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Novel water-assisting low firing MoO₃ microwave dielectric ceramics

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Abstract

MoO₃ ceramics can not be well densified via conventional solid state method and a
low relative density (ρ) was obtained ($\sim 64.5\%$ at $680\text{ }^{\circ}\text{C}$) with a permittivity (ϵ_r) \sim

7.58, a quality factor (Qf) $\sim 35,000$ GHz and a temperature coefficient of resonant frequency (TCF) ~ -39 ppm/ $^{\circ}\text{C}$. However, cold sintering at 150 $^{\circ}\text{C}$ using 4 wt. % H_2O at 150 MPa enhanced densification and give a relative $\rho \sim 76.8$ % and $\epsilon_r \sim 8.31$ but with a Qf of only ~ 900 GHz. The addition of $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ further improved densification to give a relative $\rho \sim 83.7$ % after annealing at 700 $^{\circ}\text{C}$, resulting in a $\epsilon_r \sim 9.91$ with a $Qf \sim 11,800$ GHz. We conclude therefore that oxides that are difficult to be sintered via a conventional solid state route may benefit from cold sintering but despite the higher density, lower Qf cannot be avoided due to the impurities and grain boundary phases that are introduced.

Keywords: (Ceramics, Microwave Dielectrics)

Introduction

Low temperature co-fired ceramic (LTCC) technology has become an important fabrication method for modern electronic devices due the low cost of manufacture and potential of the integration multiple microwave (MW) circuits.¹⁻⁴ LTCCs are required to have lower sintering temperatures than that of the inner metal electrodes (typically Ag, 961 $^{\circ}\text{C}$)^{5,6} but classic MW dielectric ceramics typically densify at > 1000 $^{\circ}\text{C}$.¹⁻⁷ Lowering the sintering temperature of a MW ceramic by the addition of low-melting-point glasses and oxides has been used to fabricate many commercial LTCCs.¹⁻⁷ The search for intrinsically low sintering temperature LTCC has accelerated in recent years and the so-called family of ultra-LTCC (ULTCC) compounds can be

well sintered at as low as 400 °C.⁸⁻¹¹ Most MW dielectric ceramics are oxides and their sintering temperatures are, to a simple approximation, determined by their melting points. Consequently, systems rich in low melting temperature oxides, such as TeO₂ (733°C), MoO₃ (795°C), Bi₂O₃ (817°C), B₂O₃ (450°C), P₂O₅ (340°C) and V₂O₅ (690°C), have been explored in the past decade.⁷⁻¹⁴

Despite more than 50 types ULTCC molybdates have been reported to date,^{8,10,12,14} the understanding of some simple binary compositions, such as MoO₃, is quite limited. MoO₃ powders are usually produced by roasting molybdenum disulfide in industry and take on a yellow color with a monoclinic crystal structure (space group *Pbnm*, $a = 3.962 \text{ \AA}$, $b = 13.855 \text{ \AA}$ and $c = 3.696 \text{ \AA}$).^{15,16} Its theoretical density ρ is 4.692 g/cm³ with a melting point 795 °C and many MoO₃-rich compounds have commensurately low melting points and sintering temperatures. However, when not alloyed with other binary compounds, MoO₃ can be well densified.^{10,14} Even MoO₃-rich phases in well known phase diagrams, such as the Bi₂O₃-MoO₃ binary system, struggle to achieve high density,¹⁰ e.g. Bi₂Mo₃O₁₂ which, despite its excellent MW properties ($\epsilon_r \sim 19$, $Qf \sim 21,800 \text{ GHz}$ and $TCF \sim -215 \text{ ppm/}^\circ\text{C}$), has never been synthesized with relative $\rho > 90 \%$. However, Varghese *et al.*¹³ have reported that MoO₃ sintered at 650 °C has a $\epsilon_r \sim 6.6$ and a $Qf \sim 41,000 \text{ GHz}$ at 11.3 GHz and claimed a high relative ρ ($\sim 88\%$) was achieved via traditional sintering.

Most ceramics are processed using a conventional solid-state method using dry powders at high temperature. However, the poor sinterability of MoO₃ and its partial solubility in water suggest that a solution assisted method, i.e. cold sintering,^{17,18} may be beneficial in achieving high ρ . Cold sintering can be explained as a room temperature crystallization or condensation from supersaturated solutions at grain boundaries, which has been employed in salt manufacture for more than one thousand

years. The first successful microwave dielectric ceramic densified using cold sintering was Li_2MoO_4 .^{19,20} The properties of Li_2MoO_4 conventionally sintered at 540 °C were first reported in our previous work¹⁴ with a $\epsilon_r \sim 5.5$, a $Qf \sim 46,000$ GHz and a $TCF \sim -160$ ppm/°C. In 2014, Jantunen *et al.*¹⁹ demonstrated that dense Li_2MoO_4 ceramic may be obtained at 80 °C if water is added. They also recognized that this approach permits the formation of Li_2MoO_4 -rich composite ceramics, such as $\text{Li}_2\text{MoO}_4\text{-TiO}_2$, $\text{Li}_2\text{MoO}_4\text{-BaTiO}_3$ etc.¹⁹⁻²¹ In 2016, Randall and his co-workers expanded this natural mechanism to other partially water-soluble MoO_3 and V_2O_5 based systems.^{17,18} Solubility in water determines whether a material is suitable for cold sintering. Generally speaking, the cold sintering process (CSP) is a protocol for achieving dense ceramic solids by integrating particles, particle-fluid interface control and external pressure at very low temperatures. CSP uses a transient aqueous environment to achieve densification through a mediated dissolution-precipitation process. Although MoO_3 is only slightly water soluble, ammonium molybdate is highly soluble and decomposes to MoO_3 and NH_3 (g) above 370 °C.^{22,23} Hence, it may be an ideal accelerant for cold sintering of MoO_3 ceramics.

In the present work, a comparison is made between MoO_3 ceramics prepared via a conventional solid-state method and cold sintering using water / $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$ additions. Their phase evolution, microstructure and MW dielectric properties are presented and discussed in detail.

Experimental Section

Solid state reaction method: MoO_3 (> 99%, Fisher Scientific) were ball-milled for 24 h in isopropanol with ZrO_2 balls. After drying, the powders were pressed into cylinders (20 mm in diameter and 4 ~ 5 mm in height) at 30 ~ 50 MPa. Samples were

sintered 2 h at 640 to 740 °C.

Cold sintering method: Fine MoO₃ powder was mixed with 4 wt. % water using an agate mortar. The mixture was pressed into cylinders (20 mm in diameter and 4 ~ 5 mm in height) at 100 ~ 150 MPa at 120 ~ 150 °C from 10 min to 30 min. Besides, 10 wt. % (NH₄)₆Mo₇O₂₄·4H₂O was also mixed with MoO₃ powders and water (4 wt. %) and the same cold sintering process was carried out. To prevent the reaction between MoO₃ and the steel, thin PTFE pellets were added inside the die during the cold sintering process. After cold sintering, the samples were dried at 120 °C for 24 h before measurements. Some samples were also annealed at 600 to 700 °C in air after cold sintering.

Structural, Microstructure and Electrical Characterization: Bulk density ρ was measured by the Archimedes' method (using ethanol as liquid) as well as by calculating the mass / volume from basic geometry. X-ray diffraction (XRD) was performed using with Cu K α radiation (Bruker D2 Phaser) from 5 - 65° 2 θ at a step size of 0.02 °. Natural and fractured surfaces were observed by scanning electron microscopy (SEM, FEI, Inspect F). Dielectric properties at MW frequency were measured using the TE_{01 δ} dielectric resonator method with a network analyzer (Advantest R3767CH; Advantest, Tokyo, Japan) and a home-made heating system. The temperature coefficient of resonant frequency TCF (τ_f) was calculated with the following formula:

$$TCF (\tau_f) = \frac{f_T - f_{T_0}}{f_{T_0} \times (T - T_0)} \times 10^6 \quad (1)$$

where: f_T and f_{T_0} are the TE_{01 δ} resonant frequencies at temperature T and T_0 , respectively.

Results and Discussions

MoO₃ prepared via solid state reaction method

Relative ρ , ϵ_r and Qf of MoO₃ ceramics prepared via solid state reaction method as a function of sintering temperature (640 ~ 740 °C) are shown in Fig. 1a. ϵ_r increased from 6.75 to 7.58 as sintering temperature increased from 640 °C to 680 °C and then decreased a little bit with further increase in sintering temperature. Qf reached a maximum value of 35,000 GHz at 660 °C and remained almost constant for higher sintering temperatures. TCF was ~ -39 ppm/°C and therefore the overall MW properties were similar to those reported.¹³ Although the properties are attractive for the development of MW ceramics, MoO₃ pellets could not be well densified even at temperatures close to its melting point, only with a maximum relative $\rho \sim 64.5$ % at 680 °C. An optical image of an MoO₃ pellet sintered at 680 °C and the schematic of crystal structure are shown in Fig. 1b. The pellet has a green-yellow color, similar to the starting powders. Conversely, some grains are observed which are > 100 μm in diameter which indicates that grain growth is possible but not uniform throughout the ceramic, resulting in poor mechanical strength and low fracture toughness. All the results suggest MoO₃ can not be well sintered using a conventional solid-state method even though high Qf is observed. Moreover, its true ϵ_r is likely to be far higher than the measured value (~ 7.58).

MoO₃ prepared via cold sintering with water only

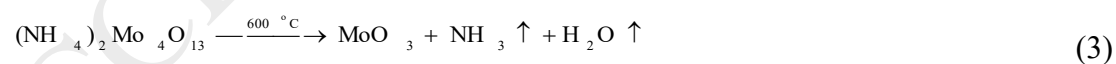
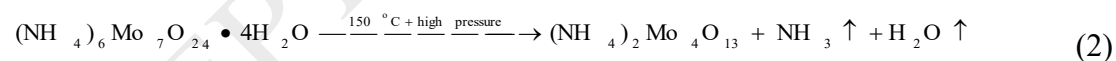
XRD patterns of the MoO₃ powders, the natural and fractured surfaces of cold sintered MoO₃ ceramics (sintered 0.5 h at 150 °C) and a sample annealed at 620 °C are shown in Fig. 2a. Scanning electron and optical images of starting powders and cold sintered MoO₃ ceramics are shown in Fig. 2b. The cold sintered MoO₃ ceramic is

black in color on its surface but its interior is deep green. XRD results showed that besides MoO₃, weak peaks of secondary phases were observed on the fracture surface, which indicates that some MoO₃ has reacted with H₂O forming secondary phases that did not decompose after 24 h drying at 150 °C. However, due to their low volume fraction they can not be identified. For the natural surface of the cold sintered MoO₃ ceramic, only XRD peaks of MoO₃ phase were observed but with evidence of some preferred orientation. The black surface color is attributed to reduction in the presence of heat, pressure and water. The starting powders adopt an acicular morphology (5 to 10 μm) which is commensurate with an anisotropic crystal structure. The fracture surfaces of cold sintered MoO₃ ceramics show little grain growth compared with the starting powder. The black surface in contrast exhibits bar shaped grains in the *a-c* plane which are presumably responsible for the increase in intensity of the (020) and (040) peaks with respect to the polycrystalline standard. After annealing above 300 °C, both the natural (outer) and fractured (interior) surfaces of cold sintered MoO₃ ceramic returned to the green-yellow color, the same with both that observed in the starting powder and for conventionally sintered MoO₃ ceramic. The relative ρ of MoO₃ ceramic cold sintered at 150 °C was ~ 76.8 % and increased to 77.4 % and 78.7 % at 600 °C and 700 °C, respectively, with an improvement over conventionally sintered MoO₃ as shown in Fig. 3a. When cold sintered ceramics were annealed above 600 °C, large crystal flakes (whiskers) grew from the edge (Fig. 2b), this phenomenon was not observed in conventionally sintered MoO₃ ceramics. Whisker formation is often related to liquid or vapor phase transport and their formation could be driven by the evolution on annealing of H₂O from trapped OH⁻ groups.²⁴⁻²⁶ ϵ_r and Q_f of the cold sintered MoO₃ (150 °C) were ~ 8.31 and ~ 900 GHz but increased to 9.02 and 19,700

GHz, respectively, after annealing at 700 °C as shown in Fig. 3b. TCF value of the cold sintered MoO₃ ceramic is about -55 ± 15 ppm/°C.

MoO₃ prepared by cold sintering with (NH₄)₆Mo₇O₂₄·4H₂O

Although cold sintering with H₂O improved relative ρ , the optimum value (78.7 %), as shown in Fig. 3a, was below the required density for commercially useful MW ceramics (> 95 %). (NH₄)₆Mo₇O₂₄·4H₂O is soluble in water and its re-crystallization may enhance densification during cold sintering. Hence, 10 wt. % (NH₄)₆Mo₇O₂₄·4H₂O was mixed with MoO₃ powders before 4 wt. % H₂O was added. XRD patterns of the (NH₄)₆Mo₇O₂₄·4H₂O powders, mixtures of MoO₃ ceramic with (NH₄)₆Mo₇O₂₄·4H₂O cold sintered for 0.5 h at 150 °C and a cold sintered sample annealed at 600 °C are shown in Fig. 4. As reported in literatures, the (NH₄)₆Mo₇O₂₄·4H₂O decomposes to (NH₄)₄Mo₅O₁₇ at ~ 130 °C and the latter decomposes to (NH₄)₂Mo₄O₁₃ at about 245 °C.^{22,23} In cold sintered MoO₃ (150 °C) sample, (NH₄)₂Mo₄O₁₃ phases were revealed in addition to those of the matrix phase but after annealing at 600 °C, only MoO₃ phases are observed, suggesting the following reaction sequence:



The relative ρ of cold sintered MoO₃ ceramic with (NH₄)₆Mo₇O₂₄·4H₂O (150 °C) addition was 82.3 % but the presence of (NH₄)₂Mo₄O₁₃ secondary phase affects this value since it has a lower ρ (3.528 g/cm³)²⁷ than that of MoO₃ (4.69 g/cm³) as shown in Fig. 3a. ϵ_r of cold sintered MoO₃ with (NH₄)₂Mo₄O₁₃ as a secondary is ~ 10, larger than that of pure MoO₃. After annealing at 700 °C, the relative ρ increased to its

highest value (83.7 %) but ε_r decreased to 9.91. Qf value of cold sintered MoO_3 with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ addition was only 500 GHz, but increased to 11,800 GHz after annealing at 700 °C. TCF value of the annealed MoO_3 ceramics is about -48 ± 10 ppm/°C, which is similar to the conventionally sintered MoO_3 ceramics.

Calculation of ε_r of MoO_3 using Shannon's additive rule

Based on the above results, we conclude that higher relative ρ results in higher ε_r but estimation of the true ε_r of MoO_3 ceramic with high porosity is inaccurate. From Shannon's additive rule,²⁸ polarizability at microwave region can be treated as the sum of both ionic and electronic components and the molecular polarizability (α) of complex substances maybe estimated by summing α of the constituent:

$$\alpha_{\text{MoO}_3} = \alpha_{\text{Mo}^{6+}} + 3\alpha_{\text{O}^{2-}} = 9.31 \text{ \AA}^3, \quad (4)$$

where the ionic polarizabilities of Mo^{6+} and O^{2-} are 3.28 \AA^3 and 2.01 \AA^3 , respectively.^{28,29} Considering the Clausius–Mosotti relation,³⁰

$$\varepsilon_{\text{cal}} = \frac{3V + 8\pi\alpha}{3V - 4\pi\alpha} \approx 10.96, \quad (5)$$

where V is the cell volume ($202.95/4 = 50.74 \text{ \AA}^3$). The calculated permittivity is 10.96, larger than the measured maximum value ~ 9.91 . Shannon's additive rule usually gives good estimation for low permittivity materials and it is worth believing that the real permittivity of MoO_3 is around 11, which is 45 % and 67 % larger than the traditional one here and reported value,¹³ respectively.

Conclusions

MoO_3 can not be well densified by conventional sintering with a relative $\rho \sim 64.5\%$ obtained at 680 °C giving a $\varepsilon_r \sim 7.58$, a $Qf \sim 35,000$ GHz and a $TCF \sim -39$ ppm/°C.

Water-assisted cold sintering method increased the relative density of MoO₃ ceramic to ~ 78 %, which was further improved to ~ 83 % by the addition of (NH₄)Mo₇O₂₄•4H₂O. However, higher temperature annealing was still required to eradicate secondary phases and / or and increase Qf . Calculated ϵ_r of MoO₃ using Shannon's additive rule is ~ 10.96, which is 10 % larger than that of the optimum cold sintered samples. Although relative ρ of MoO₃ did not achieve > 95 %, the methodology of introducing a cold sintering step for materials that are difficult to be sintered is adequately demonstrated.

ACKNOWLEDGEMENTS

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Figure Captions:

Fig. 1 a) Relative ρ , ϵ_r and Qf value of MoO_3 ceramics prepared via conventional sintering as a function of sintering temperature (640 ~ 740 °C). b) Optical images of starting powders and MoO_3 ceramic sintered at 680 °C / 2 h with its crystal structure inset.

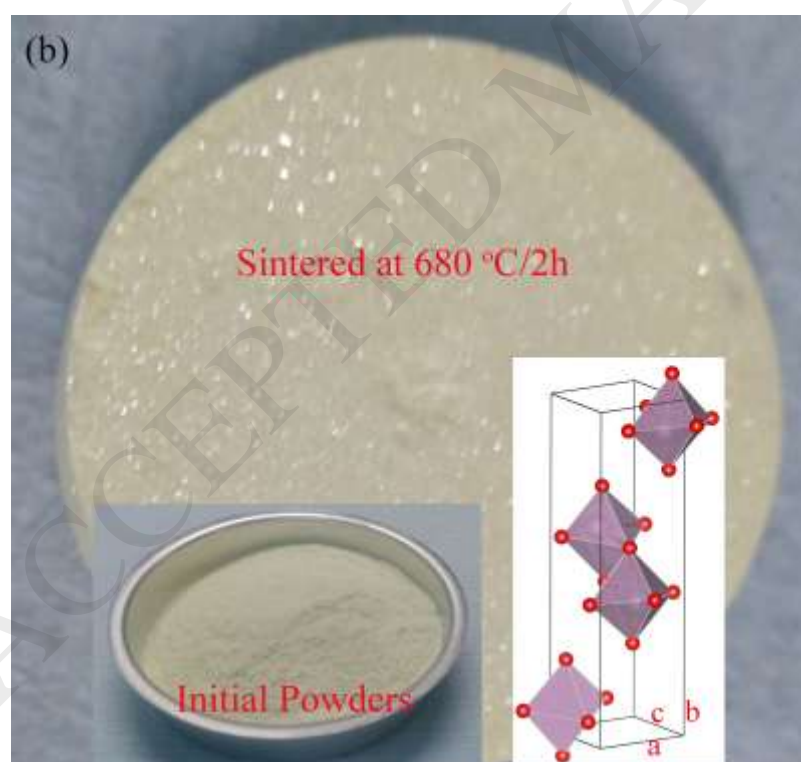
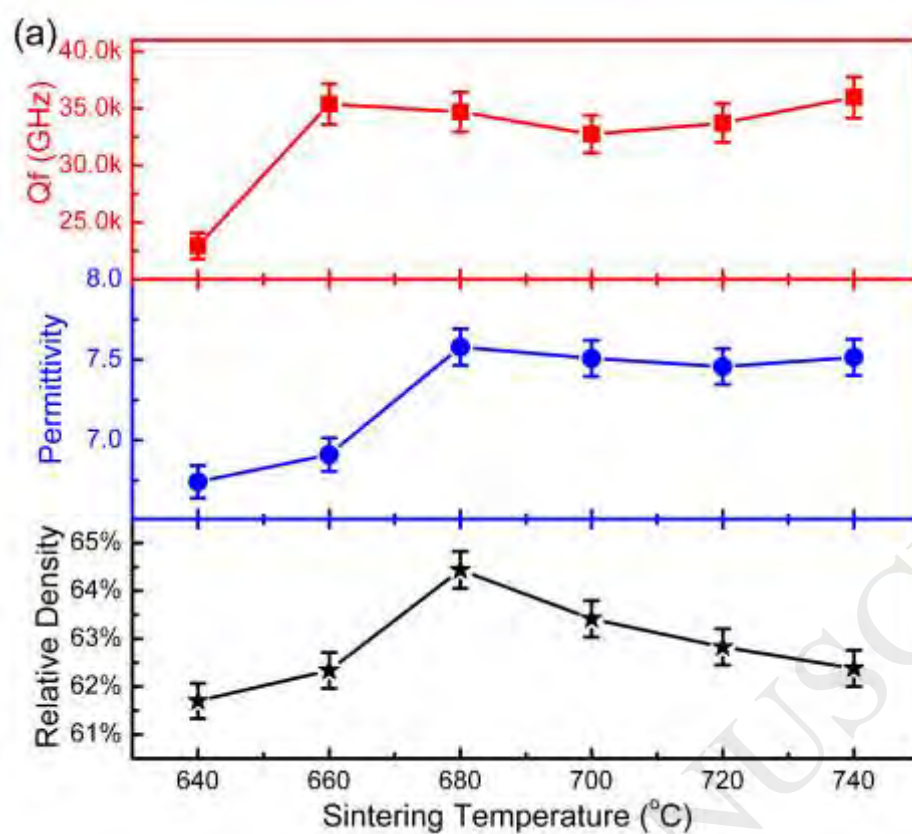
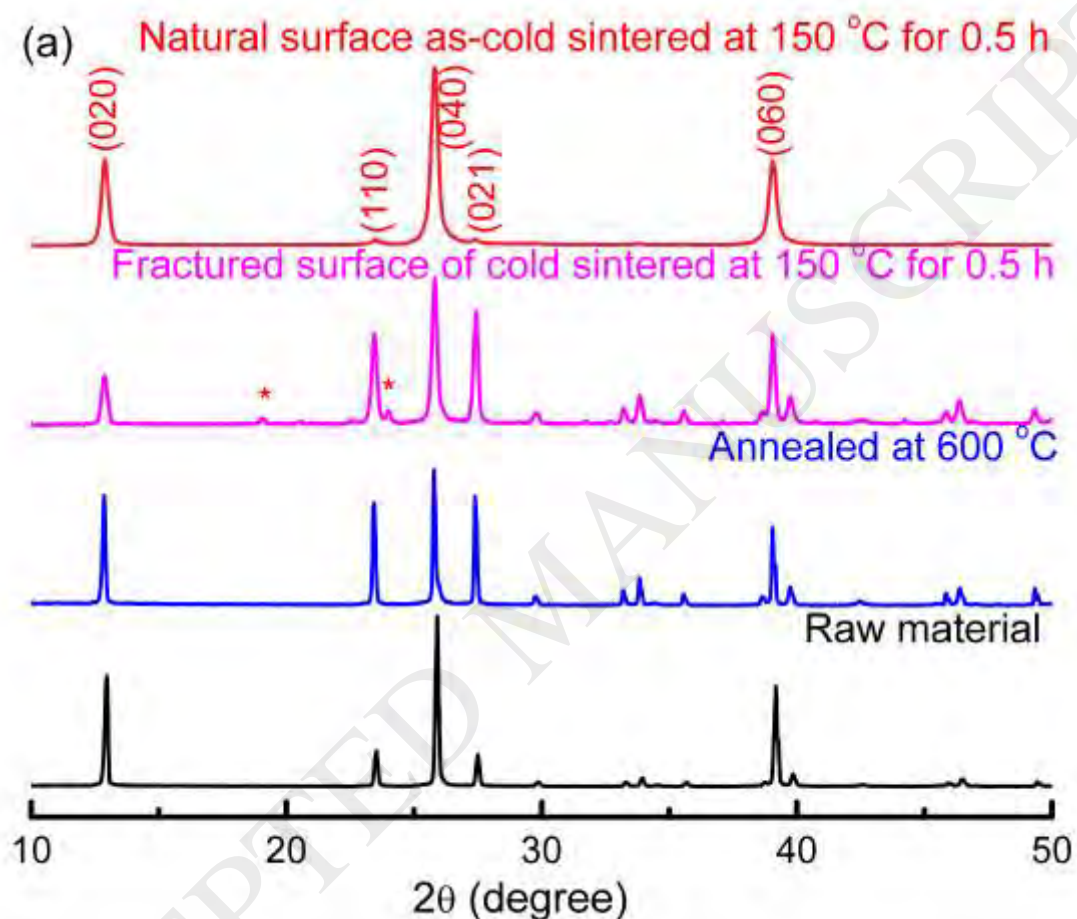


Fig. 2 a) XRD patterns of the raw MoO_3 powders, natural and fractured surfaces of cold sintered MoO_3 ceramic at 150°C for 0.5 h, and annealed sample 620°C . b) Optical and SEM images of the starting powders and cold sintered MoO_3 ceramics.



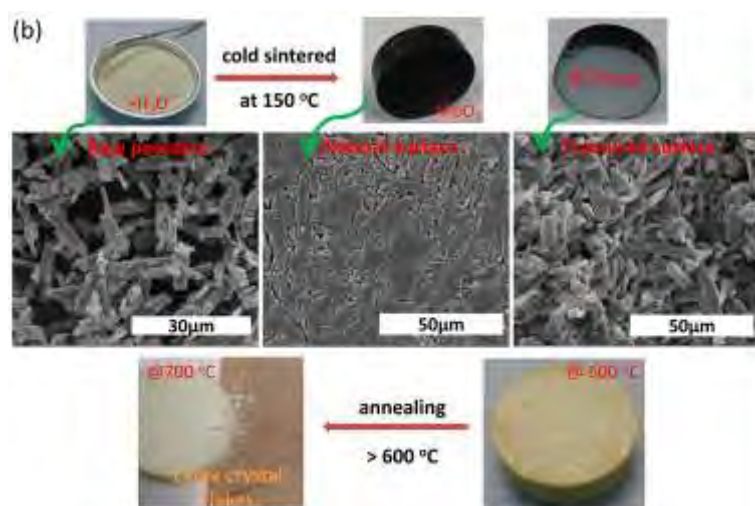
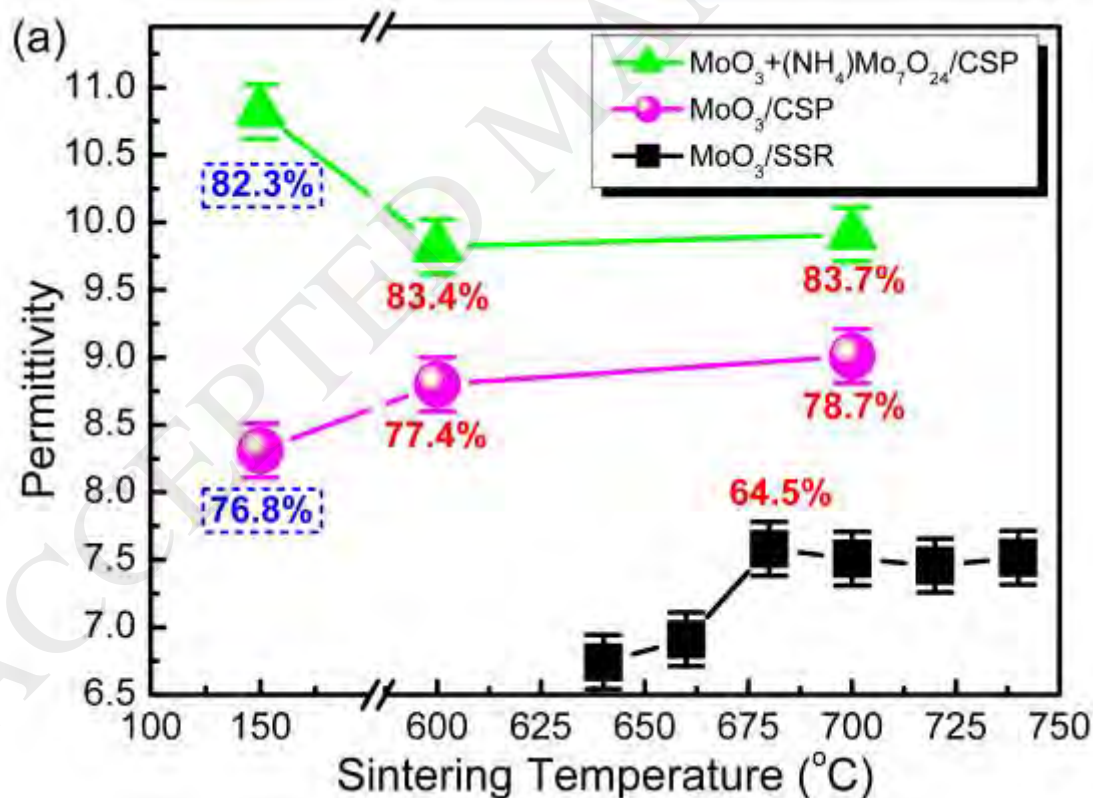


Fig. 3 a) Relative ρ , ϵ_r and b) Qf of the MoO_3 prepared via conventional and cold sintering methods as a function of sintering temperature.



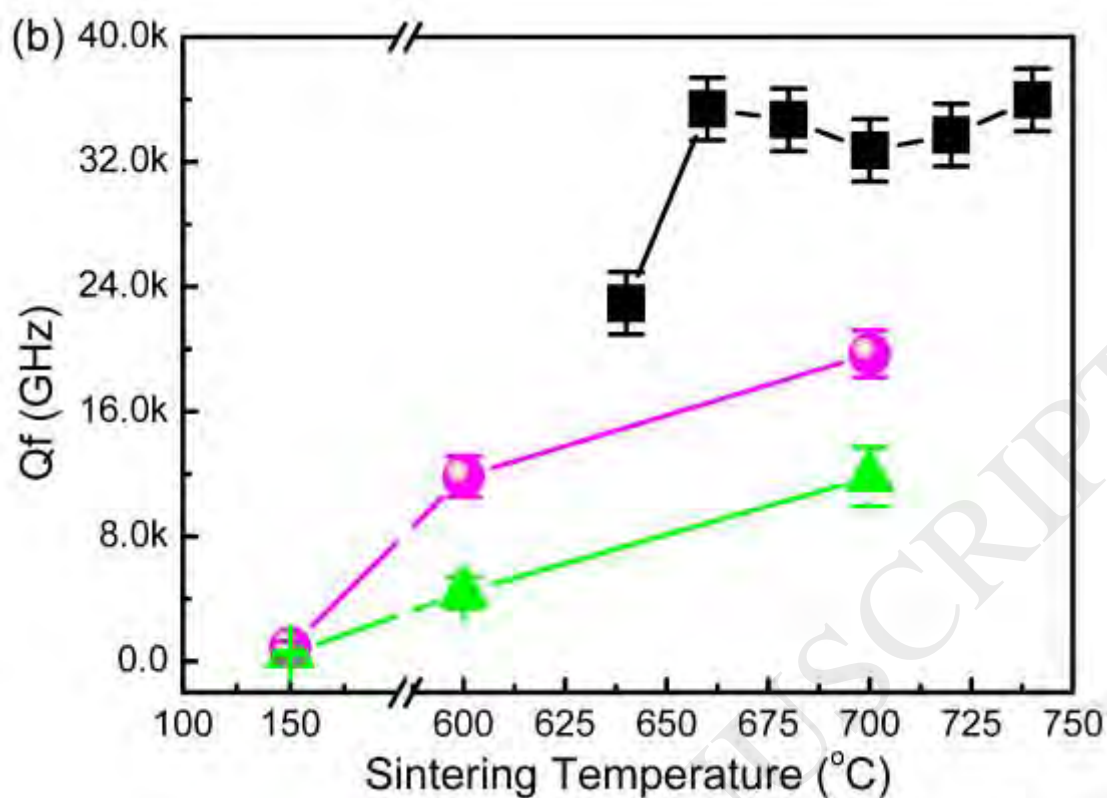
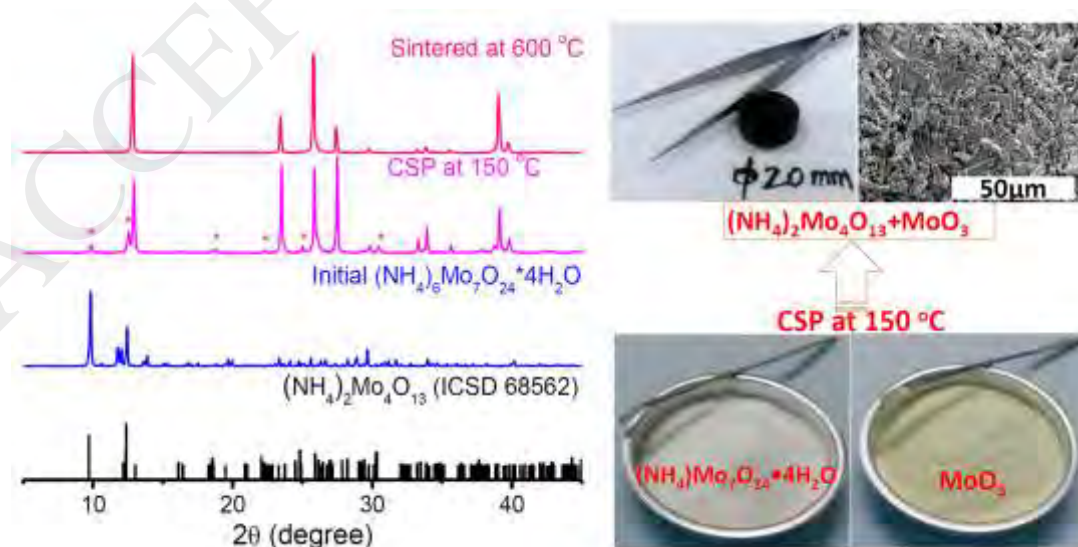


Fig. 4 XRD patterns of the starting $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ powder, cold sintered MoO_3 ceramic with $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24}\cdot 4\text{H}_2\text{O}$ (150 °C for 0.5 h) and a sample annealed at 600 °C, and optical and SEM images of the starting powders and cold sintered MoO_3 ceramics.



ACCEPTED MANUSCRIPT