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Low-temperature sintering and microwave dielectric properties of LiF-doped $Ba(Mg_{1/2}W_{1/2})O_3$–TiO_2 ceramics

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ABSTRACT

The $Ba(Mg_{1/2}W_{1/2})O_3$ (BMW)–x wt% LiF (x = 2.0, 4.0, 6.0, 8.0) ceramics were prepared by a conventional solid-state route. The effects of LiF addition on the sinterability, crystal structure, microstructures and microwave dielectric properties of BMW ceramics were investigated. With an amount of LiF addition, the sintering temperature of the ceramics was reduced to below 960 °C from 1550 °C without degradation of microwave dielectric properties, due to the enhancement of the apparent density at low temperature by liquid phase sintering. On this basis, TiO_2 was used to adjust the temperature coefficient of resonant frequency, optimized microwave dielectric properties with $\varepsilon_r = 20$, $Q\times f = 48{,}000$ GHz, and $\tau_f = 1.2$ ppm/°C for 0.96 BMW–0.04 TiO_2–4.0 wt% LiF composition. With low sintering temperature and good dielectric properties, these LiF-doped ceramics are promising materials for LTCC integration applications.

1. Introduction

With the development of modern communication technology, low-temperature co-fired ceramics (LTCC) has been generating considerable interest due to the benefits offered for the fabrication of miniature multilayer devices [1]. LTCC materials are required to have a sintering temperature below 960 °C, suitable permittivity (ε_r) (in the range of 4–100), high quality factor ($Q\times f > 1000$ GHz) for better selectivity and near-zero temperature coefficient of resonant frequency (τ_f) for stability [2–4].

Microwave dielectric properties of several 1:1 ordered compounds with the general formula $A(B'_{1/2}B''_{1/2})O_3$ (A = Ba, Sr, Ca; B' = La, Nd, Sm, Yb; B" = Ta, Nb) have been investigated by several authors [5]. Khalyavin et al. investigated the microstructure and microwave dielectric properties of ε_r = 15–17.6, $Q\times f$ = 45,200–57,300 GHz, and $\tau_f = -25$ ppm/°C for BMW [6]. In addition, a $BaWO_4$ secondary phase was also found due to the decomposition of BMW. Much attention had been attracted to study the sinterability by various A- or B-site ionic substitution, for instance, $Ba_{1-3x/2}La_x(Mg_{1/2}W_{1/2})O_3$ [7], $Ba_2Mg_{1-x}Ca_xWO_6$ [8] and $(1-x)Ba(Mg_{1/2}W_{1/2})O_{3-x}Ba(RE_{2/3}W_{1/3})O_3$ [9]. Wu et al. reported the effect of nonstoichiometry on microstructure of BMW ceramics, greatly improved the $Q\times f$ value to 140,000 GHz for the Ba-deficient or W-excessive samples [10]. However, their sintering temperatures all about 1500 °C–1600 °C were too high to be used in the LTCC multilayer devices.

In general, adding glasses with low melting point is an effective, low cost approach to lower the densification temperature of ceramics [11]. It is well known that LiF addition often makes it possible to decrease the sintering temperature of perovskite materials [12]. Therefore, in this work, LiF addition was used to lower the sintering temperature of BMW ceramics and TiO_2 (ε_r ~ 105, $Q\times f$ ~ 46,000 GHz, and τ_f ~ +465 ppm/°C [13]) was used to adjust the temperature coefficient of resonant frequency. The influences of LiF and TiO_2 on the sintering behavior, microstructure, and microwave dielectric properties of BMW ceramics were investigated.

2. Experimental procedure

The ceramics were prepared by conventional solid state reaction method from the powders of $BaCO_3$ (99%), MgO (99.99%), WO_3 (99%), LiF (99%) and TiO_2 (99%, 80 nm). Predried raw materials were weighed in stoichiometric $Ba(Mg_{1/2}W_{1/2})O_3$ and mixed in alcohol medium using zirconia balls for 8 h. The mixtures were dried and calcined at 1200 °C for 2 h. The calcined powders were reground by ball milling with various LiF–TiO_2 additions for 8 h, After drying, the powders added with PVA organic binder (5 wt%) were palletized into cylindrical compacts of 11.5 mm in diameter and 5–7 mm in thickness under uniaxial pressure of 200 MPa. The ceramic pellets were sintered at 900 °C–1000 °C for 6 h in air. The crystal

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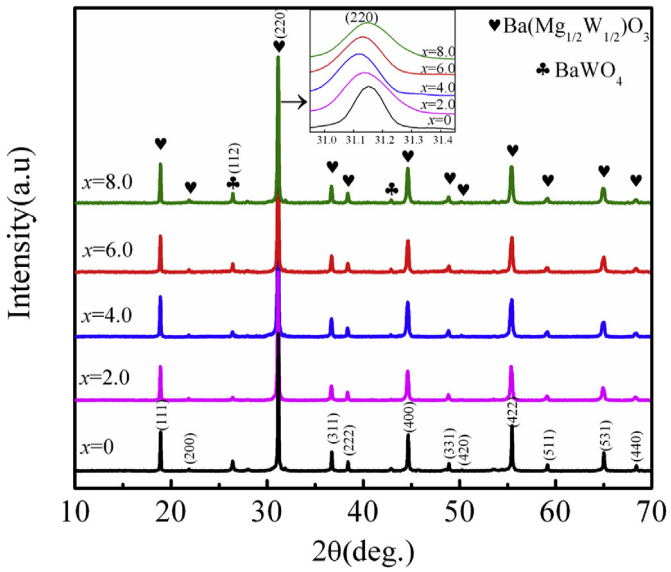

Fig. 1. Powder XRD patterns of $Ba(Mg_{1/2}W_{1/2})O_3$ ceramic sintered at 1550 °C and $Ba(Mg_{1/2}W_{1/2})O_3$–x wt% LiF ceramics sintered at 950 °C for 6 h.

structures of the specimens were analyzed by an X-ray diffractometer (XRD, Rigaku D/MAX-2400, Japan) with Cu*K*a radiation generated at 40 kV and 100 mA. The microstructure of pellets was investigated using a scanning electron microscope (SEM, Fei Nova 650, Hillsboro, US) coupled with energy dispersive spectrometer (EDS). 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 coefficient of resonant frequency (τ_f) was calculated with the following equation:

$$\tau_f = \frac{f_{80} - f_{20}}{f_{20} \times (80 - 20)}$$

where f_{80} and f_{20} are the resonant frequency at 80 °C and 20 °C, respectively.

3. Results and discussion

3.1. BMW–LiF system

Fig. 1 shows the powder XRD patterns of BMW ceramic sintered

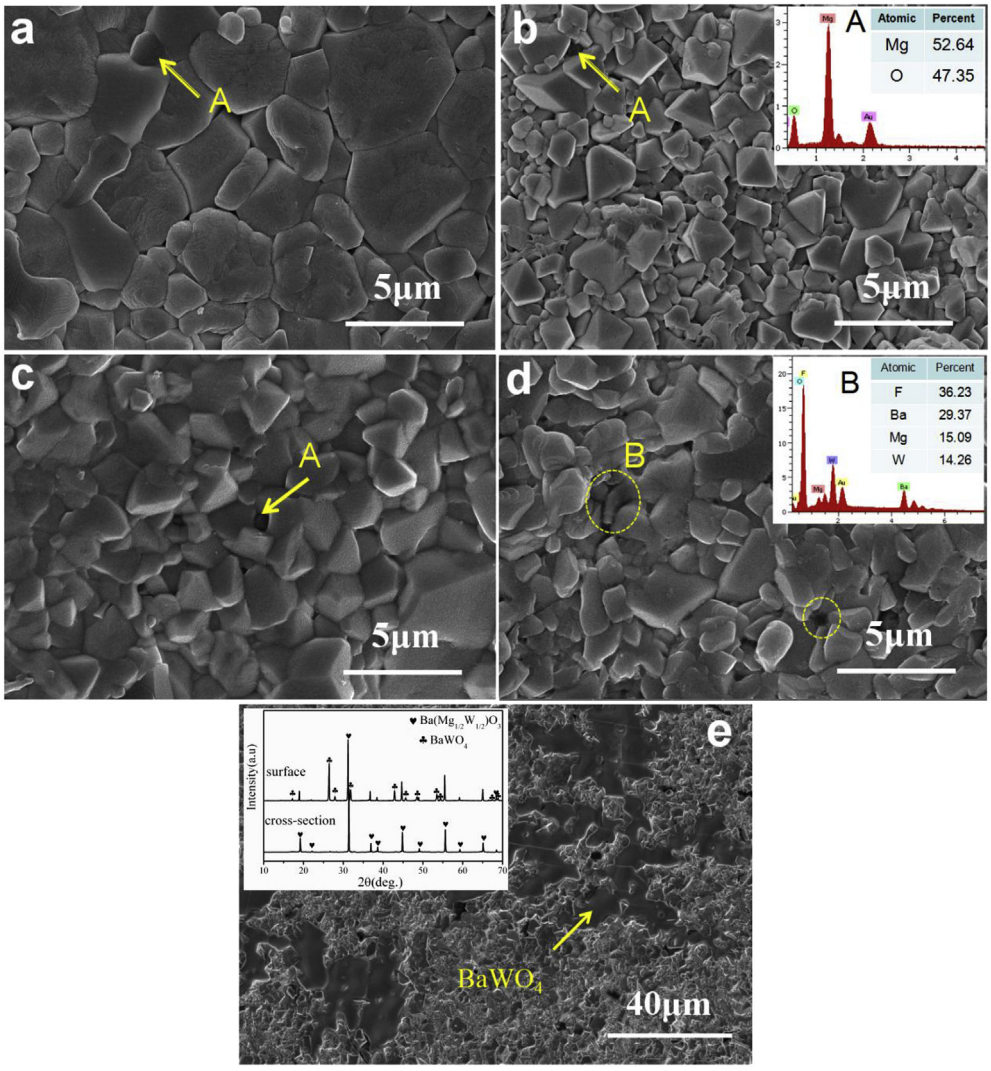

Fig. 2. SEM micrographs of polished and etched cross-section of $Ba(Mg_{1/2}W_{1/2})O_3$–x wt% LiF (a) $x = 0$, 1550 °C, (b) $x = 2.0$, 950 °C (c) $x = 4.0$, 950 °C (d) $x = 8.0$, 950 °C and (e) surface of $x = 8.0$.