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Microwave Dielectric Properties of Li_2WO_4 Ceramic with Ultra-Low Sintering Temperature

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A new ultra-low-temperature firing microwave dielectric ceramic, Li_2WO_4 with the phenacite structure, was prepared via solid-state reaction method. The Li_2WO_4 ceramic can be well sintered at 640°–660°C, with a microwave relative permittivity ~5.5, a $Q \times f$ value about 62 000 GHz, and a negative temperature coefficient of −146 ppm/°C at 15.7 GHz. From an X-ray diffraction analysis, the Li_2WO_4 ceramic was found to be chemically compatible with both silver and aluminum powders at 640°C. All the results indicate that the Li_2WO_4 ceramic is a promising candidate for ultra-low temperature cofired ceramic technology, especially for dielectric substrate application.

I. Introduction

Low-temperature cofired ceramic (LTCC) technology plays an important role in the modern microwave circuit fabrication and integration due to the cofiring between active layers, electrodes and substrates. Many microwave dielectric ceramics have been developed for use in the LTCC field in the past decades with low melting point oxide and fluoride glasses to provide sintering temperatures designed for cofiring with an electrode of Ag (961°C).[1,2] About 10 years ago, a number of researchers moved their attention to obtaining microwave dielectric ceramics with intrinsic low firing temperatures.[3] There are many good examples in TeO_2-rich, Bi_2O_3-rich, and MoO_3-rich systems.[4–9] The microwave dielectric ceramics that can be densified at ultra-low temperatures (usually below the melting point of Al 660°C) are called ultra-low firing ceramics (ULTCC). If a chemically compatible electrode can be found, the so-called ULTCC technology can be achieved. The search for new ultra-low firing microwave dielectric ceramics has attracted more and more attention.

In our previous work,[10] a series of compounds in the Li_2O–Bi_2O_3–MoO_3 ternary systems were reported to possess good microwave dielectric properties and ultra-low firing temperature. Among all the ceramics in that work, Li_2MoO_4 ceramic has the lowest sintering temperatures, about 540°C (to our knowledge it is the lowest sintering temperature reported in the literature for microwave dielectric ceramics), with a relative permittivity ~5.5, a $Q \times f$ value of 46 000 GHz, and a temperature coefficient of resonant frequency (TCF) ~−160 ppm/°C at 13 GHz. In this work, the sintering behavior, microwave dielectric properties, and chemical compatibility with Ag and Al of Li_2WO_4 ceramic are introduced as new ULTCC materials.

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II. Experimental Procedure

The Li_2WO_4 composition were prepared by mixed-oxide approach using proportionate amounts of reagent-grade starting materials of Li_2CO_3 and WO_3 (>99%, Alfa Aesar, Ward Hill, MA). 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°C for 4 h. 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 Co., Philadelphia, PA), pulverized, and sieved through a mesh screen with 180 μm openings. 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 sintered at various temperatures ranging from 580° to 660°C for 2 h under the air 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.

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

The dielectric properties were measured at microwave frequency by the postresonator method, as suggested by Hakki and Coleman,[11] with a network analyzer (HP8510 Network Analyzer, Agilent, Hewlett-Packard, Loveland, CO). The TCF was determined using a zero thermal expansion cavity with programmable temperature chamber (Delta 9023, Delta Design,

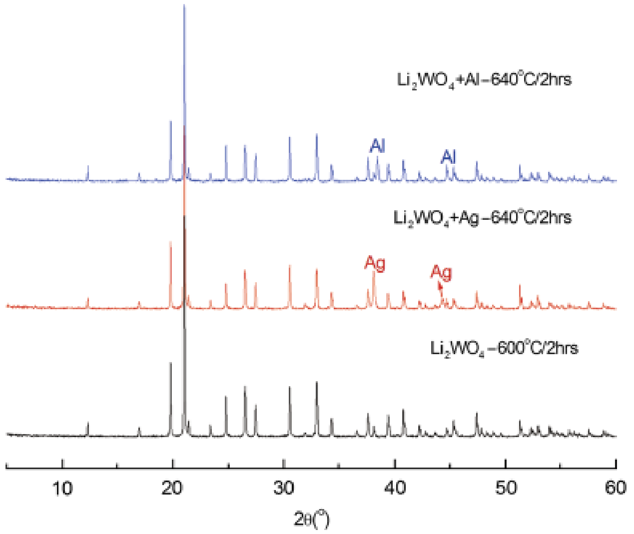

Fig. 1. X-ray diffraction patterns of Li_2WO_4 ceramics sintered at 600°C and cofired ceramics with 20 wt% Ag and 20 wt% Al at 640°C for 2 h.

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 $TE_{01\delta}$ resonant frequencies at 85° and 25°C, respectively.

III. Results and Discussions

The XRD patterns of Li_2WO_4 ceramic sintered at 600°C and cofired ceramic samples with 20 wt% silver and aluminum powders are shown in Fig. 1. Pure Li_2WO_4 ceramic sintered at 600°C/2 h shows a rhombohedral structure with $a = b = 14.360$ Å, $c = 9.599$ Å (R$\bar{3}$,No. 148), which is similar to the results reported by a structural investigation by Zachariasen and Plettinger[12] and Hartmann.[13] The theoretical density calculated from XRD data and the apparent density of the 640°C sintered Li_2WO_4 ceramics are 4.567 and 4.407 g/cm^3, respectively. The relative density is about 96.5%, and this indicates a well-densified Li_2WO_4 ceramic can be achieved though sintering at 640°C/2 h. For the cofired ceramic samples, we note the peaks of Li_2WO_4 and the respective metals, and there are no additional peaks in the XRD patterns to reflect a secondary phase formed, implying that Li_2WO_4 materials do not react with either silver or aluminum at the sintering temperature 640°C.

As shown in Fig. 2(a), there are homogeneous microstructures with almost no pores for the Li_2WO_4 ceramic sintered at 640°C/2 h. The grain size lies between 5 and 15 μm, which is similar to the results for Li_2MoO_4 ceramic sintered at 540°C/2 h. The backscattered electron imaged micrographs of Li_2WO_4 cofired ceramics with 20 wt% Ag and 20 wt% Al are shown

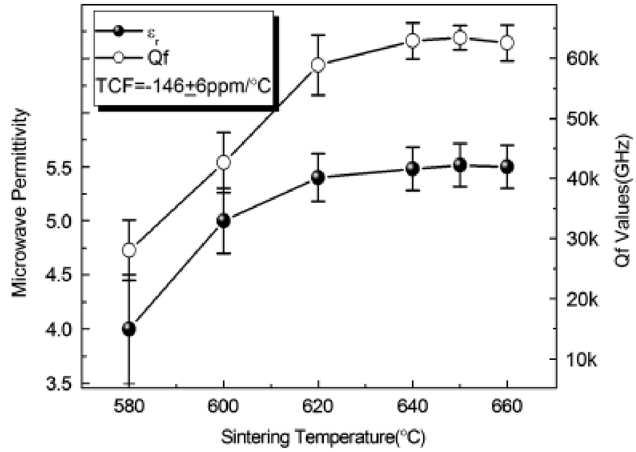

Fig. 3. Microwave dielectric properties (permittivity, $Q \times f$ value, and TCF value) of Li_2WO_4 ceramics sintered at 580°–660°C for 2 h and the SEM micrograph of as-fired surface of Li_2WO_4 ceramic sintered at 640°C/2 h.

in Figs. 2(b) and (c). The cofired ceramics were found to be composed of both Li_2WO_4 grains and metal grains coupled with EDS analysis, which further confirms no intermediate phases and the desired the chemical compatibility between Li_2WO_4 and silver/aluminum powders.

Microwave dielectric relative permittivity and $Q \times f$ values of Li_2WO_4 ceramics are shown in Fig. 3 as a function of the sintering temperature. As the sintering temperature increases, microwave dielectric constant increases and then reaches a saturated value at 640°C as is associated with the elimination of the pores. In regard to the microwave dielectric loss, there are in general two components: the intrinsic loss and the extrinsic loss. Usually, the extrinsic dielectric losses caused by the universal defects (impurities, substitution, grain boundaries, grain morphology and shape, secondary phase, pores, etc.)[14] dominate the $Q \times f$ value in ceramics. By now, it is still difficult to accurately calculate the extrinsic losses in polycrystalline samples. For the Li_2WO_4 ceramic, $Q \times f$ values become stable in sintering temperature range 640°–660°C after being well-densified. The Li_2WO_4 can be well sintered at 640°C with a microwave permittivity of 5.5, a $Q \times f$ value about 62 000 GHz, and a negative temperature coefficient TCF of −146 ppm/°C at 15.7 GHz. The influence of the porosity on the microwave permittivity could be eliminated by applying Bosman and Havinga's correction[15,16] as shown in Eq. (1)

$$\varepsilon_{Bosman} = \varepsilon_m(1 + 1.5P) \quad (2)$$

where ε_{Bosman} and ε_m are corrected and measured values of permittivity, respectively. P is the fractional porosity (0.035 in this work). The porosity corrected permittivity is about 5.79.

In the microwave region, the polarizability is the sum of both ionic and electronic components. Shannon[17] suggested that molecular polarizabilities of complex substances could be esti-

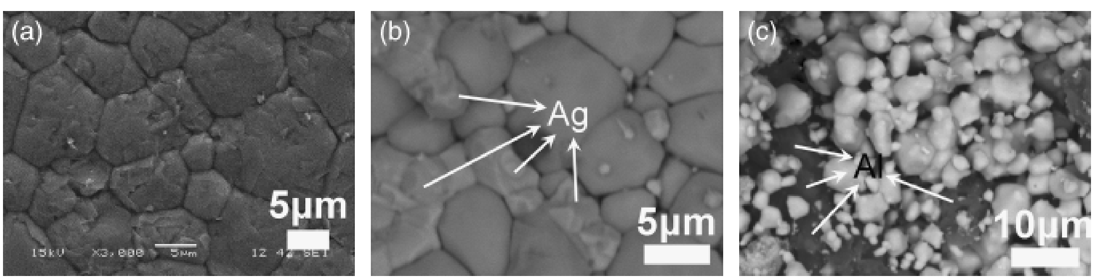

Fig. 2. Scanning electron micrograph of Li_2WO_4 ceramics sintered at 640°C for 2 h (a) and the backscattered electron image micrograph of cofired samples with 20 wt% silver (b) and 20 wt% aluminum (c) sintered at 640°C/2 h.

Table I. Comparison of Microwave Dielectric Properties of Some Compounds with Microwave Relative Permittivity between 4 and 6

Composition	S_T	F (GHz)	ε_r	$Q \times f$ (GHz)	TCF	References
$Li_3AlB_2O_6$	650	16.8	4.2	12 460	$>+100$	Ohashi *et al.*[19]
$CaO–B_2O_3–SiO_2$	900	9.9	4.1	2600	—	Hiang *et al.*[20]
$Li_3AlB_2O_6$	775	17.4	5.4	20 448	$>+100$	Ohashi *et al.*[19]
$NaAlSi_3O_8$	1025	—	5.5	11 200	≈ 0	Krzmanc *et al.*[21]
Li_2MoO_4	540	13.05	5.5	46 000	-160	Zhou *et al.*[10]
Li_2WO_4	650	15.7	5.5	62 000	-146	This work
$K_{0.9}Ba_{0.1}Ga_{1.1}Ge_{2.9}O_8$	990	12	5.9	94 100	$+12$	Krzmanc *et al.*[22]

S_T, sintering temperature; F, resonant frequency; TCF, temperature coefficient of resonant frequency.

mated by the oxide additivity rule. Then the polarizabilities of a Li_2WO_4 molecular could be calculated as follows:

$$\alpha(Li_2WO_4) = 2\alpha(Li^+) + \alpha(W^{6+}) + 4\alpha(O^{2-}) \tag{3}$$

where $\alpha(Li^+)$, $\alpha(W^{6+})$, and $\alpha(O^{2-})$ are the polarizability of Li^+ (1.20 Å^3), W^{6+} (3.20 Å^3), and O^{2-} (2.01 Å^3).[17,18] Considering the Clausius–Mosotti relation as follows:

$$\varepsilon_r = \frac{3V + 8\pi\alpha}{3V - 4\pi\alpha} \tag{4}$$

where V is the cell volume of Li_2WO_4. The theoretical permittivity calculated by the oxide additivity rule is 5.494. It is similar to both the measured value and the porosity corrected value 5.5 and 5.79, and the relative error is about 0.1% for the former and about 5.1% for the latter, which implies that there is no other polarization mechanism in the Li_2WO_4 ceramic at microwave region beside ionic and electronic displacive polarization. The comparison of microwave dielectric properties of some compounds with microwave relative permittivity between 4 and 6 is shown in Table I. It is seen that the Li_2WO_4 ceramic could be a candidate for dielectric substrate application due to its low dielectric relative permittivity, high $Q \times f$ value, and chemical compatibility with both Ag and Al. However, its large negative TCF value must be modified to near zero before its application. Design of solid solution and composite both are possible methods to achieve it.

IV. Conclusions

In summary, the phenacite structure Li_2WO_4 ceramic was prepared via traditional solid-state reaction methods. High performance of microwave dielectric properties were obtained in the Li_2WO_4 ceramics sintered at 640°–660°C with a microwave permittivity of 5.5, a $Q \times f$ value about 62 000 GHz, and a negative temperature coefficient TCF of -146 ppm/°C at 15.7 GHz. From the XRD analysis, the Li_2WO_4 ceramic was found to be chemically compatible with silver powders at its sintering temperatures. All the results indicate that the Li_2WO_4 ceramic is a promising candidate for ultra-low temperature cofired ceramic technology.

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