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Influence of Mg^{2+} substitution on the crystal structure and microwave dielectric properties of $ZnZrNb_2O_8$ ceramics

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ABSTRACT

Wolframite-structured $Zn_{1-x}Mg_xZrNb_2O_8$ ($0 \le x \le 0.1$) ceramics were synthesized by the conventional solid-state method. The effects of Mg^{2+} substitution on the sinter ability, crystal structures and microwave dielectric properties were systematically investigated. The $Q{\cdot}f$ values increased from 46,800 GHz to 53,400 GHz when the x value increased from 0 to 0.1. Based on the complex chemical bond theory, the intrinsic parameters were calculated to analyze the mechanism of dielectric loss in $Zn_{0.9}Mg_{0.1}ZrNb_2O_8$. The total lattice energy and bond energy of the $Zn_{0.9}Mg_{0.1}ZrNb_2O_8$ were higher than that of $ZnZrNb_2O_8$, which was corresponding with the decrease of dielectric loss in the wolframite-structured compounds. The dielectric constant (ε_r) and temperature coefficient of resonant frequency (τ_f) of $Zn_{1-x}Mg_xZrNb_2O_8$ ceramics were also heavily influenced by the addition of Mg^{2+}. Typically, the dense $Zn_{0.9}Mg_{0.1}ZrNb_2O_8$ ceramics sintered at 1200 °C exhibited excellent microwave dielectric properties with $\varepsilon_r = 27.82$, $Q{\cdot}f = 53{,}400$ GHz and $\tau_f = -45.82$ ppm/°C.

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1. Introduction

Microwave dielectric materials have attracted increasing interest because of the wide range of applications in mobile and satellite communications. Specifically, they have been investigated as various components for wireless communications, including duplexers, resonators, antennas and oscillators. In order to meet the requirements of low-loss wireless communication, many high-Q materials are used for dielectric substrate, filter and some wireless devices. From the point of view of the practical use, the materials should also possess higher dielectric constant and near-zero temperature coefficient of resonant frequency [1–4].

Recently, the wolframite-structured $ZnZrNb_2O_8$ ceramics have attracted great attentions for their higher $Q{\cdot}f$ values [5–11]. For instance, Liao et al. firstly reported that the $ZnZrNb_2O_8$ ceramics exhibited microwave dielectric properties with $\varepsilon_r = 30$, $Q{\cdot}f = 61{,}000$ GHz and $\tau_f = -52$ ppm/°C [5]. Tang et al. lowered the sintering temperature of the ceramics by adding 3 wt% low-melting glass of $BaCu(B_2O_5)$. A good combination of microwave dielectric properties of $\varepsilon_r = 28.4$, $Q{\cdot}f = 56{,}720$ GHz and $\tau_f = -53$ ppm/°C was obtained at 950 °C, which met the requirements of LTCC [6]. The compounds were successfully synthesized by the reaction sintering method with $\varepsilon_r \sim 28.5$, $Q{\cdot}f \sim 60{,}000$–$80{,}000$ GHz and $\tau_f > -50$ ppm/°C, which made $ZnZrNb_2O_8$ ceramics possible for practical applications [7,8]. Ionic substitution is an effective way to investigate crystal structure and improve microwave dielectric properties of matrix compounds. For instance, Li et al. reported the effects of A-site ions substitution on the microwave dielectric properties of $ZnZrNb_2O_8$ ceramics. The $Q{\cdot}f$ value of $Zn_{0.95}Mg_{0.05}ZrNb_2O_8$ ceramics sintered at 1280 °C was 81,128 GHz, which was higher than that of $ZnZrNb_2O_8$ synthesized in the same condition (61,130 GHz) [9]. Ionic radius of Mg^{2+} (0.72 Å) is similar with that of Zn^{2+} (0.74 Å) and the difference between two radii is less than 15%. In our previous reports, the $MgZrNb_2O_8$ ceramics showed the same structure as $ZnZrNb_2O_8$ [10–12]. Thus, the Mg^{2+} substitution is a suitable approach for the improvement on the dielectric loss of the matrix compounds. However, there are few report on investigating the relationship between Mg^{2+} content and microwave dielectric properties in $Zn_{1-x}Mg_xZrNb_2O_8$. In addition, it is necessary to focus on further research on the structure-property relationship of the wolframite-structured compounds.

In this work, a series of $Zn_{1-x}Mg_xZrNb_2O_8$ ($0 \le x \le 0.1$) ceramics were synthesized by the conventional solid-state method. The sintering behaviors, microstructures, phase composition and microwave dielectric properties were studied in detail. Rietveld refinement was used to analyze the structure of the crystalline phase. Based on the cell parameters and the complex chemical

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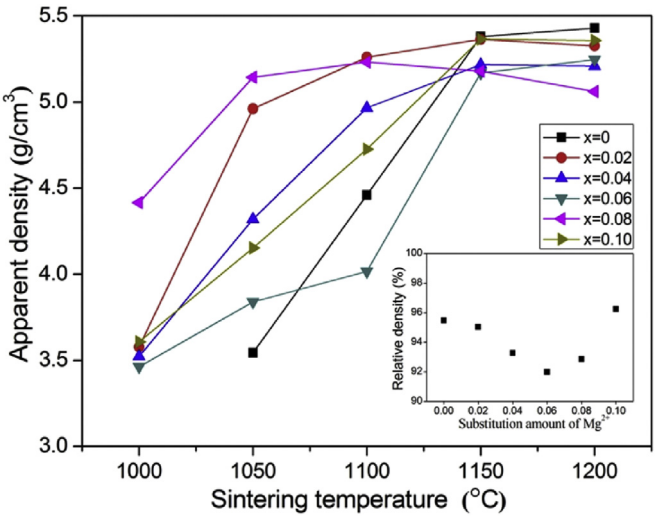

Fig. 1. The apparent density of the $Zn_{1-x}Mg_xZrNb_2O_8$ ceramics sintered at different temperatures and relative densities of ceramics sintered at 1200 °C.

bond theory, the lattice energy and bond energy were calculated to evaluate the structural stability of $ZnZrNb_2O_8$ and $Zn_{0.9}Mg_{0.1}ZrNb_2O_8$ ceramics.

2. Experimental procedure

Polycrystalline specimens of $Zn_{1-x}Mg_xZrNb_2O_8$ ($0 \leq x \leq 0.1$) were prepared via the conventional solid-state method. Proportionate amounts of the starting materials (analytical-grade ZnO, MgO, ZrO_2 and Nb_2O_5; Aladdin Shanghai Biochemical Technology Co., Ltd. Shanghai, China) were collected in an ethanol container with ZrO_2 balls. The powders were milled for 4 h with distilled water, dried and calcined at 1050 °C for 2 h in alumina crucibles. The obtained powders were reground for another 4 h, dried and mixed with 8 wt% polyvinyl alcohol as a binder. The granulated powders were pressed into cylinders of 10 mm diameter and about 6 mm height at a pressure of 200 MPa. The resultant cylinders were preheated at 500 °C for 4 h to expel the binder and sintered at 1000–1200 °C for 4 h in air at a heating rate of 5 °C/min.

Phase analysis of samples was conducted with the help of a Rigaku diffractometer (Model D/MAX-B, Rigaku Co., Japan) using Ni filtered CuKα radiation (λ = 0.1542 nm) at 40 kV and 40 mA settings. The morphology on the surface of sintered samples was examined using a scanning electron microscopy (Model FEG250, FEI Co., America). The apparent densities of the sintered samples were measured using the Archimedes method (Mettler ToledoXS64). A network analyzer (N5234A, Agilent Co., America) was used for the measurement of microwave dielectric properties. Dielectric constants were measured using Hakki-Coleman post-resonator method by exciting the TE011 resonant mode of dielectric resonator by using an electric probe as suggested by Hakki and Coleman [13]. Unloaded quality factors were measured using TE01d mode by the cavity method [14]. All measurements were made at room temperature and in the frequency of 8–12 GHz. The temperature coefficient of the resonant frequency (τ_f) was calculated from data collected in the temperature range of 25–85 °C according to $\tau_f = \Delta f/(f_0 \Delta T)$, where f_0 was the frequency at 25 °C.

3. Results and discussion

The relationship between apparent densities and sintering temperatures of $Zn_{1-x}Mg_xZrNb_2O_8$ ceramics was presented in Fig. 1, through which the optimized sintering temperature could be determined. As shown in Fig. 1, the apparent densities of the specimens gradually increased with the sintering temperature and obtained the maximum values in the temperature region of 1150–1200 °C. The scatter plot of relative density of $Zn_{1-x}Mg_xZrNb_2O_8$ ceramics sintered at 1200 °C was shown in the inset of Fig. 1. It could be observed that the relative density linearly decreased from 95.6% to 92.1% as the x value increased from 0 to 0.06 and then increased up to 94.4% for $Zn_{0.9}Mg_{0.1}ZrNb_2O_8$. The apparent density obtained in our previous work (5.41 g/cm^3, 94.1% of their theoretical density) was close to that of all the $Zn_{1-x}Mg_xZrNb_2O_8$ ceramics sintered at 1200 °C in the present work [10], which indicated that the $Zn_{1-x}Mg_xZrNb_2O_8$ ceramics could be obtained at 1200 °C with nearly full density. As representative SEM micrographs of $Zn_{0.98}Mg_{0.02}ZrNb_2O_8$ and $Zn_{0.92}Mg_{0.08}ZrNb_2O_8$ ceramics sintered at 1200 °C were chosen as examples and shown in Fig. 2. Dense and homogeneous microstructures with almost no pores were revealed in these compositions.

X-ray diffraction patterns of $Zn_{1-x}Mg_xZrNb_2O_8$ ($0 \leq x \leq 0.1$) ceramics sintered at 1200 °C were shown in Fig. 3. All diffraction peaks of compositions could be indexed with a monoclinic cell in the space group of p2/c, which matched well with JCPDS file No. 48-0324. There were no significant changes in peak positions as Mg^{2+} content increasing, reflecting the similar radius between Mg^{2+} (0.72 Å) and Zn^{2+} (0.74 Å). In order to characterize the crystal

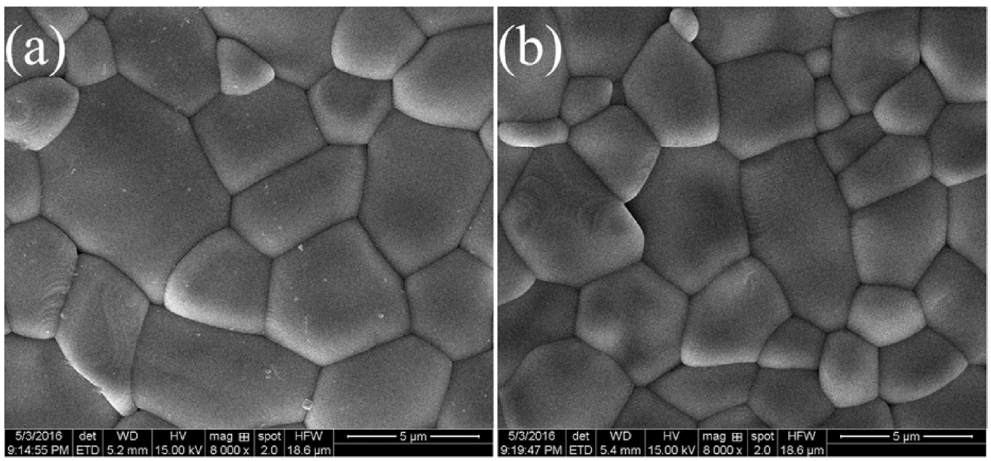

Fig. 2. SEM micrographs of ceramics sintered at 1200 °C (a) $Zn_{0.98}Mg_{0.02}ZrNb_2O_8$ and (b) $Zn_{0.92}Mg_{0.08}ZrNb_2O_8$ as representative.

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