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Microwave Dielectric Ceramics in Li_2O–Bi_2O_3–MoO_3 System with Ultra-Low Sintering Temperatures

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A series of compounds in the Li_2O–Bi_2O_3–MoO_3 ternary system were investigated with regard to the preparation, phase composition, microwave dielectric properties, and chemical compatibility with silver (Ag) and aluminum (Al) electrodes. All the ceramics in this work have sintering temperatures lower than 750°C. The sintering behaviors and microwave dielectric properties of three single phases Li_2MoO_4, $(Li_{0.5}Bi_{0.5})MoO_4$, and $Li_8Bi_2Mo_7O_{28}$ bulk ceramics, were of particular focus in this investigation. The Li_2MoO_4 ceramic can be sintered to a high density at 540°C/2 h with a relative permittivity ~5.5, a $Q \times f$ value of 46 000 GHz, and a temperature coefficient of resonant frequency (TCF) of ~−160 ppm/°C. The $(Li_{0.5}Bi_{0.5})MoO_4$ ceramic has a scheelite structure and the largest relative permittivity of 44.4 among the ceramics studied in this work with a sintering temperature around 560°C, a $Q \times f$ value of 3200 GHz, and a large positive TCF of ~+245 ppm/°C. The $Li_8Bi_2Mo_7O_{28}$ ceramic could be sintered at 540°C and has a relative permittivity of 13.6, a $Q \times f$ value of 8000 GHz, and a small negative TCF value of ~−59 ppm/°C. From the X-ray diffraction analysis of cofired ceramics, the Li_2MoO_4 ceramic does not react with either Ag or Al powders. The $Li_8Bi_2Mo_7O_{28}$ ceramic reacts with Ag but not with Al at its densification temperature. The $(Li_{0.5}Bi_{0.5})MoO_4$ ceramic was found to strongly react with Ag powder and to a limited extent with Al powders. From this study, the Li_2O–Bi_2O_3–MoO_3 ternary system has a number of attractive new materials with low sintering temperatures, high-performing microwave dielectric properties, chemical compatibility with both Ag and Al metal electrodes, nontoxicity, and low-cost constituents. All these materials can be included in the new field of ultra-low-temperature cofiring dielectrics for multilayer applications.

I. Introduction

To meet the requirement of miniaturization of microwave components for wireless communication, new developments in materials, integration, packaging, and interconnection technologies are needed. Low-temperature cofired ceramic (LTCC) technology has attracted much attention because of its predominance in enabling the fabrication of three-dimensional ceramic modules with low dielectric loss and embedded metal electrodes.[1–5]

To develop ultra-low-temperature cofiring ceramic technology (ULTCC) with aluminum (Al) electrodes as an alternative to LTCC, we will require new dielectrics with a range of dielectric properties. For microwave applications, high permittivity, low dielectric loss (high $Q \times f$ value), near-zero temperature coefficient, low sintering temperature below the melting points of Al, and chemical compatibility are required. Furthermore, the ceramics will have to be low-cost and nontoxic. In the past 20 years, a large number of ceramics with good microwave dielectric properties have been developed, such as (Ba,Sr)O–TiO_2–Nb_2O_5 system,[6,7] Li_2O–Nb_2O_5–TiO_2 system,[8,9] (Zr,Sn)TiO_4,[10,11] and $(A_1A_2)(B_1B_2)O_3$ complex perovskite system,[12–16] etc. Lowering sintering temperatures and modifying temperature coefficients are always hot topics for research, but most have considered the traditional LTCC conditions that cofire at 850°C.[17] The first dielectric to be cofired with Al was a $BaTe_4O_9$ ceramic. It can be sintered well at 550°C and cofired with Al electrodes.[18] However, TeO_2 is relatively costly and has toxicity problems. In our recent research, we found that $Bi_2Mo_2O_9$ ceramic can be sintered well at around 620°C and it possesses very good microwave dielectric properties with a permittivity around 38, $Q \times f$ value of about 12 500 GHz, and temperature coefficient of resonant frequency (TCF) of about +31 ppm/°C.[19] Furthermore, we studied the sintering behaviors together with microwave dielectric properties and chemical compatibility with Al and silver (Ag) of many compounds in a Bi_2O_3–MoO_3 binary system, which looked promising for a ULTCC technology. We found $Bi_2Mo_2O_9$ ceramic does not react with Al up to 645°C but reacts with Ag at this temperature.[20] Both $BaTe_4O_9$ and $Bi_2Mo_2O_9$ ceramics have interesting low sintering temperatures. Thus, if there are new materials that are suitable for ULTCC, it would seem that the oxide constituents require low melting temperatures, examples being TeO_2 (733°C), MoO_3 (795°C), and Bi_2O_3 (817°C) oxides, and in the phase diagrams there are eutectic or peritectic solid-phase reactions. Hence, we can speculate that there may be many new ceramics for a ULTCC technology with constituents with low-melting-temperature oxides, such as TeO_2 (733°C), MoO_3 (795°C), Bi_2O_3 (817°C), PbO (886°C), B_2O_3 (450°C) or H_3BO_3 (171°C), P_2O_5 (340°C), V_2O_5 (690°C), Li_2CO_3 (723°C), etc. Among them, the Li_2O–Bi_2O_3–MoO_3 ternary system is considered in this investigation, noting that all three constituents have low melting points.

The Li_2O–MoO_3 binary phase diagram has been studied by Hoermann,[21] Brower *et al.*,[22] Parmentier *et al.*,[23] and Moser *et al.*[24] and four compounds $Li_2Mo_4O_{13}$, $Li_4Mo_5O_{17}$, Li_2MoO_4, and Li_4MoO_5 can be formed. To our knowledge, there have been no reports on their microwave dielectric properties. Apart from the compound Li_4MoO_5, the other three compounds all have melting points below 700°C. Hence, such compounds can be sintered below 700°C. The Bi_2O_3–MoO_3 binary phase diagram has been studied by Belyaev and Smolynaninov,[25] Bleijenberg *et al.*,[26] Erman *et al.*,[27] Chen and Smith,[28] and Egashira *et al.*[29] Our recent research reported that many compounds in

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this binary system possess high-performance microwave dielectric properties and low sintering temperatures.[20] Although, many compounds have been developed in the Li_2O–Bi_2O_3 binary system using the ion-exchange reaction method, its phase diagram is still not accomplished.[30–36] Hence, the compositions in Li_2O–Bi_2O_3 system are not studied in this work. In the Li_2O–Bi_2O_3–MoO_3 ternary system, $(Li_{0.5}Bi_{0.5})MoO_4$[37,38] and $Li_8Bi_2Mo_7O_{28}$[39] are the only two single-phase compounds reported previously.

In the present work, we will introduce the sintering behaviors and microwave dielectric properties of a series of compounds in the Li_2O–MoO_3 system and the Li_2O–Bi_2O_3–MoO_3 ternary system (Li_2CO_3 was chosen as the starting material instead of Li_2O, and prepared via a solid-state reaction method). These compounds are considered for the applicability to the ULTCC field; the chemical compatibilities with Ag and Al are also studied.

II. Experimental Procedure

In the Li_2O–Bi_2O_3–MoO_3 ternary system, $Li_2Mo_4O_{13}$, $Li_4Mo_5O_{17}$, Li_2MoO_4, $(Li_{0.5}Bi_{0.5})MoO_4$, $LiBiMoO_5$, $Li_3BiMo_3O_{12}$, and $Li_8Bi_2Mo_7O_{28}$ compositions are chosen for investigation. Proportionate amounts of reagent-grade starting materials of Bi_2O_3 (>99%, Shu-Du Powders Co. Ltd., Chengdu, China), Li_2CO_3 (>99%, Guo-Yao Co. Ltd., Shanghai, China), and MoO_3 (>99%, Fuchen Chemical Reagents, Tianjin, China) were prepared according to the chosen compositions. Powders were mixed and milled for 4.5 h using a planetary mill (Nanjing Machine Factory, Nanjing, China) by setting the running speed at 150 rpm with zirconia balls (2 mm in diameter) as the milling media. After drying, the mixed oxides were calcined at 500°–550°C for 4 h. After crushing and remilling for 5 h using ZrO_2 balls and deionized water, powders were pressed into pellets and cylinders (10 mm in diameter and 5 mm in height) using a steel die under a uniaxial pressure of 200 MPa with PVA binder addition. Samples were sintered between 500° and 700°C for 2 h in an ambient atmosphere. To study the chemical compatibility with Ag and Al, ceramic samples were ground and mixed into composites with 20 wt% Ag and Al powders, and then sintered at around 550°C for 2 h.

The crystalline structures of samples (ground powders) were investigated using X-ray diffraction (XRD) with Cu$K\alpha$ radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan). Microstructures of natural surfaces (pellet sample) were observed using scanning electron microscopy (JEOL JSM-6460, Tokyo, Japan). Dielectric characteristics at microwave frequency were measured by the $TE_{01\delta}$ shielded cavity method using a network analyzer (8720ES, Agilent, Palo Alto, CA) and a temperature chamber (DELTA 9023, Delta Design, Poway, CA). The TCF was calculated by the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \quad (1)$$

where f_{85} and f_{25} were the $TE_{01\delta}$ resonant frequencies at 85°C and 25°C, respectively.

III. Results and Discussions

Figure 1 shows the compositions selected from the Li_2O–Bi_2O_3–MoO_3 ternary system for this investigation. XRD patterns of these compositions and cofired samples sintered at their respective densification temperatures are shown in Fig. 2. Pure Bi_2O_3 sintered at 680°C/2 h shows a monoclinic structure with $a = 5.847(4)$ Å, $b = 8.172(5)$ Å, $c = 7.511(4)$ Å, and $\beta = 112.96(2)$ Å (P21/c (No. 14)), which is similar to the results of Ivanov *et al.*[40] For the Li_2O–MoO_3 binary phase diagram, pure phases of Li_2MoO_4 and $Li_2Mo_4O_{13}$ can be formed at 540°C. There is no evidence of a Li_2CO_3 phase, which means that Li_2CO_3 reacted with MoO_3 fully during the sintering process at this temperature. For the Li_2O–Bi_2O_3–MoO_3 ternary

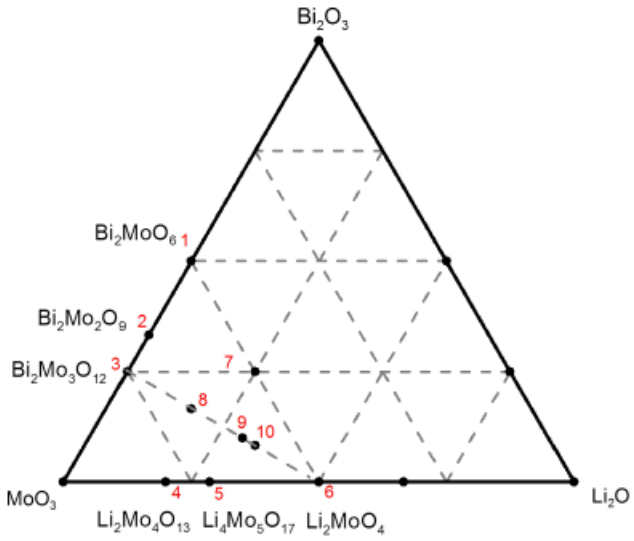

Fig. 1. Compositions chosen in the Li_2O–Bi_2O_3–MoO_3 ternary system.

system, pure phases of $(Li_{0.5}Bi_{0.5})MoO_4$ and $Li_8Bi_2Mo_7O_{28}$ can be formed at around 550°C as deduced from the XRD analysis. The $(Li_{0.5}Bi_{0.5})MoO_4$ has a $CaMoO_4$-type scheelite structure. Klevtsova[39] first reported the synthesis of $Li_8Bi_2Mo_7O_{28}$. It was found that it had a tetragonal structure with $a = 21.130$ Å and $c = 5.287$ Å (I-4 (No. 82)). In this investigation, the lattice parameters were determined as $a = 21.15$ and $c = 5.29$Å, which agreed well with Klevtsova's results. As shown in Fig. 2(a), the $Li_3BiMo_3O_{12}$ composition sample sintered at around 540°C was found to be composed of both the scheelite phase and the $Li_8Bi_2Mo_7O_{28}$ phase. The $LiBiMoO_5$ composition was found to be composed of both the Li_2MoO_4 and the Bi_2MoO_6 phases. The XRD patterns of cofired samples (just for the Li_2MoO_4, $(Li_{0.5}Bi_{0.5})MoO_4$, and $Li_8Bi_2Mo_7O_{28}$ single-phase samples, cofired with both Ag and Al powders) are shown in Figs. 2(b)–(d), respectively. For the cofired samples of Li_2MoO_4 with both Ag and Al powders, besides peaks of Li_2MoO_4 and metal, there are no additional peaks in the XRD patterns to reflect a secondary phase formed, implying that Li_2MoO_4 materials does not react with either Ag or Al at the sintering temperature. For a cofired sample of $(Li_{0.5}Bi_{0.5})MoO_4$ with Al, a very weak peak at around 28.3°C was revealed in addition to the peaks of the scheelite phase and the Al phases. This indicates that $(Li_{0.5}Bi_{0.5})MoO_4$ reacted with Al at 550°C/2 h and a secondary phase was formed, but the relative strength of the peaks either points to a slow reaction and/or a small amount of secondary phase. For the 550°C cofired sample of $(Li_{0.5}Bi_{0.5})MoO_4$ with Ag powders, besides the peaks of scheelite phase, Ag phase, and unknown phase, which also exists in Al cofired samples are observed. Several peaks of an Li_2MoO_4 phase, a Bi_2MoO_6 phase, and three other peaks of unknown phases are also noted. This result indicates that there is a complex reaction mechanism during the cofiring of $(Li_{0.5}Bi_{0.5})MoO_4$ and Ag. The appearance of an Li_2MoO_4 phase might be caused by the substitution of Ag^+ for Li^+ in the scheelite phase. The peaks of unknown phases are difficult to be indexed. From the XRD patterns in Fig. 2(d), the $Li_8Bi_2Mo_7O_{28}$ ceramic does not react with Al powder but, again, reacts deleteriously with Ag powder. After cofiring of the $Li_8Bi_2Mo_7O_{28}$ ceramic and Ag powder, peaks of the Li_2MoO_4 phase, Bi_2MoO_6 phase, scheelite phase, Ag, and the unknown phase can be observed in XRD patterns. These results all indicate that the compounds in the Li_2O–Bi_2O_3–MoO_3 system seem to be more reactive with Ag than Al, which is similar to our earlier observations in the Bi_2O_3–MoO_3 system.[20]

Microwave relative permittivity and $Q \times f$ values of samples as a function of sintering temperature are shown in Fig. 3. Densification temperatures, phase compositions, densities, and

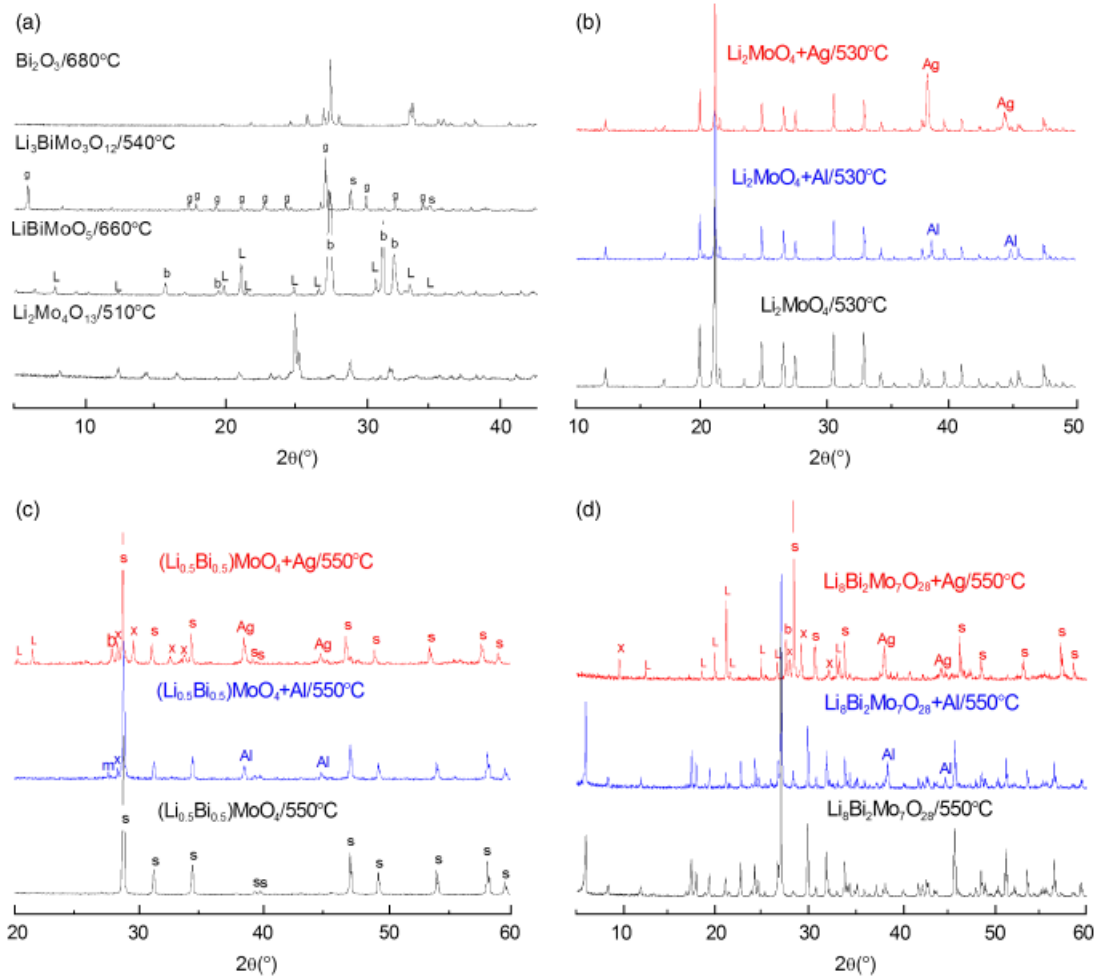

Fig. 2. X-ray diffraction (XRD) patterns of compounds in the Li_2O–Bi_2O_3–MoO_3 ternary system: Bi_2O_3/680°C, $Li_3BiMo_3O_{12}$/540°C, $LiBiMoO_5$/660°C, and $Li_2Mo_4O_{13}$/510°C (a), XRD patterns of pure Li_2MoO_4/530°C and cofired ceramics with 20 wt% Al, 20 wt% Ag (b), XRD patterns of pure $(Li_{0.5}Bi_{0.5})MoO_4$/550°C and cofired ceramics with 20 wt% Al, 20 wt% Ag (c), XRD patterns of pure $Li_8Bi_2Mo_7O_{28}$/550°C and cofired ceramics with 20 wt% Al, 20 wt% Ag (d), (L—Li_2MoO_4, b—Bi_2MoO_6, g—$Li_8Bi_2Mo_7O_{28}$, s—$(Li_{0.5}Bi_{0.5})MoO_4$ or $[(Li,Ag)_{0.5}Bi_{0.5}]MoO_4$, x—unknown phases, m—extraneous instrumental peak).

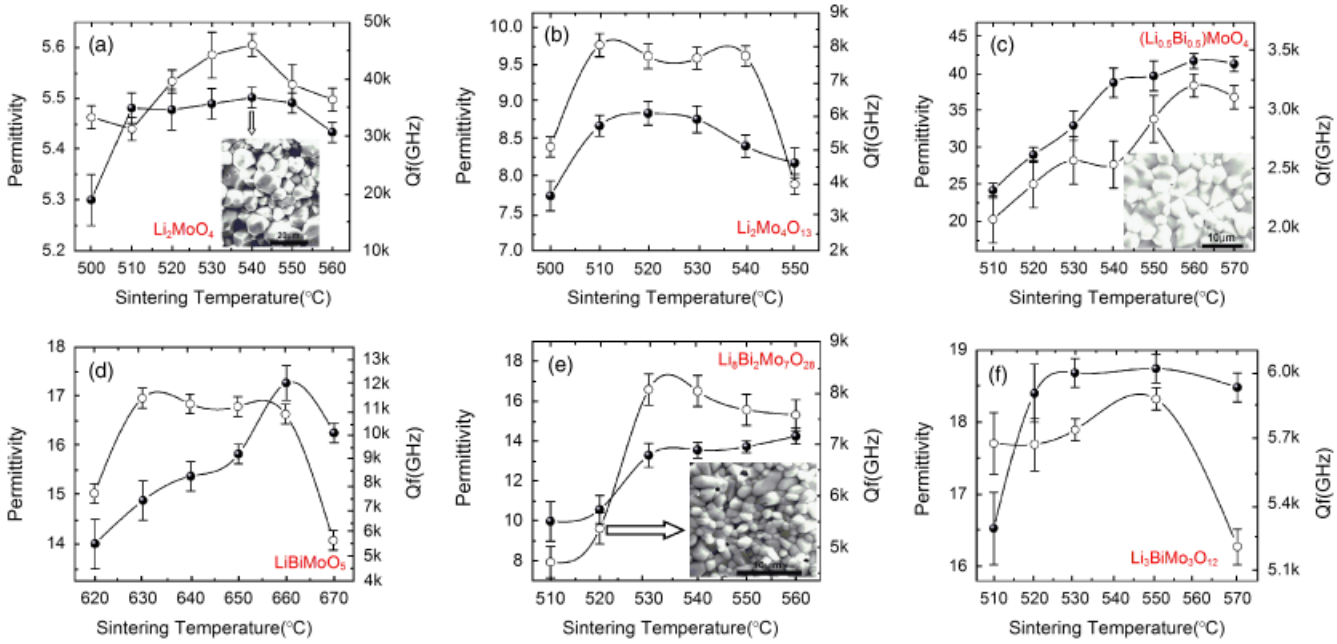

Fig. 3. Microwave dielectric properties (●, relative permittivity and ○, $Q \times f$ values) of Li_2MoO_4 (a), $Li_2Mo_4O_{13}$ (b), $(Li_{0.5}Bi_{0.5})MoO_4$ (c), $LiBiMoO_5$ (d), $Li_8Bi_2Mo_7O_{28}$ (e), and $Li_3BiMo_3O_{12}$ (f) as a function of sintering temperature.

Table I. Densification Temperatures, Phase Compositions, Densities, and Microwave Dielectric Properties of Some Compositions in the Li_2O–Bi_2O_3–MoO_3 Ternary System

No.	Composition	ST (°C)	Phase	Reaction with Al	Density (g/cm^3)	ε_r	f (GHz)	$Q \times f$ (GHz)	TCF (ppm/°C)
1†	Bi_2MoO_6	750	Pure	—	7.116	31 ± 1.2	6.434	16 700 ± 500	−114 ± 5
2†	$Bi_2Mo_2O_9$	620	Pure	No	6.250	38 ± 1.5	6.302	12 500 ± 500	+31 ± 3
3†	$Bi_2Mo_3O_{12}$	610	Pure	No	5.757	19 ± 1.2	7.577	21 800 ± 800	−215 ± 9
4‡	$Li_2Mo_4O_{13}$	520	Pure	—	—	8.8 ± 0.2	10.784	7700 ± 400	−66 ± 5
6	Li_2MoO_4	540	Pure	No (No with Ag)	2.895 (95.5%)	5.5 ± 0.05	13.051	46 000 ± 1000	−160 ± 10
7	$LiBiMoO_5$	660	Li_2MoO_4+Bi_2MoO_6	—	5.459	17.1 ± 0.5	8.002	10 800 ± 400	−112 ± 8
8	$(Li_{0.5}Bi_{0.5})MoO_4$	560	Pure	Yes	5.476 (96.7%)	44.4 ± 0.9	5.517	3200 ± 300	+245 ± 10
9	$Li_3BiMo_3O_{12}$	540	Phase8+Phase10	—	—	18.7 ± 0.3	10.150	5900 ± 300	+19 ± 3
10	$Li_8Bi_2Mo_7O_{28}$	540	Pure	No	4.286 (95.7%)	13.6 ± 0.9	9.210	8000 ± 400	−59 ± 5
11	Bi_2O_3	680	Pure	—	9.085 (97.0%)	33.5 ± 0.8	8.706	18 700 ± 800	−235 ± 10

†Data from reference[19,20]. ‡Sample is easy to hydrolyze.

microwave dielectric properties of ceramic are all summarized in Table I. Pure Bi_2O_3 could be sintered well at around 680°C with a permittivity of 33.5, a $Q \times f$ of 18 700 GHz, and a TCF of ~−235 ppm/°C at 8.706 GHz. In the Li_2O–MoO_3 binary system, the Li_2MoO_4 ceramic can be sintered at 540°C with a permittivity of $\varepsilon_r \sim 5.5$, $Q \times f$ value of ~46 000 GHz, TCF value of ~−160 ppm/°C with grains sizes between 5 and 15 μm, and $Li_2Mo_4O_{13}$ can be well densified at 510°–540°C with a permittivity of $\varepsilon_r \sim 8.8$, $Q \times f$ value of ~7700 GHz, and a TCF value of ~−66 ppm/°C. $(Li_{0.5}Bi_{0.5})MoO_4$ ceramic possesses the largest permittivity of $\varepsilon_r \sim 44.4$ among all the samples studied here. The average grain size lies between 1 and 3 μm. Because of the coexistence of a low permittivity $Li_8Bi_2Mo_7O_{28}$ phase ($\varepsilon_r \sim 13.6$) in $Li_3BiMo_3O_{12}$ composite samples, there is a decrease in the microwave relative permittivity. The grain boundaries between two different phases also deteriorated the $Q \times f$ value. A very small TCF value of +19 ppm/°C was obtained in the $Li_3BiMo_3O_{12}$ ceramic. The $LiBiMoO_5$ composite sample included both Li_2MoO_4 and Bi_2MoO_6 phases, which should be both responsible for its microwave dielectric properties. The high densification temperature (660°C) should be attributed to the Bi_2MoO_6's high sintering temperature of 750°C.[20] In general, these compositions in the Li_2O–Bi_2O_3–MoO_3 ternary system all have very low sintering temperature and high performance with regard to microwave dielectric properties.

IV. Conclusions

In the Li_2O–MoO_3 binary system and the Li_2O–Bi_2O_3–MoO_3 ternary system, a series of new compounds possessing very low sintering temperature and good microwave dielectric properties were introduced. The Li_2MoO_4 ceramic can crystallize in a single phase and be sintered well at 540°C/h with a relative permittivity of ~5.5, a $Q \times f$ value of ~46 000 GHz, and a TCF value of −160 ppm/°C. A single phase of $(Li_{0.5}Bi_{0.5})MoO_4$ has a scheelite structure and the largest relative permittivity of 44.4 with a sintering temperature around 560°C, a $Q \times f$ value of 3200 GHz, and a large positive TCF of +245 ppm/°C. Another single phase in the Li_2O–Bi_2O_3–MoO_3 ternary system $Li_8Bi_2Mo_7O_{28}$ can be sintered at 540°C and has a permittivity of 13.6, a $Q \times f$ value of 8000 GHz, and a small negative TCF value of −59 ppm/°C. Combining these three and several single phases in Bi_2O_3–MoO_3 binary system, many possibilities to design some complex phases with near-zero TCF values are available. From the chemical compatibility analysis, some compounds did not appear to react with Ag or Al at their sintering temperatures. The Li_2O–Bi_2O_3–MoO_3 ternary system provides new compounds that are promising candidates for the ULTCC field.

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