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Microwave dielectric properties of ultra-low loss $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ ceramics sintered at low temperature by LiF addition

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ABSTRACT

In this work, ultra-low loss $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ ceramics were successfully prepared via the conventional solid-state method. X-ray photoelectron spectroscopy (XPS), thermally stimulated depolarization current (TSDC) and bond energy were used to determine the distinction between intrinsic and extrinsic dielectric loss in $(Mg_{1/3}Nb_{2/3})^{4+}$ ions substituted ceramics. The addition of $(Mg_{1/3}Nb_{2/3})^{4+}$ ions enhances the bond energy in unit cell without changing the crystal structure of Li_2MgTiO_4, which results in high $Q{\cdot}f$ value as an intrinsic factor. The extrinsic factors such as porosity and grain size influence the dielectric loss at lower sintering temperature, while the oxygen vacancies play dominant role when the ceramics densified at 1400 °C. The $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ ceramics sintered at 1400 °C can achieve an excellent combination of microwave dielectric properties: ε_r = 16.19, $Q{\cdot}f$ = 160,000 GHz and τ_f = −3.14 ppm/°C. In addition, a certain amount of LiF can effectively lower the sintering temperature of the matrix, and the $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$-3 wt% LiF ceramics sintered at 1100 °C possess balanced properties with ε_r = 16.32, $Q{\cdot}f$ = 145,384 GHz and τ_f = −16.33 ppm/°C.

1. Introduction

Microwave dielectric ceramic or even films is a kind of material that operates in millimeter wave frequency range, which plays an essential role in the explosive growth of wireless communication. For the ceramics used as substrates in base station applications, higher $Q{\cdot}f$ values are required to reduce attenuation under signal processing. To meet the demand for microwave integrated devices, these materials are required to be sintered at lower temperatures for industrial production. In addition, an appropriate dielectric constant (ε_r) and a near-zero temperature coefficient of resonant frequency (τ_f) are also necessary for faster and stable signal transmission [1–3].

Nowadays, some microwave dielectric ceramics have been reported with low loss, but exploration of novel low temperature sintering and high $Q{\cdot}f$ values compounds is still ongoing [4–7]. Among several kinds of ceramic systems, the rock salt structured Li_2O-MgO-TiO_2 ternary system has attracted extensive attentions because of their stable crystal structure and excellent microwave dielectric properties [8–18]. However, the potential commercial applications for these ceramics are limited by their higher sintering temperatures as well as unbalanced comprehensive performances. Zhou et al. synthesized the $Mg_{1-x}Li_{2x}Ti_xO_{1+2\times}$ ceramics according to the partial subsolidus phase diagram reported by A.R. West, and a good combination of ε_r = 16.20, $Q{\cdot}f$ = 90,902 GHz and τ_f = −24.5 ppm/°C was found in Li_2MgTiO_4 ceramics at x = 1/2 [8,9]. In our previous works, similar results could be also testified in atmosphere-protective sintered (1-x)Li_2TiO_3-xMgO system. The Li_2MgTiO_4 ceramics sintered at 1350 °C possessed balance properties (ε_r = 15.07, $Q{\cdot}f$ = 97,629 GHz, τ_f = −3.81 ppm/°C), while the relatively low $Q{\cdot}f$ values in comparison with those of Mg-rich compounds such as $Li_6Mg_7Ti_3O_{16}$ ($Q{\cdot}f$ = 209,400 GHz, 1550 °C) and $Li_2Mg_4TiO_7$ ($Q{\cdot}f$ = 233,600 GHz, 1600 °C) [13–15]. Hence, it is meaningful to further optimize the dielectric loss in Li_2MgTiO_4 without deterioration of other properties. It has been testified that the isovalent substitution of combinations of aliovalent cations is an effective method in increasing $Q{\cdot}f$ values for dielectric materials [16–18]. For instance, the substitution of $(Mg_{1/3}Ta_{2/3})^{4+}$ for Ti^{4+} enhanced the $Q{\cdot}f$ values in Li_2MgTiO_4, and best microwave dielectric properties with ε_r = 15.73, $Q{\cdot}f$ = 184,000 GHz and τ_f = −12.54 ppm/°C were obtained in atmosphere-protective sintered $Li_2MgTi_{0.6}(Mg_{1/3}Ta_{2/3})_{0.4}O_4$ ceramics at 1500 °C. The addition of Mg^{2+} might decrease the intrinsic loss in Li_2MgTiO_4, while the higher polarizability of Ta^{5+} (4.73 Å^3) in comparison with Ti^{4+} (2.93 Å^3) might keep the permittivity unchanged [18]. However, there are few reports concerning the distinction between intrinsic and extrinsic losses in Li_2MgTiO_4 system, and the high sintering temperature still pose difficulties for industrial production. Therefore, it is essential to develop ultra-low loss Li_2MgTiO_4 based

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ceramics sintered at lower temperature. In addition, it has been reported that thermally stimulated depolarization current (TSDC) can be used to investigate the relaxation behavior of the typical microwave dielectric ceramic [19–21]. For instance, Zhang et al. reported that the significant thermally stimulated relaxation was observed in TSDC curves for $BaTi_4O_9$ and defect dipoles as well as oxygen vacancies were the main defect types in the $BaTi_4O_9$ ceramics [19].

In this work, Nb_2O_5 was used as alternative for Ta_2O_5 to reduce the cost of starting materials, and a novel $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ composition was chosen as an example from $Li_2MgTi_{1-x}(Mg_{1/3}Nb_{2/3})_xO_4$ ($0 \le x \le 0.5$) ceramics to optimize the *Q·f* values in Li_2MgTiO_4 [22]. X-ray photoelectron spectroscopy (XPS), thermally stimulated depolarization current and bond energy were adapted for $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ ceramics to analyze the dielectric loss. Besides, different weight percentages of lithium fluoride (LiF) were used as sintering aids to lower the sintering temperatures, and the relationship between microwave dielectric properties and LiF content was investigated.

2. Experimental procedure

High purity Li_2CO_3, MgO, TiO_2 and Nb_2O_5 powders (Aladdin Shanghai Biochemical Technology Co., Ltd. Shanghai, China) were mixed according to the stoichiometry of $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$. At the first stage, the starting powders were milled for 24 h with anhydrous ethanol, dried and calcined at 1050 °C for 2 h in alumina crucibles. Then, the calcined powders were ground for another 24 h, dried and mixed with 8 wt% polyvinyl alcohol for granulation. In order to lower sintering temperature, 1–5 wt% LiF were added in the matrix powders before the reground process. Thereafter, all the granulated powders were pressed into pellets (10 mm diameter, 6 mm height) under an axial pressure of 200 MPa and preheated at 500 °C for 4 h to expel the polyvinyl alcohol. In order to suppress the lithium evaporation at higher sintering temperature, the matrix samples were buried with sacrificial powders and sintered at 1300–1500 °C for 6 h in platinum crucibles. On the contrary, those LiF added samples were sintered at 850–1100 °C under air atmosphere.

The apparent density of the sintered pellets was measured using the Archimedes method (XS64, Mettler Toledo, USA). The crystal structure of $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ was examined by an X-ray diffractometer (Model D/MAX-B, Rigaku Co., Japan). The surface morphology of the sintered samples was characterized by a field-emission-scanning electron microscope (FeSEM Quanta 250, FEI Co., USA). XPS measurements were measured with the ESCALAB 250 XI system using AlKa radiation to obtain information on the chemical binding energy in samples. For TSDC measurements, the silver electrodes covered sample sheets were firstly polarized under an electric field of 85 V/mm in the temperature range of 100–225 °C for 10 min. Thereafter, these samples were locked to the starting temperature of −80 °C and depolarized for 10 min. Finally, the released currents were recorded by a pA meter under the heating rate of 5 °C/min (6517B, Keithley, Cleveland, Ohio, USA), and the temperature-dependent measurements were measured by a quatro temperature controller (Novocontrol, Montabaur Germany). A network analyzer (N5234A, Agilent Co., America) was used for measuring microwave dielectric properties. The dielectric constant was 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 [23]. The unloaded quality factor was measured using TE01d mode by the cavity method [24]. The temperature coefficients of resonant frequency of the samples were measured in the temperature range of 25–85 °C.

3. Results and discussion

Fig. 1 demonstrates the apparent density and diametric shrinkage ratio of $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ ceramics sintered at different temperatures. As the sintering temperature increases from 1300 °C to 1500 °C, the shrinkage ratio increases from 8.39% to 11.79% and the apparent density shows similar tendency with saturated values around 3.2 g/cm^3. The maximum density of $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ sample is higher than that of Li_2MgTiO_4 (< 3.0 g/cm^3 at 1350 °C) reported in our previous work [13], which is mainly caused by the higher atomic mass of $(Mg_{1/3}Nb_{2/3})^{4+}$ (70.04) in comparison with that of Ti^{4+} (47.87). Besides, the densification temperature increases from 1350 °C to 1400 °C with the addition of multi-ions, implying that the MgO might hinder the densification process.

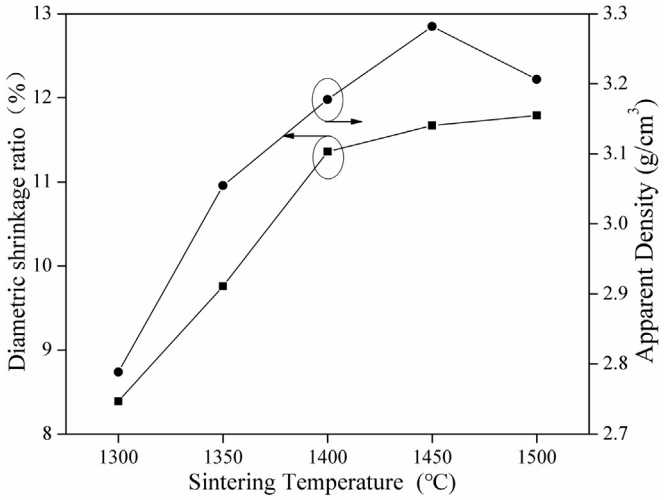

Fig. 1. Apparent density and diametric shrinkage ratio of $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ ceramics sintered from 1300 to 1500 °C.

SEM micrograph of $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ sintered at 1400 °C is illustrated in Fig. 2. Well-developed microstructure with closely-packed grains and discernable grain boundaries can be observed, which indicates that compact $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ compounds can be obtained at 1400 °C. EDS analysis about the point chosen randomly from the grains in SEM micrograph is also shown in Fig. 2. Because the beryllium window tube of detector absorbs X-ray on lightweight elements, the Li element in the ceramics cannot be detected by the EDS analyzer, the Li element in the ceramics cannot be detected by the EDS analyzer. The detected atom ratio of Mg, Ti, Nb and O (19.49%, 13.19%, 2.11% and 61.81%) correspond with the theoretical values (18.33%, 11.67%, 3.33% and 66.67%), which indicates that the pure phase $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ ceramics can be formed at 1400 °C.

Fig. 3 shows the measured XRD patterns and the corresponding Rietveld refinement plots of $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ ceramic sintered at 1400 °C, through which the effects of $(Mg_{1/3}Nb_{2/3})^{4+}$ ions addition on the crystal structure of Li_2MgTiO_4 can be determined. Typical diffraction peaks such as (200) and (220) are indexed as the cubic rock-salt structured $LiFeO_2$ (JCPDS No. 70-2711) with no secondary phases being detected. Rietveld discrepancy factors R_p, R_{wp} and R_{exp} are 10.1%, 14.0% and 2.68%, respectively, which confirms the validity of matching models. Hence, it can be concluded that the substitution of complex ions doesn't significantly influence the crystal structure in the rock-salt structured Li_2MgTiO_4 ceramics. On the other hand, due to the fact that the ionic size of $(Mg_{1/3}Nb_{2/3})^{4+}$ (0.66 Å) is larger than that of Ti^{4+} (0.605 Å), the calculated lattice parameters of $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ (a = b = c = 4.1704 Å, V_m = 72.5326 Å^3) are higher than those of Li_2MgTiO_4 (a = b = c = 4.1583 Å, V_m = 71.9005 Å^3) reported in our previous work [13]. The bond lengths calculated by lattice parameters are shown in Table 1, which will be used to investigate the nature of bonding (bond energy) in the following section.

Curves of dielectric constant and quality factors of $Li_2MgTi_{0.7}(Mg_{1/3}Nb_{2/3})_{0.3}O_4$ ceramics sintered at different temperatures are illustrated in Fig. 4. The ε_r value linearly increases from 13.96 at 1300 °C to 16.19