

# Ultra-Low Firing High-k Scheelite Structures Based on $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$ Microwave Dielectric Ceramics

Di Zhou,<sup>†,‡,§</sup> Clive A. Randall,<sup>§</sup> Hong Wang,<sup>†,‡</sup> Li-Xia Pang,<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, China

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

In this work, dense ceramic samples across the solid solution of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  system are prepared using the solid-state reaction process. The monoclinic phase region could be obtained for  $0 \leq x < 0.098$  and the scheelite tetragonal solid solution region could be obtained for  $0.098 < x \leq 1$ . When  $x = 0.098$ , the boundary composition  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  could be readily sintered at  $650^\circ\text{C}$  and also have excellent microwave properties with a high relative permittivity of 81, and a  $Q \times f$  value of 8000 GHz and a low temperature coefficient of  $+9.7$  ppm/ $^\circ\text{C}$ . This ceramic is chemically compatible with both Al and Cu electrode materials at its sintering temperature. It can be an excellent candidate for ultra-low-temperature co-fired ceramic technology and is the highest permittivity microwave material found to date with sintering considerations as low as  $650^\circ\text{C}$ .

## I. Introduction

To achieve the miniaturization of microwave components for wireless communication, low-temperature co-fired ceramic (LTCC) technology becomes an important method because of its predominance in enabling the fabrication of three-dimensional ceramic modules with a low dielectric loss and co-fired metal electrodes. The dielectric material used in LTCC must have a variety of dielectric constant materials to permit future integration and embedded passive components. A high dielectric permittivity, with a high  $Q \times f$  value ( $f$  = resonant frequency,  $Q = 1/\text{dielectric loss at } f$ ), a near-zero temperature coefficient of resonant frequency (TCF  $\approx 0$  ppm/ $^\circ\text{C}$ ), a low sintering temperature with the metal electrodes such as Al would enable miniaturization in ultra-low-temperature co-fired ceramic (ULTCC), usually the sintering temperature of ULTCC is below  $800^\circ\text{C}$  without frit addition).<sup>1–5</sup> Besides, the basic physical property requirement, the cost, and the toxicity should also be considered in these applications.

Traditionally, high-performance microwave dielectrics have high sintering temperatures (above  $1000^\circ\text{C}$ ). Although the addition of sintering aids, such as glasses and fluxes, can lower the sintering temperatures of most systems efficiently, it is still very difficult to obtain a dense dielectric material with a sintering temperature below  $900^\circ\text{C}$ , a permittivity  $\geq 80$ , a

$Q \times f \geq 5000$  GHz, a TCF  $\approx 0$  ppm/ $^\circ\text{C}$ , and chemical compatibility with an electrode material. The microwave dielectric material such as  $\text{BaO-Ln}_2\text{O}_3\text{-TiO}_2$ , where Ln is a lanthanide, meets all the property requirements, but its sintering temperature cannot be lowered to below  $1100^\circ\text{C}$  without a serious deterioration of properties.<sup>6–8</sup> Likewise, the  $(\text{Ba,Sr,Ca})\text{TiO}_3$  system has a large permittivity between 150 and 500 and high  $Q \times f$  values, but it also has high sintering temperature and large positive TCF values.<sup>9–11</sup> The  $\text{Ag}(\text{Nb,Ta,Sb})\text{O}_3$  system has a large permittivity and a low sintering temperature, but it also has a small  $Q \times f$  value ( $< 600$  GHz at 3 GHz).<sup>12</sup> To our knowledge now, the best microwave dielectric candidate possessing a permittivity around 80 for conventional LTCC technology is the  $0.88\text{TiO}_2\text{-}0.12\text{Bi}_2\text{Ti}_4\text{O}_{11}$  ceramic with 0.112 wt% CuO addition explored by Axelsson and Alford<sup>4</sup> using uncalcined nanosized anatase/rutile powders. Its TCF is very sensitive to the composition because of the large opposite TCF values of  $\text{TiO}_2$  and  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$ . This success is due to the nonreaction between  $\text{TiO}_2$  and  $\text{Bi}_2\text{Ti}_4\text{O}_{11}$  and the efficient lowering of the sintering temperature from the CuO addition.

Recently, the search for new compounds with intrinsically lower sintering temperatures has attracted much attention and some of them could co-fire with an Al electrode material instead of Ag due to their ultra-low sintering temperatures ( $< 660^\circ\text{C}$ ).<sup>13,14</sup> In our previous work, we speculated that there may be many new ceramic dielectrics and may even be resistive materials for a ULTCC technology. This offers the dielectrics community some new challenges and incentives to explore new ultra-low-temperature firing dielectric ceramics.<sup>14,15</sup>

The  $\text{BiVO}_4$  ceramic has good microwave dielectric properties with  $\sim \epsilon_r = 68$ ,  $\sim Q \times f = 6500\text{--}8000$  GHz,  $\sim \text{TCF} = -243$  to  $-260$  ppm/ $^\circ\text{C}$ , and a sintering temperature below  $900^\circ\text{C}$ .<sup>5,16</sup> However, it was found by Valant and Suvorov<sup>5</sup> that the  $\text{BiVO}_4$  ceramic reacted with Ag seriously and this limited its application in LTCC technology. Recently, we have explored an ultra-low-temperature firing  $(\text{Li}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$  ceramic, which can be sintered well at around  $550^\circ\text{C}$  with a relative permittivity of  $\epsilon_r = 44.4$ , a  $Q \times f = 3200$  GHz, and a TCF =  $+245$  ppm/ $^\circ\text{C}$ .<sup>15</sup> The ultra-low sintering temperature and the common scheelite structure, which usually has wide cation solubility make the  $\text{BiVO}_4$ , and the  $(\text{Li}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$  are very attractive constituents for the goal of developing ULTCC dielectrics. In this investigation, the phase composition, sintering behavior, microwave dielectric properties, and chemical compatibility with common electrode materials of the  $(1-x)\text{BiVO}_4\text{-}x(\text{Li}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$  system are introduced.

## II. Experimental Procedure

Proportionate amounts of reagent-grade starting materials of  $\text{Bi}_2\text{O}_3$  (99.9%, MCP Inc., Lübeck, Germany),  $\text{Li}_2\text{CO}_3$ ,  $\text{MoO}_3$ ,

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<sup>†</sup>Author to whom correspondence should be addressed. e-mails: zhoudi1220@gmail.com; hwang@mail.xjtu.edu.cn

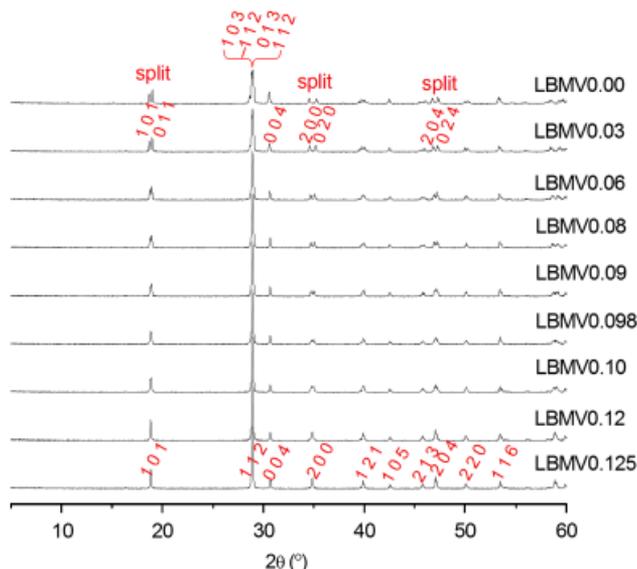


Fig. 1. XRD patterns of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics ( $0 \leq x \leq 0.125$ ).

and  $\text{V}_2\text{O}_5$  (>99%, Alfa Aesar, Ward Hill, MA) were prepared according to the stoichiometric formulation of  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  compositions. Powders were mixed and ball milled with stabilized zirconia media for 24 h. The powder mixture was then calcined at  $500^\circ\text{--}700^\circ\text{C}$  for 4 h according to the composition. The calcined powders were vibratory milled for 24 h to obtain fine powders. Then, the powders were pressed into cylinders (12 mm in diameter and 6 mm in height) in a steel die with 5 wt% PVA binder addition under a uniaxial pressure of 200 MPa. Samples were sintered in the temperature range from  $510^\circ$  to  $850^\circ\text{C}$  for 2 h. To investigate the chemical compatibility, ceramic powders were mixed with 20 wt% silver, aluminum, and copper powders and co-fired at different temperatures. XRD was performed at room temperature for structural analysis and lattice parameter determination using a Scintag PADV diffractometer with  $\text{CuK}\alpha$  radiation ( $\lambda = 1.54 \text{ \AA}$ ). Before examination, the sintered pellets were crushed in a mortar and pestle to powder. The diffraction pattern was obtained between  $5^\circ$  and  $60^\circ 2\theta$  at a step size of  $0.02^\circ$ . Lattice parameters were calculated using the JADE software (Materials Data Inc., Livermore, CA). To examine the grain morphology, as-fired surfaces were examined using scanning electron microscopy (SEM) (Hitachi S-3000H, Hitachi High-Technologies Co., Tokyo, Japan), and the chemical composition in localized areas of the samples was characterized by energy-dispersive spectroscopy (EDS). Dielectric behaviors at the microwave frequency

were measured with the  $\text{TE}_{011}$  parallel plate dielectric resonator method using a network analyzer (HP 8510 Network Analyzer, Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023, Delta Design, Poway, CA). The temperature coefficient of resonant frequency  $\tau_f$  (TCF) was calculated using 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  $\text{TE}_{011}$  resonant frequencies at  $85^\circ$  and  $25^\circ\text{C}$ , respectively.

### III. Results and Discussions

Figure 1 shows the XRD patterns of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  powdered ceramics ( $0 \leq x \leq 0.125$ ) sintered at their specific optimal sintering temperatures. As seen from Fig. 1, when  $x$  becomes  $\leq 0.10$ , the structure of  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics changes from a tetragonal scheelite structure to a monoclinic structure. This is reflected through the data with the splitting of several reflection peaks, such as (1 0 1) peak splitting into (1 0 1) and (0 1 1) peaks, (2 0 0) peak splitting into (2 0 0) and (0 2 0) peaks, etc. The unit cell parameter  $a$  of the tetragonal structure transforms into  $a$  and  $b$  of the monoclinic structure. Figure 2 shows the dependence of cell parameters on the  $x$  value in  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics ( $0 \leq x \leq 1$ ) and the crystal structure of both  $(\text{Li}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$  and  $\text{BiVO}_4$ . The  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics with  $x = 0.10, 0.098$ , and  $0.09$  were indexed both by tetragonal and monoclinic scheelite structures. It is observed that in both scheelite tetragonal and monoclinic solid solution regions, the cell parameters change almost linearly with the composition, mostly consistent with Vegard's law. The structure parameters of  $(\text{Li}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$  ( $a = b = 5.105 \text{ \AA}$ ,  $c = 11.577 \text{ \AA}$ , and  $\gamma = 90^\circ$ ) and  $\text{BiVO}_4$  ( $a = 5.1935 \text{ \AA}$ ,  $b = 5.0898 \text{ \AA}$ ,  $c = 11.6972 \text{ \AA}$ , and  $\gamma = 90.39^\circ$ ) ceramics are related through a compositional variation of the transition temperature between the paraelastic tetragonal phase and the low-temperature ferroelastic monoclinic phase.<sup>17–19</sup> The compositional solid solution approach minimizes the positive volume distortion of the unit cell of the  $\text{BiVO}_4$  and transforms into the tetragonal structure. It is interesting to recall the work of Mariathan *et al.*<sup>19</sup> who demonstrated that  $\text{BiVO}_4$  transforms under a high pressure to a tetragonal structure with lattice parameters  $a = b = 5.08 \text{ \AA}$ ,  $c = 11.49 \text{ \AA}$ , and  $\gamma = 90^\circ$ . In the scheelite tetragonal solid solution region, the unit cell volume increases as the  $x$  value increases and this should be attributed to the bigger ionic radius of  $\text{Mo}^{6+}$  ( $0.41 \text{ \AA}$ ) than  $\text{V}^{5+}$  ( $0.355 \text{ \AA}$ ). Thus, there is a phase boundary at room temperature near the composition  $x = 0.098$ , and at this boundary, the unit cell volume is at a minimum value.

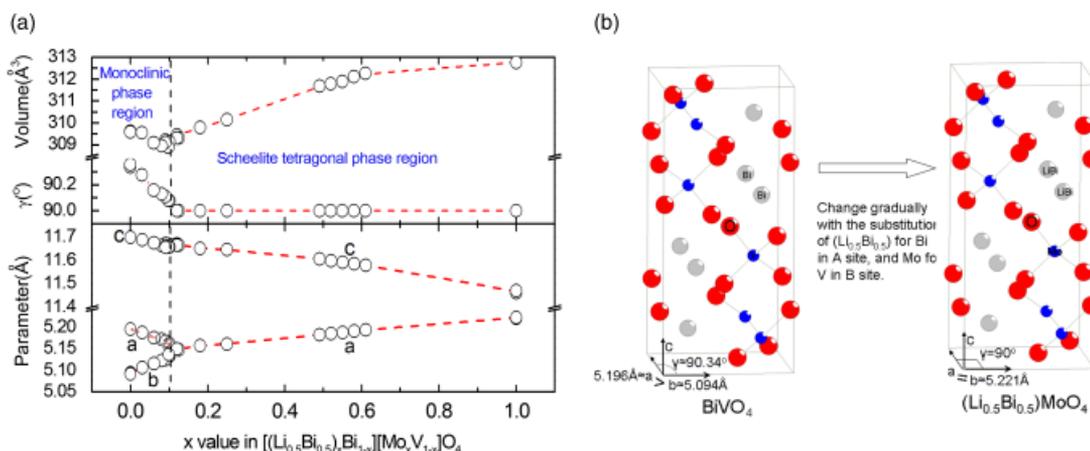
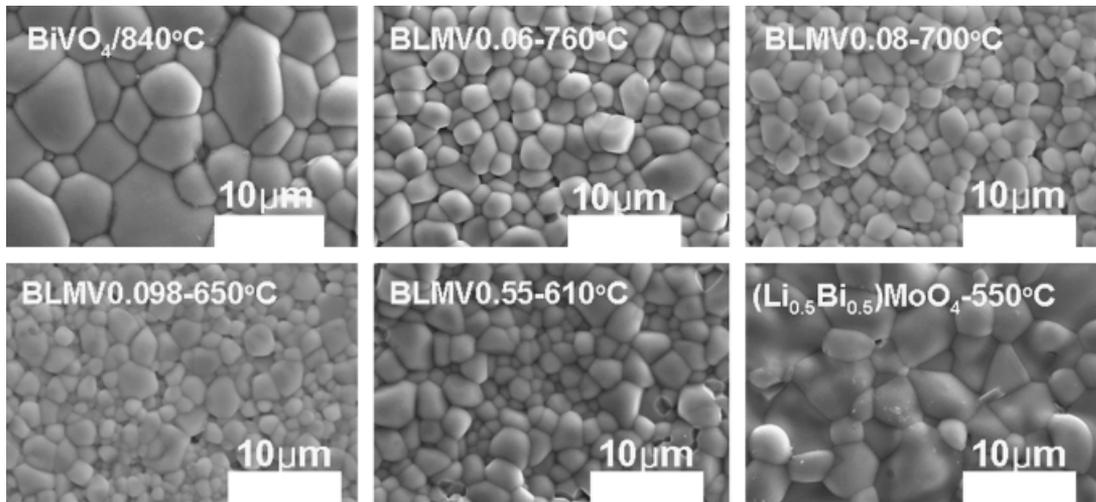


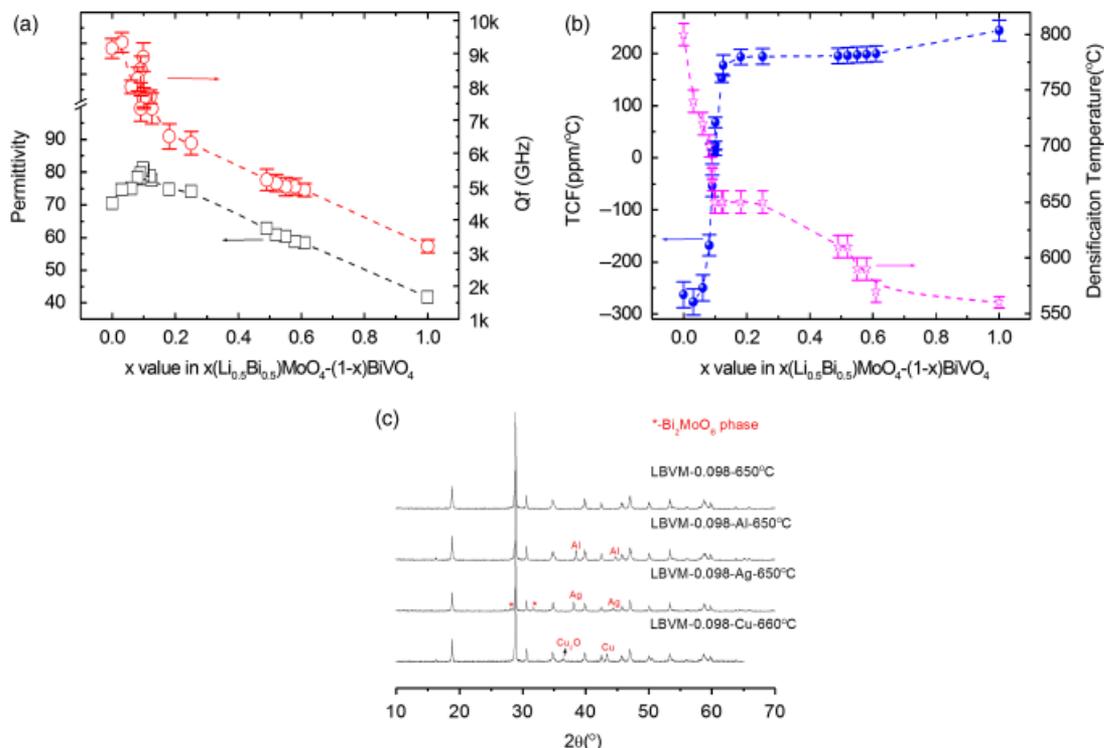
Fig. 2. Cell parameters (a) and crystal structure (b) of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  solid solution.



**Fig. 3.** Scanning electron microscopy photos of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics ( $x = 0, 0.06, 0.08, 0.098, 0.55,$  and  $1$ ) sintered at different temperatures but to optimal density.

Through a careful scanning and refinement of XRD analysis, with the techniques and processing used here, there was no evidence of mixed phases of tetragonal and monoclinic phase or any other phases in this region. SEM micrographs of as-fired surfaces demonstrate the microstructure of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics ( $x = 0, 0.06, 0.08, 0.098, 0.55,$  and  $1$ ) sintered at different temperatures as shown in Fig. 3. Dense and homogeneous microstructures could be revealed in all compositions. The grains of both  $\text{BiVO}_4$  ceramic sintered at  $840^\circ\text{C}$  for 2 h and  $(\text{Li}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$  ceramic sintered at  $550^\circ\text{C}$  for 2 h have the similar morphology and size lying between 3 and 8  $\mu\text{m}$ . For  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics with  $x = 0.06, 0.08, 0.098,$  and  $0.55$ , the grain sizes are a little smaller and vary between 1 and 3  $\mu\text{m}$ . In fact, the EDS analysis shows very close chemical composition for the grains with different sizes in ceramic with  $x = 0.098$ , and therefore no evidence of mixed phases was found from the EDS results.

Microwave dielectric permittivity,  $Q \times f$  value, TCF, and densification temperatures of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics ( $0 \leq x \leq 1$ ) as a function of  $x$  value are shown in Figs. 4(a) and (b). In the monoclinic solid-solution region, microwave permittivity of  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics increased linearly from 70 to 81 as the  $x$  value increased from 0.0 to 0.098 to a maximum, and then decreased to 44.4 at the  $(\text{Li}_{0.5}\text{Bi}_{0.5})\text{MoO}_4$  end member. The  $Q \times f$  values decreased approximately linearly from 9500 GHz at  $x = 0.0$  to 3200 GHz at  $x = 1.0$ . The increase of disordering caused by the substitution of  $(\text{Li}_{0.5}\text{Bi}_{0.5})$  may be responsible for the continuous decrease in  $Q \times f$  value in this system. As the  $x$  value decreased from 1.0 to 0.18, the temperature coefficient of resonant frequency decreased from  $+245$  to  $+194$  ppm/ $^\circ\text{C}$ . This indicates that scheelite structure ceramics in the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  system usually have large positive TCF values. When  $x$  decreased from 0.125 to 0.06, the TCF shifted sharply from  $+178$  to  $-250$  ppm/ $^\circ\text{C}$ .



**Fig. 4.** (a) Microwave dielectric permittivity and  $Q \times f$  value, (b) temperature coefficient of resonant frequency and densification temperature of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics ( $0 \leq x \leq 1$ ) as a function of  $x$  value, and (c) the XRD patterns of co-fired samples of  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  (LBVM0.098) with 20 wt% Al, Ag, and Cu powders sintered at  $650^\circ$  and  $660^\circ\text{C}$ .

and a near-zero TCF +9.7 ppm/°C was obtained in the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  ceramic. This indicates that the structure change near the boundary of scheelite and monoclinic phase have a strong influence on the TCF value. In the perovskite family, ferroelastic phase transition temperature also influences the TCF value strongly, as there is a maximum value in the permittivity at the phase transition point, which reverses the sign of the TCF value similar to the phenomenon observed in the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  system.<sup>20</sup> We speculate that the ferroelastic transition temperature undergoes a compositional variation from 250°C in the  $\text{BiVO}_4$ <sup>21</sup> to room temperature at  $x = 0.098$ ; beyond this, the composition suppresses the transition to below room temperature. This phenomenon will be studied in our future work. The densification temperature of  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics decreased exponentially from around 800°C to near 550°C as the  $x$  value increased from 0.0 to 1.0, using similar processing conditions. The detailed relation among the crystal structure, microwave dielectric properties, and sintering temperature needs to be studied further, but it is clear that this is a most interesting system with extraordinary sintering and dielectric properties combined. The best microwave dielectric properties were obtained in the composition of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  ceramic with a microwave permittivity of 81, a  $Q \times f$  value of 8000 GHz, a TCF of +9.7 ppm/°C, and a sintering temperature of 650°C. The densification temperature is far lower than any high-permittivity microwave dielectric such as a  $\text{TiO}_2\text{-Bi}_2\text{Ti}_4\text{O}_{11}$  ceramic with dielectric properties of ( $\epsilon_r = 80$ ,  $Q \times f = 9000$  GHz, and  $\tau_f = 0$ ).<sup>4</sup> The low sintering temperature also offers the opportunity to co-fire with the aluminum electrode.

Finally, a brief and preliminary investigation of the chemical compatibility of the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  ceramic with common metal electrode materials is made. This was assessed by mixing 20 wt% Ag, 20 wt% Al, and 20 wt% Cu powders with  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  ceramic samples, which were co-fired at 650°C for Ag and Al under an air atmosphere, at 660°C for Cu under an  $\text{N}_2$  atmosphere. The XRD patterns of co-fired ceramics are shown in Fig. 4(c). For co-fired ceramic with Ag powders, several peaks of the  $\text{Bi}_2\text{MoO}_6$  phase were observed. It can be seen that the Ag partially reacted with the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  ceramic and we conclude that Ag cannot be used as the internal electrode material in this system. For a co-fired ceramic with Al powders, only pure  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  and Al phases were observed, indicating a compatible electrode system for ULTCC. For a co-fired ceramic with Cu powders, a very weak peak of  $\text{Cu}_2\text{O}$  phase was revealed besides pure  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  and Cu phases; a better reducing atmosphere control would permit Cu to be a candidate too.

#### IV. Conclusions

Thus, in summary, in a solid solution investigation of  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_x\text{Bi}_{1-x}][\text{Mo}_x\text{V}_{1-x}]\text{O}_4$  ceramics, a monoclinic scheelite phase was found for  $0.0 \leq x < 0.098$  and a tetragonal scheelite solid solution was found for  $0.098 < x \leq 1.0$ . A continuous cell

parameter change existed near the phase boundary at  $x = 0.098$ . The cell volume was also a minimum at this boundary. Furthermore, the best microwave dielectric properties were obtained in the  $[(\text{Li}_{0.5}\text{Bi}_{0.5})_{0.098}\text{Bi}_{0.902}][\text{Mo}_{0.098}\text{V}_{0.902}]\text{O}_4$  ceramic compositions with a microwave permittivity of 81, a  $Q \times f$  value of 8000 GHz, a TCF of +9.7 ppm/°C, and a very low sintering temperature of 650°C. It can also be compatible with both Al and Cu electrode materials without a reaction at around its sintering temperature. This material is an excellent candidate for ultra-low-temperature co-fired ceramic technology.

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