The structure and microwave dielectric properties of $\text{Li}_2\text{MoO}_4\text{-SiO}_2$ ceramics without addition of glass as sintering aids

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SiO_2 ceramic is one of the most important candidate materials for high-frequency microwave ceramics with very low dielectric constant (ϵ_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, $\text{Li}_2\text{MoO}_4\text{-(1+\delta)SiO}_2$ ($\delta = -0.5, -0.2, 0, 0.2, 0.5$ 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_2MoO_4 and SiO_2 phases. The ϵ_r values decrease with increased δ , which agree with the Lichtenecker logarithmic rule. The quality factor ($Q \times f$) value initially increased and then decreased with increased δ . When evaluated as a microwave dielectric material, the $\text{Li}_2\text{MoO}_4\text{-(1+\delta)SiO}_2$ ceramics show excellent dielectric performance with a low dielectric constant ($\epsilon_r = 4.807$) and high $Q \times f$ values of ~ 21000 GHz at $\delta = 0$ 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 ϵ_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 $\text{K}_x\text{Ba}_{1-x}\text{Ga}_{2-x}\text{Ge}_{2+x}\text{O}_8$ [7,8], $(\text{K}_{0.5}\text{Ln}_{0.5})\text{MoO}_4$ ($\text{Ln} = \text{Nd}$ and Sm) [9], $\text{Ba}_2\text{ZnSi}_2\text{O}_7$ [10], LiMnPO_4 [11] and $\text{Mg}_2\text{Al}_4\text{Si}_5\text{O}_{18}$ [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_2O_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_2MoO_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_2MoO_4 ceramic have been reported with the ultra-low sintering temperature of 540 °C, exhibiting $\epsilon_r = 5.5$ and a $Qf \sim 46000$ GHz and TCF ~ 160 ppm/°C [23]. Nonetheless, information about the dielectric properties of $\text{Li}_2\text{MoO}_4\text{-SiO}_2$ composite ceramics at low sintering temperature is scarce. Thus, there is a need to investigate in more detail the dielectric properties of $\text{Li}_2\text{MoO}_4\text{-SiO}_2$ composite ceramics.

In this work, the $\text{Li}_2\text{MoO}_4\text{-(1+\delta)SiO}_2$ ($\delta = -0.5, -0.2, 0, 0.2, 0.5$ 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

$\text{Li}_2\text{MoO}_4\text{-(1+\delta)SiO}_2$ ($\delta = -0.5, -0.2, 0, 0.2, 0.5$ mole) ceramics were prepared by conventional solid-state ceramic route. Stoichiometric amounts of high-purity 99.9% Li_2CO_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.

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 K α 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 $\sim 0.3 \text{ cm}^{-1}$. 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. ϵ_r and $Q \times f$ 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 $\text{Li}_2\text{MoO}_4\text{-(1+\delta)SiO}_2$ 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 Li_2MoO_4 (ICDD No. 12-0763) and SiO_2 (ICDD No. 89-8935), suggesting that the two phases can exist individually and display very good chemical compatibility.

Fig. 1 The XRD patterns of $\text{Li}_2\text{MoO}_4\text{-(1+\delta)SiO}_2$ ceramics.

Rietveld refinement was performed using the FullProf package [24], which involved constraining the refinement within the rhombohedral structure model of Li_2MoO_4 with space group R-3 and cell parameters $a = b = 1.4318 \text{ nm}$, $c = 0.9576 \text{ nm}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$ and the hexagonal structure model of SiO_2 with space group $P3_121$ and cell parameters $a = b = 0.4916 \text{ nm}$, $c = 0.5408 \text{ nm}$, $\alpha = \beta = 90^\circ$ and $\gamma = 120^\circ$, respectively. As a representative, the refined XRD patterns of the ceramics with $\delta = 0$ are shown in Fig. 2. The refined XRD parameters and lattice constants were presented in Table 1. The reasonably small χ^2 factors suggest that mixed-phase Li_2MoO_4 and SiO_2 obtained under our experimental process have different stoichiometric ratio from the results of the refinement. As a representative,

the crystal structure of Li_2MoO_4 and SiO_2 with $\delta = 0$ is shown in Fig. 3. Li_2MoO_4 crystal structure consists of a three-dimensional network of corner linked slightly distorted LiO_4 and fairly regular MoO_4 tetrahedra with a narrow open channel along the crystallographic c-axis. SiO_2 crystal structure consists of a three-dimensional network of SiO_4 tetrahedra shown in Fig. 3(b).

Fig. 2 Rietveld analysis of the $\text{Li}_2\text{MoO}_4\text{-(1+\delta)SiO}_2$ ceramics with $\delta = 0$.

Fig. 3 The crystal structure of Li_2MoO_4 (a) and SiO_2 (b) phases with $\delta = 0$.

The morphology of $\text{Li}_2\text{MoO}_4\text{-(1+\delta)SiO}_2$ ceramics was characterised by SEM. Fig. 4 presents SEM micrographs of the $\text{Li}_2\text{MoO}_4\text{-(1+\delta)SiO}_2$ ceramics with $\delta = -0.5, 0.0$ and 0.5 . The SEM images show that two phases can be distinguished clearly by the different morphology. Since the sintering temperature of Li_2MoO_4 ceramics (540 °C) was lower than 800 °C [23], the SiO_2 ceramics was higher than 800 °C. Thus, when sintered at 800 °C, it was reasonable that the ceramics proceeded over sintering of Li_2MoO_4 and an in-completed grain growth of SiO_2 , resulting in Li_2MoO_4 ceramics present in the liquid phase and SiO_2 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 SiO_2 , and Si ions were also detected in the matrix of Li_2MoO_4 , probably because of the ions diffusion between two phases. In addition, SiO_2 containing more Mo ions than those Si ions in the matrix of Li_2MoO_4 . The low melting point Li_2MoO_4 , which form liquid phases during sintering, can be easier to diffuse. Therefore, according to SEM and EDS, the particle of SiO_2 embedding the Li_2MoO_4 matrix is noteworthy, which is in accordance with the XRD.

Table 1 Lattice parameters from Rietveld refinement for $\text{Li}_2\text{MoO}_4-(1+\delta)\text{SiO}_2$ ceramics.

		-0.5	-0.2	0.0	0.2	0.5
Li_2MoO_4	a(nm)	1.4340	1.4337	1.4338	1.4335	1.4339
	c(nm)	0.9592	0.9590	0.9591	0.9589	0.9591
	V(nm ³)	1.7083	1.7072	1.7076	1.7065	1.7076
	wt%	86.88	72.98	70.76	63.63	57.67
SiO_2	a(nm)	0.4917	0.4916	0.4915	0.4917	0.4918
	c(nm)	0.5411	0.5406	0.5412	0.5406	0.5409
	V(nm ³)	0.1133	0.1132	0.1132	0.1132	0.1133
	wt%	13.12	27.02	29.24	36.37	42.33
	R _p (%)	14.4	14.5	15.8	11.9	13.9
	R _{wp} (%)	18.5	18.8	20.6	16.0	18.1
	R _{exp} (%)	10.97	10.92	10.81	10.53	10.73
	χ^2	2.83	2.96	3.64	2.29	2.83
Relative density (%)		97.11	96.74	95.24	94.62	93.12

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

Fig. 5 displays the Raman spectra for the $\text{Li}_2\text{MoO}_4-(1+\delta)\text{SiO}_2$ ceramics. According to Zachariasen, lithium molybdate belongs to the trigonal system (space group R-3) and is isostructural with Be_2SiO_4 , Zn_2SiO_4 , Li_2BeF_4 , Li_2WO_4 and some other phenacite-type compounds [25]. The theoretical number of optical modes of Li_2MoO_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:

$$\Gamma_{\text{Opt}} = 21A_g(R) + 20A_u(IR) + 21E_{1g}(R) + 21E_{2g}(R) + 20E_{1u}(IR) + 20E_{2u}(IR) \quad (1)$$

where A and B denote nondegenerate vibrational modes, and E denotes doubly degenerate vibrational modes. Symmetric and antisymmetric modes for the centre of inversion are denoted by subscripts g and u, respectively. R and IR represent the Raman and infrared active, respectively. According to selection rules, the aforementioned irreducible representations indicate that 63 vibrational modes are Raman active, whereas 60 vibrational modes are IR active. The free $[\text{MoO}_4]^{2-}$ tetrahedron has a T_d symmetry and four normal modes

which are assigned as $\nu_1(A_1)$, $\nu_2(E)$, $\nu_3(F_2)$, $\nu_4(F_2)$ and $F_1(\text{rot})$ where A_1 , E and F_2 are Raman permitted and F_2 is also IR active. ν_1 , ν_2 , ν_3 and ν_4 are denoted as nondegenerate symmetrical stretching mode, doubly degenerate symmetrical bending mode, triply degenerate anti-symmetrical stretching and anti-symmetrical bending vibrations, respectively [27]. In addition, the theoretical number of possible optical modes of SiO_2 is possible according to the following irreducible representations:

$$\Gamma_{\text{Opt}} = 4A_1(R) + 4A_2(IR) + 17E(R, IR) \quad (2)$$

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

Fig. 5 The Raman spectra of $\text{Li}_2\text{MoO}_4-(1+\delta)\text{SiO}_2$ ceramics.

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 $\text{Li}_2\text{MoO}_4-(1+\delta)\text{SiO}_2$ ceramics. Other bands were not detected as their extremely low intensity precluded their observation or was overlapped. Moreover, a part of bands for Li_2MoO_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 and translational modes of the $[\text{MoO}_4]^{2-}$ ions, respectively, whereas the bands at 205 and 268 cm^{-1} can be ascribed as the translational modes of the lithium [28,29]. The bands around 370 and 387 cm^{-1} are assigned to the bending $\nu_2(E)$ vibration of MoO_4 tetrahedra, respectively [28,30]. The $\nu_4(F_2)$ and $\nu_2(E)$ bending vibrations are placed in the region 275–335

cm⁻¹ and 350–450 cm⁻¹, whereas $\nu_1(A_1)$ and $\nu_3(F_2)$ stretching vibrations of [MoO₄]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 $\nu_2(\text{MoO}_4) + \nu_4(\text{MoO}_4)$, 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 MoO₄ tetrahedra and O–Si–O bonds, respectively [31–34]. Overall, the Raman spectra of Li₂MoO₄ and SiO₂ 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 Li₂MoO₄ Raman peaks significant more than those of SiO₂, which means a good crystal quality for Li₂MoO₄. One possible reason is the lower sintering temperature of Li₂MoO₄ than SiO₂. The Li₂MoO₄ ceramics have higher degree of crystallisation at the same sintering temperature, which lead to the stronger Raman peaks than those of SiO₂ ceramics. The results of the Raman spectra are in accordance with those from the SEM.

Dielectric constants (ϵ_r) as a function of composition in Li₂MoO₄-(1+ δ)SiO₂ ceramics are shown in Fig. 6. The relative dielectric constants decrease linearly from 5.1 at $\delta = -0.5$ to 4.1 at $\delta = 0.5$. 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]:

$$\log \epsilon = V_1 \log \epsilon_1 + V_2 \log \epsilon_2 \quad (3)$$

where ϵ , ϵ_1 and ϵ_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 δ as dielectric constants of Li₂MoO₄ and SiO₂ are 5.5 and 3.8, respectively, at microwave frequencies. Fig. 6 also compares the measured and theoretical values of dielectric constant of Li₂MoO₄-(1+ δ)SiO₂ composites. The theoretical values (based on batch composition and XRD refinement) give the same trend as that of 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 Li₂MoO₄-(1+ δ)SiO₂ ceramics as a function of δ are shown in Fig. 6. With increased δ , 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-SiO₂ end member. However, this value was still much lower than the reported 46000 and 70600 GHz for pure Li₂MoO₄ and B₂O₃-modified SiO₂ 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 the number of grain boundary with increased SiO₂ 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 $\delta = 0-0.5$.

Fig.6 The microwave dielectric properties of Li₂MoO₄-(1+ δ)SiO₂ ceramics.

4. CONCLUSIONS

The microstructure and microwave dielectric properties of Li₂MoO₄-(1+ δ)SiO₂ ($\delta = -0.5, -0.2, 0, 0.2, 0.5$ mole) ceramics has been studied as a function of SiO₂ content. The mixed phases, Li₂MoO₄ and SiO₂, were observed through XRD, SEM, EDS and Raman spectra. The dielectric constants decrease with increased δ , which agree with the Lichtenecker logarithmic rule. The Q×f value initially increased and then decreased with increased δ . When evaluated as a microwave dielectric material, the Li₂MoO₄-(1+ δ)SiO₂ ceramics show an excellent dielectric performance with a low dielectric constant ($\epsilon_r = 4.807$) and good Q×f values of ~21 000 GHz at $\delta = 0$ with sintering at 800 °C.

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