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Microwave dielectric properties of $(\text{ABi})_{1/2}\text{MoO}_4$ ($A = \text{Li, Na, K, Rb, Ag}$) type ceramics with ultra-low firing temperatures

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ABSTRACT

A series of $(\text{ABi})_{1/2}\text{MoO}_4$ ($A = \text{Li, Na, K, Rb, Ag}$) compositions were studied in regard to the sintering behavior, phase composition, microwave dielectric properties and chemical compatibility with silver and/or aluminum for electrodes. All the $(\text{ABi})_{1/2}\text{MoO}_4$ ($A = \text{Li, Na, K, Rb, Ag}$) ceramics could be sintered below 700 °C with relative densities above 93%. Whereas the $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic can be sintered to a high density at around 630 °C/2 hrs with a relative permittivity ~ 37 , a Qf value of 4000 GHz and a temperature coefficient of resonant frequency (TCF) $\sim +117$ ppm/°C. Furthermore, from the XRD analysis of co-fired ceramics, the $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic reacts with silver but not with aluminum at its densification temperature. The $(\text{ABi})_{1/2}\text{MoO}_4$ ($A = \text{Li, Na, K, Rb, Ag}$) type ceramics can all be considered into the new field of ultra-low temperature co-firing dielectrics for multilayer applications.

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1. Introduction

With the development and continued implementation in high end consumer products such as the I-phone with low temperature co-fired ceramic technology (LTCC), there is a search for new microwave dielectric ceramics with low sintering temperature. In general the physical characteristics include sintering temperatures that are lower than the melting point of metal electrodes, a range of relative permittivity, low dielectric loss (high Qf value, $Q = 1/\text{dielectric loss}$, $f = \text{resonant frequency}$), near-zero temperature coefficient of resonant frequency (TCF ≈ 0 ppm/°C), chemical compatibility with low cost metal electrodes with high conductivities, and cost effective constitute raw materials [1–4].

Although unsustainable, high cost and toxic the TeO_2 -based materials illustrated that the LTCC technology could transit into a novel field of ultra-low temperature co-fired ceramic technology [5–7], so-called ULTCC. Recently, a series of Mo-based microwave dielectric ceramics with ultra-low firing temperatures have been explored [8–12]. Due to the relative low cost of MoO_3 , the Mo-based microwave dielectric ceramics might provide a replacement strategy for Te-based system. In the present work, the synthesis, sintering behavior, phase composition, chemical compatibility with

Al and Ag powders, along with the microwave dielectric properties of $(\text{ABi})_{1/2}\text{MoO}_4$ ($A = \text{Li, Na, K, Rb, Ag}$) type ceramics with Scheelite or Scheelite-related structures were studied.

2. Experimental

Proportionate amounts of reagent-grade starting materials were prepared by a mixed-oxide approach according to the following stoichiometric compositions, $(\text{ABi})_{1/2}\text{MoO}_4$ ($A = \text{Li, Na, K, Rb, Ag}$). 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 then vibratory milled with yttrium-stabilized zirconia media in the nylon bottles for 24 h to increase the reactivity and homogeneity and following this the particulates were granulated with 2–5 wt.% acryloid polymer binder (Acrylic Resin, Rohm and Haas Chemicals LLC, Philadelphia, PA, USA), and sieved through a mesh screen with 180 μm openings. This was done 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 (from room temperature to 500 °C at a rate of 1 °C/min⁻¹ and the incubation time is about 3 h) the samples were then sintered at various temperatures ranging from 510 °C to 700 °C for 2 h in ambient atmosphere. To investigate the chemical compatibility of these compounds with electrode metal powders, 20 wt.% Ag and 20 wt.% Al were mixed with the different compounds and held at the sintering temperatures for 4 h.

The phase determination was made from X-ray diffraction (XRD) patterns obtained on a Scintag PADV and X2 diffractometers (Scintag Inc., Cupertino, CA) with Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). Prior to examination sintered pellets were crushed in a mortar and pestle to powder. Microstructures of co-fired ceramics were observed on the fracture surfaces with a scanning electron microscopy (SEM) (Hitachi S-3000H, Hitachi High-Technologies Co., Tokyo, Japan).

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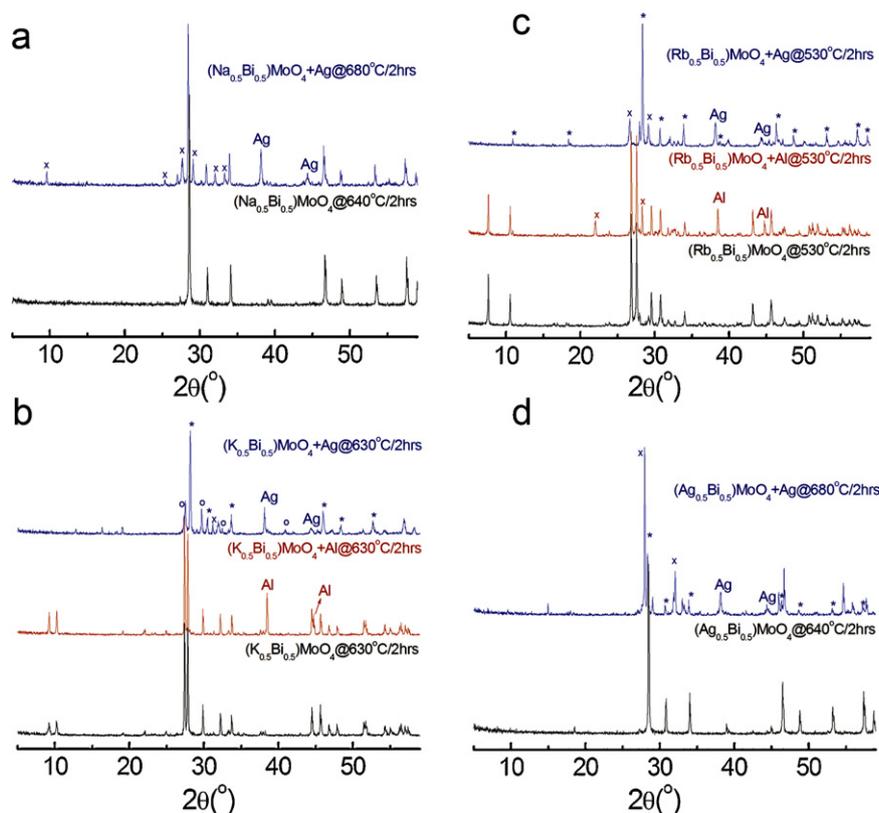


Fig. 1. X-ray diffraction patterns of $(\text{ABi})_{1/2}\text{MoO}_4$ ($A=\text{Na}$ (a), K (b), Rb (c), and Ag (d)) ceramics and co-fired ceramics with 20 wt.% Ag and 20 wt.% Al sintered at various temperatures for 2 h (*-Scheelite phase, o- $\text{K}_5\text{Bi}(\text{MoO}_4)_4$, x-unknown phase).

The dielectric properties were measured at microwave frequencies by the post-resonator method as suggested by Hakki and Coleman with a network analyzer (HP8510 Network Analyzer, Agilent, Hewlett-Packard, Palo Alto, CA). The temperature coefficient of resonant frequency (TCF) was determined using a zero thermal expansion cavity with programmable temperature chamber (Delta 9023, Delta Design, Poway, CA) in the temperature range of 25–85 °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 resonant frequencies at 85 °C and 25 °C, respectively. A closed-cycle helium cryostat was used to measure the microwave dielectric properties over the temperature range 10–300K with a heating rate of 0.5 K/min⁻¹.

3. Results and discussions

The X-ray diffraction patterns for $(\text{ABi})_{1/2}\text{MoO}_4$ ($A=\text{Na}, \text{K}, \text{Rb},$ and Ag) compounds and co-fired ceramics with 20 wt.% Ag and 20 wt.% Al sintered at various temperatures for 2 h are shown in Fig. 1. Similar to the $(\text{LiBi})_{1/2}\text{MoO}_4$ ceramic as reported in our previous work [10], the $(\text{NaBi})_{1/2}\text{MoO}_4$ and $(\text{AgBi})_{1/2}\text{MoO}_4$ ceramics crystallized in a CaMoO_4 type Scheelite structure, which corresponds well with the reported work [13–15]. The Scheelite structure has a space group $I4_1/a$ (No. 88) and much flexibility for ion substitution on both A and B sites as described in Leight and Linn's work [16]. As shown in Fig. 1(b), the Scheelite phase cannot be obtained in $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic by solid state reaction method and this result is similar to Klevtsov's report [14]. In fact, the $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic crystallized with a monoclinic structure. From Klevtsov and Vinokurov's high temperature XRD analysis [17], the low temperature monoclinic phase of $(\text{KBi})_{1/2}\text{MoO}_4$ continuously transforms to the high temperature tetragonal Scheelite structure over a broad temperature range and is completed at

660 °C. The $(\text{RbBi})_{1/2}\text{MoO}_4$ ceramics also crystallized in a monoclinic structure with a space group $P2_1/c$ as suggested by Klevtsov et al. [14]. From the XRD analysis for co-fired ceramics, it is seen that all the $(\text{ABi})_{1/2}\text{MoO}_4$ ($A=\text{Na}, \text{K}, \text{Rb},$ and Ag) compounds reacted with silver to form new secondary phases at their respective densification temperatures, which is similar to the case described in $(\text{LiBi})_{1/2}\text{MoO}_4$ [10]. The $(\text{RbBi})_{1/2}\text{MoO}_4$ ceramics also reacted with aluminum and two new diffraction peaks at 21.9° and 28.4° were observed in XRD results for the co-fired ceramic. Only the $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic seems not to react with aluminum at 630 °C and there is no XRD peaks observed for secondary phases. This is only a preliminary investigation for the chemical compatibility between the $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic and aluminum powders but in our previous experience it is an effective screen. To apply the $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic in LTCC technology using aluminum as inner electrode, much work needs to be done in the future to study the reaction mechanism and diffusion between ceramic and metal electrode.

SEM micrographs of $(\text{ABi})_{1/2}\text{MoO}_4$ ($A=\text{Li}, \text{Na}, \text{K}, \text{Rb},$ and Ag) ceramics sintered at their respective densification temperatures are shown in Fig. 2. There is a homogeneous microstructure with low levels of porosity revealed in the $(\text{ABi})_{1/2}\text{MoO}_4$ ($A=\text{Li}, \text{Na}, \text{K},$ and Rb) ceramics sintered at the optimal sintering temperatures. The $(\text{AgBi})_{1/2}\text{MoO}_4$ cannot be well densified until it starts to melt above a temperature of 720 °C. Grains of $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic sintered at 630 °C/2 h show regular morphologies and with sizes between 1–5 μm, which is much smaller than that of $(\text{LiBi})_{1/2}\text{MoO}_4$ ceramic sintered at 550 °C/2 h.

Microwave dielectric relative permittivity (a) and Qf value (b) of $(\text{ABi})_{1/2}\text{MoO}_4$ ($A=\text{Li}, \text{Na}, \text{K}, \text{Rb},$ and Ag) ceramics are plotted as a function of sintering temperature in Fig. 3. As the sintering temperature increases, microwave relative permittivity

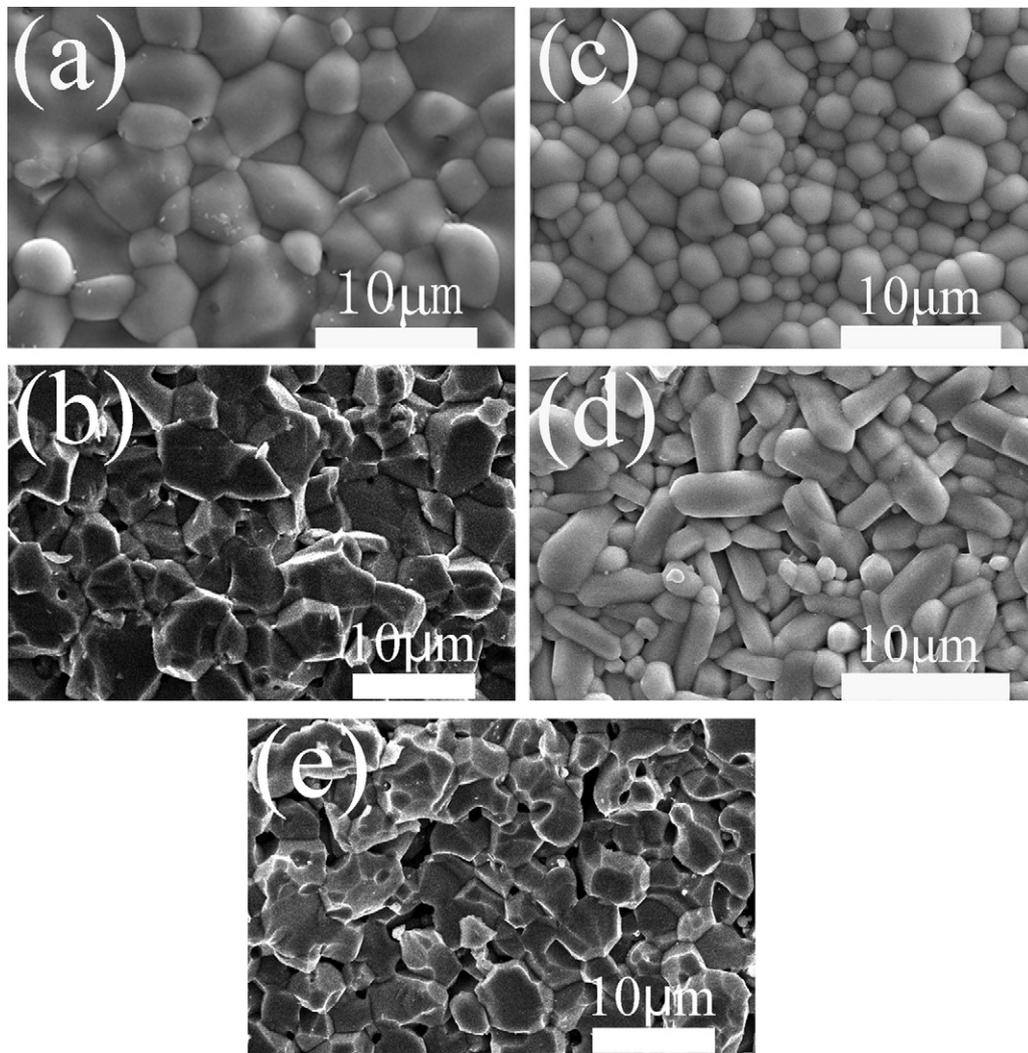


Fig. 2. SEM micrographs for $(\text{LiBi})_{1/2}\text{MoO}_4$ ceramic sintered at $550^\circ\text{C}/2\text{ h}$ (a) (from Ref. [11]), $(\text{NaBi})_{1/2}\text{MoO}_4$ ceramic sintered at $700^\circ\text{C}/2\text{ h}$ (fractured surface) (b), $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic sintered at $630^\circ\text{C}/2\text{ h}$ (c), $(\text{RbBi})_{1/2}\text{MoO}_4$ ceramic sintered at $550^\circ\text{C}/2\text{ h}$ (d), and $(\text{AgBi})_{1/2}\text{MoO}_4$ ceramic sintered at $700^\circ\text{C}/2\text{ h}$ (fractured surface) (e).

increases and then reaches a saturated value as there is an elimination of the pores. The microwave dielectric permittivity usually keeps stable after the pores being eliminated from ceramic and decreases slight with further increase of sintering temperature. In regard to the microwave dielectric loss there are in general two parts: an intrinsic loss and an extrinsic loss. Intrinsic losses are caused by absorptions of phonon oscillation within the lattice and extrinsic losses are associated with defects (impurities, substitution, grain boundaries, grain morphology and shape, secondary phase, pores etc.). Due to the complex influence of grain size, secondary grain growth and grain size distribution, the Q_f usually keeps high value in a temperature range observed here. The sintering temperature, phase composition, microwave dielec-

tric properties (relative permittivity, Q_f value and TCF value), and chemical compatibility for $(\text{ABi})_{1/2}\text{MoO}_4$ ($A = \text{Li, Na, K, Rb, and Ag}$) ceramics are all summarized in Table 1. Due to the high reactivity between Ag and Mo, all the Scheelite-related phases here react with silver seriously. Comparatively, Al has weak reactivity with the Mo-based phases. In particular the $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic seems not to react or have limited reactivity with Al at its sintering temperature. From our previous study [11], the modification of $(\text{LiBi})_{1/2}\text{MoO}_4$ ceramic with BiVO_4 substitution also demonstrated a chemical stability with Al and Cu. Although most of the $(\text{ABi})_{1/2}\text{MoO}_4$ ($A = \text{Li, Na, K, Rb, and Ag}$) ceramics might not be applied directly in LTCC technology, they will play an important role in the study of the ultra-low temperature co-fired ceramics

Table 1

The sintering temperature, phase composition, microwave dielectric properties (relative permittivity, Q_f value and TCF value), and chemical compatibility is qualitatively accessed from the second phase formation assessment in XRD.

Composition	S.T. ($^\circ\text{C}$)	Phase	Al	Ag	ϵ_r	f (GHz)	Q_f (GHz)	TCF (ppm/ $^\circ\text{C}$)
$(\text{LiBi})_{1/2}\text{MoO}_4$	560	Scheelite	Weak	Serious	41.7	5.5	3200	+240
$(\text{NaBi})_{1/2}\text{MoO}_4$	690	Scheelite	–	Serious	34.4	7.5	12,300	+43
$(\text{KBi})_{1/2}\text{MoO}_4$	630	Monoclinic	No	Serious	37.0	7.5	4000	+117
$(\text{RbBi})_{1/2}\text{MoO}_4$	550	Monoclinic	Weak	Serious	21.4	9.0	6200	–30
$(\text{AgBi})_{1/2}\text{MoO}_4$	690	Scheelite	–	Serious	30.4	8.7	12,600	+57

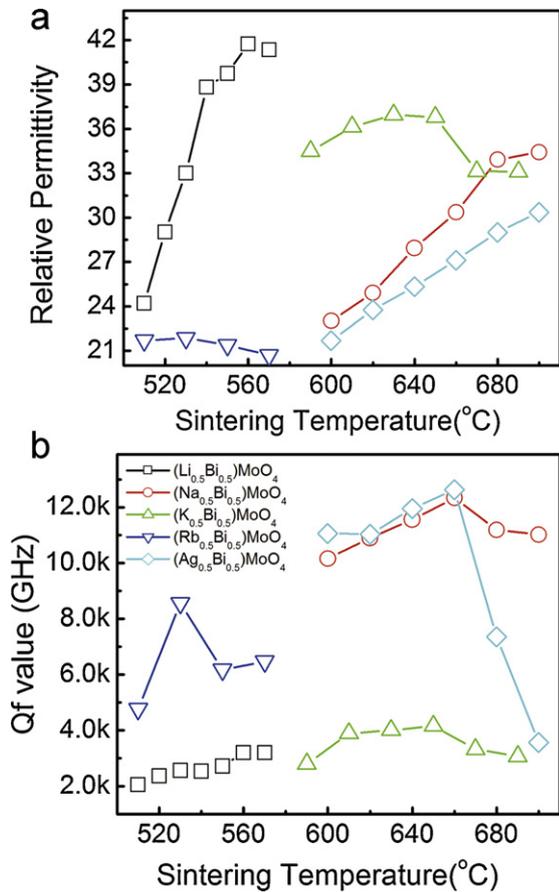


Fig. 3. Microwave dielectric relative permittivity (a) and Qf value of $(\text{ABi})_{1/2}\text{MoO}_4$ (A = Li, Na, K, Rb, and Ag) ceramics as a function of sintering temperature.

technology and offer possibilities to design some new ULCC systems.

The temperature coefficients of $(\text{ABi})_{1/2}\text{MoO}_4$ (A = Li, Na, K, Rb, and Ag) ceramics are listed in the Table 1. To further understand the origin of TCF, the microwave dielectric relative permittivity and Qf value of $(\text{ABi})_{1/2}\text{MoO}_4$ (A = Li, Na, K, Rb, and Ag) ceramics as a function of temperature (10–290 K) are shown in Fig. 4. The TCF value can be obtained as follows:

$$\tau_f(\text{TCF}) = -(\alpha_L + \frac{1}{2} \tau_\epsilon) \quad (2)$$

where α_L is the linear thermal expansion coefficient, and τ_ϵ is the temperature coefficient of relative permittivity. Compared with the τ_ϵ value, α_L is usually smaller and can be ignored for substrate dielectric applications with oxides. Hence, the TCF value in most systems is determined by the τ_ϵ value. As shown in Fig. 4(a), dielectric permittivities of $(\text{LiBi})_{1/2}\text{MoO}_4$, $(\text{KBi})_{1/2}\text{MoO}_4$, $(\text{NaBi})_{1/2}\text{MoO}_4$ and $(\text{AgBi})_{1/2}\text{MoO}_4$ ceramics decreased almost linearly in the temperature between 100 K and 290 K, which means that their TCF values were positive and the slopes are determine the magnitude of the TCF. For the $(\text{RbBi})_{1/2}\text{MoO}_4$ ceramic, the dielectric permittivity increased slightly with temperature and its TCF value is about $-30 \text{ ppm}/^\circ\text{C}$. As discussed in our previous work [18], the peak value of dielectric permittivity of $(\text{LiBi})_{1/2}\text{MoO}_4$ ceramic is due to a ferroelastic phase transition at around 43 K. There is no apparent phase transition observed from the relative permittivity–temperature curve for other compositions in the temperature range 10–290 K. However, an abnormal change in Qf value is observed around 25 K for $(\text{RbBi})_{1/2}\text{MoO}_4$ ceramic as shown in Fig. 4(b). This phenomenon

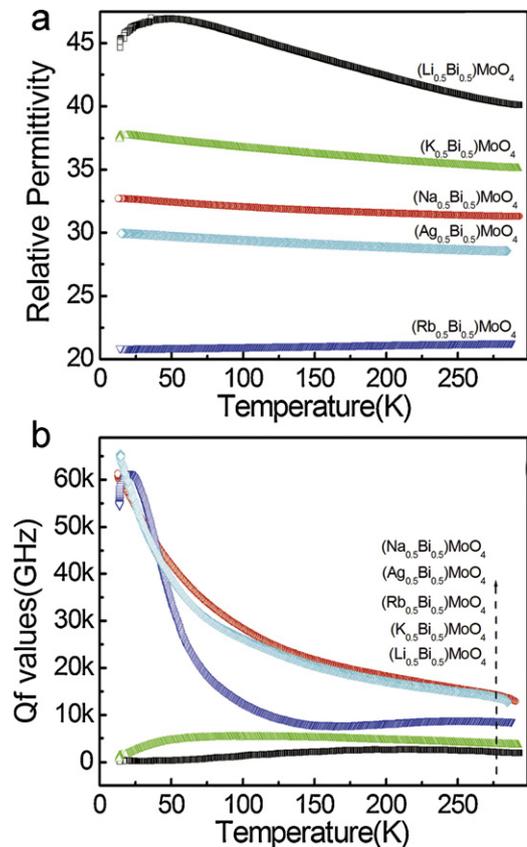


Fig. 4. Microwave dielectric relative permittivity (a) and Qf value of $(\text{ABi})_{1/2}\text{MoO}_4$ (A = Li, Na, K, Rb, and Ag) ceramics as a function of temperature (10–290 K).

needs further study, but is beyond the general compositional investigation of this work

4. Conclusions

The $(\text{LiBi})_{1/2}\text{MoO}_4$ and $(\text{NaBi})_{1/2}\text{MoO}_4$ ceramics crystallize in the pure Scheelite structure and can be well densified at 560°C and 690°C , respectively. Although the Scheelite phase $(\text{AgBi})_{1/2}\text{MoO}_4$ can also be formed at low temperatures below 700°C , it is not easy to obtain dense ceramic via the solid state reaction method. The $(\text{KBi})_{1/2}\text{MoO}_4$ and $(\text{AgBi})_{1/2}\text{MoO}_4$ ceramics crystallize in a Scheelite-related monoclinic structure and can be sintered to high densities at 630°C and 550°C , respectively. The 630°C sintered $(\text{KBi})_{1/2}\text{MoO}_4$ ceramic does not react with the Al powders from the XRD analysis and it possesses good microwave dielectric properties with a permittivity of 37, a Qf value of 4000 GHz and a temperature coefficient of $+117 \text{ ppm}/^\circ\text{C}$. This system offers possibilities for new ultra-low temperature firing ceramics for microwave application. The temperature coefficients must be modified to near zero due to the temperature stability requirement for ULCC technology.

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