High-Q Li$_2$Mg$_2$(MoO$_4$)$_3$ dielectrics for LTCC applications at microwave frequencies

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ABSTRACT

Li$_2$Mg$_2$(MoO$_4$)$_3$ dielectric was prepared via the conventional solid-state method, and its dielectric properties were investigated in the microwave frequency region. The XRD patterns of the sintered samples revealed single-phase formation with an orthorhombic structure and a space group belonging to Pnma(62). Lattice parameters, bond length, and Raman spectra of the ceramics were also investigated. The dielectric properties exhibited significant dependence on the sintering conditions. The $\tau_r$ values (resonant frequency temperature coefficient) remained in a range from $\sim$ 60 to $\sim$ 69 ppm/°C for all specimens because the changes in the unit cell volume were small. Excellent microwave dielectric properties ($\varepsilon_r \sim 9.5$, $Q \times f \sim 80,000$ GHz and $\tau_r \sim$ $-69$ ppm/°C) can be obtained for Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics sintered at 880°C for 4 h. This constitutes a very promising material for LTCC applications.

1. Introduction

Low-temperature co-fired ceramics (LTCC) technology has been widely used in the fabrication of multi-layer devices for modern wireless communication components in the last two decades. LTCC multi-layer devices are normally composed of layers of alternating microwave dielectric ceramics and internal electrodes. Owing to its high conductivity and low cost, Ag is generally chosen as the internal electrode material for LTCC application. In order to avoid the migration of Ag, the sintering temperature of the ceramics should be lower than the melting temperature of the Ag electrode (melting point $\sim$961°C) [1–3].

In addition, other major requirements for LTCC materials include a low dielectric constant ($\varepsilon_r<10$), a high $Q \times f$ value, and a near-zero resonant frequency ($\tau_r$) temperature coefficient. In order to lower the sintering temperature of microwave dielectric ceramics for LTCC application, sintering aids addition is a common approach. However, with the sintering aids addition, the degradation of the dielectric properties, especially $Q \times f$ value, is worth paying attention. As a result, the demand for new ceramics with intrinsic low sintering temperature and excellent microwave dielectric properties is desired than ever.

Complex tungstates and molybdates crystals are well-known laser host materials. Moreover, ABO$_4$ ($A =$ Ca, Sr, Ba and $B =$ Mo, W) compounds, having a tetragonal scheelite-structure and a space-group $I4_1/a$, are functional materials in scintillation detectors, phosphors, lasers, photo-catalysts, lithium-ion batteries, and microwave dielectric ceramics [4]. Furthermore, the AMo$_4$ ($A =$ Ca, Sr, Ba) family was found to have good combinations of microwave dielectric ceramics ($\varepsilon_r \sim 9–11$, $Q \times f \sim 37,000–90,000$ GHz and $\tau_r \sim 57–87$ ppm/°C) [5]. It is worth noting that the sintering temperature of dielectrics is relatively low (800–1100°C), which makes them a potential candidate material for LTCC applications [6,7]. In addition, double molybdates such as NaLa(MoO$_4$)$_2$ and NaBi(MoO$_4$)$_2$ have also been reported to be suitable photoluminescence and LTCC dielectrics [6]. This motivated the present investigation of other LTCC dielectrics in the molybdates family. The crystal of lithium metal triple molybdates with the chemical formula Li$_2$Mg$_2$(MoO$_4$)$_3$, having a lyonsite-type orthorhombic structure, has been studied as a potential host for Eu$^{3+}$ ions in PL applications [8]. However, their microwave dielectric properties have not been studied yet.

In this paper, the crystal structure and the microwave dielectric properties of Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics were firstly investigated. The surface morphology, XRD patterns, and Raman spectrum were also studied. Crystalline information was estimated from the X-ray profile refined by the GSAS program. In addition, a U-type bandpass filter using the Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramic substrate was designed and implemented to further verify the performance of the proposed dielectric.
2. Materials and methods

Specimens of a Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramic were processed with high-purity Li$_2$CO$_3$, MgO, and MoO$_3$ oxide powders (>99.9%) using a conventional solid-state reaction method. The starting materials were weighed according to the desired stoichiometry and were then mixed and ball-milled with distilled water and zirconia balls in an anion container for 24 h. The mixtures of Li$_2$Mg$_2$(MoO$_4$)$_3$ were dried and calcined at 600°C for 2 h in air. After drying and mixing with 5 wt% of a 10% PVA solution as a binder, the prepared powders were granulated by sieving through a 200 mesh and pressed into 5 mm thick pellets measuring 11 mm in diameter using an automatic uniaxial hydraulic press at 2000 psi. The Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics were sintered at 820–940°C for 4 h. The crystal structures of the sintered ceramics were analyzed with a Siemens D5000 diffractometer (Munich, Germany) with Cu Kα radiation operated at 40 kV and 40 mA. Raman spectra were excited with a 532 nm Raman Spectrometer light source (Jobin Yvon/Labram HR). The microstructures were evaluated using scanning electron microscopy (UHR–SEM; HitachiSU-8000), and the composition of the samples was analyzed with an energy-dispersive X-ray spectrometer (EDS, Philips). The bulk densities of the ceramics were measured using the Archimedes method.

Measurements of the dielectric constant ($\varepsilon_r$) and the unloaded quality factor values ($Q_0$) on TE$_{011}$ mode at 14–17 GHz were accomplished using the post resonant method developed by Hakkii-Coleman [9] and Courtney [10]. It consisted of two parallel conducting plates and coaxial probes connected to a HP8757D network analyzer and a HP8350B sweep oscillator. By measuring the TE$_{015}$ resonant frequency at 25°C and 80°C, the temperature coefficient of resonant frequency $\tau_f$(ppm/°C) could be obtained as

$$\tau_f = (f_2 - f_1)/(f_1(T_2 - T_1))$$

where $f_1$ and $f_2$ represent the resonant frequencies at $T_1$ and $T_2$, respectively. The entire test setup was then placed over a thermostat in a temperature range of 25–80°C. Rietveld refinement of the powder X-ray diffraction data was performed with the General Structure and Analysis (GSAS) system. The patterns were refined for the lattice parameters, scale factor, background, bond length, bond angle, and atomic coordinates.

3. Results and discussion

The relative densities and $\varepsilon_r$ values of Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics as a function of sintering temperature are shown in Figure 1. It can be seen that the relative densities of the specimens initially increased with increasing in the sintering temperature and reached a maximum of 96% at 880°C, which was due to the grain growth and the decrease in the number of pores (whose $\varepsilon_r$ near to 1), as shown in Figure 2(a–e). However, the relative densities decreased slightly thereafter, suggesting that 880°C is the optimal sintering temperature. Variations in $\varepsilon_r$ were consistent with those of the relative density, because a higher density represented lower porosity, indicating that density might be a primary factor affecting $\varepsilon_r$ in this experiment. A maximum $\varepsilon_r$ value of ~9 was obtained for the specimen sintered at 880°C for 4 h.

Figure 2 provides SEM micrographs of Li$_2$Mg$_2$(MoO$_4$)$_3$ specimens at different sintering temperatures. It can be seen that the specimen sintered at 820°C has a distribution of comparably small grain sizes and a noticeable amount of intergranular porosity. Grain size increases with increases in the sintering temperature, leading to the grains being closely packed with
only a small amount of porosity and showing a dense, uniform microstructure that could be observed at 880°C. Further increases in the sintering temperature degraded grain uniformity, and abnormal grain growth began to appear at 940°C. The $Q \times f$ values of Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics at different sintering temperatures

![Figure 2. SEM micrographs of Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics sintered at (a) 820°C, (a) 850°C, (c) 880°C, (d) 910°C, (e) 940°C for 4 h, and (f) EDS data.](image)

![Figure 3. $Q \times f$ values of Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics sintered at different temperatures for 4 h.](image)
are illustrated in Figure 3. The measured microwave dielectric loss represents the overall loss, including not only intrinsic loss related to the lattice vibration modes, but also extrinsic contributions related to density, second phases, impurities, surface morphology, and the lattice defect [11,12]. The variations in $Q \times f$ showed a similar trend to that of the relative density, which suggests that the dielectric loss was mainly controlled by the densification and that the maximum $Q \times f$ of 80,000 GHz could be achieved for specimens sintered at 880°C for 4 h.

Since there is no second phase detected in the Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics, crystal structure may play an important role in the dielectric properties. Accordingly, the $\tau_f$ values of the specimens (Figure 4) ranged stably from $-60$ ppm/°C to $-69$ ppm/°C since the variations in the lattice parameters and cell volumes were limited and within 0.5%, as shown in Table 1.

The Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics, single orthorhombic structure, belongs to the space group Pnma(62) [8]. In order to further clarify the crystal structure of Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics, Rietveld refinements were carried out using GSAS software, for which the refined plot of the specimen sintered at 880°C is illustrated in Figure 5. The refined lattice parameters, molecular volume, reliability factors, and goodness of fit indicators are presented in Table 1. The variations in the lattice parameters and cell volumes were limited and within 0.5%, and the goodness of fit indicator values ($\chi^2$) were all <2. As can be seen, the results from Figure 5 are identical to the crystallographic data achieved from Rietveld refinement, as shown in Table 1. These results also confirmed the formation of a single orthorhombic structure phase.

Based on crystal structural considerations, the $Q \times f$ values also maybe largely dependent on the relative density. In the microcosm study, the packing density (shown in Table 1) is more related to the crystal structure system. The results confirmed the dependence of the $Q \times f$ on the packing density of the ceramics, and their variations were similar.

Moreover, Shannon reported that the dielectric constant is directly proportional to the ionic polarizabilities ($\alpha_D$) and inversely proportional to the molecular volume ($V_m$), as is known from the Clausius–Mosotti equation [13]:

$$
\alpha_D = V_m(\varepsilon_r - 1)/[b(\varepsilon_r + 2)]
$$

where $\varepsilon_r$ is the corrected dielectric constant, and $b$ is a constant value $4\pi/3$. The experimental dielectric

![Figure 4](image-url). $\tau_f$ values of Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics sintered at different temperatures for 4 h.

| Sintering temp.(°C) | 820   | 850   | 880   | 910   | 940   |
|--------------------|-------|-------|-------|-------|-------|
| a (Å)              | 5.135 | 5.122 | 5.128 | 5.125 | 5.125 |
| b (Å)              | 10.479| 10.468| 10.475| 10.474| 10.472|
| c (Å)              | 17.647| 17.620| 17.638| 17.638| 17.625|
| cell volume (Å$^3$)| 949.7 | 947.4 | 944.8 | 945.9 | 946.8 |
| packing density (%)| 45.631| 45.741| 45.867| 45.814| 45.770|
| $R_{wp}$ (%)       | 9.78  | 11.27 | 10.6  | 11.03 | 11.84 |
| $R_p$ (%)          | 1.83  | 1.53  | 1.38  | 1.56  | 1.58  |
| $V_m$ (Å$^3$)      | 237.43| 236.85| 236.20| 236.48| 236.70|
| $\varepsilon_r$    | 7.3   | 8.3   | 9.5   | 9.0   | 8.5   |
| $\varepsilon_{rc}$ | 9.2   | 9.7   | 10.0  | 9.6   | 9.3   |
| $\alpha_D$ (Å$^3$) | 41.44 | 42.04 | 42.29 | 41.85 | 41.50 |

$R_{wp}$: the reliability factor of weighted patterns; $R_p$: the reliability factor of patterns; $\chi^2$: goodness of fit indicator = ($R_{wp}/R_{exp}$)$^2$.
constant can be corrected by porosity using the following equation [12]:

\[ \varepsilon_r = \varepsilon_{rc} \left[ 1 - 3P(\varepsilon_{rc} - 1)/(2\varepsilon_{rc} + 1) \right] \quad (3) \]

where \( \varepsilon_r \) is the measured dielectric constant, and \( P \) is the fractional porosity. The \( \varepsilon_{rc} \) exhibited a similar trend in variations to that of \( \alpha_D \), as shown in Table 1. The results suggest that the dielectric constant is mainly controlled by the porosity and ionic polarizability rather than by the molecular volume.

Figure 6 illustrates the Raman spectrum of the \( \text{Li}_2\text{Mg}_2(\text{MoO}_4)_3 \) ceramics recorded at room temperature. \( \text{M–O} \) \((\text{M} = \text{V}, \text{Mo}, \text{W}, \text{etc.})\) stretching Raman bands generally appear at \( \sim 900-1040 \text{ cm}^{-1} \). As can be seen, the Raman bands are distributed in two distinct regions between 828 and 995 cm\(^{-1}\) corresponding to the \( \text{MoO}_4 \) symmetric stretching modes, between 326 and 370 cm\(^{-1}\) representing the \( \text{MoO}_4 \) bending modes. In addition, the 971 cm\(^{-1}\) and 995 cm\(^{-1}\) bands both are \( \text{Mo–O–} \)-type with Mg and Li to the left, respectively.

For LTCC applications, an U-type band-pass filter with stubs at the input and output ports are designed and fabricated to verify the performance of the proposed ceramics. The filter was designed to have a fractional bandwidth of 7.5\% at a center frequency of 2.4 GHz and was fabricated on the \( \text{Li}_2\text{Mg}_2(\text{MoO}_4)_3 \) ceramic substrate. Figure 7 and Table 2 illustrates the physical layout and corresponding parameters of the designed filter for which the response was simulated by the software. Photos and corresponding results of the filter prototype are provided in Figures 8 and 9, respectively. The measurements indicated a band-pass

![Figure 5](image_url)  
Figure 5. Structural refinement pattern of \( \text{Li}_2\text{Mg}_2(\text{MoO}_4)_3 \) ceramics sintered at 880°C for 4 h.

![Figure 6](image_url)  
Figure 6. Raman spectrum of \( \text{Li}_2\text{Mg}_2(\text{MoO}_4)_3 \) ceramics recorded at room temperature.
center frequency of 2.42 GHz with a 3-dB pass-band width of 6.2%, compared with simulated values of 2.4 GHz and 7.5%, respectively. In addition, the measured insertion loss and return loss are –1.35 dB and –24.5 dB, compared with a simulated value of –0.7 dB and 25.3 dB, respectively. The results indicated that the measured response was influenced by the surface roughness of the

Figure 7. Layout of the U-type band-pass filter with on Li$_2$Mg$_2$(MoO$_4$)$_3$ substrate.

Table 2. The corresponding parameters of the designed filter.

| L (mm) | b (mm) | c (mm) | d (mm) | b$_2$ (mm) | p (mm) | e (mm) | k (mm) | u (mm) | j (mm) |
|--------|--------|--------|--------|------------|--------|--------|--------|--------|--------|
| 9.9    | 2      | 4.9    | 2      | 2          | 0.6    | 0.4    | 9.8    | 1.5    | 9.6    |
| g (mm) | i (mm) | n (mm) | b$_2$ (mm) | a (mm) | b$_1$ (mm) | q (mm) | m (mm) | h (mm) |
| 3.3    | 6.5    | 3.9    | 2.5    | 8          | 1.6    | 6.6    | 5.3    | 1.6    |

Figure 8. Simulated and measured frequency responses of the filter on Li$_2$Mg$_2$(MoO$_4$)$_3$ substrate.
substrate, the conductor thickness, the electric contact, and the substrate shrinkage.

4. Conclusion

The microwave dielectric properties of Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics were investigated in the present study. A single-phase, which corresponded to an orthorhombic structure, belonging to the space group Pnma (62), was identified for all the specimens at different sintering temperatures. A highest ε$_r$ of 9 and a maximum Q×f value of 80,000 GHz could be achieved for specimens sintered at 880°C for 4 h. The τ$_f$ values stably ranged from –60 ppm/°C to –69 ppm/°C since no second phase was formed, and variations in the lattice parameters and cell volumes were also limited. Li$_2$Mg$_2$(MoO$_4$)$_3$ ceramics not only offer excellent dielectric properties (ε$_r$~9.5, Q×f~80,000 GHz and τ$_f$~–69 ppm/°C), but also features a low sintering temperature. Together, this makes it a promising material for LTCC applications as verified with the fabricated band-pass filter.

Disclosure statement

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Funding

This work was financially supported by the Ministry of Science and Technology of Taiwan under grant MOST 105-2221-E-006-055-MY3.

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