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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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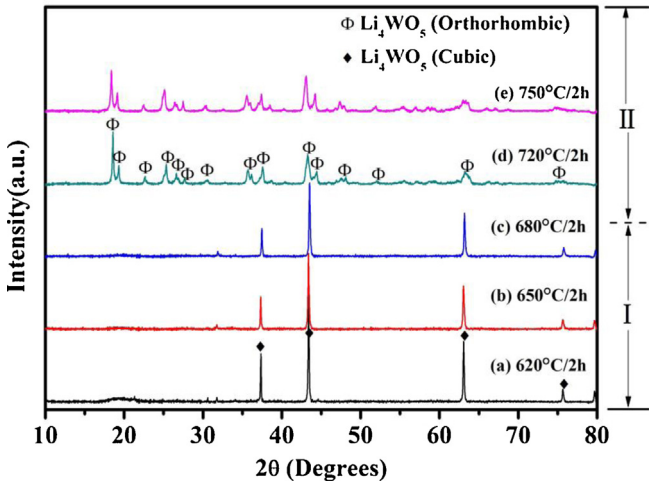

Fig. 1. The XRD patterns of the Li_4WO_5 powders calcined at 620–750 °C for 2 h.

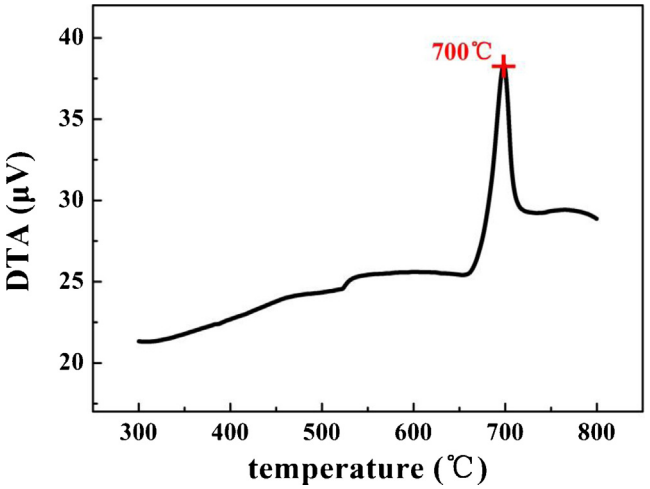

Fig. 2. Differential thermal analysis (DTA) curve of the Li_4WO_5 powders calcined at 620 °C.

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

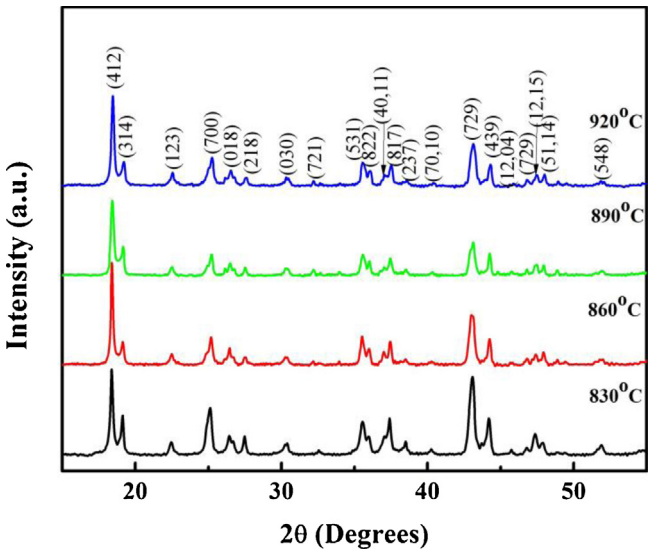

Fig. 3. XRD patterns of the Li_4WO_5 ceramics sintered at various temperatures from 830–920 °C for 2 h.