

# Microwave Dielectric Properties of $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$ and $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$ ( $\text{M} = \text{Zn}, \text{Ca}, \text{Al},$ and $\text{In}$ ) Lyonsite-Related-Type Ceramics with Ultra-Low Sintering Temperatures

Di Zhou,<sup>†,‡,§</sup> Clive A. Randall,<sup>§</sup> Li-Xia Pang,<sup>¶</sup> Hong Wang,<sup>‡</sup> Xin-Guang Wu,<sup>‡</sup> Jing Guo,<sup>‡</sup> Gao-Qun Zhang,<sup>‡</sup> Li Shui,<sup>‡</sup> and Xi Yao<sup>‡</sup>

<sup>‡</sup>Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, Shaanxi, China

<sup>§</sup>Center for Dielectric Studies, Materials Research Institute, The Pennsylvania State University, University Park, Pennsylvania 16802

<sup>¶</sup>Micro-optoelectronic Systems Laboratories, Xi'an Technological University, Xi'an 710032, Shaanxi, China

In this work, the  $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$  and  $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$  ( $\text{M} = \text{Zn}, \text{Ca}, \text{Al},$  and  $\text{In}$ ) lyonsite-related structures were prepared using a solid-state reaction method. Single-phase lyonsite materials were formed for the following compositions  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$ ,  $\text{Li}_3\text{AlMo}_3\text{O}_{12}$ , and  $\text{Li}_3\text{InMo}_3\text{O}_{12}$  ceramics. Whereas, the  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  batched compositions produced  $\text{Li}_2\text{MoO}_4$  and  $\text{CaMoO}_4$  phases. All the four ceramics did not react with Ag and Al powders at their optimal sintering temperatures, which will permit the possibility of cofired electrodes with these metallurgies. The  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  ceramic can be sintered at 630°C with a relative permittivity of 11.1, a  $Q \times f$  value of  $\sim 70\,000$  GHz, and a temperature coefficient of  $-90$  ppm/°C at 14.6 GHz. The  $\text{Li}_3\text{AlMo}_3\text{O}_{12}$  ceramic sintered at 570°C has a relative permittivity of 9.5, a  $Q \times f$  value of  $\sim 50\,000$  GHz, and a temperature coefficient of  $-73$  ppm/°C at 14.1 GHz. The  $\text{Li}_3\text{InMo}_3\text{O}_{12}$  ceramic sintered at 630°C has a relative permittivity of 9.8, a  $Q \times f$  value of  $\sim 36\,000$  GHz, and a temperature coefficient of  $-73$  ppm/°C at 15.0 GHz. These ceramics are a good candidate for the expanding family of ultra-low temperature cofired ceramic technologies, for filter and substrate applications at the high-frequency range.

## I. Introduction

OVER the past half century, microwave dielectric ceramics have been widely used as dielectric resonators, filters, dielectric waveguides, microstripline substrates, and all dielectric metamaterials.<sup>1–3</sup> To meet the miniaturization and integration requirements for rapidly developing mobile and satellite communication, low-temperature cofired ceramic (LTCC) technology has become an important fabricating method to integrate the passive components with microstripline packaged with IC chips mounted on the surface. By this technology, microwave dielectrics are stacked in multilayers and cofired with internal electrodes, such as Ag, Cu, Au, and more recently special patterns to control transmission and filtering microwave transmission.<sup>4–7</sup> The microwave dielectric materials used in LTCC field

have a range of dielectric permittivities, high  $Q \times f$  value ( $f =$  resonant frequency,  $Q = 1/\text{dielectric loss at } f$ ,  $Q \times f > 50\,000$  GHz), and a near-zero temperature coefficient of resonant frequency (TCF  $\approx 0$  ppm/°C), with a low sintering temperature (below the melting points of electrode metals with chemical compatibility between the metal electrodes and the dielectric). Additional issues include environment and economic considerations.<sup>8–13</sup>

In our previous work,<sup>14–16</sup> many  $\text{MoO}_3$ -rich oxides were reported to possess good microwave dielectric properties and ultra-low sintering temperatures, such as 540°C sintered  $\text{Li}_2\text{MoO}_4$  ceramic with a relative permittivity of  $\sim 5.5$ , a  $Q \times f$  value of 46 000 GHz at 13 GHz, and a TCF of  $\sim -160$  ppm/°C. In this work, we introduce a lyonsite family with  $\text{MoO}_3$  chemistries with ultra-low sintering temperature, and the associated properties with various chemistries.

## II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials were prepared by a mixed-oxide approach according to the following stoichiometric  $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{2+} = \text{Zn}$  and  $\text{Ca}$ ) and  $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{3+} = \text{Al}$  and  $\text{In}$ ) compositions. Powders were mixed and ball milled with stabilized zirconia media (Tosoh Ceramics, Tokyo, Japan) for 24 h. The powder mixture was then calcined at 500°–600°C for 4 h for each of the different compositions. The calcined powders were vibratory milled for 24 h to increase reactivity and better homogeneity and then granulated with 2–5 wt% acryloid polymer binder (Acrylic Resin, Rohm and Hass Chemicals LLC, Philadelphia, PA), pulverized, and sieved using a mesh screen with 180  $\mu\text{m}$  openings. This was performed to aid pressing and producing high green density. Then, the powders were pressed into cylinders (12 mm in diameter and 6 mm in height) in a steel die under a uniaxial pressure of 200 MPa. After debinding, the samples were then sintered at various temperatures ranging from 510° to 690°C for 2 h in ambient atmosphere. To investigate the chemical compatibility of these compositions with electrode metal powders, 20 wt% Ag and 20 wt% Al were mixed with the different compositions and held at the sintering temperatures for 4 h.

Phase determination was made using X-ray diffraction (XRD) (Scintag PADV and X2 diffractometers, Scintag Inc., Cupertino, CA) with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54$  Å). Before examination sintered pellets were crushed in a mortar and pestle to powder. Microstructures of cofired ceramics were observed on the fracture surface with scanning electron microscopy (SEM) (Hitachi S-3000H, Hitachi High-Technologies Co., Tokyo, Japan).

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<sup>†</sup>Author to whom correspondence should be addressed e-mail: zhoudi1220@gmail.com

The dielectric properties were measured at microwave frequency by the postresonator method as suggested by Hakki and Coleman<sup>17</sup> with a network analyzer (HP8510 Network Analyzer, Agilent, Hewlett-Packard, Palo Alto, CA). The TCF was determined using a zero thermal expansion cavity with programmable temperature chamber (Delta 9023, Delta Design, Poway, CA) in the temperature range of +25° to +85°C and a closed-cycle helium cryostat in the temperature range of -190° to +20°C. The TCF was calculated by the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times (85 - 25)} \times 10^6 \quad (1)$$

where  $f_{85}$  and  $f_{25}$  were the  $\text{TE}_{018}$  resonant frequencies at 85° and 25°C, respectively.

### III. Results and Discussions

The room-temperature XRD patterns for pure  $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{2+} = \text{Zn}$  and  $\text{Ca}$ ),  $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{3+} = \text{Al}$ ,  $\text{La}$ , and  $\text{In}$ ) ceramics and their mixtures with metal powders (20 wt% Al and Ag) sintered at different temperatures are also shown in Fig. 1. Only a single orthorhombic phase can be indexed in  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$ ,  $\text{Li}_3\text{AlMo}_3\text{O}_{12}$ , and  $\text{Li}_3\text{InMo}_3\text{O}_{12}$  ceramics. In fact, it is a ubiquitous adaptive structure type and got its name from the mineral lyonsite  $\alpha\text{-Cu}_3\text{Fe}_4(\text{VO}_4)_6$ .<sup>18,19</sup> The general formula for lyonsite-based oxides can be written as  $\text{A}_{16}\text{B}_{12}\text{O}_{48}$ , in which three different A sites are usually in low-oxidation-state (+1, +2, and +3) metal cations and the two B sites usually occupy high-oxidation-state (+5 and +6) metal cations. The lyonsite crystal structure is based on an array of pseudo-hexagonal oxygen atoms, and built up of isolated  $\text{BO}_4$  tetrahedra linked by  $\text{AO}_6$  chains as shown in Fig. 1(e).<sup>18</sup> The largest group of the existing lyonsite-type compounds are molybdates, which was first discovered and recognized as a new structure for  $\text{NaCo}_{2.31}(\text{MoO}_4)_3$  back in 1964.<sup>20</sup> Now, there are many lyonsite-based molybdates including  $\text{Li}_2\text{M}_2^{2+}(\text{MoO}_4)_3$  ( $\text{M} = \text{Fe}$ ,  $\text{Mg}$ ,  $\text{Mn}$ ,  $\text{Co}$ ,  $\text{Ni}$ ,  $\text{Cu}$ , and  $\text{Zn}$ ),  $\text{Li}_3\text{M}^{3+}(\text{MoO}_4)_3$  ( $\text{M} = \text{Fe}$ ,  $\text{Al}$ ,  $\text{Cr}$ ,  $\text{Ga}$ ,  $\text{Sc}$ ,  $\text{In}$ , and  $\text{Co}$ ), and  $\text{Li}_2\text{M}^{4+}(\text{MoO}_4)_3$  ( $\text{M} = \text{Ti}$ ,  $\text{Zr}$ , and  $\text{Hf}$ )<sup>21-30</sup> were discovered. For the cofired samples of  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$ ,  $\text{Li}_3\text{AlMo}_3\text{O}_{12}$ , and  $\text{Li}_3\text{InMo}_3\text{O}_{12}$  with both Ag

and Al powders, only X-ray peaks of the lyonsite phase and metal were observed, implying that these lyonsite materials did not react with either the silver or aluminum metal phase at the sintering temperatures. For the 630°C-sintered  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  sample, there was no lyonsite-type phase formed and it was found to be composed of both Scheelite  $\text{CaMoO}_4$  and  $\text{Li}_2\text{MoO}_4$  phases. As we reported previously,  $\text{Li}_2\text{MoO}_4$  does not react with either Ag or Al at 530°C.<sup>16</sup> In this work, the  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  sample, which is a mixture of  $\text{CaMoO}_4$  and  $\text{Li}_2\text{MoO}_4$ , also did not react with either Ag or Al powders at 630°C as shown in Fig. 1(d).  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$ ,  $\text{Li}_3\text{AlMo}_3\text{O}_{12}$ ,  $\text{Li}_3\text{InMo}_3\text{O}_{12}$  lyonsite compounds and  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  composition can cofire with Ag and Al in multilayers devices due to their chemical compatibility.

Figure 2 shows the SEM micrographs of  $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{2+} = \text{Zn}$  and  $\text{Ca}$ ) and  $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{3+} = \text{Al}$  and  $\text{In}$ ) ceramics sintered at the optimal temperatures that provide the maximum densities, the BEI micrographs of cofired ceramics, and the related EDS analysis. Homogeneous grain microstructures were revealed in all ceramic samples. The grains of  $\text{Li}_3\text{AlMo}_3\text{O}_{12}$  ceramic sintered at 550°C/2 h exhibit bar-shape and the length of bar-shaped grains lies between 3 and 7  $\mu\text{m}$ . The grains of  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  and  $\text{Li}_3\text{InMo}_3\text{O}_{12}$  ceramics sintered at 630°C/2 h have similar shape and their grain sizes scatter between 3–7 and 1–3  $\mu\text{m}$ , respectively. Generally speaking, all the three lyonsite-type ceramics have some similarity in grain morphology. It is seen from Fig. 2(d) that there are two different kinds of grain morphology in the  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  ceramic sintered at 630°C/2 h. One kind has a small grain size about 1.5  $\mu\text{m}$ , corresponding to  $\text{CaMoO}_4$  to grain according to an EDS analysis. The other kind has a grain size > 5  $\mu\text{m}$ , which corresponds to  $\text{Li}_2\text{MoO}_4$  grains according to the EDS analysis. The grain size of  $\text{CaMoO}_4$  ceramic sintered at 1100°C for 2 h lies between 2 and 5  $\mu\text{m}$  according to the SEM micrograph reported by Choi *et al.*<sup>31</sup> Pure  $\text{Li}_2\text{MoO}_4$  ceramic sintered at 540°C ranges between 5 and 15  $\mu\text{m}$  from our previous work.<sup>16</sup> The BEI photo of  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  cofired ceramic with 20 wt% Ag is shown in Fig. 2(g). The cofired ceramic was found to be composed of both  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  grains (with black color) and Ag (with white color) grains, which further confirms the chemical compatibility between  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  and silver. The BEI photo of  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  cofired ceramic with 20 wt% Ag is shown in Fig. 2(e).

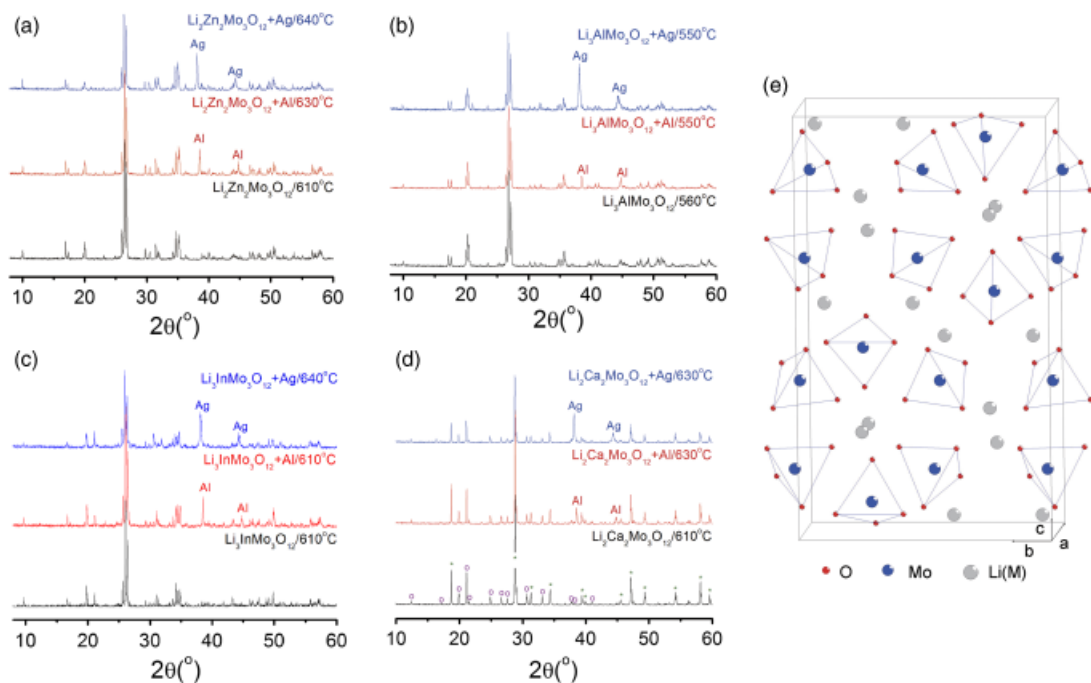
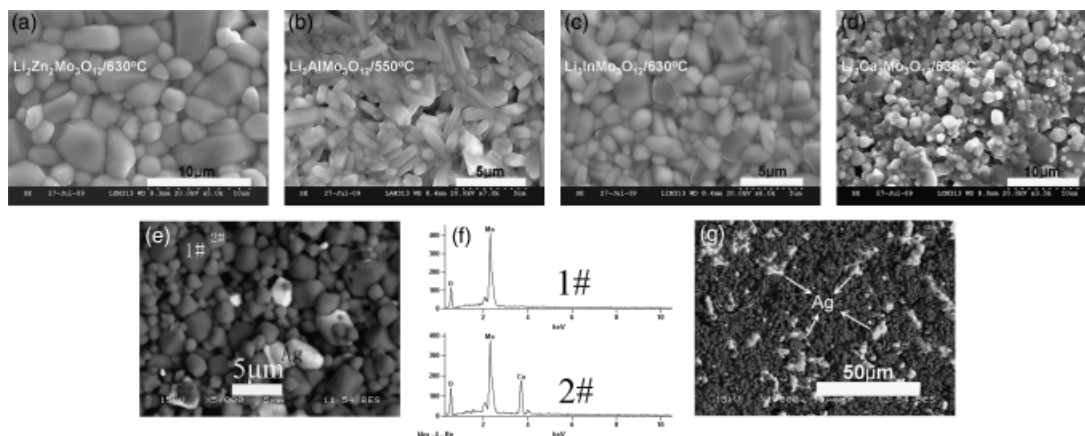


Fig. 1. XRD patterns of ceramic samples and their cofired samples with both Ag and Al powders for  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  (a),  $\text{Li}_3\text{AlMo}_3\text{O}_{12}$  (b),  $\text{Li}_3\text{InMo}_3\text{O}_{12}$  (c), and  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  (d) and crystal structure for lyonsite (e) (o— $\text{Li}_2\text{MoO}_4$  phase, \* $\text{CaMoO}_4$  phase).

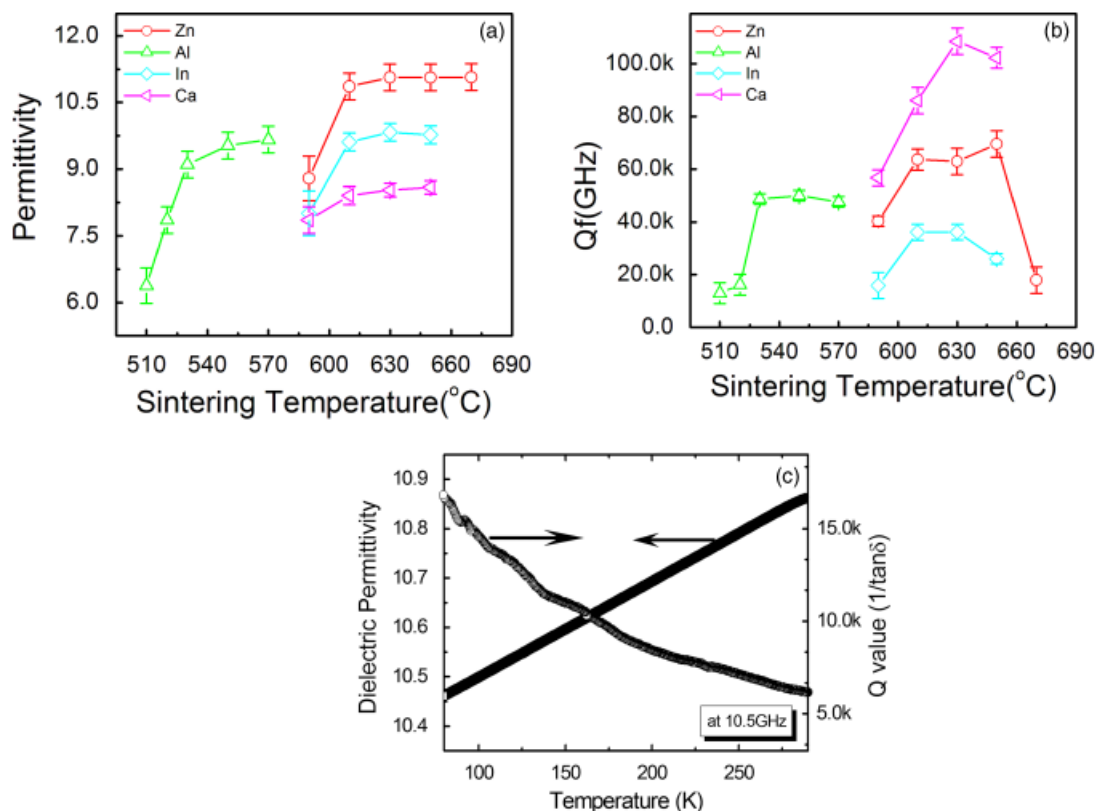


**Fig. 2.** SEM micrographs of  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  ceramic sintered at  $630^\circ\text{C}/2\text{ h}$  (a),  $\text{Li}_3\text{AlMo}_3\text{O}_{12}$  ceramic sintered at  $550^\circ\text{C}/2\text{ h}$  (b),  $\text{Li}_3\text{InMo}_3\text{O}_{12}$  ceramic sintered at  $630^\circ\text{C}/2\text{ h}$  (c),  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  ceramic sintered at  $630^\circ\text{C}/2\text{ h}$  (d), BEI photo of  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  cofired ceramic with 20 wt% Ag sintered at  $630^\circ\text{C}/2\text{ h}$  (e), EDS analysis of marked part in (e) (f), and BEI photo of  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  cofired ceramic with 20 wt% Ag sintered at  $630^\circ\text{C}/2\text{ h}$  (g).

There are three kinds of grains observed. One is the Ag grain and it takes on a white color. The other two kinds of grains take on the similar color with different grain sizes. The one with larger grain size has a color a little heavier than the one with smaller grain size, which means that the former one contains a lighter element than the latter one. The EDS analysis further confirms that the large grains belong to  $\text{Li}_2\text{MoO}_4$  phase (actually, lithium can not be detected by EDS) and the small grains belong to  $\text{CaMoO}_4$  phase, which corresponds well with the XRD analysis.

Microwave relative permittivity and  $Q \times f$  values of  $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{2+} = \text{Zn}$  and  $\text{Ca}$ ) and  $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{3+} = \text{Al}$  and  $\text{In}$ ) ceramics measured as a function of sintering temperature are shown in Fig. 3. Densification temperatures, phase compositions, and microwave dielectric properties of ce-

ramic are all summarized in Table I. All the ceramics studied here possess microwave relative permittivities  $\sim 10$  and high  $Q \times f$  values above 30 000 GHz. Such materials could be applied to substrates for high-speed devices due to the low permittivity near 10 for reducing the signal delay time, the high quality factors ( $Q \times f$ ) for frequency selectivity, and the chemical compatibility with Ag and Al. However, the large negative TCF is harmful to the temperature stability. The microwave dielectric permittivity and  $Q$  value of  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  ceramic in the temperature range  $-190^\circ$  to  $20^\circ\text{C}$  are shown in Fig. 3(c) to further understand the wide temperature range dependence of the microwave dielectric behaviors of lyonsite ceramics. It is seen that as the temperature increases from  $-190^\circ$  to  $20^\circ\text{C}$ , the microwave dielectric permittivity linearly increases from 10.46 to 10.85 and the  $Q$  value decreases from 17 000 to 6 500. The temperature



**Fig. 3.** Microwave relative permittivity (a) and  $Q \times f$  value (b) of  $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{2+} = \text{Zn}$  and  $\text{Ca}$ ) and  $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{3+} = \text{Al}$  and  $\text{In}$ ) ceramics as a function of sintering temperature, and microwave dielectric behaviors of  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  ceramic in a temperature range of  $190^\circ$  to  $+20^\circ\text{C}$ .

**Table I. Microwave Dielectric Properties of  $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{2+} = \text{Zn}$  and  $\text{Ca}$ ) and  $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$  ( $\text{M}^{3+} = \text{Al}$  and  $\text{In}$ ) Ultra-Low-Temperature Firing Ceramics**

Compositions	Phase	ST (°C)	$f$ (GHz)	$\epsilon_r$	$Q \times f$ (GHz)	TCF (ppm/°C)
$\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$	Pure	$630 \pm 10$	14.628	$11.1 \pm 0.3$	$70\,000 \pm 5000$	$-90 \pm 7$
$\text{Li}_3\text{AlMo}_3\text{O}_{12}$	Pure	$570 \pm 10$	14.130	$9.5 \pm 0.4$	$50\,000 \pm 2000$	$-73 \pm 8$
$\text{Li}_3\text{InMo}_3\text{O}_{12}$	Pure	$630 \pm 10$	15.019	$9.8 \pm 0.2$	$36\,000 \pm 3000$	$-73 \pm 4$
$\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$	$\text{Li}_2\text{MoO}_4 + \text{CaMoO}_4$	$630 \pm 20$	13.231	$8.5 \pm 0.2$	$108\,000 \pm 4000$	$-89 \pm 7$

ST, sintering temperature;  $f$ , resonant frequency; TCF, temperature coefficient of resonant frequency.

coefficient of microwave dielectric permittivity calculated from a similar equation to formula (1) is about +183 ppm/°C, which is similar two times of the TCF value and has an opposite sign. One method to modify the TCF is to form lyonsite solid solutions. Another good method is to fabricate two phase composite materials by adding another microwave dielectric with the opposite sign of TCF value.<sup>32,33</sup> We performed a preliminary work on the composite of  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$  ceramic with rutile  $\text{TiO}_2$  ceramic. It was found that the TCF could be shifted to  $-49$  ppm/°C by 20 mol% addition of rutile  $\text{TiO}_2$ . Both methods could be used in future work on the modification of TCF value of lyonsite-phase microwave dielectrics.

#### IV. Summary and Conclusions

In this work, the  $\text{Li}_2(\text{M}^{2+})_2\text{Mo}_3\text{O}_{12}$  and  $\text{Li}_3(\text{M}^{3+})\text{Mo}_3\text{O}_{12}$  ( $\text{M} = \text{Zn}, \text{Ca}, \text{Al},$  and  $\text{In}$ ) ceramics were studied with regard to the phase composition, microwave dielectric properties, and chemical compatibility with Ag and Al. The  $\text{Li}_2\text{Zn}_2\text{Mo}_3\text{O}_{12}$ ,  $\text{Li}_3\text{AlMo}_3\text{O}_{12}$ , and  $\text{Li}_3\text{InMo}_3\text{O}_{12}$  were found to belong to the lyonsite family. The  $\text{Li}_2\text{Ca}_2\text{Mo}_3\text{O}_{12}$  was composed of  $\text{Li}_2\text{MoO}_4$  and  $\text{CaMoO}_4$  phases. All the four ceramics can be well sintered below 650°C and demonstrated low relative permittivities near 10, high  $Q \times f$  values above 30 000 GHz, large negative temperature coefficients near  $-80$  ppm/°C, and chemical compatibility with Ag and Al at the optimal sintering temperatures. These are all good candidate materials for ultra-LTCC technology, filters, all dielectric metamaterials, and packaging applications in high frequencies.

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