Journal

Preparation and Microwave Dielectric Properties of Ultra-low Temperature Sintering Ceramics in K₂O–MoO₃ Binary System

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A series of microwave dielectric ceramics in the compositions of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ in K_2O–MoO_3 binary system with ultra low sintering temperatures were prepared using the solid-state reaction method. Their synthesis, phase composition, compatibility with metal electrodes, microstructures, and microwave dielectric properties were investigated. The $K_2Mo_2O_7$ ceramic sintered at 460°C with a triclinic structure has a relative permittivity of 7.5, a $Q \times f$ value of 22 000 GHz, and a τ_f value of -63 ppm/°C. The X-ray diffraction patterns indicate that $K_2Mo_2O_7$ does not react with Ag and Al electrodes at the co-fired temperatures. The $K_2Mo_3O_{10}$ ceramic can be sintered well at 520°C with a relative permittivity of 5.6, a $Q \times f$ value of 35 830 GHz, and a τ_f value of -92 ppm/°C. It has compatibility with Ag electrode. The $K_2Mo_4O_{13}$ ceramic sintered at 540°C possesses good microwave dielectric properties with a relative permittivity of 6.8, a $Q \times f$ value of 39 290 GHz and a τ_f value of -67 ppm/°C and it is compatible with Al electrode. For $K_2Mo_2O_7$ and $K_2Mo_4O_{13}$, it is found that the grain sizes and the number of grain boundaries play an important role in the dielectric loss. From this study, it can be seen that the three ceramics in K_2O–MoO_3 system have good microwave dielectric properties, ultra-low sintering temperatures, non-toxic, and low-cost characteristics. So they can be potentially applied to ultra-LTCC devices.

I. Introduction

WITH the development of modern communication technology, higher requirements to realize miniaturization, portability, versatility, high reliability, and low cost are proposed for dielectric materials. Low temperature co-fired ceramics are mainly used for highly integrated electronic packaging circuits with high performance, and have enormous potential for flexibility, wiring density, and reliability.[1] Microwave dielectric ceramics as the crucial base material are required with a low sintering temperature (<960°C), an appropriate permittivity, a high-quality factor, a near zero temperature coefficient of frequency and excellent chemical stability cofired with metal electrodes.[2–4] However, most of the traditional electronic ceramics have high sintering temperatures. Therefore, developing low sintering temperature ceramics has aroused researchers' interests.

Generally, there are four main ways to obtain low sintering temperature ceramics, i.e., doping sintering aids (low melting point oxides or low melting point glasses), preparing

samples by wet chemical method, using nanopowders method and using hot pressing sintering method.[1,5,6] However, considering the cost and complexity of technology, the last three ways are not suitable for industrial production. The first way is commonly used in low sintering temperature ceramics, due to its low cost and simple process. But the sintering aids will often deteriorate the dielectric and mechanical properties of ceramics. So, the search for new microwave dielectric systems of inherent low sintering temperatures, especially the materials with ultra-high permittivity (>100) or ultra-low permittivity (3–5), is one of the hot focuses of developing novel microwave dielectrics.

The microwave dielectric ceramic systems reported with ultra-low sintering temperatures mainly are Bi_2O_3–TeO_2 system, TiO_2–TeO_2 system, Bi_2O_3–TiO_2–TeO_2 system, BaO–TeO_2 system, BaO–TiO_2–TeO_2 system, CaO–TeO_2 system, ZnO–TeO_2 system, Bi_2O_3–MoO_3 system, Li_2O–Bi_2O_3–MoO_3 system, and Bi_2O_3–WO_3 system etc.[5–16] In the above systems, $Li_2Mo_4O_{13}$ with the lowest sintering temperature of 520°C has a permittivity of 8.8, a $Q \times f$ value of 7700 GHz and a τ_f value of -66 ppm/°C.[15] Due to the expensive price and high toxicity, Te-base materials are unsuited for mass production. From the previous works, a common characteristic in these ultra-low sintering temperature ceramic systems is that all of them contain at least one low melting point oxide. Therefore, the K_2O–MoO_3 system with low melting point compounds attracted our attention of exploring its potential microwave dielectric properties.

In the previous works, the phase diagram of K_2O–MoO_3 system has been studied by Caillet and Spitsyn *et al.*[17,18] There are four stable compounds in the system, namely K_2MoO_4, $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$, and two unstable phases $K_2Mo_6O_{19}$ and $K_2Mo_8O_{25}$. The compounds $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ in the system show very low reaction temperatures and low melting temperatures below 600°C. However, the preparation process of dielectric ceramics and their microwave dielectric properties in this system have not been studied and reported before.

In this work, the synthesis, phase composition, microstructure and microwave dielectric properties of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ ceramics have been investigated. The derived K_2O–MoO_3 based ceramics possess good microwave dielectric properties with the minimum sintering temperature of 460°C, which is the lowest one among those of microwave dielectrics to the best of our knowledge. The chemical compatibility of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ with Ag and Al electrodes has also been studied and presented.

II. Experimental Procedure

The powders of K_2O–MoO_3 system were prepared using solid-state reaction method. Reagent-grade materials of K_2CO_3 (>99%; SINOPHARM Chemical Reagent, Shanghai,

China) and MoO_3 (>99.5%; Yutong Chemical Reagents, Tianjin, China) were weighted according to the stoichiometric compositions of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$. The mixed powders were milled in absolute ethyl alcohol solution with zirconia balls (2 mm in diameter) as milling media using polyethylene jars and planetary mill (QM-1F; Nanjing Machine Factory, Nanjing, China) for 4 h at a running speed of 150 rpm, subsequently calcined in air at 400°C–450°C for 4 h respectively. After being crushed, the powders were remilled for 5 h with the same condition of the first milling. Then the dried powders granulated with 5 wt% polyvinyl alcohol (PVA) were uniaxially pressed into cylinders (12 mm in diameter and 5 mm in height) in a steel die under pressure of 300 MPa. PVA was burnt out at 390°C–400°C, respectively, for 5 h with heating rate of 1°C/min. Then the cylinders were sintered at 440°C–550°C in air for 2 h, depending on their composition. The chemical compatibility of the ceramics with Ag and Al electrodes was also studied. The ground samples were mixed with 20 wt% Ag and 20 wt% Al, and then were sintered at 440°C–540°C for 1 h.

The phase composition was studied using X-ray diffraction with CuKα radiation (SHIMADZU XRD-7000, Tokyo, Japan). Diffraction spectrums were measured according to the lattice parameters precise calculation requirements with the scanning angle range of 5°–70°. Phase identification, background subtraction, Kα2 subtraction, smoothing, and spectrum fitting were operated by using Jade 6.0 (Jade Software Corporation Limited, Christchurch, New Zealand). The lattice parameters were preliminary calculated by cell refinement with the relative error of 4%.

The microstructures of the natural and fractured surface of the samples were examined using scanning electron microscopy (SEM, JSM-6460; Jeol, Tokyo, Japan). The bulk density of the sintered specimens was determined by the Archimedes' method and the basic method (measurement of size and weight). The microwave dielectric properties of sintered ceramics were measured at microwave frequency using the $TE_{01\delta}$ shielded cavity method with a network analyzer (8720ES; Agilent, Palo Alto, CA) and a temperature chamber (Delta 9023; Delta Design, Poway, CA). The τ_f was calculated by the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \times 10^6 (\text{ppm}/°C) \qquad (1)$$

here 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 XRD patterns of samples sintered at different temperatures. The pure phase of $K_2Mo_2O_7$ was formed at 440°C–480°C and identified on the base of PDF card 36-0347 as in Fig. 1(a). Magarill and Klevtsova reported that the $K_2Mo_2O_7$ had a triclinic structure with unit cell dimensions of $a = 7.51$ Å, $b = 7.24$ Å, $c = 6.95$ Å, $\alpha = 92°$, $\beta = 112°$, $\gamma = 82.5°$, $Z = 2$.[19] In our experiment, the lattice parameters were determined as $a = 7.5$ Å, $b = 7.2$ Å, $c = 6.9$ Å, $\alpha = 94.0°$, $\beta = 111.0°$, $\gamma = 82.0°$, $Z = 2$, which were consistent with the results reported. For the samples of $K_2Mo_2O_7$ co-fired with 20 wt% Ag and 20 wt% Al, respectively, only the pure $K_2Mo_2O_7$, silver, and aluminum phases were identified, indicating that there was no chemical reaction between them. As it is known that molybdenum oxide is easy to react with Ag and Al, but the $K_2Mo_2O_7$ compound restrains their reaction at the ultralow temperature. In Fig. 1(b), the pure phase of $K_2Mo_3O_{10}$ was identified on the base of PDF card 37-1467 at the sintering temperature 520°C–540°C. It has been reported that $K_2Mo_3O_{10}$ crystallizes in a monoclinic system, space group $C2/c$, with lattice parameters $a = 13.092$ Å, $b = 7.914$ Å, $c = 8.845$ Å,
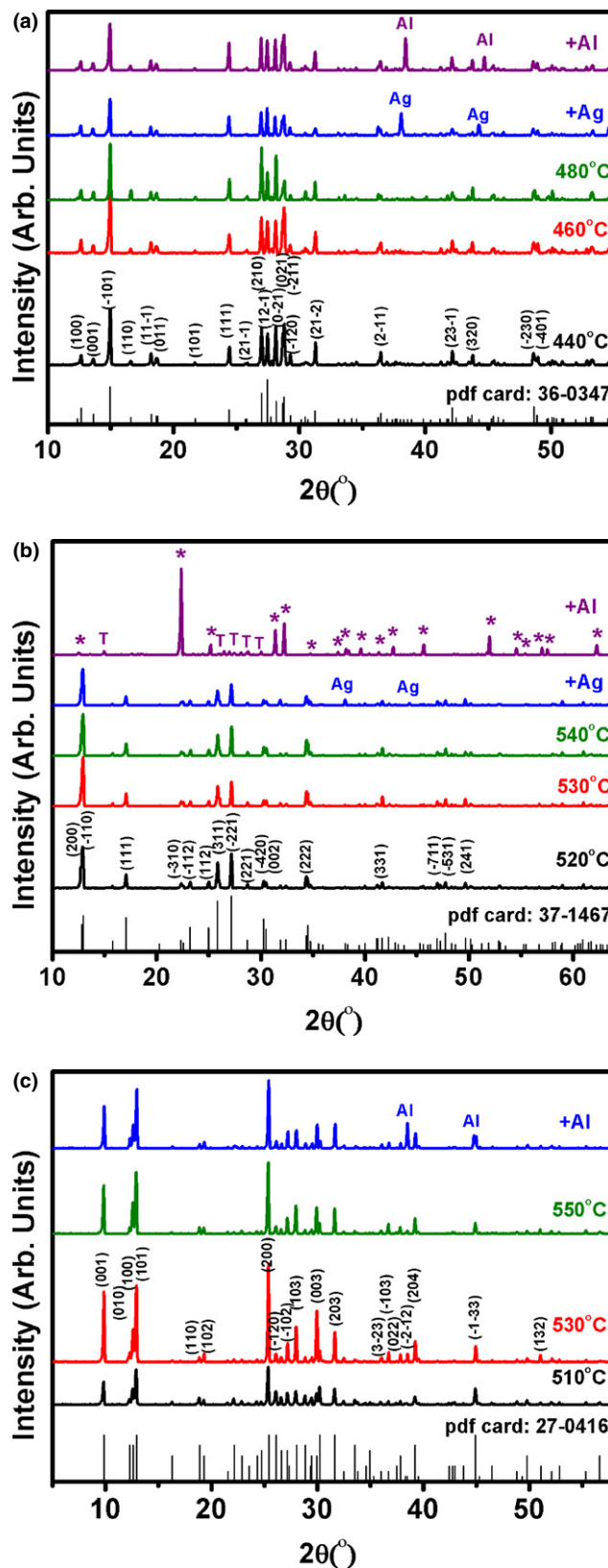
Fig. 1. XRD patterns of (a) $K_2Mo_2O_7$, (b) $K_2Mo_3O_{10}$, and (c) $K_2Mo_4O_{13}$ ceramics and their co-firing with 20 wt% Ag and 20 wt% Al sintered at various temperatures (*, $KAl(MoO_4)_2$; T, $K_2Mo_2O_7$).

$\beta = 98.83°$.[20] Here the results with $a = 13.9$ Å, $b = 7.9$ Å, $c = 8.9$ Å, $\beta = 99.0°$ approximate the reported results. The XRD pattern of $K_2Mo_3O_{10}$ cofired with 20 wt% Ag at 520°C shows only pure $K_2Mo_3O_{10}$ phase and Ag peaks. But $K_2Mo_3O_{10}$ reacted with Al at 520°C and formed new phase $KAl(MoO_4)_2$ marked with "*". At the same time, there are
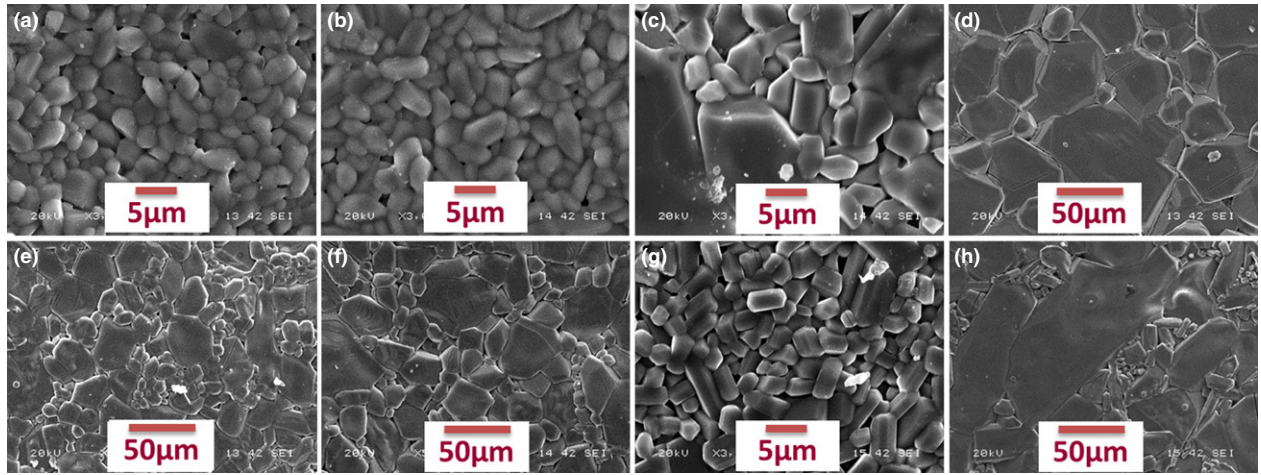
Fig. 2. SEM images of (a)–(d) K$_2$Mo$_2$O$_7$, (e)–(f) K$_2$Mo$_3$O$_{10}$, and (g)–(h) K$_2$Mo$_4$O$_{13}$ ceramics sintered at various temperatures. (a) ST: 450°C, (b) ST: 460°C, (c) ST: 470°C, (d) ST: 480°C, (e) ST: 520°C, (f) ST: 540°C, (g) ST: 540°C, (h) ST: 550°C.
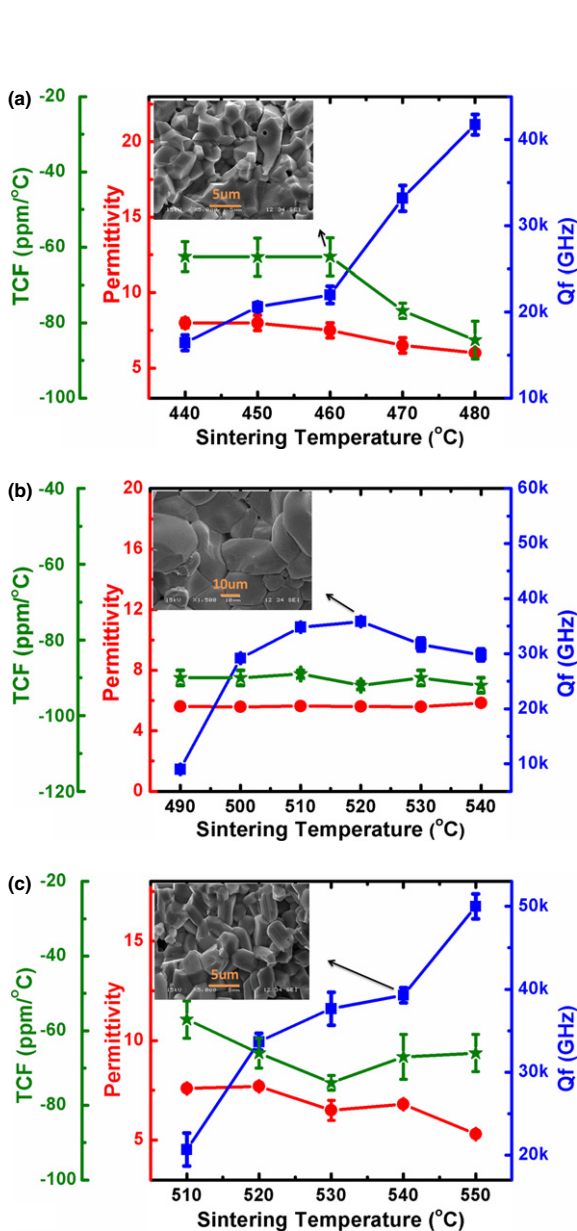

Fig. 3. Microwave dielectric properties(■: $Q \times f$ values, ●: permittivity, ★: TCF values) of (a) K$_2$Mo$_2$O$_7$, (b) K$_2$Mo$_3$O$_{10}$, and (c) K$_2$Mo$_4$O$_{13}$ ceramics as a function of sintering temperature and SEM images of fractured surface (inserts).
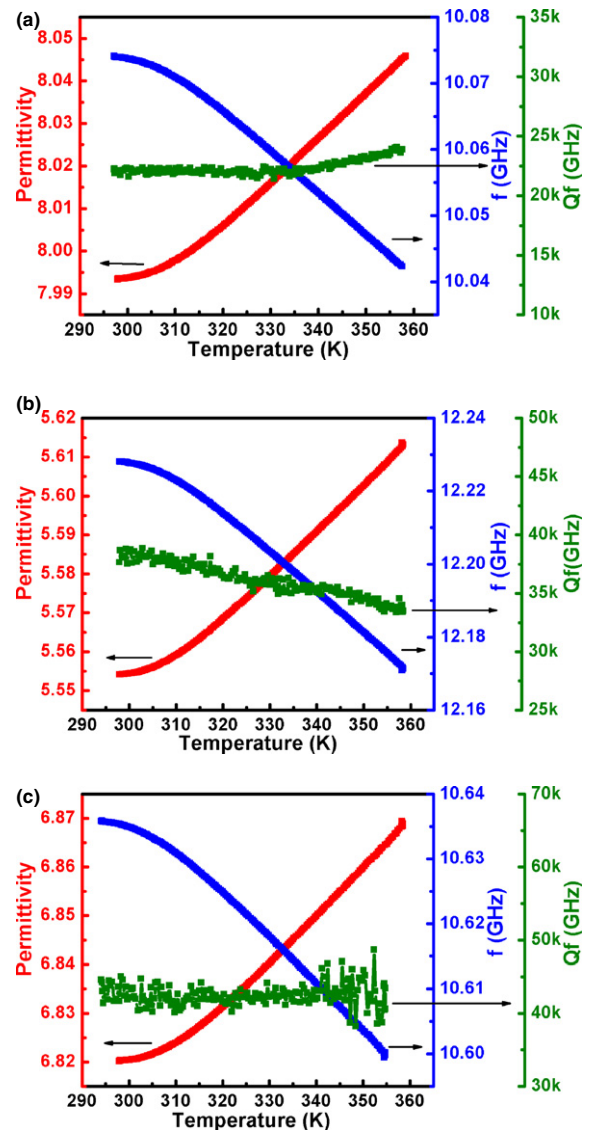

Fig. 4. Microwave dielectric permittivity, resonant frequency and $Q \times f$ values of (a) K$_2$Mo$_2$O$_7$, (b) K$_2$Mo$_3$O$_{10}$, and (c) K$_2$Mo$_4$O$_{13}$ ceramics as a function of temperatures.

some small peaks marked with "T" which belong to the phase $K_2Mo_2O_7$. The above results indicate that $K_2Mo_3O_{10}$ has compatibility only with Ag. In Fig. 1(c), pure $K_2Mo_4O_{13}$ phase was gained at sintering temperature 510°C–550°C showing a triclinic structure, space group p-1, with $a = 8.0$ Å, $b = 8.3$ Å, $c = 11.0$ Å, $\alpha = 119.4°$, $\beta = 62.6°$, $\gamma = 109.8°$, $Z = 2$, which are similar to the results of Gatehuose *et al.* with $a = 7.972$ Å, $b = 8.352$ Å, $c = 10.994$ Å, $\alpha = 119.41°$, $\beta = 62.70°$, $\gamma = 109.80°$, $Z = 2$.[21] The XRD patterns of $K_2Mo_4O_{13}$ cofired with Al at 540°C are shown in Fig. 1(c). For the sample of $K_2Mo_4O_{13}$ with Al, no impurity peak was detected except pure $K_2Mo_4O_{13}$ and Al phases. But the sample of $K_2Mo_4O_{13}$ with Ag melts at 540°C. These results illustrate that the pure phase of the three ceramics can be synthesized at ultra-low temperatures by solid-state reaction method and the compounds in $K_2O–MoO_3$ system have different compatibility with Ag and Al electrodes.

Figure 2 shows the SEM micrographs of the surfaces of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ ceramics sintered at each temperature for 2 h. For $K_2Mo_2O_7$ sintered at 450°C and 460°C, the ceramics exhibit homogeneous structures and a grain size of 2–5 μm. With the sintering temperature increasing, some of the grains grow rapidly with the grain sizes of 30–50 μm at 470°C and 480°C, indicating the grain abnormal growth. For $K_2Mo_3O_{10}$ sintered at 510°C–540°C, it shows slow grain growth and the grain morphology of samples at 520°C is more uniform than the others. For $K_2Mo_4O_{13}$, the full range of sizes is examined from 1 to 3 μm at sintering temperature 520°C–540°C. And the grains are in the shape of long rods. At 550°C, abnormal growth appears with some very large grains.

The microwave dielectric properties of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ ceramics sintered at different temperatures are shown in Fig. 3. In the $K_2O–MoO_3$ binary system, the $K_2Mo_2O_7$ can be sintered well at 460°C with a permittivity of 7.5, a $Q \times f$ value of 22 000 GHz, a τ_f value of −63 ppm/°C and a grain size of 2–5 μm. Although the $Q \times f$ values of $K_2Mo_2O_7$ ceramics increase a lot at 470°C–480°C, the density of them decreases from 3.22 to 3.08 g/cm³ at the same time, which is caused by the increasing closed pores in the very large grains with abnormal growth at 470°C–480°C. Dielectric loss is influenced by porosity, grain boundary, grain size, liquid phase etc., reported in many articles.[22,23] Here the grain sizes increase rapidly from 5 to 50 μm at 470°C–480°C as shown in Fig. 2, and the number of grain boundaries decreases, which diminishes the dielectric loss. Thus for $K_2Mo_2O_7$ ceramics sintered at 470°C–480°C, the grain size and the number of grain boundaries play important roles in the dielectric loss. The $K_2Mo_3O_{10}$ sintered

at 520°C possesses the best property with a permittivity of 5.6, a $Q \times f$ value of 35 830 GHz, and a τ_f value of −92 ppm/°C. And the $K_2Mo_4O_{13}$ can be sintered well at 540°C with a permittivity of 6.8, a $Q \times f$ value of 39 290 GHz, and a τ_f value of −67 ppm/°C. The similar reason as that of $K_2Mo_2O_7$ enlarges the $Q \times f$ value of $K_2Mo_4O_{13}$ at 550°C. The three ceramics in the $K_2O–MoO_3$ system have very narrow sintering temperature ranges, as shown in Figs. 2 and 3, so it is important to control the sintering temperature precisely.

Microwave dielectric properties of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ ceramics as a function of test temperature are shown in Fig. 4. For $K_2Mo_2O_7$ ceramics, the $Q \times f$ values increase slightly from 22 230 GHz at 298 K to 24 000 GHz at 358 K. The $Q \times f$ values of $K_2Mo_3O_{10}$ decrease slightly from 37 650 GHz at 298 K to 34 000 GHz at 358 K. And the $Q \times f$ values of $K_2Mo_4O_{13}$ fluctuate within a range of 40 000–44 000 GHz. The relationship between the temperature coefficients of frequency and the temperature coefficients of permittivity can be described as follows[24]:

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

here α_L is the linear thermal expansion coefficient and usually smaller than τ_ε. So τ_f is mainly determined by τ_ε in most systems. As shown in Fig. 4, the permittivity increases linearly and resonant frequency decreases linearly with the temperature rising from 298 to 358 K. The temperature coefficients of frequency of the $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ ceramics are −63 ppm/°C, −92 ppm/°C, and −67 ppm/°C, respectively. And the temperature coefficients of permittivity of the three ceramics are 146 ppm/°C, 210 ppm/°C, and 147 ppm/°C, respectively. τ_f is approximately equal to the negative half of the τ_ε, which complies with the above formula.

For microwave dielectric ceramics, the permittivity mainly results from ionic displacement polarization and electronic displacement polarization. It can be expressed as follows:

$$\varepsilon_r \approx \varepsilon_i + \varepsilon_e \quad (3)$$

ε_e and ε_i can be expressed as follows[25]:

$$\varepsilon_e \approx 1 + \frac{n_{0e}\alpha_e E_e}{\varepsilon_0 E} \quad (4)$$

$$\varepsilon_i \approx 1 + \frac{n_{0i}\alpha_i E_e}{\varepsilon_0 E} \quad (5)$$

here n_{0e} and n_{0i} are the number of polarized particles per unit volume. α_e and α_i are electronic polarizability and ionic

Table I. The Sintering Temperatures, Permittivity, $Q \times f$ Values and Temperature Coefficients of Resonance Frequency of the Low Temperature Co-Fired and Low Permittivity Microwave Dielectric Ceramics

No.	Composition	S.T. (°C)	ε_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	Reference
1	$K_2Mo_2O_7$	460	7.5	22 000 ± 800	−63 ± 10	This work
2	$K_2Mo_3O_{10}$	520	5.6	35 830 ± 120	−92 ± 2	This work
3	$K_2Mo_4O_{13}$	540	6.8	39 290 ± 1000	−67 ± 7	This work
4	$Li_2Mo_4O_{13}$	520	8.8	7700	−66	[15]
5	Li_2MoO_4	540	5.5	46 000	−160	[15]
6	$Li_3AlB_2O_6$	650	4.2	12 460	−290	[26]
7	$45\%Al_2O_3 + 55\%SiO_2–B_2O_3–Al_2O_3$	875	6.3	11 500	−33	[27]
8	$Zn_2P_2O_7$	875	7.5	50 000	−204	[28]
9	$95MgTiO_3–5CaTiO_3 + 55ZnO–25B_2O_3–20SiO_2$	880	8.67	3380	8.5	[29]
10	$Ca_{0.9}Mg_{0.1}SiO_3 + 9\%Li_2CO_3–Bi_2O_3$	890	6.92	27 566	−43.6	[30]
11	$CaCuP_2O_7$	900	7.33	71 624	−76	[31]
12	$(MgCo_2)(VO_4)_2$	900	9.5	78 906	−94.5	[32]
13	$BaWO_4$	900	8.27	30 229	−70	[33]
14	$MgMoO_4$	900	7.07	79 100	−46	[34]
15	$MnMoO_4$	900	8.55	54 100	−74	[34]
16	$BaMoO_4$	900	9.3	37 200	−79	[34]

S.T., sintering temperature.

polarizability. E_e is local electric field acted on particles, and E is macroscopic average electric field. With the temperature increasing, n_{0e} and n_{0i} decrease and α_i increases. α_e is independent of temperature. So the ε_e decreases with temperature rising. Because the ε_r of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ ceramics increase linearly, the ε_i of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ ceramics increase with temperature rising. That indicates α_i has a greater influence on ε_i than n_{0i} in the three ceramics. And α_i is proportional to the cubic of the sum of the radii of the positive and negative ions. This further indicates that the τ_ε of $K_2Mo_2O_7$, $K_2Mo_3O_{10}$, and $K_2Mo_4O_{13}$ ceramics is related with the ionic radius. So the τ_f of the three ceramics can be adjusted by ions doping to change the ionic radius, which is also under ongoing investigation.

Table I summarizes the sintering temperatures, permittivity, $Q \times f$ values and temperature coefficients of resonance frequency of the low temperature co-fired and low permittivity microwave dielectric ceramics in this work and other related works. At present, the study on microwave dielectric ceramics with low sintering temperature and low permittivity focuses on Al_2O_3 system, silicate systems, $MTiO_3$ systems, AWO_4, $M_3(VO_4)_2$, AMP_2O_7, and $MMoO_4$ systems.[15,26–34] What's more, these materials are widely applied to many microwave components, such as dielectric resonator, oscillator, antenna, balun, multilayer ceramic capacitor, and dielectric filter. Compared with other compositions in Table I, the three compositions in the $K_2O–MoO_3$ system possess ultra-low sintering temperatures without any sintering aids. To the best of our knowledge, the sintering temperature of $K_2Mo_2O_7$ is the lowest in the current reported microwave dielectric ceramics. The three compositions in $K_2O–MoO_3$ system have not only good microwave dielectric properties but also ultra-low sintering temperature which will greatly reduce energy consumption and improve productivity. All the results indicate that they are promising candidates for ultra-low temperature co-fired ceramic technology, especially for LTCC microwave component application.

IV. Conclusion

A series of ceramics with ultra-low sintering temperature below 550°C in $K_2O–MoO_3$ system were obtained using solid-state reaction method. Among them, $K_2Mo_2O_7$ can be sintered well at 460°C with a ε_r of 7.5, a $Q \times f$ of 21 995 GHz, a τ_f of −63 ppm/°C and compatibility with Ag and Al electrodes. $K_2Mo_3O_{10}$ sintered at 520°C exhibits a ε_r of 5.6, a $Q \times f$ of 35 830 GHz, a τ_f of −92 ppm/°C and does not react with Ag. $K_2Mo_4O_{13}$ sintered at 540°C has a ε_r of 6.8, a $Q \times f$ of 39 290 GHz, a τ_f of −67 ppm/°C and chemical compatibility with Al electrode. During the grains growth of the three ceramics, the porosity and the number of grain boundaries have a big influence on microwave dielectric loss. The analysis of the dielectric temperature spectra explains that the τ_f of the three compositions in $K_2O–MoO_3$ system can be adjusted by ions doping to change the ionic radius. The good microwave dielectric properties, ultra-low sintering temperatures, non-toxic and low cost characteristics make the three ceramics promising candidates for LTCC.

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