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Journal

Microwave Dielectric Ceramics $Li_2MO_4-TiO_2$ (M = Mo, W) with Low Sintering Temperatures

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In this work, novel series of (1 – x)Li_2MO_4–$x$$TiO_2$ (M = Mo, W; x = 0.3, 0.4, 0.45, 0.5, 0.6) ceramics were developed for microwave dielectric application. They were prepared via the mixed-oxide process and the phase composition, microstructures, sintering behaviors, and microwave dielectric properties were investigated. The X-ray diffraction (XRD) pattern and scanning electron microscope analysis indicated that the Li_2MO_4 (M = Mo, W) did not react with rutile TiO_2 and a stable two-phase composite system Li_2MO_4–TiO_2 (M = Mo, W) was formed. The XRD pattern of cofired ceramics revealed that some parts of Li_2MoO_4 phase and very small part of Li_2WO_4 phase react with Ag to form Ag_2MoO_4 phase and Ag_2WO_4 phase, respectively. At x = 0.45–0.5, temperature stable microwave dielectric materials with low sintering temperature (700°C–730°C) were obtained: ε_r = 10.6–11.0, Qf = 30 060–32 800 GHz, and temperature coefficient of resonant frequency ~0 ppm/°C.

I. Introduction

Over the past decades, microwave dielectric ceramics have been paid extensive attention due to the rapid development of wireless communication technology. To fabricate miniaturized and integrated microwave devices, low-temperature cofired ceramic technology emerged and has been widely investigated. Besides possessing a low sintering temperature (<960°C), the microwave dielectric material for substrate application should have a low dielectric constant to avoid the signal delay, a high-quality factor ($Q \times f$) value (a low dielectric loss) to ensure the frequency selectivity and reduce the insertion loss, and a near-zero temperature coefficient of resonant frequency (TCF/$\tau_f \approx 0$ ppm/°C) to assure the temperature stability.[1–3]

As one of glass-free low firing ceramics, TeO_2-rich compounds have been studied for more than 10 yr.[4–7] Recently, for the purpose of low cost and low toxicity, a number of new oxide systems have been developed, such as MoO_3/WO_3-rich compounds, Bi_2O_3-rich compounds, V_2O_5-rich compounds, B_2O_3-rich compounds, and P_2O_5-rich compounds.[8–17] Among them, many MoO_3/WO_3-rich ceramics exhibit good microwave dielectric properties. Especially, Li_2MoO_4 and Li_2WO_4 have ultralow sintering temperature and high-quality factors (Li_2MoO_4: ST = 540°C, $Q \times f$ = 46 000 GHz; Li_2WO_4: ST = 650°C, $Q \times f$ = 62 000 GHz).[10,11] However, the large negative TCF values (Li_2MoO_4: TCF = −160 ppm/°C; Li_2WO_4: TCF = −146 ppm/°C) have limited their applications in the microwave devices. One of the easy and effective methods to achieve temperature stable microwave dielectric materials is combining two component materials with opposite TCF values. Our recent research showed that rutile TiO_2 is a good candidate to compensate the negative TCF values of MoO_3-rich ceramics.[18–20] It has a large permittivity (~105), a high Qf value (~46 000 GHz), and a large positive TCF value (~+465 ppm/°C).[21,22] Therefore, it is expected that a temperature stable material system with high $Q \times f$ values may be obtained by mixing Li_2MO_4 (M = Mo, W) with TiO_2. In this work, the synthesis, phase compositions, microstructures, microwave dielectric properties, and the chemical compatibility with silver of (1 − x)Li_2MO_4–$x$$TiO_2$ (M = Mo, W) composite ceramics were studied.

II. Experimental Procedure

The ceramics based on the (1 − x)Li_2MO_4–$x$$TiO_2$ (M = Mo, W) system were synthesized by the conventional solid-state reaction. Reagent-grade powders Li_2CO_3 (>98%, Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), MoO_3, WO_3 (>99.5%, Fuchen Chemical Reagents, Tianjin, China), and rutile TiO_2 (>99.9%, Linghua Co. Ltd., Zhaoqing, China) were used as starting materials. According to the composition of (1 − x)Li_2MO_4–$x$$TiO_2$ (M = Mo, W, 0.3 mol ≤ x ≤ 0.6 mol; LMT and LWT were used for abbreviations), powders were milled with ZrO_2 milling media in ethanol for 4 h using a planetary ball mill. Then, the slurry was dried and calcined in air at 500°C–550°C for 4 h. After remilling for 4 h using zirconia balls and ethanol, the powders were mixed with 5 wt% Polyvinyl Alcohol binder and then pressed into cylindrical pellets (12 mm in diameter and 5 mm–6 mm in height) under uniaxial pressing. These specimens were sintered at 650°C–750°C for 2 h with a heating rate of 3°C/min in air. Finally, to study the chemical compatibility with silver, the Li_2MO_4–TiO_2 (M = Mo, W) composites were mixed with 20 wt% Ag and sintered at 700°C–730°C for 2 h.

The phase compositions of sintered samples were investigated using X-ray diffraction (XRD) with Cu$K\alpha$ radiation (Rigaku D/MAX-2400 X-ray diffractometer, Tokyo, Japan) in the 10°–70° 2θ range (at a step size of 0.02°). The microstructures of sintered ceramics on the fractures were observed with a scanning electron microscope (SEM, FEI, Quanta 250 F; FEI, Hillsboro, OR), and the chemical constitution was examined by energy-dispersive spectrometer. The permittivity and $Q \times f$ value at microwave frequencies were measured according to the $TE_{01\delta}$ shielded cavity method using a network analyzer (8720ES, Agilent, Palo Alto, CA). The TCF value was measured with a network analyzer and a temperature chamber (Delta 9023, Delta Design, Poway, CA) in the temperature range 25°C–85°C, and was calculated by the following equation:

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$$TCF = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \times 10^6 (\text{ppm}/^\circ\text{C}) \quad (1)$$

where f_{25} and f_{85} are the resonant frequencies at 25°C and 85°C, respectively.

III. Results and Discussions

Figure 1 presents the XRD patterns of sintered Li_2MO_4–TiO_2 (M = Mo, W) ceramics with various amounts of TiO_2. It is known that Li_2MO_4 (M = Mo, W) has a rhombohedral structure with space-group symmetry *R*-3 (No. 148) and rutile TiO_2 has a tetragonal structure with space-group symmetry $P4_2/mnm$ (No. 136).[10,11,20] For Li_2XO_4 (X = Mo, W), each B-site ion is surrounded by four oxygen ions. Based on Shannon's report, the ionic radius of W^{6+} (0.42 Å) is a little larger than that of Mo^{6+} (0.41) Å.[23] As a consequence, the diffraction lines slightly shift to lower angles when W^{6+} cation (Li_2WO_4) replaces Mo^{6+} cation (Li_2MoO_4). From the XRD results, it is seen that only Li_2MO_4 (M = Mo, W) phase and rutile TiO_2 phase can be observed. When x value increases from 0.3 to 0.6, no other impurity phase can be detected and the diffraction intensities of TiO_2 increase gradually. Therefore, the rutile TiO_2 can coexist with Li_2MO_4 (M = Mo, W) and a stable two-phase system Li_2MO_4–TiO_2 can be formed.

Figure 2 shows the backscattered electron images of the fractures of $0.55Li_2MoO_4$–$0.45TiO_2$ and $0.55Li_2WO_4$–$0.45TiO_2$ composite ceramics sintered at 700°C/2 h and 730°C/2 h, respectively. In accordance with the XRD patterns, two kinds of grains with different shapes coexist with each other. Due to the different atomic weight of Mo/W (95.94/183.84) and Ti (47.9), the light-color grains marked as A are rich in Mo/W (Li_2MoO_4/Li_2WO_4 phase), and the dark-color ones marked as B are rich in Ti (TiO_2 phase). Almost all the large grains belong to Li_2BO_4 (B = Mo, W) phase and most of the small grains belong to TiO_2 phase. This phenomenon may result from that the sintering temperature of pure TiO_2 ceramic (about 1400°C)[21] is much higher than that of pure Li_2MoO_4 (540°C) and Li_2WO_4 (650°C) ceramic.[10,11] It is also seen that the grain boundary is not clear, especially for $0.55Li_2MoO_4$–$0.45TiO_2$ sample, which reveals that the sintering temperature of $0.55Li_2MoO_4$–$0.45TiO_2$/$0.55Li_2WO_4$–$0.45TiO_2$ specimen is close to the melting point of Li_2MoO_4/Li_2WO_4 (705°C/742°C) crystals.

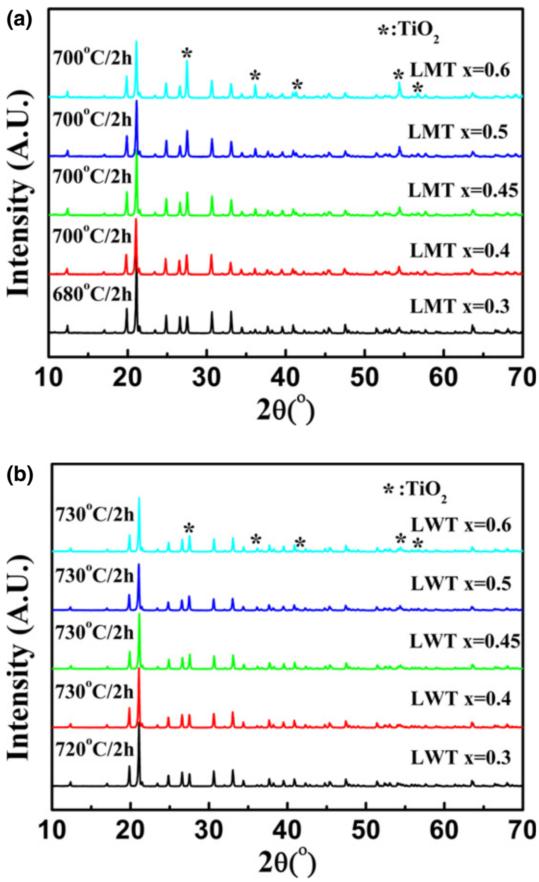

Fig. 1. X-ray diffraction patterns of sintered $(1-x)LiMoO_4$–$xTiO_2$ (a) and $(1-x)LiWO_4$–$xTiO_2$ (b) ceramics [LMT: $(1-x)LiMoO_4$–$xTiO_2$, LWT: $(1-x)LiWO_4$–$xTiO_2$].

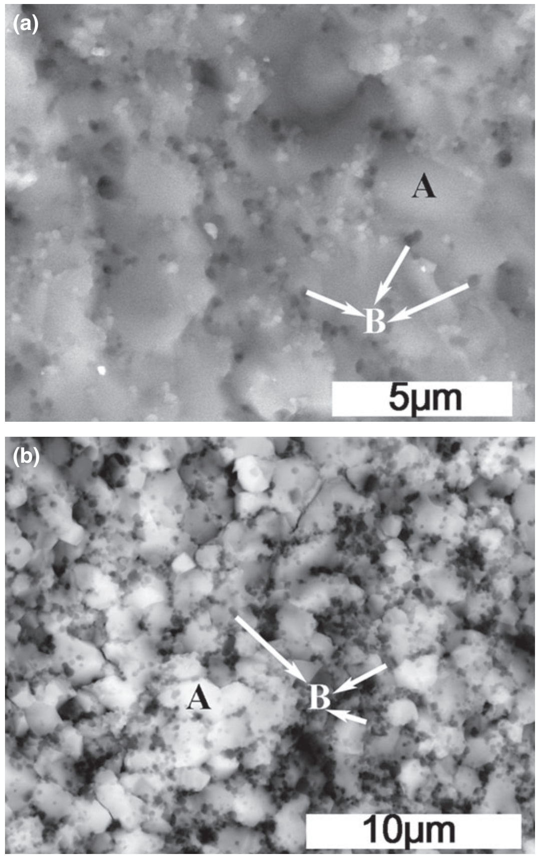

Fig. 2. Backscattered electron micrographs of fractures of (a) $0.55Li_2MoO_4$–$0.45TiO_2$ compounds sintered at 700°C/2 h and (b) $0.50Li_2WO_4$–$0.50TiO_2$ ceramics sintered at 730°C/2 h.

The microwave dielectric properties of the Li_2MO_4–TiO_2 (M = Mo, W) composites sintered at their optimal temperatures for 2 h are plotted in Fig. 3. As x value increases from 0.3 to 0.6, the dielectric constant of Li_2MO_4–TiO_2 (M = Mo, W) ceramics rise step by step. There are a lot of models to predict the effective permittivity of a mixture. Among them, Lichtenecker empirical logarithmic rule is a simple one to calculate the theoretical permittivity of a two-phase composite:

$$1g\varepsilon = y_1 1g\varepsilon_1 + y_2 1g\varepsilon_2 \quad (2)$$

where ε_1 and ε_2 are permittivities of material 1 and material 2, respectively; y_1 and y_2 represent the volume fractions of corresponding materials. Figure 3 illustrates that, when x value goes up from 0.3 to 0.6, the calculated permittivity of the mixture changes from around 7.9 to around 14.5. Although the measured permittivity is different from the calculated one, they are close to each other, which indicates that the measured values are generally in accordance with the Lichtenecker formula. As known to all, the mixing rule of TCF values can be described as follows:

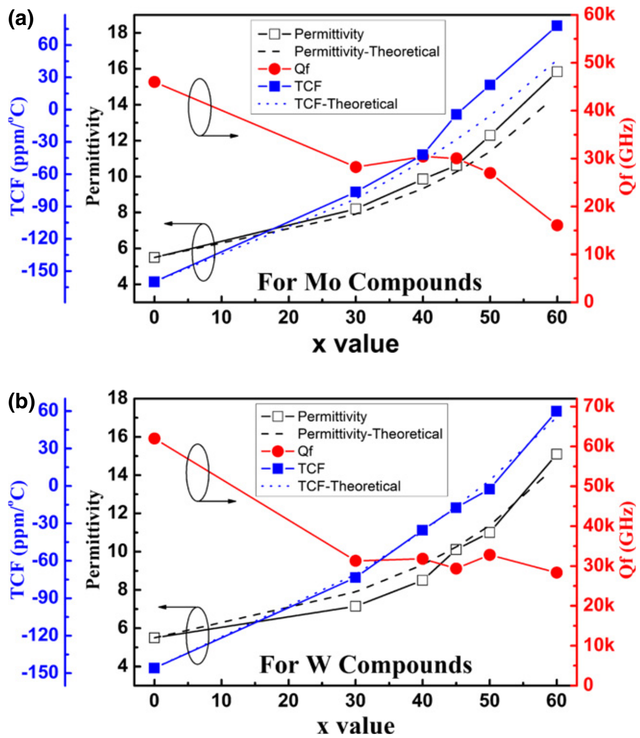

Fig. 3. Microwave dielectric properties of $(1 - x)$LiMoO$_4$–xTiO$_2$ (a) and $(1 - x)$LiWO$_4$–xTiO$_2$ (b) compounds as a function of x values.

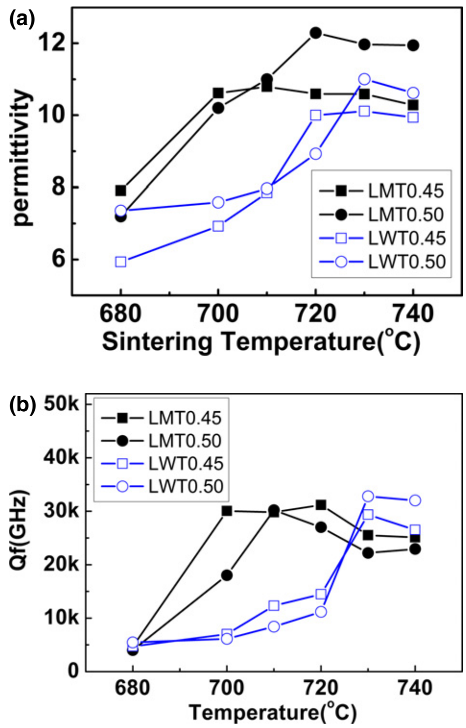

Fig. 4. Microwave permittivity (a) and $Q \times f$ values (b) of temperature stable $(1 - x)$LiMO$_4$–xTiO$_2$ (M = Mo, W; x = 0.45–0.5) ceramics as a function of sintering temperature.

$$\tau_f = y_1\tau_{f1} + y_2\tau_{f2} \quad (3)$$

where τ_{f1} and τ_{f2} represent the TCF values of material 1 and material 2, respectively. As x value changes from 0.3 to 0.6, there are steady increases in the TCF values of Li_2MO_4–TiO_2 (M = Mo, W) composites. For Li_2WO_4–TiO_2 samples, the measured TCF values are similar to the theoretical ones. For Li_2MoO_4–TiO_2 samples, the measured TCF values are a little higher. As shown in Fig. 3, the $Q \times f$ values of the compounds show a downtrend with x. This is probably due to the differences in the $Q \times f$ values and sintering temperatures of the two phases. In a word, the microwave dielectric properties of the two-phase system mainly depend on the concentration of the constituents and the temperature stable ceramics (near-zero TCF values) have been obtained at x = 0.45–0.50.

The microwave dielectric constants and $Q \times f$ values of temperature stable ceramics $(1 - x)Li_2MO_4$–$xTiO_2$ (M = Mo, W; x = 0.45–0.5) as a function of sintering temperature are shown in Fig. 4. With the sintering temperature increasing from 680°C to 740°C, the permittivity of both $(1 - x)$LiMoO$_4$–xTiO$_2$ and $(1 - x)$LiWO$_4$–xTiO$_2$ (x = 0.45–0.5) ceramics climb up first and then remain stable, which is caused by the densification process of ceramics. When the sintering temperature exceeds 740°C, these composites will melt partially. The curve of $Q \times f$ value versus sintering temperature is similar to that of permittivity versus sintering temperature. After the $Q \times f$ value reaches the peak, it decreases slowly, which may result from that the defects increase when the temperature is much high. From Fig. 4 and Table I, it is also seen that the $(1 - x)Li_2MO_4$–$xTiO_2$ (M = Mo, W; x = 0.45–0.5) ceramics can be sintered well at low temperatures and have good microwave dielectric properties. The $0.55Li_2MoO_4$–$0.45TiO_2$ sample sintered at 700°C has a permittivity of 10.6, a $Q \times f$ value of 30 060 GHz, and a TCF value of −4.5 ppm/°C. The $0.50Li_2WO_4$–$0.50TiO_2$ specimen sintered at 730°C has a permittivity of 11.0, a $Q \times f$ value of 32 800 GHz, and a TCF value of −2.6 ppm/°C.

Figure 5 demonstrates the XRD patterns of $0.55Li_2MO_4$–$0.45TiO_2$ (M = Mo, W) compounds with 20 wt% Ag addition sintered at 700°C–730°C. It is observed that besides the peaks of Li_2MO_4 (M = Mo, W) phase, TiO_2 phase, and silver phase, some other phases ($LiTi_2O_4$ phase, Ag_2MoO_4 phase and Ag_2WO_4 phase) also exist in the cofired ceramics. The previous report shows that Li_2MoO_4 and Li_2WO_4 are chemical compatible with Ag and Al at their sintering temperatures. However, in this study, the Li_2MoO_4 phase and Li_2WO_4 phase partially react with Ag to form Ag_2MoO_4 phase and Ag_2WO_4 phase, respectively. This phenomenon may be caused of the high sintering temperature. In the Li_2MO_4–TiO_2 (M = Mo, W) system, the sintering temperature is much higher than that of pure Li_2MoO_4 (540°C) and Li_2WO_4 (650°C) ceramics and close to the melting point of Li_2MoO_4 (705°C) and Li_2WO_4 (742°C) crystals. Hence, the reactive activity of Li_2MoO_4 and Li_2WO_4 with Ag may be enhanced and the excess of Li reacts with TiO_2 to form $LiTi_2O_4$ phase. From Fig. 5, it is also seen that only small part of Li_2WO_4 reacts with Ag and the peak intensity of

Table I. Microwave Dielectric Properties of Temperature Stable Ceramics $(1 - x)$LiBO$_4$–xTiO$_2$ (x = 0.45–0.5)

Composition	ST (°C)	Permittivity	$Q \times f$ (GHz)	τ_f (ppm/°C)	References
Li_2MoO_4	540	5.5	46 000	−160	[10]
$0.55Li_2MoO_4$–$0.45TiO_2$	700	10.6	30 060	−4.5	This work
$0.50Li_2MoO_4$–$0.50TiO_2$	720	12.3	27 000	+23.0	This work
Li_2WO_4	650	5.5	62 000	−146	[11]
$0.55Li_2WO_4$–$0.45TiO_2$	730	10.1	29 370	−17.4	This work
$0.50Li_2WO_4$–$0.50TiO_2$	730	11.0	32 800	−2.6	This work

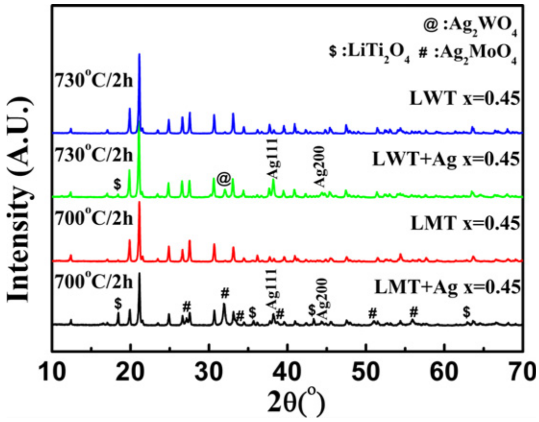

Fig. 5. -ray diffraction patterns of sintered $0.55Li_2MO_4$–$0.45TiO_2$ (M = Mo, W) ceramics with 20 wt% Ag.

impurity phases of Li_2WO_4–TiO_2–Ag compounds is much lower than that of Li_2MoO_4–TiO_2–Ag compounds.

IV. Conclusion

This study introduced a new series of material system $(1-x)$ Li_2MO_4–$xTiO_2$ (M = Mo, W) with low sintering temperature and good microwave dielectric properties. The XRD pattern and SEM analysis indicated that the Li_2MoO_4 phase and Li_2WO_4 phase with rhombohedral structure could coexist with the rutile TiO_2 phase and no other impurity phase could be detected. From the XRD pattern of cofired ceramics, it was found that some parts of Li_2MoO_4 phase and very small part of Li_2WO_4 phase react with Ag to form Ag_2MoO_4 phase and Ag_2WO_4 phase, respectively. The microwave dielectric properties were strongly determined by the relative content of Li_2MO_4 (M = Mo, W) and TiO_2 in the mixtures. The dielectric constant and TCF values increased with a rise of x, and the $Q \times f$ values showed a downtrend with x. The $(1-x)$ Li_2MO_4–$xTiO_2$ (M = Mo, W; x = 0.45–0.5) ceramics with low sintering temperature (700°C–730°C) possess good microwave dielectric properties with permittivities of 10.6–11.0, $Q \times f$ values from 30 060 to 32 800 GHz, and TCF values from −2.6 ppm/°C to −4.5 ppm/°C.

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