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Low-firing and microwave dielectric properties of a novel glass-free MoO_3-based dielectric ceramic for LTCC applications

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Abstract
A novel glass-free MoO_3-based dielectric ceramic of $Li_2Ni_2(MoO_4)_3$ was prepared by the conventional solid-state route. The phase compositions, microstructures and microwave dielectric properties were investigated. The XRD data analysis shown that $Li_2Ni_2(MoO_4)_3$ belongs to an orthorhmbic lyonsite-type structure with Pmcn (62) space group during the sintering temperature range from 650 to 725 °C. The $Li_2Ni_2(MoO_4)_3$ ceramic could be well densification at 700 °C for 2 h with 96.8% relative density and exhibited excellent microwave dielectric properties: $\varepsilon_r = 9.2$, $Q \times f = 41{,}064$ GHz, $\tau_f = -68.86$ ppm/°C. Moreover, the $Li_2Ni_2(MoO_4)_3$ ceramic shown excellent compatible with Ag electrode, which makes it a promising candidate for advanced substrate materials in low temperature co-fired ceramic applications.

1 Introduction

With the rapid development in wireless communication industry, the microwave electronic components for integration, multifunctional and lightweight are the necessary growing trend. To date, the low temperature co-fired ceramic (LTCC) technology, as a key approach to fabricating highly integrated and high-performance devices with a compact multilayer ceramic structure, has attracted significant attention. To meet the LTCC technology, materials with a high quality factor ($Q \times f > 10{,}000$ GHz), an appropriate dielectric constant, a near-zero temperature coefficient of resonant frequency ($|\tau_f| \leq 10$ ppm/°C), low sintering temperature (Ts < 961 °C) and chemical compatibility with Ag electrode should be absolutely taken into account [1–5].

The traditional microwave dielectric ceramics, which usually have high performance and most of them have been widely used in practice. However, the high sintering temperatures (≥ 1200 °C) prohibits these ceramics application in LTCC. For purpose of lower the sintering temperature, there are several methods which including: (1) reducing the particle sizes of the raw materials; (2) chemical synthesis methods; (3) addition of low-melting glasses, etc. Among in these methods, adding low-melting glasses is the most effective approach and has been extensively used, but the microwave dielectric properties of ceramics always be seriously deteriorated [4, 6]. In addition, there are many microwave dielectric materials have been limited available for many practical applications by reasons of the today's demands for energy saving, nontoxicity and low cost etc. [7]. Without questions, searching for new microwave dielectric ceramics with intrinsic low firing temperatures, non-toxicities and low costs are the significant and fascinating research topic for development the LTCC technology.

Recently, owing to the low-melting (MoO_3 melting at 795 °C) and price advantage of molybdate, a series of MoO_3-based compounds, such as: A_2O–MoO_3 (A = Na, K, Ag) binary systems [8–10], PbO–MoO_3 binary systems [11, 12], Bi_2O_3–MoO_3 binary systems [13] and Li_2O–Bi_2O_3–MoO_3 ternary systems [14] etc., without any sintering aids have been found to be with satisfactory microwave dielectric properties sintered at the temperature range from 440 to 700 °C for 2–4 h. Unfortunately, there are still some problems in these systems, For examples: (1) in the PbO–MoO_3 binary systems, the toxicity of lead prohibits its further applications; (2) in the A_2O–MoO_3 (A = Li, Na) binary systems,

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although many ceramics have been reported shown a good microwave dielectric properties, such as: $2Na_2O–MoO_3$ ($\varepsilon_r = 5.8$, $Q \times f = 23{,}000$ GHz, $\tau_f = -115$ ppm/°C), Na_2MoO_4 ($\varepsilon_r = 4.3$, $Q \times f = 36{,}000$ GHz, $\tau_f = -76$ ppm/°C) [8] and $Li_2Mo_4O_{13}$ ($\varepsilon_r = 8.8$, $Q \times f = 7700$ GHz, $\tau_f = -66$ ppm/°C) [14], these ceramics are easy to moisture absorption or hydrolyze; (3) chemical incompatibility with Ag electrodes, such as: $Bi_2Mo_2O_9$ [13] and $(Li_{0.5}Bi_{0.5})MoO_4$ [14] etc. Therefore, further searching for new MoO_3-based ceramic systems are needed.

In the present work, a novel glass-free MoO_3-based microwave dielectric ceramics of $Li_2Ni_2(MoO_4)_3$ was synthesized via the conventional solid-state route. Furthermore, the phase compositions, microstructures, microwave dielectric properties and co-fired with Ag were investigated systematic. Up to now, a large quantity surveys of literature available shows that the $Li_2Ni_2(MoO_4)_3$ ceramic for LTCC applications have not been reported. As well, the microwave dielectric properties of $Li_2Ni_2(MoO_4)_3$ ceramic have not been reported too.

2 Experimental

$Li_2Ni_2(MoO_4)_3$ powders were synthesized via the conventional solid-state route. Analytical grade powders of Li_2CO_3 (99%), NiO (99%) and MoO_3 (99.5%) as raw materials. Stoichiometric Li_2CO_3, NiO and MoO_3 were mixed according to the formula of $Li_2Ni_2(MoO_4)_3$ with ZrO_2 balls and ethanol by ball mill for 4 h. The mixtures were dried and then calcined at 600 °C for 4 h. Subsequently, the calcined powders were reground for 4 h and then dried, mixed with 5 wt% PVA binder, pelleted to 15 mm diameter and 8 mm green body at 5 MPa by hydraulic pressing. The green body samples were heated at 550 °C for 2 h to remove the binder and then sintered at 650–725 °C for 2 h in ambient atmosphere at a heating rate of 5 °C/min.

The phase compositions of the sintered specimens were analyzed by X-ray diffractometer (PANalytical Empyrean Series 2, UK) with CuKa radiation. The microstructures of sintered ceramics were performed by scanning electron microscope (SEM, JSM-6460LV, Japan) coupled with energy-dispersive X-ray spectrometer (EDS, Philips). The bulk densities of the samples were measured by the Archimedes method. Dielectric properties measurements were carried out using a network analyzer (HP83752A, USA) in a wide frequency (1–20 GHz). The ε_r and Q values were measured in the TE011 mode by using the Hakki–Coleman dielectricresonator method. The temperature coefficients of resonant frequency (τ_f) were measured with changing temperatures from 20 to 60 °C defined as follows:

$$\tau_f = \frac{f_{60} - f_{20}}{40 \times f_{20}} \times 10^6 (\text{ppm/}^{\circ}\text{C})$$

where the f_{20} and f_{60} represent the resonant frequency at 20 and 60 °C, respectively.

3 Results and discussion

Powder XRD patterns of $Li_2Ni_2(MoO_4)_3$ ceramics sintered at 650–725 °C for 2 h are illustrated in Fig. 1. The XRD peaks of $Li_2Ni_2(MoO_4)_3$ can be well indexed based on JCPDS file number 70-0452 with an orthorhmbic lyonsite-type structure (space group Pmcn (62)) and the lattice parameters are: a = 10.425 (3) Å, b = 17.513 (4) Å, c = 5.085 (1) Å, which in accordance with the reported by Ozima and Zoltai [15]. At the same time, no other second phases are detected when the sintering temperature between 650 and 725 °C for 2 h. These results evidenced that a phase purity $Li_2Ni_2(MoO_4)_3$ ceramic can be obtained with a relatively low temperature.

Microstructure images (SEM) of $Li_2Ni_2(MoO_4)_3$ ceramics sintered at 650–725 °C for 2 h are displayed in Fig. 2. Figure 2a,b shows the microstructure is not dense and some isolated pores are also found. As the temperature increases, the microstructure become more compact and the grains become larger, a dense microstructure with evidently identifiable grain boundaries are obtained with two kinds of grains shape shows in Fig. 2c when the sintering temperature reaches 700 °C. Some rod-shaped grains with a diameter of 3–6 μm and a length of 10–20 μm and some of the hexagon-shape grains with 1–4 μm coexist in the microstructure. However, some abnormal growth grains with the size over 20 μm are observed in Fig. 2d as the sintering temperature increases to 725 °C.

The phase purity of $Li_2Ni_2(MoO_4)_3$ ceramic is further confirmed by the EDS. Figure 3 shows the EDS results of $Li_2Ni_2(MoO_4)_3$ ceramics sintering at 700 °C

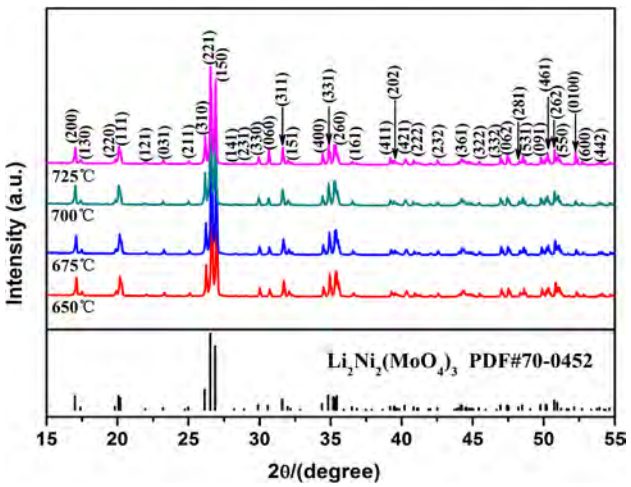

Fig. 1 XRD patterns of $Li_2Ni_2(MoO_4)_3$ sintered at different temperatures for 2 h

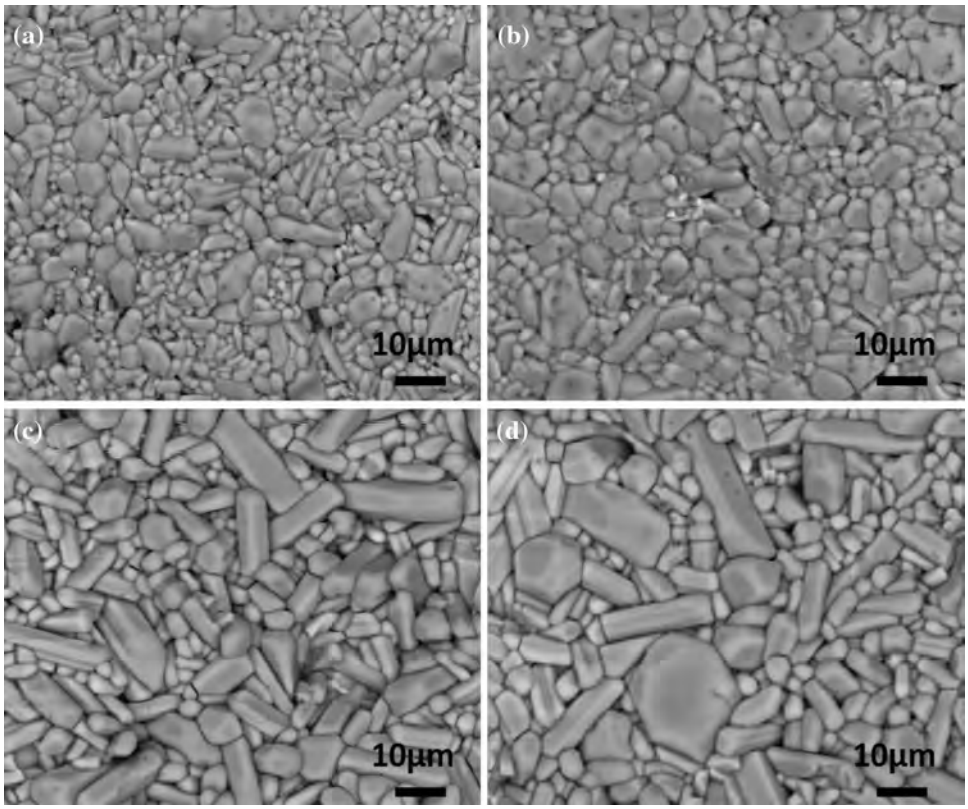

Fig. 2 The SEM micrographs of $Li_2Ni_2(MoO_4)_3$ ceramics sintered at different temperatures: **a** 650 °C, **b** 675 °C, **c** 700 °C, **d** 725 °C for 2 h

for 2 h. As shown in Fig. 3a, the SEM morphology of the $Li_2Ni_2(MoO_4)_3$ ceramics indicated two different grain types, which are rod-shaped grains (spot A) and hexagon-shape grains (spot B). On the basis of the EDS results show in Fig. 3b, the spot A show that consisted of Ni, Mo, and O, with a Ni:Mo:O ratio of about 1:1.5:6, and it correspond to the $Li_2Ni_2(MoO_4)_3$ crystal. The elemental composition of spot B is the same as that of spot A. Combing the results of XRD patterns from Fig. 1, indicating that both the grains are the $Li_2Ni_2(MoO_4)_3$ crystal. That is to say, a phase purity $Li_2Ni_2(MoO_4)_3$ ceramic is obtained. These results are consistent with the reported by Zhou et al. [16].

The variations in the relative density, dielectric constant (ε_r), quality factor ($Q\times f$), and temperature coefficient of resonant frequency (τ_f) of the $Li_2Ni_2(MoO_4)_3$ ceramics as a function of the sintering temperature are shown in Fig. 4. As shown in Fig. 4a, the relative density of $Li_2Ni_2(MoO_4)_3$ ceramics gradually increases during the sintering temperature range from 650 to 700 °C, and reaches a maximum value of 96.8% at 700 °C, and then decreased slightly to 95.6% at 725 °C caused by the abnormal grain growth, which in agreement with the SEM micrographs variation shown in Fig. 2. There is a similar variation tendency of the ε_r, and the $Q\times f$ with the relative density. During the sintering temperature changes from 650 to 700 °C, the ε_r increase from 8.2 to 9.2, and then slightly decreased to 9.0 at 725 °C (Fig. 4b). The lower permittivity at low temperature may be given the credit to the pores. Values of the $Q\times f$ increase from 26,326 GHz at 650 °C to a maximum value of 41,064 GHz at 700 °C, further increase in sintering temperature decreased the $Q\times f$ value to 35,064 GHz at 725 °C (Fig. 4c). Many factors are classified as two parts: the intrinsic loss and the extrinsic loss, have been reported to affect the microwave dielectric properties. In general, the intrinsic loss is caused by lattice vibration modes whereas the extrinsic loss is mainly caused by second phase, grain sizes, and densification etc [17, 18]. According to the XRD and EDS results, the influence of impurity and second phases could be eliminated. Therefore, the densification may be believed the mainly factor to affect the $Q\times f$ value in this work. With the sintering temperature increasing from 650 to 725 °C, the τ_f value of the $Li_2Ni_2(MoO_4)_3$ ceramic showed a not obvious varies and fluctuated in the range from -69.91 to -67.03 ppm/°C (Fig. 4d). Generally, excellent microwave dielectric properties of the $Li_2Ni_2(MoO_4)_3$ ceramic with $\varepsilon_r = 9.2$, $Q\times f = 41{,}064$ GHz, and $\tau_f = -68.86$ ppm/°C obtained as sintered at 700 °C for 2 h.

In order to verification the chemical compatibility of the $Li_2Ni_2(MoO_4)_3$ ceramic with silver electrode. Ag paste was printed on the surface of the unsintered $Li_2Ni_2(MoO_4)_3$ pellets and then cofired. Figure 5 shows the XRD pattern, SEM image and EDS line scan of the $Li_2Ni_2(MoO_4)_3$ ceramic cofired at 700 °C for 2 h with Ag electrode. The XRD pattern shows that only a cubic silver phase is detected in Fig. 5a. As

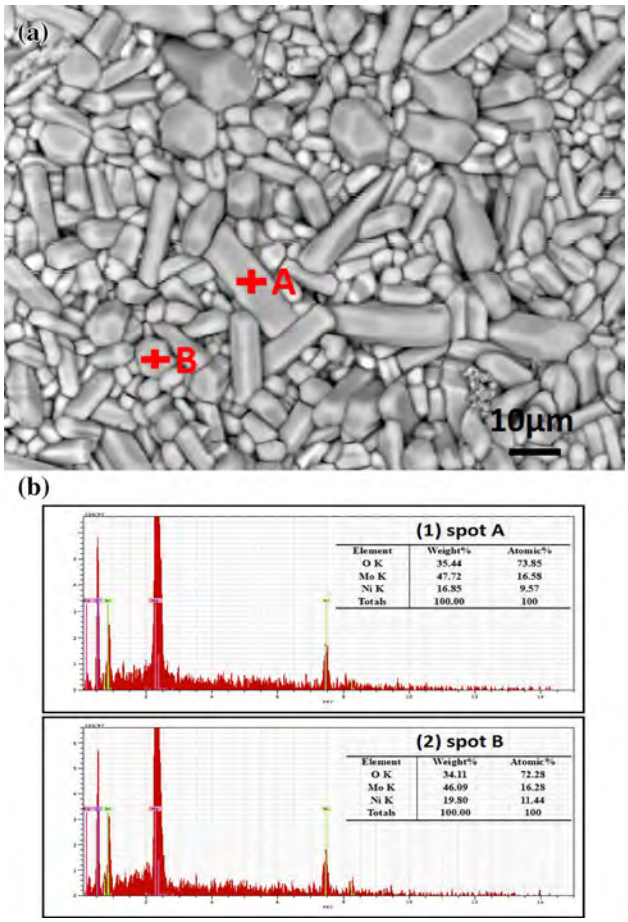

Fig. 3 The marks of SEM for the $Li_2Ni_2(MoO_4)_3$ ceramics sintered at 700 °C for 2 h (**a**); **b** EDS data of $Li_2Ni_2(MoO_4)_3$ ceramics for spots A and B

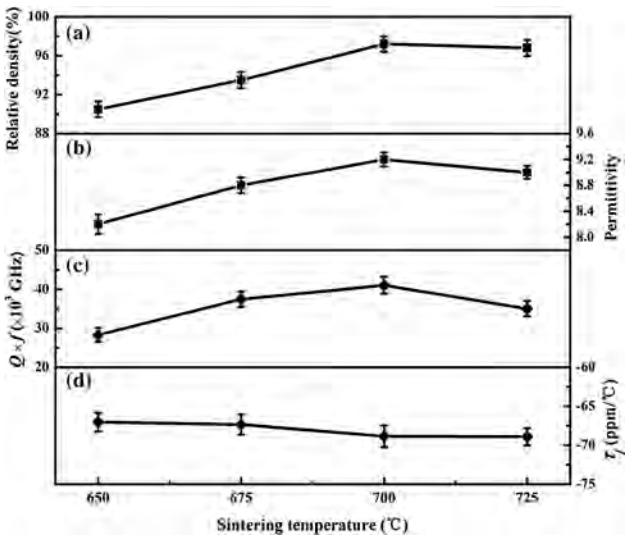

Fig. 4 The relative density and microwave dielectric properties (ε_r, $Q\times f$ and τ_f) of $Li_2Ni_2(MoO_4)_3$ ceramics as a function of sintering temperature

shown in Fig. 5b, the SEM image result shows that between the $Li_2Ni_2(MoO_4)_3$ ceramic and the Ag layer, a clear interface can be found. In addition, the EDS line scan result reveals that no new phases appear in the interface between ceramic and Ag during the co-fired processing. All results demonstrate that the $Li_2Ni_2(MoO_4)_3$ ceramic not only have a good chemical compatibility with silver electrode but also is a very promising candidate material for LTCC applications.

Table 1 lists the sintering temperatures, microwave dielectric properties and chemical compatibility with Ag electrode of some MoO_3-based ceramics. From Table 1, the permittivity of these ceramics are between 9.2 and 38. The sintering temperature are between 610 and 1100 °C. Although the ceramics of $PbMoO_4$, Pb_2MoO_5 and $Bi_2Mo_2O_9$ has a ultra-low sintering temperature between 610 and 650 °C, the toxicity of lead or chemical incompatibility with Ag electrode prohibits its further applications. It is worth noting that the $Li_2Ni_2(MoO_4)_3$ ceramic not only have a low permittivity, high quality factor and low sintering temperature but also chemical compatibility with Ag electrode. In addition, the raw materials of $Li_2Ni_2(MoO_4)_3$ ceramic are environment-friendly. Which further indicate that the $Li_2Ni_2(MoO_4)_3$ ceramic is a very potential candidate materials in LTCC application.

4 Conclusions

A novel glass-free MoO_3-based $Li_2Ni_2(MoO_4)_3$ ceramic was prepared with a low sintered temperature range from 650 to 725 °C for 2 h by the conventional solid-state route. When sintered at 700 °C for 2 h, the $Li_2Ni_2(MoO_4)_3$ ceramic could be well densification with 96.8% relative density and exhibited excellent microwave dielectric properties: $\varepsilon_r = 9.2$, $Q\times f = 41{,}064$ GHz, and $\tau_f = -68.86$ ppm/°C. In addition, the $Li_2Ni_2(MoO_4)_3$ ceramic has a good chemical compatibility with silver. All of these merits make the $Li_2Ni_2(MoO_4)_3$ ceramic to be a very potential candidate for advanced substrate materials in LTCC application.

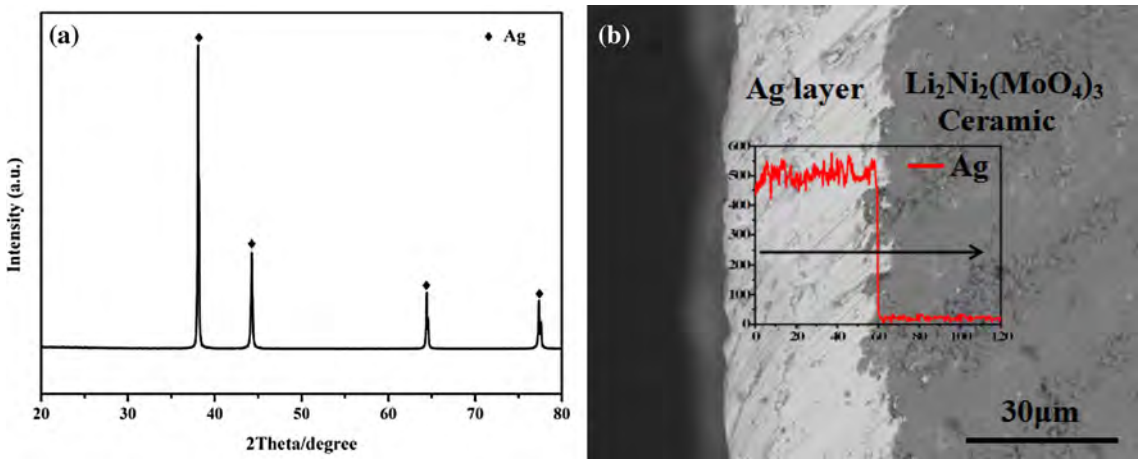

Fig. 5 XRD pattern of the surface of the Ag paste printed on the $Li_2Ni_2(MoO_4)_3$ ceramic after co-firing at 700 °C for 2 h (**a**), SEM and EDS line scan (**b**) of the cross-section of the $Li_2Ni_2(MoO_4)_3$ ceramic co-fired with Ag electrode at 700 °C for 2 h

Table 1 Comparison of the microwave dielectric properties and chemical compatibility with Ag electrode of some MoO_3-based ceramics

Composition	*S.T.* (°C)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	Reaction with Ag	References
$CaMoO_4$	1100	10.8	89,700	−57	–	[19]
$SrMoO_4$	1050	9.5	61,000	−67	–	[19]
$PbMoO_4$	650	26.7	42,830	+6.2	No	[11]
Pb_2MoO_5	610	19.1	21,960	−60	No	[12]
$Bi_2Mo_2O_9$	620	38	12,500	+31	Yes	[13]
$Li_2Ni_2(MoO_4)_3$	700	9.2	41,064	−68.9	No	This work

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