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Short communication

Li_4WO_5: A temperature stable low-firing microwave dielectric ceramic with rock salt structure

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ABSTRACT

A Li_4WO_5 ceramic with rock salt structure was prepared by the solid-state reaction method and its microwave dielectric properties was demonstrated for the first time. It could be well densified at relatively low sintering temperature (~890 °C). XRD and DTA analysis revealed a phase transformation from cubic to orthorhombic occured at 700 °C. Excellent microwave dielectric properties with a near-zero temperature coefficient of resonant frequency ~−2.6 ppm/°C, a relative permittivity ~8.6 and a quality factor ~23,100 GHz (at 11.0 GHz) was obtained. Li_4WO_5 was found to be chemically compatible with silver powders when sintered at 890 °C. All the results indicate that the Li_4WO_5 ceramic is a promising candidate as a base material in low temperature cofired ceramic technology.

1. Introduction

Low-temperature cofired ceramic (LTCC) technology has played an important role in the modern microwave circuit fabrication and integration due to the co-firing between active layers, electrodes and substrates [1]. In LTCC, a low-firing temperature (<961 °C, the melting temperature of Ag electrode) and suitable microwave dielectric properties (an appropriate relative permittivity, a high quality factor, and a near-zero temperature coefficient of resonant frequency) are strongly desired for practical application [2,3]. Unfortunately, the most commonly used microwave dielectric ceramics, such as BZT ($BaZn_{0.33}Ta_{0.67}O_3$) [4], BMT ($BaMg_{0.33}Ta_{0.67}O_3$) [5], usually have sintering temperatures higher than 1000 °C, which limits their applications in LTCC. Addition of low melting point glass, effectively reduces the sintering temperature, but degrades the microwave properties, especially the quality factor [6]. Thus, searching for Glass-free LTCC materials with improved microwave dielectric properties is strongly desired [7].

The recent development in low-firing microwave dielectric ceramics has been mainly focused on the materials consisting of low-melting constituents, such as V_2O_5-rich [8,9], TeO_2-rich [10,11], Bi_2O_3-rich [12,13], Li_2O-rich [14,15] and WO_3-rich compounds [16,17], etc. Among them, some Li-containing compounds with rock salt structure, such as Li_2TiO_3 and Li_3NbO_4, were reported to exhibit a combination of low sintering temperature and excellent microwave dielectric properties [18–20]. For example, Li_2TiO_3 had a permittivity of 22, $Q \times f$ value of 63,500 GHz (at 8.6 GHz), and τ_f value of 20.3 ppm/°C [18]. Li_3NbO_4 could be well sintered at 930 °C with good microwave dielectric properties: $\epsilon_r = 16.4$, $\tau_f = -45$ ppm/°C and $Q \times f = 47{,}179$ GHz (8.7 GHz) [21]. The rock salt structure is one of the most common and well-known structure types. It is characterized by edge shared octahedrons coordinated for both cations and anions to form three-dimensional network [18]. A site can be occupied by two or three crystallographically distinct types of cations, e.g., Li_2TiO_3 and Li_3NbO_4. Li_4WO_5 belongs to the family of rock salt. Feng et al. firstly reported that Li_4WO_5 crystallized into a rock salt structure and it could be calcined at a low temperature ~700 °C [22]. And, Li_4WO_5 ceramics have been extensively investigated as promising luminescence materials [23]. To the best of our knowledge, however, no microwave dielectric properties of Li_4WO_5 have been reported yet. With a purpose to

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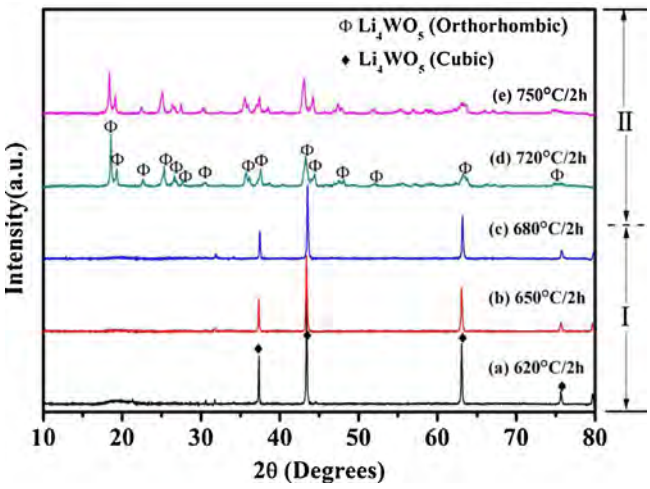

Fig. 1. The XRD patterns of the Li_4WO_5 powders calcined at 620–750 °C for 2 h.

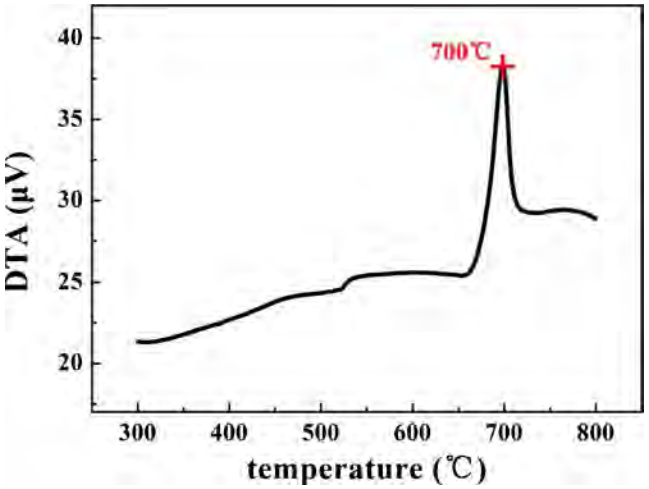

Fig. 2. Differential thermal analysis (DTA) curve of the Li_4WO_5 powders calcined at 620 °C.

develop novel LTCC materials, Li_4WO_5 ceramics were prepared and the sintering behavior, phase transition, and microwave dielectric properties were reported in the present paper. The chemical compatibility of Li_4WO_5 ceramic with Ag was also investigated.

2. Experimental procedure

Li_4WO_5 ceramic was prepared by conventional solid state reaction route. Reagent-grade raw materials of Li_2CO_3, and WO_3 with high-purity (>99%, Guo–Yao Co., Ltd., Shanghai, China) were weighed according to the stoichiometry and ball milled in alcohol medium for 4 h in a plastic bottle using zirconia balls as a grinding medium. Then the mixture was dried and calcined at various temperatures (620 ~ 750 °C) for 2 h in air. The calcined powders were vibratory milled for 6 h. Polyvinyl alcohol (PVA, 5 wt%) was added as a binder to the powders, then dried and ground. The milled powder was pressed into cylindrical pellets of 12 mm diameter and 7 mm thickness under a pressure of 200 MPa. These pellets were heated to 550 °C for 2 h to remove the organic binder, and then sintered at different temperatures from 780 to 920 °C for 2 h in air. To investigate the chemical compatibility of these compounds with electrode metal powders, 10 wt% Ag was mixed with Li_4WO_5 compounds and sintered at 860 °C for 2 h.

The phase composition and crystal structure were examined by X-ray diffraction (XRD) with CuKα1 radiation (Model X'Pert PRO, PANalytical, Almelo, The Netherlands). The phase transition temperature of the Li_4WO_5 was investigated using differential thermal analysis (DTA, PerkinElmer STA-8000, Massachusetts, America). The bulk densities were measured using the Archimedes method. Scanning electron micro-scope (SEM, Model JSM6380-LV, JEOL, Tokyo, Japan) was used to study the surface morphology of the specimens. The microwave dielectric properties were measured by a network analyzer (Model N5230A, Agilent Co., Palo Alto, California) and a temperature chamber (Delta 9039, Delta Design, San Diego, California). The temperature coefficients of resonant frequency τ_f values were calculated by the equation:

$$\tau_f = \frac{f_{85} - f_{25}}{60 \times f_{25}} \quad (1)$$

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

3. Results and discussion

Fig. 1 shows the room-temperature XRD patterns of the calcined Li_4WO_5 powders at 620–750 °C for 2 h. As observed, the crystal structure exhibited a strong dependence on the calcination temperature. With increasing temperature, two phase regions were identified and marked as phase I and II in Fig. 1. For the powders calcined at 620–680 °C, all the observed peaks matched well with the JCPDS No. 21-0531 card for the cubic Li_4WO_5 without additional peaks detected. This suggests the formation of single-phase cubic Li_4WO_5 within the limitation of XRD. Interestingly, the cubic phase changed to an orthorhombic phase after calcined at higher temperatures (720 °C). In order to clarify the phase transition, DTA was conducted on the Li_4WO_5 powders calcined at 620 °C, as shown in Fig. 2. An exothermic peak at ~700 °C was observed in DTA curve during heating, indicating the phase transformation from cubic to orthorhombic. XRD and DTA analysis reveals that the orthorhombic Li_4WO_5 phase can be formed at temperatures higher than 680 °C and the orthorhombic phase is stable to room temperature. This is further confirmed from the room-temperature XRD patterns of the sintered ceramics at 830–920 °C (as shown in Fig. 3). All the patterns

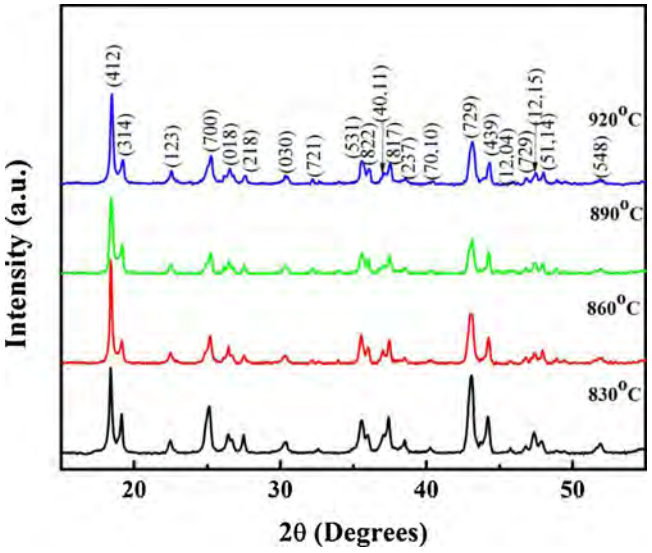

Fig. 3. XRD patterns of the Li_4WO_5 ceramics sintered at various temperatures from 830–920 °C for 2 h.

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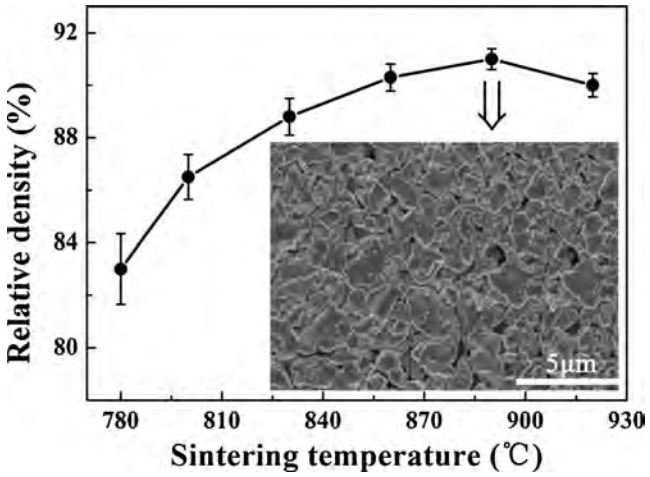

Fig. 4. The relative densities of the ceramics as a function of the sintering temperature and the SEM image of the fractured surface of ceramic sintered at 890 °C.

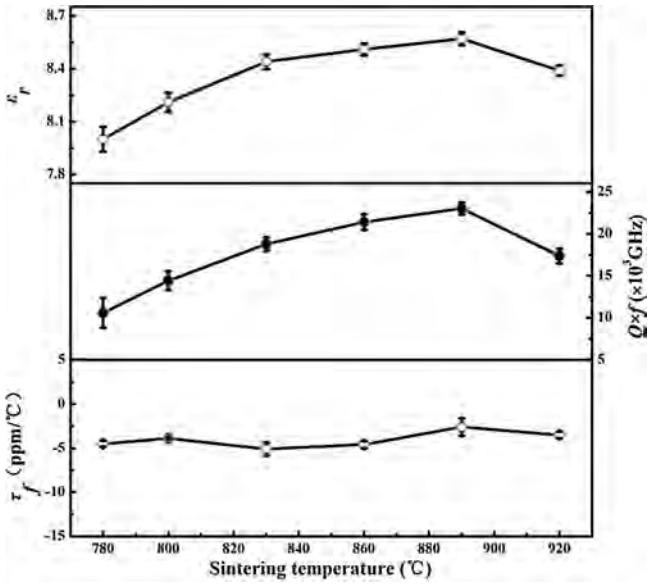

Fig. 5. The microwave dielectric properties (ϵ_r, $Q\times f$, and τ_f values) of the Li_4WO_5 ceramics sintered at various temperatures for 2 h.

could be indexed with the orthorhombic Li_4WO_5 phase. Thus, all the following measurements were performed on the orthorhombic Li_4WO_5 ceramics.

The relative densities of the ceramics are shown in Fig. 4 as a function of the sintering temperature. The sample sintered at 780 °C had a low density ~4.11 g/cm^3 that was about 83% of the XRD theoretical density (~4.95 g/cm^3). With increasing sintering temperature to 920 °C, the relative density monotonously increased to a maximum values of 91%, and then decreased slightly. The inset of Fig. 4 shows SEM image of the fractured surface of the ceramic sintered at 890 °C. As seen, a relatively dense microstructure with some porosity was observed. A similar porous microstructure was reported in Li_2TiO_3 ceramic [18]. The authors ascribed the porosity to the evaporation of lithium at elevated temperatures and the phase transition.

Fig. 5 shows the microwave dielectric properties (ϵ_r, $Q\times f$, and τ_f values) of the Li_4WO_5 ceramics sintered at various temperatures for 2 h. The relative permittivity of Li_4WO_5 ceramic increased from 8.0 at 780 °C to a maximum value ~8.6 at 890 °C, then slightly decreased when the sintering temperature exceeded 890 °C. The relationship between the permittivity and the sintering temperature followed the same trend as that of the relative density. The lower permittivity at low temperature could be attributed to the existence of pores. The influence of the porosity on ϵ_r could be eliminated by applying Bosman and Having's correction [24]:

$$\epsilon_{\text{corrected}} = \epsilon_{\text{m}}(1 + 1.5p) \quad (2)$$

where p is the fractional porosity (in this work $p = 0.09$ for the pellet sintered at 890 °C), $\epsilon_{\text{corrected}}$ and ϵ_{m} are the corrected and measured values of relative permittivity, respectively. The calculated $\epsilon_{\text{corrected}}$ is about 9.7 for Li_4WO_5.

In regard to the factors effecting the microwave dielectric loss, there are in general two components: the intrinsic loss and the extrinsic loss. It is well accepted that the extrinsic dielectric losses are caused by the defects, such as impurities, substitution, grain boundaries, grain morphology and shape, secondary phase, pores, etc. [25], which have significant affect on the $Q\times f$ value. For the as-sintered Li_4WO_5 ceramics, the variation of $Q\times f$ values displayed similar behavior as those of the density and the permittivity with increasing sintering temperature. A maximum value ~23,100 GHz was obtained for sample sintered at 890 °C. This might be related to the density of the sample. The τ_f values of Li_4WO_5 ceramics did not change remarkably with increasing sintering temperature and remained stable at ~−2.6 ppm/ °C. The comparison of microwave dielectric properties of some compounds with rock salt structure is shown in Table 1. It is seen that the Li_4WO_5 ceramic mainly has two advantages over the other compounds: one is near-zero temperature coefficient of resonant frequency, and the other is the relatively low sintering temperature.

In order to study the chemical compatibility of Li_4WO_5 ceramic with the commonly used silver electrodes, XRD patterns of the Li_4WO_5 ceramic and the cofired ceramic with 10 wt% silver powders sintered at the same temperature 890 °C are compared (shown in Fig. 6a). The Li_4WO_5 ceramic sintered at 890 °C crystallized into an orthorhombic structure based on the JCPDS card No. 021-0530. For the cofired ceramic samples, additional peaks belonging to the silver were detected, suggesting the cofired ceramic was composed of both Li_4WO_5 and silver phase. Fig. 6b shows the SEM image of the cofired ceramic with 10 wt% silver sintered at 860 °C for 2 h. Two distinct grains with different sizes were observed. The larger grains were detected to be Ag. This result further implies that Li_4WO_5 ceramic is chemically compatible with silver at the sintering temperature of 860 °C. Therefore, it is evident that Li_4WO_5 ceramic is a promising candidate for base material in LTCC technology.

Table 1
Comparison of the densification temperature and microwave dielectric properties of some compounds with rock salt structure.

Composition	S.T. (°C)	ϵ_r	$Q\times f$ (GHz)	τ_f (ppm/°C)	References
Li_4WO_5	890	8.6	23100	−2.6	This work
Li_2TiO_3	1300	22	63500	20.3	[18]
$0.7Li_2TiO_3 + 0.3LiF$	1200	22.0	60000	−30	[19]
$0.7Li_2TiO_3 + 0.3MgO$	1300	19.0	90000	−10	[18]
$0.4Li_3NbO_4 + 0.6Li_2TiO_3$	1250	19.8	91200	−24	[26]
$0.3Li_3NbO_4 + 0.7Li_2SnO_3$	1200	13.5	61600	29	[26]
Li_3NbO_4	1150	16.4	47100	−45	[20]

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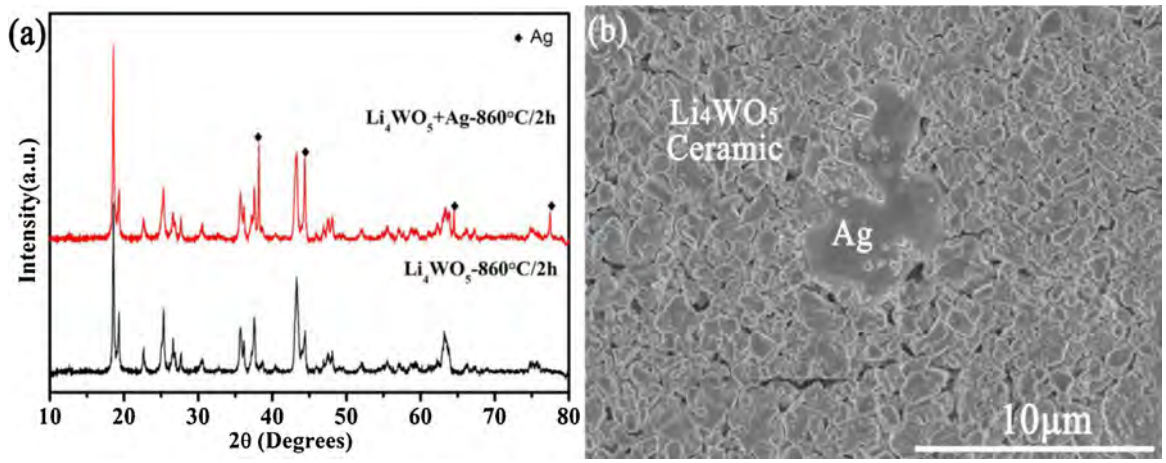

Fig. 6. (a) XRD patterns of Li_4WO_5 ceramic sintered at 860 °C and the cofired ceramic samples with 10 wt% silver powders at 860 °C for 2 h; (b) SEM image of the cofired ceramic.

In spite of the above significant results, it is worth noting that the porosity microstructure of Li_4WO_5 ceramic is still a challenge. It is expected that the quality factor will be improved if a denser microstructure with a higher relative density is obtained. Thus, further efforts are still needed to enhance the density of Li_4WO_5 ceramic.

4. Conclusions

In summary, the rock salt structure Li_4WO_5 ceramic was prepared via traditional solid-state reaction method. High performance microwave dielectric properties were obtained in the Li_4WO_5 ceramic sintered at 890 °C with a relative permittivity of 8.6, a $Q \times f$ value of 23,100 GHz, and a near zero temperature coefficient τ_f of −2.6 ppm/°C at 11.0 GHz. From the XRD analysis, the Li_4WO_5 ceramic was found to be chemically compatible with silver powders at 860 °C. All the results indicate that the Li_4WO_5 ceramic is a promising candidate for LTCC technology.

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