Preparation, crystal structure, and dielectric characterization of $\text{Li}_2\text{W}_2\text{O}_7$ ceramic at RF and microwave frequency range

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Single phase $\text{Li}_2\text{W}_2\text{O}_7$ with anorthic structure was prepared by the conventional solid-state reaction method at 550°C and the anorthic structure was stable up to 660°C . The dielectric properties at radio frequency (RF) and microwave frequency range were characterized. The sample sintered at 640°C exhibited the optimum microwave dielectric properties with a relative permittivity of 12.2, a quality factor value of 17,700 GHz (at 9.8 GHz), and a temperature coefficient of the resonant frequency of -232 ppm/ $^\circ\text{C}$ as well as a high relative density $\sim 94.1\%$. Chemical compatibility measurement indicated $\text{Li}_2\text{W}_2\text{O}_7$ did not react with aluminum electrodes when sintered at 640°C for 4 h.

Keywords: Microwave dielectric ceramics; LTCC; anorthic structure.

1. Introduction

In recent years, low-temperature co-fired ceramic (LTCC) technology has attracted much attention because of its crucial role in the fabrication of modern electronic devices due to its ability to fabricate three-dimensional ceramic modules with low dielectric loss and embedded low-cost metal electrodes, such as silver and aluminum.^{1–4} In LTCC, a sintering temperature lower than the melting points of the inner metals and suitable microwave dielectric properties (an appropriate relative permittivity ϵ_r , a high quality factor $Q \times f$, and a near-zero temperature coefficient of resonant frequency τ_f) are strongly required for practical applications.^{5–8} Thus, searching for novel microwave dielectric ceramics with low sintering temperatures and promising properties is still a hot issue.

Tungstates are stable crystalline compounds and have been reported to possess good microwave dielectric properties along with relatively low sintering temperatures, especially those simultaneously containing Li_2O and WO_3 , such as $\text{Li}_2\text{O}-\text{WO}_3$ binary systems.^{9–11} Among them, Li_2WO_4 could be well densified at 640°C with a high relative density $\sim 96.5\%$, a relatively high $Q \times f \sim 62,000$ GHz, a small

permittivity $\epsilon_r \sim 5.5$ and a negative $\tau_f \sim -146$ ppm/ $^\circ\text{C}$. Additionally, it was found to be chemically compatible with both silver and aluminum powders at 640°C .⁹ Thus, it is important to continue to search for novel low-firing microwave dielectric ceramics in $\text{Li}_2\text{O}-\text{WO}_3$ binary system.

$\text{Li}_2\text{W}_2\text{O}_7$ was reported for the first time in 1928 by Hoermann.¹² Until 1975, its crystal structure with a triclinic space group $P-1$ was determined based on the X-ray diffractometry (XRD) analysis of $\text{Li}_2\text{W}_2\text{O}_7$ crystal synthesized at 800°C .¹³ The structure of $\text{Li}_2\text{W}_2\text{O}_7$ is built up of WO_6 octahedra and LiO_4 tetrahedra. Up to date, the microwave dielectric properties of $\text{Li}_2\text{W}_2\text{O}_7$ ceramics have not been investigated yet. With an attempt to develop new low-firing microwave dielectric ceramics, $\text{Li}_2\text{W}_2\text{O}_7$ ceramic was prepared and its crystal structure, sintering behavior and microwave dielectric properties were studied in detail in this work.

2. Experimental Procedure

The conventional solid-state ceramic route was applied to prepare $\text{Li}_2\text{W}_2\text{O}_7$ ceramics. Proportionate amounts of

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reagent-grade raw materials of Li_2CO_3 (>98%, Guo-Yao Co. Ltd., Shanghai, China) and WO_3 (>99%, Guo-Yao Co. Ltd., Shanghai, China) were weighted, mixed and ball-milled in alcohol medium for 4 h in nylon bottle with zirconia balls. The powder mixture was dried and calcined at 550°C for 4 h. Then the calcined powders were re-milled, added with 5 wt.% polyvinyl alcohol (PVA) as binder, and uniaxially pressed into disks of 12 mm in diameter and 7 mm in thickness under a pressure of 200 MPa. The samples were heated to 550°C for 4 h to remove the organic binder and then sintered at 620 – 660°C for 4 h.

The phase purity and crystal structure were evaluated using an XRD ($\text{CuK}\alpha 1$, 1.54059 Å, Model X'Pert PRO, PANalytical, Almelo, The Netherlands). The microstructure of the samples was observed by a Scanning Electron Microscope (SEM, Model JSM6380-LV, JEOL, Tokyo, Japan). The bulk densities of the ceramics were determined by the Archimedes method. The impedance spectra were recorded in the frequency range of 100 Hz–1 MHz (Agilent 4294A Impedance Analyzer) and silver paste was applied on both the sides of the ceramics (sintered at 550°C for 0.5 h). The microwave dielectric properties were measured using a network analyzer (Model N5230A, Agilent Co., Palo Alto, Canada) and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). The temperature coefficients of resonant frequency were calculated by equation

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \times 10^6 (\text{ppm}/^\circ\text{C}), \quad (1)$$

where f_1 and f_2 represent resonant frequencies at temperatures T_1 and T_2 , respectively.

3. Results and Discussion

Figure 1 shows the room-temperature XRD patterns of $\text{Li}_2\text{W}_2\text{O}_7$ recorded on the calcined samples at 550°C and sintered ceramics over temperature range 620 – 660°C for 4 h. All the observed diffraction peaks matched well with the PDF file number 01-070-0869 for $\text{Li}_2\text{W}_2\text{O}_7$ and no additional peaks are observed. The indexing was based on the standard PDF card. This result suggests the formation of single-phase $\text{Li}_2\text{W}_2\text{O}_7$.

Figure 2 shows the SEM images performed on the surfaces of the $\text{Li}_2\text{W}_2\text{O}_7$ ceramics sintered at 620°C , 630°C , 640°C , and 650°C , respectively. When sintered at 620°C , a porous microstructure with many pores and small grains (~ 3 – $6 \mu\text{m}$) was developed. With increasing sintering temperature, the porosity decreased gradually along with obvious grain growth. When the sintering temperature reached 640°C , a uniform and dense microstructure was obtained as shown in Fig. 2(c). With further increase in sintering temperature to 650°C , abnormal grain growth appeared with large grains $\sim 10 \mu\text{m}$. The change in microstructure would partially affect the bulk density and microwave dielectric properties.

Fig. 1. X-ray diffraction pattern of $\text{Li}_2\text{W}_2\text{O}_7$ powder calcined at 550°C and patterns of ceramics sintered at 620 – 660°C for 4 h.

It should be noted that some snowflake-like grains could be observed, which might be related to the surface precipitates at elevated temperatures.

The frequency dependencies (in log scale) of the relative permittivity (ϵ_r) and dielectric loss tangent ($\tan \delta$) at radio frequency (RF) region are shown in Fig. 3. It is observed that both ϵ_r and $\tan \delta$ decreased with increase in frequency. At 1 MHz, the relative permittivity and loss tangent were about 14.5 and 0.0018, respectively, which were much higher compared with those values at microwave frequency region. It is well known that several polarization mechanisms responding at different frequency regions contribute to the permittivity including instantaneous polarizations and relaxation polarizations.^{14,15} At higher frequency region, the relaxation polarizations (e.g., space charge polarization) cannot follow the electric field, thus make no contribution to the net polarization, and hence result in decrease in the permittivity and dielectric loss. A similar result was previously reported in LiMnPO_4 ceramics.¹⁶

The bulk density and microwave dielectric properties (ϵ_r , $Q \times f$, and τ_f) are shown in Fig. 4 as a function of sintering temperature. At 620°C , the bulk density was about 5.58 g/cm^3 that was only $\sim 91.7\%$ of the theoretical density ($\sim 6.08 \text{ g/cm}^3$). As the sintering temperature increased to 640°C , the bulk density reached its maximum density $\sim 5.72 \text{ g/cm}^3$ with a relative density $\sim 94.1\%$, followed by a slight decrease to 93.3% at 660°C . Combined with the SEM analysis, the increase in density might be explained by the elimination of the pores, while the subsequent decline might be related to the abnormal grain growth.

The change in relative permittivity (ϵ_r) with the sintering temperature exhibited a similar trend as that of the bulk density. The relative permittivity increased from 10.8 at 620°C to 11.3 at 630°C . A maximum value of 12.2 was obtained in the sample sintered at 640°C . The relative permittivity decreased with further increase in sintering

Fig. 2. SEM micrographs of the surfaces of $\text{Li}_2\text{W}_2\text{O}_7$ ceramics sintered at different temperatures.

temperature. Similarly, $\text{Li}_2\text{W}_2\text{O}_7$ ceramic sintered at 640°C had a maximum $Q \times f$ value of 17,700 GHz (at 9.8 GHz). Generally, the dielectric properties at microwave frequency region could be affected by several factors, including crystal structure and extrinsic factors such as pore, density, second phases, grain sizes and impurities.^{17–20} In the present work, it is proposed that the main factor affecting the relative permittivity and quality factor is densification. Similar results were reported in $\text{Li}_2\text{O}-\text{WO}_3$ system.¹² No remarkable change in τ_f was found with increasing sintering temperature value and they fluctuated around a constant value of $-232 \text{ ppm}/^\circ\text{C}$.

Fig. 3. The frequency dependencies (in log scale) of the relative permittivity (ϵ_r) and dielectric loss tangent ($\tan \delta$) at RF region.

In order to evaluate the chemical compatibility of $\text{Li}_2\text{W}_2\text{O}_7$ ceramic with aluminum electrode, it was co-fired with 20 wt.% Al powders at 640°C for 4 h. XRD pattern, the backscattered electron image and energy dispersive X-ray spectroscopy (EDS) analysis of the co-fired ceramic are shown in Fig. 5. XRD patterns revealed that only the peaks of $\text{Li}_2\text{W}_2\text{O}_7$ and Al were detected. Two kinds of grains with different element contrasts could be observed from the BSEM micrograph. According to the energy dispersive X-ray spectroscopy (EDS) analysis, the larger dark grains ($\sim 20 \mu\text{m}$)

Fig. 4. Variations in the bulk density, ϵ_r , $Q \times f$, and τ_f of $\text{Li}_2\text{W}_2\text{O}_7$ ceramics as a function of sintering temperature.

Fig. 5. XRD pattern, the backscattered electron image and EDS analysis of the co-fired $\text{Li}_2\text{W}_2\text{O}_7$ ceramic with 20 wt.% Al powders.

belonged to Al electrodes and the smaller grains were $\text{Li}_2\text{W}_2\text{O}_7$ -based phase. Chemical compatibility measurement indicated $\text{Li}_2\text{W}_2\text{O}_7$ did not react with aluminum electrodes when sintered at 640°C for 4 h. From the application point of view, however, τ_f values are still too large for practical application. Further efforts are needed to tune the large negative τ_f value of $\text{Li}_2\text{W}_2\text{O}_7$ ceramic to be near zero by forming composite materials such as TiO_2 or CaTiO_3 with positive sign of τ_f values.

4. Conclusions

A novel microwave dielectric ceramic $\text{Li}_2\text{W}_2\text{O}_7$ with anorthic structure was prepared by the conventional solid-state reaction method. The crystal structure, sintering behavior and microwave dielectric properties of $\text{Li}_2\text{W}_2\text{O}_7$ ceramic were investigated. XRD results indicate that single phase $\text{Li}_2\text{W}_2\text{O}_7$ could be obtained at 600°C and the anorthic structure was stable up to 660°C . The sample sintered at 640°C exhibited the optimum microwave dielectric properties with a relative permittivity of 12.2, a quality factor value of 17,700 GHz (at 9.8 GHz), and a temperature coefficient of the resonant frequency of $-232 \text{ ppm}/^\circ\text{C}$ as well as a high relative density $\sim 94.1\%$.

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