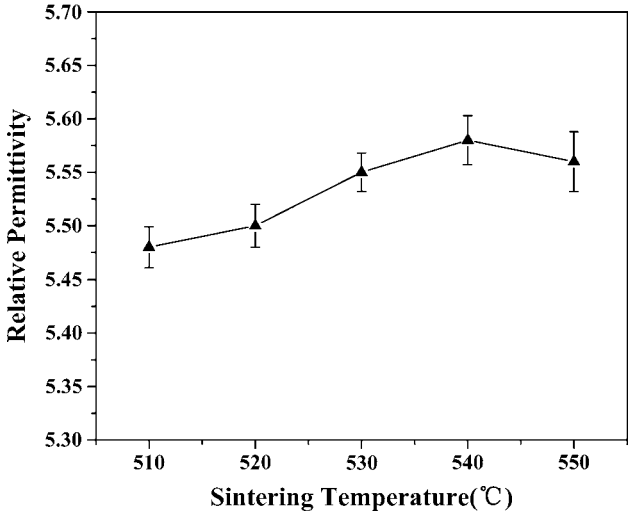

Fig. 4 Relative permittivity of Li_2MoO_4 ceramics as a function of sintering temperature

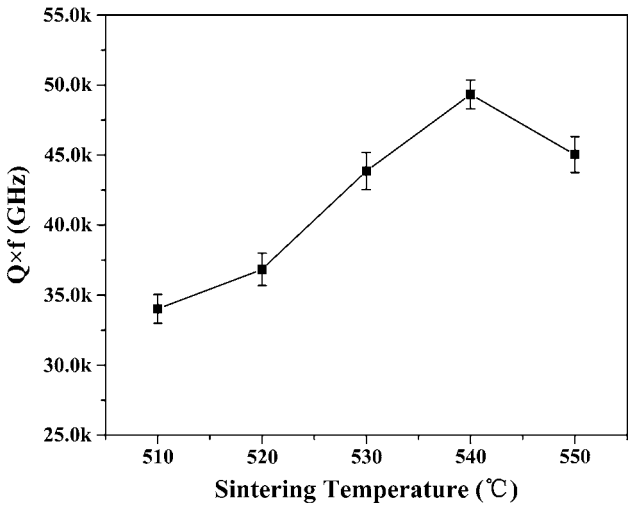

Fig. 5 Q × f values of Li_2MoO_4 ceramics as a function of sintering temperature

Microwave dielectric properties of Li_2MoO_4 ceramics prepared by conventional solid-state reaction method and the aqueous solution method are listed in Table 1 for comparison. Comparing with the conventional solid-state method, the aqueous solution method is a simple, economical and effective route to obtain Li_2MoO_4 ceramics with high density and excellent microwave dielectric properties.

This method may be interesting for the preparation of Li_2WO_4 and ABO_4 (A=Mg^{2+}, Ca^{2+}, B=Mo, W) ceramics, which have been synthesized via conventional solid-state reaction method and sintered for microwave dielectric application by other researchers [8, 19–21].

Table 1 Microwave dielectric properties of Li_2MoO_4 ceramics prepared by various methods

	Proposed by Zhou et al. [13]	This work
Processing	Conventional solid-state method	Aqueous solution method
Milling process	First milling/4.5 h, remilling/5 h	No milling
Calcination temp./time	500–550 °C/4 h.	No calcining
Sintering temp./time	540 °C/2 h	540 °C/2 h
Relative density	95.5 %	95.63 %
Relative permittivity	5.5	5.58
Q × f (GHz)	46,000	49,328
τ_f (ppm/°C)	−160	−168

4 Conclusions

A novel aqueous solution method was used to prepare Li_2MoO_4 powder, which was pressed and sintered at 540 °C/2 h into dense ceramic with the maximum bulk density of 2.898 g/cm^3 (95.63 % of the theoretical value) and excellent microwave dielectric properties of $\varepsilon_r = 5.58$, $Q \times f = 49{,}328$ GHz, $\tau_f = -168$ ppm/°C ($f = 10.17$ GHz). In this study, Li_2MoO_4 ceramic sintered at 540 °C/2 h has the maximum $Q \times f$ value of 49,328 GHz that is higher than that of 46,000 GHz for Li_2MoO_4 ceramic prepared by conventional solid-state reaction method, which can be attributed to the significant decrease of impurity content. Therefore, the aqueous solution method is a simple, low-cost and effective method to produce Li_2MoO_4 ceramics.

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