The structure and microwave dielectric properties of Li$_2$MoO$_4$–SiO$_2$ ceramics without addition of glass as sintering aids

Yuanming Lai$^{a}$, Xiaoli Tang$^{a}$, Huaiwu Zhang$^{a}$, Xiaofeng Liang$^{b}$, Xin Huang$^{a}$, Jie Li$^{a}$, Hua Su$^{a,*}$

$^{a}$State Key Laboratory of Electronic Thin Films and Integrated Devices, University of Electronic Science and Technology of China, Chengdu 610054, China.

$^{b}$Analytical and Testing Center, Southwest University of Science and Technology, Mianyang 621010, PR China

* Corresponding author: Tel.: +86 2883203793, E-mail address: uestcsz77@163.com

SiO$_2$ ceramic is one of the most important candidate materials for high-frequency microwave ceramics with very low dielectric constant ($\varepsilon_r$) at around 3.8 and low dielectric loss. However, a high sintering temperature must be provided during the preparation, which restricted their further application in low temperature co-fired ceramic (LTCC) field. In the present work, Li$_2$MoO$_4$–(1+δ)SiO$_2$ (δ = -0.5, -0.2, 0, 0.2, 0.5 mole) ceramics were prepared by solid-state reaction method and sintered at 800 °C. XRD, SEM, EDS and Raman spectroscopy techniques were used to study the phase composition and crystal structure. The ceramic samples were composed of both Li$_2$MoO$_4$ and SiO$_2$ phases. The $\varepsilon_r$ values decrease with increased δ, which agree with the Lichtenecker logarithmic rule. The quality factor (Q×f) value initially increased and then decreased with increased δ. When evaluated as a microwave dielectric material, the Li$_2$MoO$_4$–(1+δ)SiO$_2$ ceramics show excellent dielectric performance with a low dielectric constant ($\varepsilon_r$ = 4.807) and high Q×f values of $\sim$21000 GHz at δ = 0 as sintered at 800 °C, which is a possible candidate for LTCC.

Key words: Microwave dielectric ceramics, Structure, Dielectric properties, Raman spectroscopy

1. INTRODUCTION

With the rapid development of mobile telecommunications, the low-permittivity, low-loss materials have attracted extensive attention owing to their potential use as a substrate material [1]. For the microwave propagation in a substrate, the phase delay is proportional to $\varepsilon_r$. Thus, microwave substrate materials with lower dielectric constant are urgently demanded with the development of microwave communication technology towards higher frequencies [2]. Polymers and porous materials with low dielectric constants are also potential candidates as substrate materials. However, their Qf values are usually relatively low [3–6]. Recently, ceramic systems with originally low sintering temperature have been investigated for microwave application. These systems include K$_2$Ba$_{1-x}$Ga$_x$Ge$_2$O$_7$ [7,8], (K$_{0.5}$Ln$_{0.5}$)MoO$_4$ (Ln = Nd and Sm) [9], Ba$_2$ZnSi$_2$O$_7$ [10], LiMnPO$_4$ [11] and Mg$_3$Al$_5$Si$_7$O$_{18}$ [12] ceramics. These ceramics require high sintering temperature during preparation or the dielectric constants still exceed 5.0.

SiO$_2$ ceramics are important insulating materials with very low dielectric constant at around 3.8 and low dielectric loss, indicating their possible applications as microwave substrates [1]. Recently, varying Qf values from several to tens of thousands GHz have been reported for fused silica [13,14]. Low dielectric constant and high Qf value, through B$_2$O$_3$-modified amorphous SiO$_2$ or high-temperature sintering SiO$_2$, were obtained [1,15]. However, a high sintering temperature (1100 °C and 1650 °C) must be provided during the preparation, which restricted their further application in LTCC field. Thus, there is always much interest in searching for ceramic systems with much better sintering and microwave dielectric properties.

LTCC technology imposes the additional requirement of a low sintering temperature: lower than 960 °C [16,17]. The low sintering temperature of LTCC substrate materials can be achieved by recrystallisation or by the addition of low-melting-point glass. However, the presence of a glassy phase in both cases, the dielectric losses are higher than in glass-free material. Although Li$_2$MoO$_4$ materials have been extensively researched in high-performance rechargeable batteries [18–20], these materials have only been recently recognised as potential candidates for low-dielectric-constant microwave applications [21,22]. Recently, the microwave dielectric properties of Li$_2$MoO$_4$ ceramic have been reported with the ultra-low sintering temperature of 540 °C, exhibiting $\varepsilon_r = 5.5$ and a Qf ~46000 GHz and TCF ~160 ppm/°C [23]. Nonetheless, information about the dielectric properties of Li$_2$MoO$_4$–SiO$_2$ composite ceramics at low sintering temperature is scarce. Thus, there is a need to investigate in more detail the dielectric properties of Li$_2$MoO$_4$–SiO$_2$ composite ceramics.

In this work, the Li$_2$MoO$_4$–(1+δ)SiO$_2$ (δ = -0.5, -0.2, 0, 0.2, 0.5 mole) ceramics were prepared by conventional solid-state ceramic route. The microstructure and microwave dielectric properties were investigated by XRD, SEM, EDS, Raman spectra and microwave resonant cavity.

2. EXPERIMENTAL PROCEDURE

Li$_2$MoO$_4$–(1+δ)SiO$_2$ (δ = -0.5, -0.2, 0, 0.2, 0.5 mole) ceramics were prepared by conventional solid-state ceramic route. Stoichiometric amounts of high-purity 99.9% Li$_2$CO$_3$, SiO$_2$ and MoO$_3$ were used as starting materials and were weighed and wet mixed in distilled water using zirconia balls in a plastic container.

(Continued on the next page...
for 4 h. The slurry was dried and calcined in alumina crucibles in 700 °C for 4 h. The calcined powders were well ground into fine form and were pressed under a uniaxial pressure of 10 MPa into cylindrical disks with 12 mm diameter and 5–6 mm height. The compacts were sintered at 800 °C for 4 h in a high-temperature furnace.

The crystalline phase of the ceramics was confirmed using PANalytical X’Pert PRO with Cu Kα radiation at room temperature. The 2θ angle scans were made between 10° and 120°, step width of 0.02° and a time per step of 1.0 s. SEM and EDS were performed at an accelerating voltage of 20 kV to obtain section images of all samples to explore the section morphology. The Raman spectra were obtained using a Renishaw InVia Raman spectrophotometer with argon ion laser as the excitation light. Raman shifts are measured with a precision of ~0.3 cm⁻¹. The spectral resolution is of the order 1 cm⁻¹. The spectra were recorded in the 100–1200 cm⁻¹ range. The microwave dielectric properties were measured by a vector network analyzer. εᵣ and Qₛᵣ of the samples were determined, respectively, by Hakki–Coleman dielectric resonator method and cavity methods.

3. RESULTS AND DISCUSSION

The phases of samples were investigated by XRD patterns. The XRD patterns of the Li₂MoO₄–(1+δ)SiO₂ ceramics are exhibited in Fig. 1. It can be observed from the XRD patterns that the main phase can be identified as the structure of phenacite Li₂MoO₄ (ICDD No. 12-0763) and SiO₂ (ICDD No. 89-8935), suggesting that the two phases can exist individually and display very good chemical compatibility.

![Fig. 1 The XRD patterns of Li₂MoO₄–(1+δ)SiO₂ ceramics.](image)

Rietveld refinement was performed using the FullProf package [24], which involved constraining the refinement within the rhombohedral structure model of Li₂MoO₄ with space group R-3 and cell parameters a = b = 1.4318 nm, c = 0.9576 nm, α = β = 90° and γ = 120° and the hexagonal structure model of SiO₂ with space group P3121 and cell parameters a = b = 0.4916 nm, c = 0.5408 nm, α = β = 90° and γ = 120°, respectively. As a representative, the refined XRD patterns of the ceramics with δ = 0 are shown in Fig. 2. The refined XRD parameters and lattice constants were presented in Table 1. The reasonably small χ² factors suggest that mixed-phase Li₂MoO₄ and SiO₂ obtained under our experimental process have different stoichiometric ratio from the results of the refinement. As a representative, the crystal structure of Li₂MoO₄ and SiO₂ with δ = 0 is shown in Fig. 3. Li₂MoO₄ crystal structure consists of a three-dimensional network of corner linked slightly distorted LiO₆ and fairly regular MoO₄ tetrahedra with a narrow open channel along the crystallographic c-axis. SiO₂ crystal structure consists of a three-dimensional network of SiO₄ tetrahedra shown in Fig. 3(b).

![Fig. 2 Rietveld analysis of the Li₂MoO₄–(1+δ)SiO₂ ceramics with δ = 0.](image)

![Fig. 3 The crystal structure of Li₂MoO₄ (a) and SiO₂ (b) phases with δ = 0.](image)

The morphology of Li₂MoO₄–(1+δ)SiO₂ ceramics was characterised by SEM. Fig. 4 presents SEM micrographs of the Li₂MoO₄–(1+δ)SiO₂ ceramics with δ = -0.5, 0.0 and 0.5. The SEM images show that two phases can be distinguished clearly by the different morphology. Since the sintering temperature of Li₂MoO₄ ceramics (540 °C) was lower than 800 °C [23], the SiO₂ ceramics was higher than 800 °C. Thus, when sintered at 800 °C, it was reasonable that the ceramics proceeded over sintering of Li₂MoO₄ and an in-completed grain growth of SiO₂, resulting in Li₂MoO₄ ceramics present in the liquid phase and SiO₂ present in the inhomogeneous grain size in specimens. The result of EDS analysis [Fig. 4(e) and (f)] shows that particle (Spot A) mainly contain Si and O elements, homogeneous matrix (Spot B) are dominantly composed of Mo and O elements, in which the Li element belongs to the ultra-light elements so that it cannot be detected by EDS. From the EDS results, it can be also found that some Mo ions were detected in the grain of SiO₂, and Si ions were also detected in the matrix of Li₂MoO₄, probably because of the ions diffusion between two phases. In addition, SiO₂ containing more Mo ions than those Si ions in the matrix of Li₂MoO₄. The low melting point Li₂MoO₄, which form liquid phases during sintering, can be easier to diffuse. Therefore, according to SEM and EDS, the particle of SiO₂ embedding the Li₂MoO₄ matrix is noteworthy, which is in accordance with the XRD.
Table 1 Lattice parameters from Rietveld refinement for Li$_2$MoO$_4$–(1+δ)SiO$_2$ ceramics.

<table>
<thead>
<tr>
<th></th>
<th>-0.5</th>
<th>-0.2</th>
<th>0.0</th>
<th>0.2</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li$_2$MoO$_4$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a(nm)</td>
<td>1.4340</td>
<td>1.4337</td>
<td>1.4338</td>
<td>1.4335</td>
<td>1.4339</td>
</tr>
<tr>
<td>c(nm)</td>
<td>0.9592</td>
<td>0.9590</td>
<td>0.9591</td>
<td>0.9591</td>
<td>0.9591</td>
</tr>
<tr>
<td>V(nm$^3$)</td>
<td>1.7083</td>
<td>1.7072</td>
<td>1.7076</td>
<td>1.7065</td>
<td>1.7076</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>V(nm$^3$)</td>
<td>0.868</td>
<td>0.4917</td>
<td>0.5411</td>
<td>0.5406</td>
<td>0.5400</td>
</tr>
<tr>
<td>Relative density (%)</td>
<td>97.11</td>
<td>96.74</td>
<td>95.24</td>
<td>94.62</td>
<td>93.12</td>
</tr>
</tbody>
</table>

Fig. 4 SEM of the Li$_2$MoO$_4$–(1+δ)SiO$_2$ ceramics with (a) δ = -0.5, (b) δ = 0.0, (c) δ = 0.5 and EDS analysis with δ = -0.5 (e) Spot A, (f) Spot B.

Fig. 5 displays the Raman spectra for the Li$_2$MoO$_4$–(1+δ)SiO$_2$ ceramics. According to Zachariasen, lithium molybdate belongs to the trigonal system (space group R-3) and is isostructural with Be$_2$SiO$_4$, Zn$_2$SiO$_4$, Li$_2$BeF$_4$, Li$_2$WO$_4$ and some other phenacite-type compounds [25]. The theoretical number of optical modes of Li$_2$MoO$_4$ that crystallises in the space group R-3 can be deduced via symmetry analysis using the Bilbao Crystallographic Server [26]. Through factor group analysis, optical modes are possible according to the following irreducible representations:

$$\Gamma_{opt} = 4A_1 \Gamma + 4A_2 \Gamma + 17E \Gamma$$

(2)

The symmetry analysis of the aforementioned irreducible representations indicates that 13 vibrational modes are Raman active and 12 vibrational modes are IR active.

It can be noted that the maximum number of 20 Raman peaks, which is less than the theoretical number of Raman modes, is observed for Li$_2$MoO$_4$–(1+δ)SiO$_2$ ceramics. Other bands were not detected as their extremely low intensity precluded their observation or was overlapped. Moreover, a part of bands for Li$_2$MoO$_4$ and SiO$_2$ overlapped, resulting in a lesser Raman bands observed as compared to the theoretical number. The bands at 127 and 158 cm$^{-1}$ can be assigned librational bands. Other bands were not detected as they were extremely low intensity precluded their observation or was overlapped. Moreover, a part of bands for Li$_2$MoO$_4$ and SiO$_2$ overlapped, resulting in a lesser Raman bands observed as compared to the theoretical number. The bands at 127 and 158 cm$^{-1}$ can be assigned librational modes of Li$_2$MoO$_4$–(1+δ)SiO$_2$ tetrahedra, respectively [28,30]. The ν$_E$(F$_2$) and ν$_E$(E) bending vibrations are placed in the region 275–335 cm$^{-1}$.
The structure and microwave dielectric properties of Li$_2$MoO$_4$-SiO$_2$ ceramics without addition of glass as sintering aids

...cm$^{-1}$ and 350–450 cm$^{-1}$, whereas $\nu$(A$_1$) and $\nu$(F$_2$) stretching vibrations of [MoO$_3$]$^2$ are observed at 903 cm$^{-1}$ and in the region 800–885 cm$^{-1}$, respectively [27]. In addition, the band at 354 cm$^{-1}$ can be attributed to the vibration of $\nu$(MoO$_3$) + $\nu$(MoO$_4$), whereas the band near 463 cm$^{-1}$ can be assigned to Li-O stretching vibration and O-Si-O bending vibration. Furthermore, the band located around 952 and 1122 cm$^{-1}$ can be owing to the symmetric stretching mode of MoO$_4$ tetrahedra and O-Si-O bonds, respectively [31–34]. Overall, the Raman spectra of Li$_2$MoO$_4$ and SiO$_2$ can be well-defined in Fig. 5 as the two-phase mixtures. This agrees well with the result from the XRD, SEM and EDS analysis. Particularly, it can be noted that the number of Li$_2$MoO$_4$ Raman peaks significative more than those of SiO$_2$, which means a good crystal quality for Li$_2$MoO$_4$. One possible reason is the lower sintering temperature of Li$_2$MoO$_4$ than SiO$_2$. The Li$_2$MoO$_4$ ceramics have higher degree of crystallisation at the same sintering temperature, which lead to the stronger Raman peaks than those of SiO$_2$ ceramics. The results of the Raman spectra are in accordance with those from the SEM.

Dielectric constants ($\varepsilon$) as a function of composition in Li$_2$MoO$_4$-(1+δ)SiO$_2$ ceramics are shown in Fig. 6. The relative dielectric constants decrease linearly from 5.1 at $\delta = -0.5$ to 4.1 at $\delta = 0$. According to the Lichtenecker empirical logarithmic rule, when two kinds of materials are uniformly mixed after being finely divided, the dielectric constant of this system can be calculated [35]:

$$\log \varepsilon = V_1 \log \varepsilon_1 + V_2 \log \varepsilon_2$$

(3)

where $\varepsilon$, $\varepsilon_1$ and $\varepsilon_2$ are the dielectric constants for the two-phase material (phase 1 and phase 2), $V_1$ and $V_2$ are, respectively, the volume fractions of phase 1 and phase 2 in the material, and $V_1+V_2 = 1$. Equation (3) is only applicable to the situation where the values of the dielectric constants of the two phases are not very large. As expected, the dielectric constants decrease with increased $\delta$ as dielectric constants of Li$_2$MoO$_4$ and SiO$_2$ are 5.5 and 3.8, respectively, at microwave frequencies. Fig. 6 also compares the measured and theoretical values of dielectric constant of Li$_2$MoO$_4$-(1+δ)SiO$_2$ composites. The theoretical values (based on batch composition and XRD refinement) give the same trend as that of the measured curve. The measured values show large deviation from theoretical predictions for composition owing to inhomogeneous mixing and porosity [36].

The Q×f values of the Li$_2$MoO$_4$-(1+δ)SiO$_2$ ceramics as a function of $\delta$ is shown in Fig. 6. With increased $\delta$, Q×f value firstly increased linearly from 14 905 GHz at $\delta = -0.5$ to 21 006 GHz at $\delta = 0$ and then decreased to 9 473 GHz at $\delta = 0.5$. As expected, the Q×f value gradually increased with the increase in high Q-SiO$_2$ end member. However, this value was still much lower than the reported 46000 and 70600 GHz for pure Li$_2$MoO$_4$ and B$_2$O$_3$-modified SiO$_2$ ceramic. As it is well known, Q×f values are usually influenced by internal and external causes, such as grain boundary, defect and ordering structure [37]. The increased number of grain boundary with increased SiO$_2$ content also could lead to deterioration of the Q×f value, since the preferable place for the aggregation of voids and lattice defects was [38]. Therefore, the Q×f value decreased when $\delta = 0–0.5$.

4. CONCLUSIONS

The microstructure and microwave dielectric properties of Li$_2$MoO$_4$-(1+δ)SiO$_2$ ($\delta = -0.5$, -0.2, 0, 0.2, 0.5 mole) ceramics has been studied as a function of SiO$_2$ content. The mixed phases, Li$_2$MoO$_4$ and SiO$_2$, were observed through XRD, SEM, EDS and Raman spectra. The dielectric constants decrease with increased $\delta$, which agree with the Lichtenecker logarithmic rule. The Q×f value initially increased and then decreased with increased $\delta$. When evaluated as a microwave dielectric material, the Li$_2$MoO$_4$-(1+δ)SiO$_2$ ceramics show an excellent dielectric performance with a low dielectric constant ($\varepsilon_r = 4.807$) and good Q×f values of $\approx 21 000$ GHz at $\delta = 0$ with sintering at 800 °C.

ACKNOWLEDGEMENTS

This work was supported by National Natural Science Foundation of China under Grant Nos. 51372031 and 61471096, Science and Technology Department of Sichuan Province 2016JQ0016 and 2016GZ0258, National High-tech R&D Program of China under Grant No. 2015AA034102, National Key Research and Development Plan No. 2016YFA0300801.

REFERENCES

(2007).

(Received September 5, 2017; Accepted November 18, 2017; Published Online February 1, 2018)