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$LiAlW_2O_8$: A novel temperature stable low-firing microwave dielectric ceramic

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ABSTRACT

A novel temperature stable microwave dielectric ceramic $LiAlW_2O_8$ was prepared by a conventional solid-state reaction method with a low temperature range from 740 °C to 800 °C. A monoclinic structure was observed for $LiAlW_2O_8$ ceramic coupled with a minor of second unknown phase. The ceramics could be well sintered at 780 °C for 4 h with 95.6% relative density and exhibited excellent microwave dielectric properties with permittivity (ε_r) of 11.7, $Q \times f$ value of 23,000 GHz (at 9.0 GHz), and temperature coefficient of resonant frequency (τ_f) of −5.3 ppm/°C.

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1. Introduction

With the rapid development of wireless communication technology, microwave dielectric ceramics have been paid extensive attention. Microwave materials are required to have suitable permittivity (ε_r), high quality factor ($Q \times f$) for better selectivity and near-zero temperature coefficient of resonant frequency (τ_f) for stability, preferably with a low sintering temperature [1–2]. Recently a large number of researchers are paying attention to develop new microwave dielectric ceramics with intrinsic low sintering temperature for application in LTCC [3–5], such as WO_3-based and Li_2O-based materials [6–7]. In Li_2O-M_2O_3-WO_3 systems, Li_2WO_4 [8] and double tungstates $LiMW_2O_8$ (M=Y, Nd, Sm, Bi) [9–12] were reported to have a low sintering temperature (650–900 °C), but a large negative τ_f value of −146 ppm/°C for Li_2WO_4 and a positive value (+63.8 ppm/°C ~ +142 ppm/°C) for M=Y, Nd, Sm. In order to improve the $Q \times f$ values and adjust the temperature coefficient of resonant frequency, AWO_4 (A=Ca, Ba, Zn) was added to $LiMW_2O_8$, but simultaneously increased the sintering temperature.

$LiAlW_2O_8$ was first reported by Mokhosoev et al. [13]. Its appearance and crystal growth occurred at 600–820 °C according to the temperature regions of phase crystallization in the system Li_2O-Al_2O_3-WO_3 [14]. Still now, there are no reports on the microwave dielectric properties of it. In this work, a new microwave dielectric ceramic $LiAlW_2O_8$ was prepared at low temperature (740–800 °C) exhibiting a near-zero τ_f value of −5.3 ppm/°C. The sintering behavior, crystal phase, microstructure, and microwave dielectric properties of the material were investigated.

2. Experimental procedure

The $LiAlW_2O_8$ ceramics were prepared by a conventional solid state reaction method from the oxide powders of Li_2CO_3 (99.99%), Al_2O_3 (99.99%), and WO_3 (99%). Stoichiometric proportions of raw materials were mixed in alcohol medium using zirconia balls for 12 h. The mixtures were dried and calcined at 700 °C for 2 h. The calcined powders were reground by ball milling for 12 h, dried, mixed with 3 wt% PVA binder, and pressed under the pressure of about 200 MPa into disks measuring 11 mm in diameter and 6 mm in thickness. The ceramic pellets were sintered at 740–800 °C for 4 h in air. The crystal structures of the specimens were analyzed by an X-ray diffractometer (Rigaku D/MAX-2400, Japan) with CuKa radiation. The microstructure of pellets was investigated using a scanning electron microscope (SEM, Fei Quanta 200, Eindhoven, Holland). The bulk densities of the sintered samples were measured by the Archimedes method. The microwave dielectric properties of sintered samples were measured using a network analysis (ZVB20, Rohde & Schwarz, Munich, Germany) with the $TE_{01\delta}$ cavity method. The temperature coefficients of the resonant frequency of the specimens were measured in the temperature

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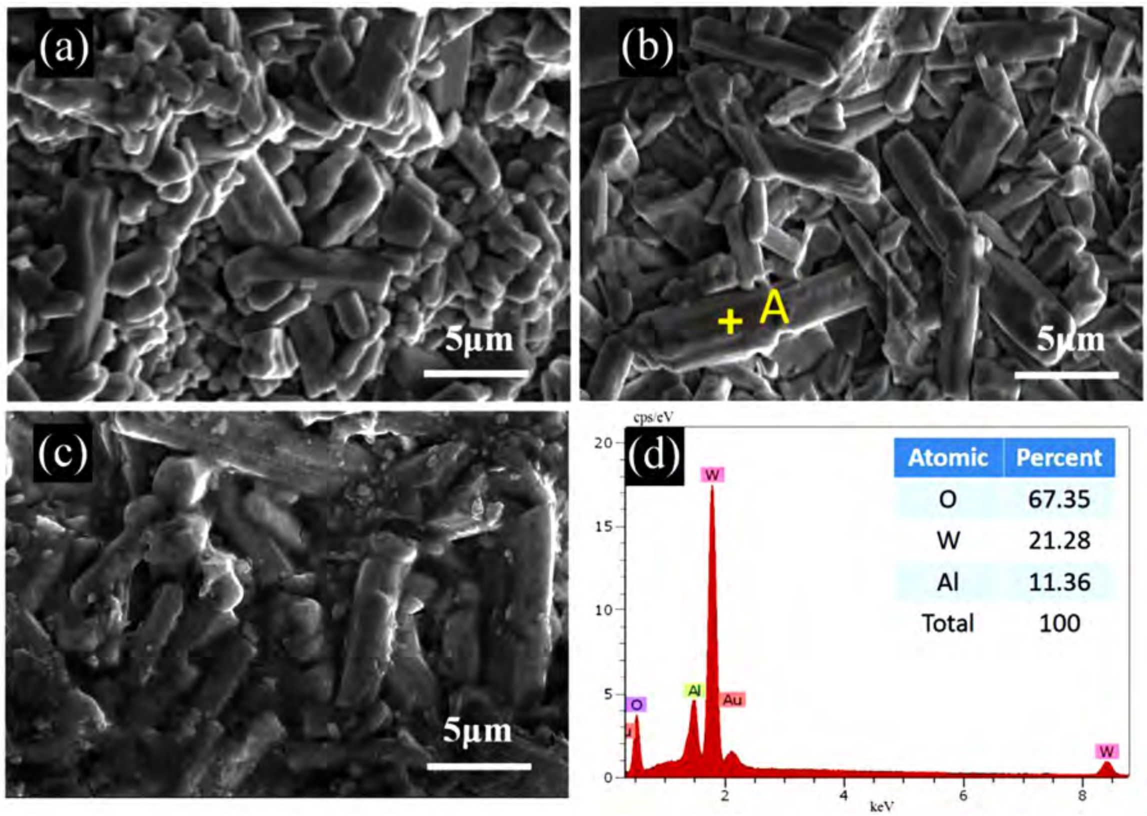

Fig. 2. SEM micrographs of $LiAlW_2O_8$ ceramics sintered at (a) 740 °C, (b) 780 °C, (c) 800 °C for 4 h, and (d) EDS spectra of spot A.

range 25–80 °C.

3. Results and discussion

Fig. 1 shows the XRD patterns of $LiAlW_2O_8$ powder calcined at 700 °C for 2 h and ceramic sintered at 780 °C for 4 h. The obtained patterns closely match with that of double tungstate $LiAlW_2O_8$ (PDF#28–0025) considered to be monoclinic. In addition, small amounts of unknown impurity phase was detected from the XRD patterns, which is consistent with the results reported by Lee et al. [15].

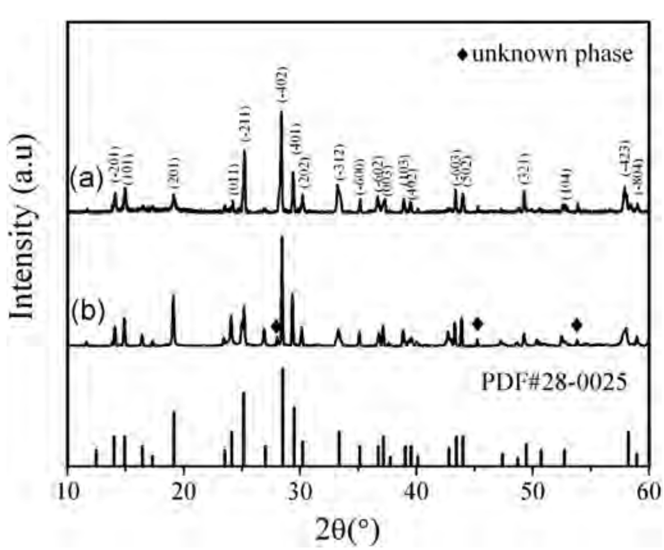

Fig. 1. XRD patterns of $LiAlW_2O_8$ (a) powder calcined at 700 °C for 2 h and (b) ceramic sintered at 780 °C for 4 h.

Fig. 2(a)–(c) presents the surface SEM images of $LiAlW_2O_8$ ceramics sintered at different temperatures. All samples have a similar morphology which consists of rod-shaped grains. The microstructure with some pores existing could be observed sintered at 740 °C for 4 h. With increasing temperature to 780 °C, the pores decreased and the grain sizes enlarged with a diameter of 1–3 μm and a length of 3–6 μm. However, when the sintering temperature reached 800 °C, some grains began to melt and the excess grain growth was observed. Fig. 2(d) shows the energy dispersive spectroscopy (EDS) analysis of spot A. Al and W elements were detected at a ratio of ~1:2, which confirms the $LiAlW_2O_8$ phase.

Fig. 3 illustrates the bulk density and relative density of $LiAlW_2O_8$ ceramics as a function of sintering temperature. The theoretical density calculated by the aid of XRD analysis software.

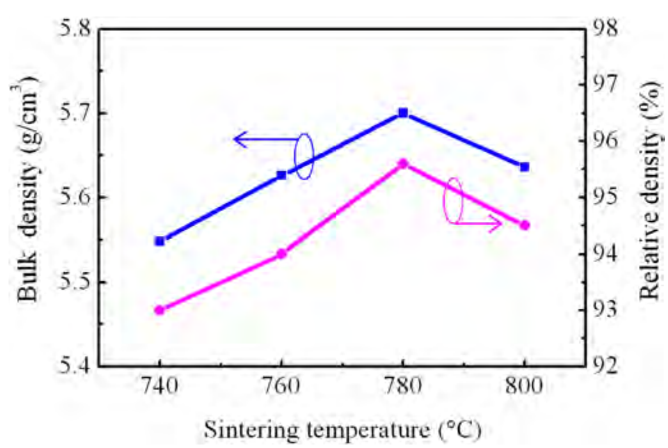

Fig. 3. Bulk density and relative density of $LiAlW_2O_8$ ceramics as a function of sintering temperature.

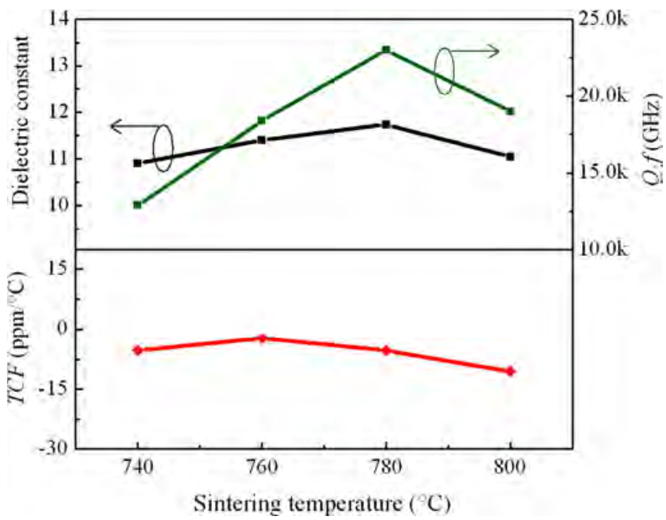

Fig. 4. Permittivity (ε_r), $Q\times f$ and τ_f values of $LiAlW_2O_8$ ceramics as a function of sintering temperature.

It can be seen that as the sintering temperature increases from 740 °C to 800 °C, the densities of samples firstly increased and reached to a maximum value of 5.7 g/cm^3 (95.6% theoretical density) at 780 °C for 4 h. After then, it slightly decreased with further increasing of the sintering temperature, which may be attributed to over-burning and abnormal grain growth. Therefore, the optimum sintering temperature of $LiAlW_2O_8$ ceramics was considered to be 780 °C.

Fig. 4 exhibits the microwave dielectric properties of $LiAlW_2O_8$ ceramics sintered at different temperatures for 4 h. The ε_r is dependent on the relative density, dielectric polarizabilities, and structural characteristics such as grain boundaries, phase composition, and compositional homogeneity [16]. In this study, the ε_r values versus sintering temperature of $LiAlW_2O_8$ ceramics showed a similar trend with that between bulk density and sintering temperature. Considering the Clausius-Mosotti relation [17], the value of theoretical permittivity was calculated to be 7.8, smaller than the measured value of 11.7. With the increase of sintering temperature, the $Q\times f$ increased to a maximum value of 23,000 GHz at 780 °C and decreased thereafter probably owing to the abnormal grain growth. The temperature coefficient of resonant frequency (τ_f) is related to the composition, the additives, and the second phase of the material [18]. The τ_f values of $LiAlW_2O_8$ ceramics did not change remarkably with increasing sintering temperature and remained stable at about -2.2 ppm/°C to -10.5 ppm/°C, because no additives and significant compositional change was observed. Compared with other $LiMW_2O_8$ (M=Y, Nd, Sm, Bi) ceramics [9–12], in addition to the ultra-low sintering temperature, $LiAlW_2O_8$ ceramics exhibited near-zero temperature coefficient of resonant frequency (τ_f).

4. Conclusions

$LiAlW_2O_8$ ceramics were prepared by a solid state reaction method within a low temperature range from 740 °C to 800 °C for 4 h in air. When sintered at 780 °C, the new dielectric ceramic could be well densified and exhibited good microwave dielectric properties: $\varepsilon_r=11.7$, $Q\times f=23{,}000$ GHz (at 9.0 GHz) and $\tau_f=-5.3$ ppm/°C. This novel temperature stable material is an attractive candidate of low-firing microwave dielectrics application.

Acknowledgments

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