

Improvements and Modifications to Room-Temperature Fabrication Method for Dielectric Li_2MoO_4 Ceramics

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Dielectric properties of lithium molybdate disks fabricated by moistening water-soluble Li_2MoO_4 powder, compressing it, and postprocessing the samples at 120°C, were improved by the optimization of powder particle size, sample pressing pressure, and postprocessing time. It appeared that the postprocessing temperature of the Li_2MoO_4 ceramics could be chosen so as to be applicable to the associated integrated materials as long as the postprocessing time was adequately adjusted to ensure the removal of the residual water. In addition, the dielectric properties of Li_2MoO_4 ceramic were modified with an inclusion of suitable additives. For example, at 1 GHz the relative permittivity of Li_2MoO_4 disks fabricated at room temperature and postprocessed at 120°C was increased from 6.4 to 8.8 with an addition of 10 vol% of rutile TiO_2 and to 9.7 with an addition of 10 vol% of BaTiO_3 . At the same time the loss tangent value increased from 0.0006 to 0.0014 and to 0.011, respectively.

I. Introduction

MICROWAVE dielectric lithium molybdate (Li_2MoO_4) ceramics are conventionally prepared by solid-state synthesis from Li_2CO_3 and MoO_3 at the ultra-low sintering temperature of 540°C, and exhibit a relative permittivity of $\epsilon_r \sim 5.5$ and a $\tan \delta$ value of 0.00028 at 13.051 GHz.^{1,2} Li_2MoO_4 has been sintered in combination with $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at 685°C for magneto-dielectric composites,² with Li_2WO_4 at 600°C for use in humidity sensors,³ and with rutile TiO_2 at 700°C–730°C to form ceramics for microwave dielectric applications.⁴ TiO_2 is widely researched with different additives and in glass ceramic composites when high permittivity for LTCCs is needed.⁵ Also BaTiO_3 has been used to increase the permittivity, for example, in BaTiO_3 –BBSZ (BaO_3 – Bi_2O_3 – SiO_2 – ZnO) glass ceramic compositions with an ultra-low sintering temperature of 450°C for dielectric applications.⁶ However, these sintering temperatures are still too high for seamless integration with silicon technology or organic substrates.

In our recent paper,⁷ a fabrication method for dense Li_2MoO_4 ceramics based on dissolution and recrystallization was presented. Even though the pressed disks were postprocessed at room temperature, at 120°C, and at 540°C, the samples exhibited very similar densities and microwave dielectric properties, that is, a relative permittivity of 4.6–5.2 and a $Q \times f$ value of 10 200–18 500 GHz at 9.6 GHz, depending on the postprocessing temperature. The related loss tangent values were 0.0009 and 0.0005, respectively. In this work, we introduce an optimized fabrication method.

The effects of water content of the Li_2MoO_4 powder, pressure in the compaction of a sample, postprocessing time, as well as powder particle size have been studied to improve the dielectric properties of the samples postprocessed at 120°C. Modification in the dielectric properties of Li_2MoO_4 with BaTiO_3 and TiO_2 is also presented. The crystal structures, microstructures, and dielectric properties of the fabricated samples are investigated.

II. Experimental Procedure

Li_2MoO_4 powder (99+%, Alfa Aesar, Karlsruhe, Germany) was ground with a mortar and pestle, and sieved with mesh sizes of 180, 90, and 45 μm . According to a laser diffraction particle size distribution measurement (LS 13320; Beckman Coulter, Brea, CA), in the original commercial powder at least 95% of the particles were smaller than 500 μm , and that at least 95% of the particles of the sieved powders were smaller than the chosen mesh size. For the Li_2MoO_4 – TiO_2 ceramic composite powder, 10 vol% of TiO_2 (rutile, 99.8%; Alfa Aesar) was mixed with a mortar and pestle with Li_2MoO_4 powder (<180 μm) in ethanol and dried in an oven at 100°C. The same procedure was repeated with 10 vol% of BaTiO_3 (>99.7%; Alfa Aesar) to produce a Li_2MoO_4 – BaTiO_3 ceramic composite powder. All the powders were moistened by spraying with deionized water and mixed with a spatula as in our recent paper.⁷ The moistened powders were then pressed uniaxially in a steel mold to produce disks (diameter 20 mm, height about 3 mm). The disks were dried at 120°C for 24 h. Reference samples from powders sieved with different mesh sizes were sintered at 540°C for 2 h. All the samples were thinned and polished with a P800 carborundum paper (EcoWet, KWH Mirka Ltd, Jeppo, Finland) using ethanol.

In preparation for microstructure imaging with a field-emission scanning electron microscope (FESEM; Zeiss Sigma, Carl Zeiss, Germany) the samples were further polished with water-free diamond solution. The crystal structure of the samples was studied by X-ray diffraction (XRD) using CuK_α radiation (Bruker D8 Discover X-Ray Diffractometer, Karlsruhe, Germany). At 1 GHz, the relative permittivity and loss tangent were measured with an RF impedance/material analyzer (E4991A; Agilent Technologies, Santa Clara, CA). Silver electrodes were sputtered on both sides of the samples for the measurements. Dielectric properties at higher frequency were measured by a noncontact method using a resonant mode technique utilizing a Split Post Dielectric Resonator (QWED, Warsaw, Poland), with a nominal resonant frequency of 9.97 GHz.

III. Results and Discussion

To optimize the room-temperature fabrication method, including moistening and pressing, the effect of different pressures and powder moisture contents was evaluated. The pres-

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sure applied to the moistened Li_2MoO_4 powder affected the density of the samples. From 30 to 180 MPa, the density increased from 2.54 to 2.83 g/cm³ (from 84% to 93% of the theoretical bulk density) reaching its maximum value at a pressure of 150 MPa. The effect of the water content of the Li_2MoO_4 was studied by moistening the powder with different amounts of deionized water. However, the density of the samples stayed at the same level even though the water content of the powder before pressing the samples changed from 2% to 15% by weight. Therefore it is assumed that as long as the powder is moistened, the effect of the amount of added water is not significant. The samples pressed from dry Li_2MoO_4 powder with the same pressure of 150 MPa typically acquired a density of about 80% of the theoretical bulk density, leaving the samples still difficult to handle.

In our earlier research⁷ it was assumed that the increase in loss tangent values as the postprocessing temperature decreased indicated the presence of residual water in the samples. In this research it was noticed that, for the samples postprocessed at 120°C, the increase in time from 4 to 24 h decreased the loss tangent value from 0.0007 to 0.0004 at 9.6 GHz.

The effect of particle size on the dielectric properties of the sintered samples was clear. A smaller particle size enhanced sintering, resulting in higher density and permittivity, as well as in lower loss tangent values. Permittivities of 5.3 and 5.1 as well as loss tangent values of 0.0003 and 0.0004 at the frequency of 9.6 GHz were measured for the samples prepared from the powders sieved with mesh sizes of 45 μm and 180 μm , respectively, and sintered at 540°C for 2 h. Considering the difference in measuring techniques and frequency, the loss tangent value for the sintered sample made from the <45 μm powder was similar to that earlier reported by Zhou *et al.*,¹ $\tan \delta = 0.00028$ at 13.051 GHz. Overall, for the samples postprocessed at the sintering temperature of 540°C, the dielectric properties improved as the particle size of the powder decreased. However, this was not the case with the samples postprocessed at 120°C for 24 h. At 9.6 GHz, these samples showed a decrease in permittivity from 5.1 to 4.2, and an increase in loss tangent values from 0.0004 to 0.0032 as the particle size of the used powder decreased from <180 μm to <45 μm . Small particle sizes complicated the even moistening of the powder, resulting in clay-like clusters and nonuniform density leading to sample warpage and cracking. It can be concluded that when fabricating Li_2MoO_4 disks with the moistening and pressing method, a larger particle size is advantageous.

It should be noted that the relative permittivity and the loss tangent values were the same for the samples fabricated from the powder with the particle size of <180 μm and postprocessed at 540°C for 2 h as they were for the samples postprocessed at 120°C for 24 h. This indicates that with this fabrication method the postprocessing temperature is not decisive and mainly affects the time needed to remove the residual water from the samples.

The dielectric properties of the Li_2MoO_4 with a particle size <180 μm were modified with 10 vol% of TiO_2 and with 10 vol% of BaTiO_3 additions. Figures 1(a) and (b) show the backscattered electron images of these composites, respectively. In Fig. 1(a) the dark gray particles belong to the TiO_2 phase and in Fig. 1 (b) the light-colored particles belong to the BaTiO_3 phase. The difference between the particle size of the Li_2MoO_4 powder and that of the additive powders results in a belt-like distribution of the additives. During the mixing, the smaller particles of TiO_2 and BaTiO_3 powders attach to the surface of the larger sized Li_2MoO_4 particles. When the samples are pressed, the additives are incorporated between the Li_2MoO_4 particles attached to each other.

The phases illustrated in the FESEM images can also be identified from the XRD patterns of the Li_2MoO_4 powder, Li_2MoO_4 with 10 vol.% of TiO_2 , and Li_2MoO_4 with 10 vol % of BaTiO_3 , as shown in Fig. 2. Only the peaks arising

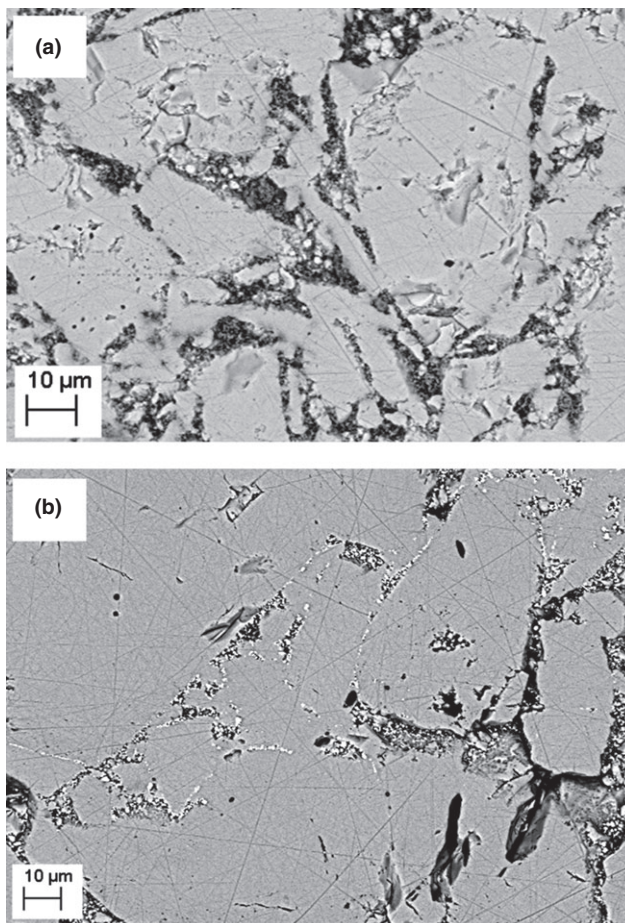


Fig. 1. Backscattered electron images of Li_2MoO_4 with an addition of (a) 10 vol% of TiO_2 and (b) 10 vol% of BaTiO_3 .

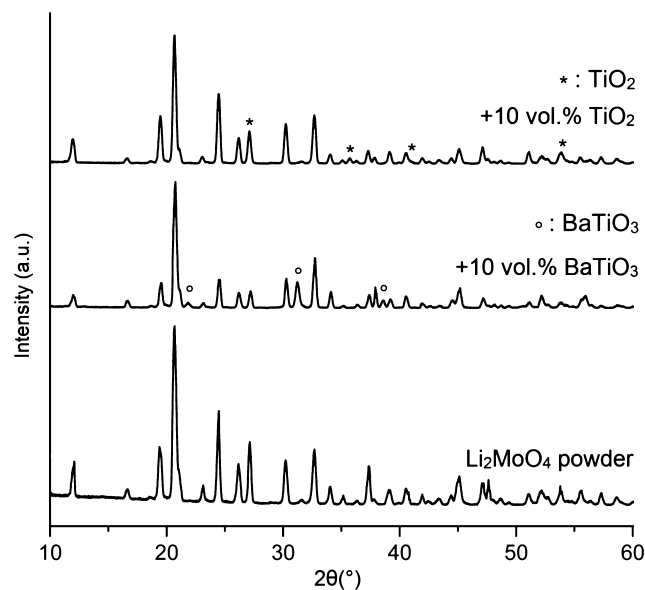


Fig. 2. X-ray diffraction pattern for Li_2MoO_4 powder, Li_2MoO_4 with 10 vol% of TiO_2 , and Li_2MoO_4 with 10 vol% of BaTiO_3 .

from the Li_2MoO_4 powder and from TiO_2 and BaTiO_3 can be detected, indicating that Li_2MoO_4 does not react with the additives at 120°C. The suitability of Li_2MoO_4 with TiO_2 was earlier reported by Guo *et al.*⁴ However, they also reported a reaction between Li_2MoO_4 and TiO_2 occurring in the presence of silver particles, forming LiTi_2O_4 and Ag_2MoO_4 extra phases, allegedly due to the high sintering temperature of 700°C–730°C. Thus cofiring of silver elec-

Table I. Dielectric Properties of the Prepared Li₂MoO₄ Ceramics

	Li ₂ MoO ₄		+10 vol% TiO ₂		+10 vol% BaTiO ₃	
<i>f</i> (GHz)	1	9.6	1	9.4	1	9.2
ε _r	6.4	5.1	8.8	6.7	9.7	8.2
tan δ	0.0006	0.0004	0.0014	0.0014	0.011	0.026

trodes could be problematic. However, it can be assumed that the low fabrication temperature used in our research could have prevented the formation of unwanted extra phases with silver.

The permittivity of Li₂MoO₄ was increased with an addition of 10 vol% of TiO₂ and BaTiO₃. Dielectric properties of the Li₂MoO₄ ceramic samples prepared with the optimized room-temperature fabrication method and samples with an addition of 10 vol.% of TiO₂ or BaTiO₃ (dried at 120°C for 24 h), are presented at Table I. The theoretical permittivity of a two-phase composite can be calculated by Lichtenecker's empirical logarithmic rule:

$$\lg \varepsilon = y_1 \lg \varepsilon_1 + y_2 \lg \varepsilon_2 \quad (1)$$

where y_1 and y_2 define the volume fractions of materials 1 and 2, and ε_1 and ε_2 refer to the permittivities of the materials, respectively. In this case, with a relative permittivity of ~100 for TiO₂,⁸ the calculated relative permittivity of the TiO₂-Li₂MoO₄ composite is 8.4 at 1 GHz and 6.9 at 9.4 GHz. Likewise, the calculated relative permittivity of the BaTiO₃-Li₂MoO₄ composite is 11.8 at 1 GHz and 9.6 at 9.2 GHz, assuming a relative permittivity of ~3000 for the used BaTiO₃.⁶ The measured relative permittivities of Li₂MoO₄ with an addition of 10 vol% of TiO₂ are in good accordance with the calculated theoretical permittivities of a two-phase composite at both measurement frequencies. However, the measured relative permittivities of Li₂MoO₄ with an addition of 10 vol% of BaTiO₃ are smaller than the calculated values. According to McNeal *et al.*,⁹ for BaTiO₃ with an average grain size of about 2 μm, the relative permittivity begins to decrease significantly with increasing frequency at above 100 kHz, making it not feasible to measure the dielectric properties at a frequency above 100 MHz. Therefore the assumed relative permittivity of 3000 is probably not correct in our case and the actual permittivity of the used BaTiO₃ powder at the measurement frequencies used in this research was much lower.

IV. Conclusions

The dielectric properties of Li₂MoO₄ ceramics fabricated at room temperature and post-processed at 120°C improved with increases in the powder particle size, sample compaction pressure, and postprocessing time. These resulted in higher Li₂MoO₄ sample density and elimination of the residual water. Results indicate that the actual postprocessing temperature is not decisive, meaning that a suitable temperature for the selected application can be chosen as long as the postprocessing time is adjusted accordingly. However, a low postprocessing temperature is thought to prevent the formation of extra phases, resulting in an easier prediction of permittivity and controllability of the phases of a ceramic composite. The results suggest that the dielectric properties of Li₂MoO₄ ceramics fabricated at room temperature and post-processed at 120°C can be further modified with suitable additives providing a number of useful materials for seamless integration of ceramics and polymers.

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