INTRODUCTION

Due to the requirement of miniaturization and integration of microwave passive components and devices, low-temperature co-fired ceramics (LTCC) technology has become more important and been widely used in the fabrication of multi-layer devices for today’s communication systems in the last two decades. LTCC multi-layer devices are normally composed of layers of alternating microwave dielectric ceramics and internal Ag electrodes. To avoid the migration of Ag, sintering temperatures of the devices must be lower than the melting point of Ag (melting point ~ 960°C).1,2,3,4 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 ($\tau_f$) temperature coefficient. These requirements are also valid for ultra-low-temperature co-fired ceramics (ULTCC) applications (<700°C).5 Thus, the research to enable co-firing either using additives or developing new materials has been widely conducted. However, low-melting glass additions need to go through a prior glass preparation followed by a synthesizing condition of sintering and normally it also degrades the microwave dielectric properties of the ceramics, in particular the $Q \times f$ value, which would limit its applications at high-frequency regime such as 5G system. As a result, the demand for new materials with excellent microwave dielectric properties and low sintering temperature is desired than ever.

Several molybdates crystal systems, such as AMoO$_4$ (A = Mg, Zn, Mn, Ca, Sr, Ba), Li$_2$(M$^{2+}$)$_2$(MoO$_4$)$_3$, and Li$_3$(M$^{3+}$)(MoO$_4$)$_3$ (M = Zn, Ca, Al, In), have been investigated as intrinsic low-temperature sintering dielectrics for microwave applications.6,7,8 In addition, double molybdates...
such as NaLa(MoO₄)₂ and NaBi(MoO₄)₂ were also reported to be suitable LTCC dielectrics. This motivated the present investigation of other LTCC and ULTCC dielectrics in the molybdates family. Li₂M₂(MoO₄)₃ (M = Co, Ni) dielectrics were reported as a high-performance positive electrode asymmetric supercapacitors for renewable energy storage systems. However, their microwave dielectric properties have yet to be studied.

In this paper, the crystal structure and the microwave dielectric properties of Li₂M₂(MoO₄)₃ (M = Co, Ni) ceramics were firstly investigated. The XRD patterns, surface morphology, and Raman spectrum were also reported. In addition, small amount Zn was employed to replace Ni to lower the microwave dielectric loss of the specimens.

## EXPERIMENTAL PROCEDURE

The Li₂M₂(MoO₄)₃ (M = Co, Ni) ceramics were prepared by the solid-state reaction method. The starting materials of high-purity Li₂CO₃, CoO, NiO, ZnO, and MoO₃ oxide powders (>99.9%) were weighed and ball-milled using distilled water and zirconia balls in an anion container for 24 hours. The mixtures were dried and calcined at 500°C for 2 hours, mixing with 5 wt% of a 10% PVA solution as a binder, and granulated by sieving through a 200 mesh and pressed into pellets with 5 mm in thickness and 11 mm in diameter using an automatic uniaxial hydraulic press at 2000 kg/cm². These pellets were sintered at 600–900°C for 4 hours. The finished sample was performed by the following test. Relative density is the ratio of the density of the sample to the density of the Li₂M₂(MoO₄)₃ (M = Co, Ni). The density of the Li₂Co₂(MoO₄)₃ and Li₂Ni₂(MoO₄)₃ is 4.3418 and 4.3797 g/cm³, respectively. The crystal structures of the sintered ceramics were analyzed with a Siemens D5000 diffractometer 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. The dielectric constant (εr) and the quality factor values (Q) at microwave frequencies were measured using the dielectric resonator method suggested by Hakki-Coleman and Courtney. A system combining a HP8757D network analyzer and a HP8350B sweep oscillator was employed in the measurement. An identical technique was applied to the measurement of the resonant frequency (f₀) temperature coefficient. Tf (ppm/°C) can be calculated by considering the change in resonant frequency (Δf), for which the resonant frequency (f₀) temperature coefficient can be defined as.

\[
T_f = \frac{(f_2 - f_1)}{f_1 (T_2 - T_1)}
\]

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 to 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.

## RESULTS AND DISCUSSION

Figures 1 and 2 show the XRD patterns of Li₂M₂(MoO₄)₃ (M = Co, Ni) ceramics sintered at different temperatures for 4 hours. The peaks are indexed based on the standard ICDD-PDF #01-085-0059 and #04-010-2828 for Li₂Co₂(MoO₄)₃ and Li₂Ni₂(MoO₄)₃, respectively. It is observed that there are several XRD peaks slightly shifting toward higher angles. This distortion might be induced from a compressed lattice volume owing to materials sintering process. The specimens exhibited homogeneous orthorhombic phase but belonged to different space groups which are Pnma(62) for Li₂Co₂(MoO₄)₃ and Pmcn(62) for Li₂Ni₂(MoO₄)₃. To further
clarify the crystal structure of Li₂M₂(MoO₄)₃ (M = Co, Ni) ceramics, and demonstrate the lattice size decreased, Rietveld refinements were carried out using GSAS software and the refined lattice parameters, molecular volume, reliability factors, and goodness-of-fit indicators are illustrated in Tables 1 and 2. The variations of lattice parameters and cell volumes were limited and within 0.5%, and the goodness-of-fit indicator values ($\chi^2$) were almost in the range 0.83–1.79, indicating that the structural model is valid and the refinement result is reliable. Also, the refined plots of the specimens are shown in Figure 2 and the results are identical to the crystallographic data achieved from Rietveld refinement, as shown in Tables 1 and 2. These results also confirmed the formation of a single orthorhombic structure phase.

Figures 3 and 4 demonstrate SEM images of Li₂M₂(MoO₄)₃ (M = Co, Ni) specimens sintered at different temperatures for 4h. As can be seen that the Li₂Co₂(MoO₄)₃ specimen at 840°C exhibits typical uniform polygonal grains along with some small grains and both are corresponding to a single Li₂Co₂(MoO₄)₃ phase as further confirmed by the EDS results (Figure 3f). As the temperature is up to 870°C or higher, the grain starts to melt, and a little secondary phase precipitates at the grain boundary (shown in Figure 3d,e), which is bad for grain densification (which will be shown in Figure 7). For Li₂Ni₂(MoO₄)₃ specimens sintered from 600°C to 720°C, well-densified microstructures were developed and there was no second phase for the entire temperature range; also, both round and bar grains have same composition which agrees with the EDS results (Figure 4f). Specimen at 720°C was found to have an obviously larger grain size and a less uniform morphology because of a higher sintering temperature. The influence of grain growth on the relative density is not obvious because of the little grain size change (which will be discussed in Figure 7). As a result, these materials have individual optimum sintering temperature for densification.

Figures 5 and 6 illustrate the Raman spectrum of the Li₂M₂(MoO₄)₃ (M = Co, Ni) ceramics recorded at room temperature. The Raman bands of Co-contained specimen are apparently distributed in three distinct regions: between 316 and 360 cm⁻¹ corresponding to the MoO₄ bending vibration modes, between 801 and 886 cm⁻¹ representing the MoO₄ anti-symmetric stretching modes, and between 948 cm⁻¹ and 970 cm⁻¹ in response of the MoO₄ symmetric stretching modes. In comparison with that of Co-contained specimen, small pattern shift was observed for Li₂Ni₂(MoO₄)₃ ceramic due to the radius difference between Co and Ni.

The relative densities and $\varepsilon_r$ values of the orthorhombic Li₂M₂(MoO₄)₃ (M = Co, Ni) ceramics as a function of sintering temperature are shown in Figure 7. The relative density was very low at approximately 86% of the theoretical

### Table 1

| Sinter temp. (°C) | 780  | 810  | 840  | 870  | 900  | Ref    |
|------------------|------|------|------|------|------|--------|
| a(Å)             | 5.088| 5.078| 5.088| 5.091| 5.087| 5.102  |
| b(Å)             | 10.468| 10.475| 10.475| 10.470| 10.466| 10.464 |
| c(Å)             | 17.599| 17.580| 17.607| 17.622| 17.609| 17.584 |
| Cell volume (Å³) | 937.330| 935.100| 938.418| 939.263| 937.617| 938.763 |
| $R_{wp}$ (%)     | 4.53 | 5.50 | 5.39 | 6.20 | 5.25 | —     |
| $\chi^2$         | 0.83 | 1.02 | 1.02 | 1.08 | 0.98 | —     |
| $\varepsilon_r$  | 7.70 | 8.40 | 9.10 | 9.20 | 8.70 | —     |
| $\varepsilon_{rc}$ | 9.40 | 9.80 | 9.90 | 10.30 | 10.50 | —     |
| $V_m$ (Å³)       | 234.3| 233.7| 234.6| 234.8| 234.4| 234.7 |
density for the Li$_2$Co$_2$(MoO$_4$)$_3$ specimen sintered at 780°C most likely due to the porous microstructure as shown in Figure 3. However, it increased with increases in the sintering temperature, reaching a maximum of 93.3% at 840°C, and decreased thereafter due to the secondary phase precipitation. Variation of $\varepsilon_r$ was consistent with that of the relative density. TABLE 2 The refined lattice parameters, molecular volume, goodness of fit, and reliability factors of the Li$_2$Ni$_2$(MoO$_4$)$_3$ ceramics sintered at different temperature

**FIGURE 3** The SEM images of Li$_2$Co$_2$(MoO$_4$)$_3$ specimens sintered at (A) 780°C, (B) 810°C, (C) 840°C, (D) 870°C, (E) 900°C for 4 h, and corresponding EDS results (F).
FIGURE 4  The SEM images of Li$_2$Ni$_2$(MoO$_4$)$_3$ specimens sintered at (A) 600°C, (B) 630°C, (C) 660°C, (D) 690°C, (E) 720°C for 4 h, and corresponding EDS results (F).

FIGURE 5  The Raman spectrum of the Li$_2$Co$_2$(MoO$_4$)$_3$ ceramic recorded at room temperature.

FIGURE 6  The Raman spectrum of the Li$_2$Ni$_2$(MoO$_4$)$_3$ ceramic recorded at room temperature.
density indicating that density might be a primary factor affecting $\varepsilon_r$ in this experiment. In addition, the relative density of Li$_2$Ni$_2$(MoO$_4$)$_3$ specimen also shows a maximum of 91% at 660°C and slightly decreases at temperatures higher than 660°C corresponding to a less uniform morphology, suggesting that 660°C is the optimal sintering temperature, and a maximum $\varepsilon_r$ value of ~9.6 was obtained.

The $Q \times f$ and $T_f$ values of Li$_2$M$_2$(MoO$_4$)$_3$ (M = Co, Ni) ceramics at different sintering temperatures are illustrated in Figure 8. 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. The variations of $Q \times f$ values for both specimens were consistent with their relative densities suggesting that the dielectric loss was mainly controlled by the densification of the specimens. Maximum $Q \times f$ of 34 000 GHz and 28 000 GHz were obtained for Co-contained and Ni-contained specimens, respectively. Moreover, crystal structure may also play an important role in affecting the dielectric properties. Because there is no obvious second-phase precipitation in the pure orthorhombic Li$_2$M$_2$(MoO$_4$)$_3$ (M = Co, Ni) ceramics, accordingly, the $T_f$ values of the specimens showed no significant change and ranged from −72ppm/°C to −94ppm/°C and −61ppm/°C to −71ppm/°C for Co-contained and Ni-contained specimens, respectively, since the variations in the lattice parameters and cell volumes were limited and within 0.5%.
Small amount of Zn was employed to partially replace Ni in the Li$_2$Ni$_{2-x}$Zn$_x$(MoO$_4$)$_3$ ($x = 0–0.1$) ceramics to improve its microwave dielectric properties, and the XRD patterns of the specimens sintered at 660°C for 4 hours are shown in Figure 9. All the specimens can be identified as a single Li$_2$Ni$_2$(MoO$_4$)$_3$ phase with the orthorhombic structure. However, expecting peak shift due to the ionic radius difference was not observed, which might be because of the substitution amount was small and could not be identified from the XRD patterns. The cell volumes, lattice parameters, and reliability factors of specimens after Rietveld refinements are listed in Table 3, and the variations of lattice parameters and cell volumes were all less

| $x$     | 0    | 0.01 | 0.03 | 0.05 | 0.07 | 0.1  |
|---------|------|------|------|------|------|------|
| a(Å)    | 10.406 | 10.387 | 10.407 | 10.407 | 10.403 | 10.412 |
| b(Å)    | 17.521 | 17.483 | 17.504 | 17.510 | 17.513 | 17.521 |
| c(Å)    | 5.080  | 5.070  | 5.074  | 5.076  | 5.079  | 5.085  |
| Cell volume (Å$^3$) | 926.230 | 924.069 | 924.314 | 925.044 | 925.325 | 926.617 |
| $R_{wp}$ (%) | 8.52 | 7.63 | 5.39 | 7.96 | 9.88 | 7.70 |
| $\chi^2$ | 1.11 | 1.01 | 1.02 | 1.05 | 1.38 | 1.08 |
| $\epsilon_r$ | 10.90 | 10.90 | 10.90 | 10.90 | 10.90 | 10.90 |
| $V_m$ (Å$^3$) | 231.6 | 231.0 | 231.1 | 231.3 | 231.3 | 231.7 |
than 0.3%. In addition, the goodness-of-fit indicator values ($\chi^2$) were in the range 1.01–1.38, suggesting that the structural model is valid and the refinement result is reliable.

Figure 10 shows the relative densities and $\varepsilon_r$ values of the Li$_2$Ni$_{2-x}$Zn$_x$(MoO$_4$)$_3$ ($x = 0–0.1$) ceramics at different sintering temperatures. For all specimens, with increasing sintering temperature the relative density increased to a maximum value at 660–690°C and then slightly decreased and it showed a relative density of 93% for $x = 0.05$ at 660°C. The $\varepsilon_r$ value also exhibited a similar variation trend with that of the relative density and a $\varepsilon_r$ of 10.9 can be obtained for $x = 0.05$ at 660°C. Instead of intrinsic factor, it suggests that the $\varepsilon_r$ value was mainly controlled by the extrinsic factor, which is relative density in this case.

The $Q \times f$ values and packing fractions of the Li$_2$Ni$_{2-x}$Zn$_x$(MoO$_4$)$_3$ ($x = 0–0.1$) ceramics are demonstrated in Figure 11. The packing fraction, defined by summing the volume of packed ions over the volume of a primitive unit cell, can be expressed as:

$$\text{Packing fraction} (%) = \frac{\text{volume of packed ions}}{\text{volume of primitive unit cell}} \times Z$$

where $Z$ is the number of formula units per unit cell. Accordingly, the dependence of the $Q \times f$ on the packing fraction of the ceramics is weak. The maximum $Q \times f$ of 56 000 GHz was obtained at 660°C for $x = 0.05$. In comparison with that of $x = 0$, it shows a 100% enhancement in the

**FIGURE 11** The $Q \times f$ values and related packing fractions of the Li$_2$Ni$_{2-x}$Zn$_x$(MoO$_4$)$_3$ ($x = 0–0.1$) ceramics

**FIGURE 12** The $T_f$ value and related sintering temperature of the Li$_2$Ni$_{2-x}$Zn$_x$(MoO$_4$)$_3$ ($x = 0–0.1$) ceramics
Q × f value which would make it a more promising dielectric material for high-frequency applications such as 5G system. The $T_f$ value of the specimen as shown in Figure 12 was functions of Zn contain and sintering temperature and it ranged from $-54$ppm/°C to $-84$ppm/°C.

The SEM images and related EDS results of Li$_2$Ni$_{2-x}$Zn$_x$(MoO$_4$)$_3$ ($x = 0.05$) ceramics sintered at 660°C are illustrated in Figure 13. The morphologies of the specimens are similar, and no significant difference was observed. Corresponding to EDS results, large and small grains were confirmed as the same Li$_2$Ni$_{2-x}$Zn$_x$(MoO$_4$)$_3$ ($x = 0.05$) composition (Figure 13b).

4 | CONCLUSION

For Li$_2$M$_2$(MoO$_4$)$_3$ (M = Co, Ni) specimens sintered at 600–900°C for 4 hours, a single orthorhombic structure with different space groups belonging to Pnma(62) and Pmcn(62), respectively, was detected. Contrast to Li$_2$Co$_2$(MoO$_4$)$_3$ having a higher $Q \times f$ value, a much lower sintering temperature (660°C) was required to obtain single Li$_2$Ni$_2$(MoO$_4$)$_3$ phase, which is more attractive for the ULTCC applications. The dielectric properties are correlated with the temperatures, the densities, and the microstructures of the specimens. Moreover, a small Zn substitution in the Li$_2$Ni$_{2-x}$Zn$_x$(MoO$_4$)$_3$ ($x = 0.05$) composition could effectively increase its $Q \times f$ (28 000 GHz for pure one) by 100% to a value of 56 000 GHz that would make it a more promising dielectric material for high-frequency applications such as 5G system.

ACKNOWLEDGMENTS

The work was financially sponsored by Ministry of Science and Technology of Taiwan under the projects MOST 105-2221-E-006-055-MY3.

ORCID

Meng-Hung Tsai https://orcid.org/0000-0002-7917-0728

REFERENCES

1. Kang IY, Seo IT, Cha YJ, Choi JH, Nahm S, Sung TH, et al. Low temperature sintering of ZnO and MnO2-added (Na0.5K0.5)NbO3 ceramics. J Eur Ceram Soc. 2012;2(10):2381–7.
2. Zhou HF, Liu XB, Chen XL, Fang L, Wang YL. ZnLi$_{2/3}$Ti$_{4/3}$O$_4$: A new low loss spinel microwave dielectric ceramic. J Eur Ceram Soc. 2012;32(2):261–5.
3. Zou D, Zhang QL, Yang H, Li SC. Low temperature sintering and microwave dielectric properties of Ba$_2$Ti$_3$Nb$_4$O$_{18}$ ceramics for LTCC applications. J Eur Ceram Soc. 2008;28(1):277–82.
4. Liu WQ, Zuo RZ. A novel low-temperature fireable La$_2$Zr$_3$(MoO$_4$)$_9$ microwave dielectric ceramic. J Eur Ceram Soc. 2018;38(1):339–42.
5. Zhang GQ, Wang H, Guo J, He L, Wei DD, Yuan QB. Ultra-low sintering temperature microwave dielectric ceramics based on Na$_2$O-MoO$_3$ binary system. J Am Ceram Soc. 2015;98(2):528–33.
6. Choi GK, Kim JR, Yoon SH, Hong KS. Microwave dielectric properties of scheelite (A=Ca, Sr, Ba) and wolframite (A=Mg, Zn, Mn) AMoO$_4$(O) compounds. J Eur Ceram Soc. 2007;27(8–9):3063–7.
7. Kim ES, Chun BS, Freer R, Cernik RJ. Effects of packing fraction and bond valence on microwave dielectric properties of A(2+)(2)B(6+)(O4) (A(2+): Ca, Pb, Ba; B6+: Mo, W) ceramics. J Eur Ceram Soc. 2010;30(7):1731–6.
8. Zhou D, Randall CA, Pang LX, Wang H, Wu XG, Guo J, et al. Microwave dielectric properties of Li-2(M2+)(2)Mo3O12 and
Li-3(M3+)Mo3O12 (M=Zn, Ca, Al, and In) lyonsite-related-type ceramics with ultra-low sintering temperatures. J Am Ceram Soc. 2011;94(3):802–5.

9. Li WB, Zhou D, Xi HH, Pang LX, Structure YX. Infrared reflectivity and microwave dielectric properties of (Na0.5La0.5)MoO4-(Na0.5Bi0.5)MoO4 Ceramics. J Am Ceram Soc. 2016;99(6):2083–8.

10. Du DW, Lan R, Xie K, Wang HT, Tao SW. Synthesis of Li2Ni2(MoO4)(3) as a high-performance positive electrode for asymmetric supercapacitors. Rsc Adv. 2017;7(22):13304–11.

11. Ozima M, Sato S, Zoltai T. Crystal-structure of a lithium-nickel molybdate, Li2ni2mo3o12, and systematics of structure type. Acta Crystallogr. 1977;33:2175–81.

12. Wiesmann M, Svoboda I, Weitzel H, Fuess H. Crystal-structure of lithium cobalt molybdate, Li2co2(Moo4)(3). Z Kristallogr. 1995;210(7):525–25.

13. Hakki BW, Coleman PD. A dielectric resonator method of measuring inductive capacities in the millimeter range. IRE Trans Microw Theory Tech. 1960;8(4):402–10.

14. Courtney WE. Analysis and evaluation of a method of measuring the complex permittivity and permeability microwave insulators. IEEE Trans Microw Theory Tech. 1970;18(8):476–85.

15. Li Y, Tanga RL, Li NN, Li H, Zhao XD, Zhu PW, et al. Pressure-induced amorphization of metavanadate crystals SrV2O6 and BaV2O6. J Appl Phys. 2015;118(3):035902–1–6.

16. Mcbride JR, Hass KC, Poindexter BD, Weber WH. “Raman and X-Ray Studies of Ce1-XReO2-Y, Where Re=La, Pr, Nd, Eu, Gd, and Tb. J Appl Phys. 1994;76(4):2435–41.

17. Silverman BD. Microwave absorption in cubic strontium titanate. Phys Rev. 1962;125(6):1921–30.

18. Penn SJ, Alford NM, Templeton A, Wang XR, Xu MS, Reece M, et al. Effect of porosity and grain size on the microwave dielectric properties of sintered alumina. J Am Ceram Soc. 1997;80(7):1885–88.

19. Liao Q, Li L, Ren X, Ding X. New low-loss microwave dielectric material ZnTiNbTaO8. J Am Ceram Soc. 2011;94(10):3237–40.

How to cite this article: Huang C-L, Liou J-N, Tsai M-H, Huang W-C. Microwave dielectric properties of Li2M2(MoO4)3 (M = Co, Ni) for LTCC applications. Int J Ceramic Eng Sci. 2020;2:130–139. https://doi.org/10.1002/ces.2.10044