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Crystal structure and enhanced microwave dielectric properties of non-stoichiometric $Li_3Mg_{2+x}NbO_6$ ceramics

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ABSTRACT

Non-stoichiometric $Li_3Mg_{2+x}NbO_6$ ceramics were prepared by the solid-state reaction process. The effects of additional magnesium contents on the microstructure, sintering behavior and dielectric performance of $Li_3Mg_{2+x}NbO_6$ ceramics were investigated systematically. XRD patterns and Rietveld refinement indicated that all of the samples exhibited a single-phase orthorhombic structure. The ε_r was dependent on the density and $Q \times f$ values were affected by the microstructure and density. Additionally, the τ_f values were related to the NbO_6 octahedron distortion. Remarkably, the $Li_3Mg_{2.04}NbO_6$ ceramics sintered at 1100 °C had outstanding microwave dielectric characteristics: ε_r = 16, $Q \times f$ = 140,000 GHz, τ_f = −5.6 ppm/°C, making these ceramics promising candidates for millimeter-wave applications.

1. Introduction

In recent decades, microwave dielectric materials have received more attention duo to the demand for the rapid development of advanced wireless communication systems, including Internet of things and mobile communication, which have expanded the carrier frequency to the millimeter-wave range for 5G applications [1,2]. Nowadays, microwave dielectric materials have been adopted as dielectric resonators (DR), capacitors, substrates, duplexers and filters to assume functions in microwave integrated circuits. To satisfy the demands of practical applications, the some extraordinarily significant characteristics possessed for microwave dielectric ceramics should be proposed: an appropriate dielectric constant to meet the requirements for size and sign delay, a high quality factor to suppresses signal attenuation and a near-zero temperature coefficient of resonant frequency to ensure the thermal stability [3]. Therefore, it is essential to modify or improve these properties by addition and substitution as well as explore and investigate new materials systems [4–6].

The lithium containing $Li_3Mg_2NbO_6$ ceramics have attracted considerable attentions duo to its excellent dielectric characteristics: ε_r = 16.8, $Q \times f$ = 79643 GHz, τ_f = −27.2 ppm/°C [7]. Afterwards, many methods have been employed to modify and enhance the microwave dielectric performance by addition and substitution. Wu et al. reported that the Co-modified $Li_3(Mg_{0.98}Co_{0.02})_2NbO_6$ ceramic had excellent microwave dielectric properties: ε_r = 15.22, $Q \times f$ = 127600 GHz, τ_f = −3.64 ppm/°C [8]. Alternatively, introducing non-stoichiometric composition has also been proposed to improve performance [9]. However, the effect of non-stoichiometry on $Li_3Mg_2NbO_6$ ceramics has not yet been reported.

In present work, non-stoichiometric $Li_3Mg_{2+x}NbO_6$ ceramics were synthesized through the solid-state reaction process. The effects of non-stoichiometric on the microstructure, sintering behavior, phase composition and microwave dielectric properties were studied in detail.

2. Experiment procedure

Non-stoichiometric $Li_3Mg_{2+x}NbO_6$ (x = 0, 0.02, 0.04, 0.06, 0.08) ceramics were synthetized by the solid-state reaction process using predecessors of MgO, Li_2CO_3, and Nb_2O_5 (all purity > 99%). The raw materials weighted by the stoichiometric ratio of $Li_3Mg_{2+x}NbO_6$ ceramics were ball-milled with distilled water for 4 h. The dried mixtures were sieved and calcined at 1000 °C for 4 h. Afterwards, the obtained powers were re-milling another 4 h and pressed into cylindrical disks (12 mm × 6 mm). The sample were sintered at 1050 °C, 1075 °C, 1100 °C, 1125 °C and 1150 °C for 4 h.

The crystalline phase was determined by X-ray diffraction (XRD: Model Miniflex 600, Rigaku Co., Japan). The apparent densities were measured by Archimedes method. The morphology,

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microstructure and grain sizes were analyzed by scanning electron microscope (JSM-6490, Japan). The microwave dielectric properties were measured with a network analyzer (Agilent N5230A, USA) and the temperature coefficient of resonant frequency (τ_f) could be calculated by $\tau_f = \Delta f/(f_0\Delta T)$.

3. Results and discussion

Fig. 1 demonstrates the XRD diffraction patterns of the non-stoichiometric $Li_3Mg_{2+x}NbO_6$ (x = 0, 0.02, 0.04, 0.06, 0.08) ceramics sintered at 1100 °C. The measured diffraction patterns of all samples could be indexed as a single orthorhombic structure $Li_3Mg_2NbO_6$ phase (JCPDS#86-0346). Besides, there existed no obvious second phase within the detection limit of the instrument. These results indicate that pure phase $Li_3Mg_2NbO_6$ ceramics could be synthesized throughout the entire composition range. Additionally, excessive MgO could not be observed as the second phase, which mismatch hypothetical result and kept inconsistent with previous literature [10]. The phenomenon may be attributed to the insufficient amount of MgO and forming of solid solutions. That is because $Li_3Mg_2NbO_6$ and MgO belong to syngony of rock salt structure phases and solid solutions are expected to form in $Li_3Mg_2NbO_6$ systems.

Fig. 2(a) shows the schematic diagram of the crystal structure for $Li_3Mg_2NbO_6$ ceramics. Li/Mg cations occupy 8b and 16g Wyckoff positions as well as Nb cations occupy 8a Wyckoff position. Li/Mg/Nb cations are octahedrally coordinated with six oxygen atoms [11]. Based on the crystal model, Rietveld refinements were conducted using GSAS suit with EXPGUI software. Fig. 2(b) exhibits the refinement pattern of $Li_3Mg_{2.04}NbO_6$ ceramics sintered at 1100 °C. The refined XRD diffraction patterns agreed well with the measured data and the positions of Bragg reflections were nearly consistent with the indexed peaks, indicating that pure-phase $Li_3Mg_2NbO_6$ ceramics are obtained. Table 1 shows the cells parameters and reality factors. The cells parameters of all the samples (x > 0) are larger than that of pure $Li_3Mg_2NbO_6$ ceramics and the cell parameters first increased and then decreased. The increased trend was attributed to interstice-occupied Mg and the decreased tendency relied on forming of solid solutions with smaller ionic size of Mg^{2+}(0.72 Å) compared with Li^+(0.76 Å).

Fig. 3 reveals the surface SEM micrographs of the $Li_3Mg_{2+x}NbO_6$ ceramics. As shown, all of the samples possessed clear grain boundaries and no obvious liquid phase existed. For x ≤ 0.04, the average gain size increased and dense microstructures with no

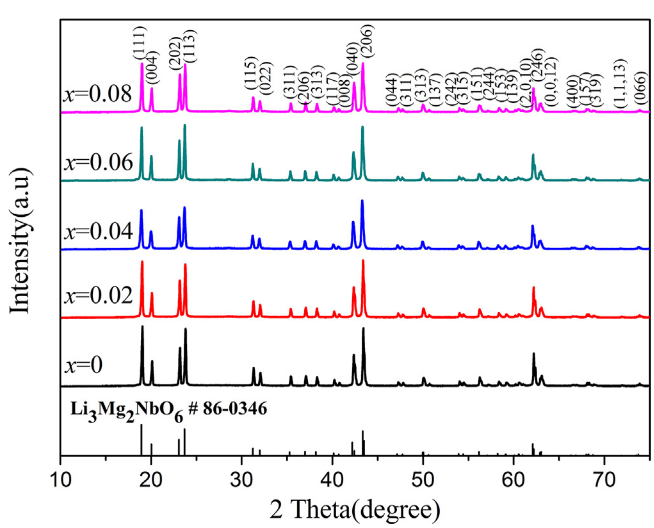

Fig. 1. XRD patterns of the $Li_3Mg_{2+x}NbO_6$ ceramics sintered at 1100 °C.

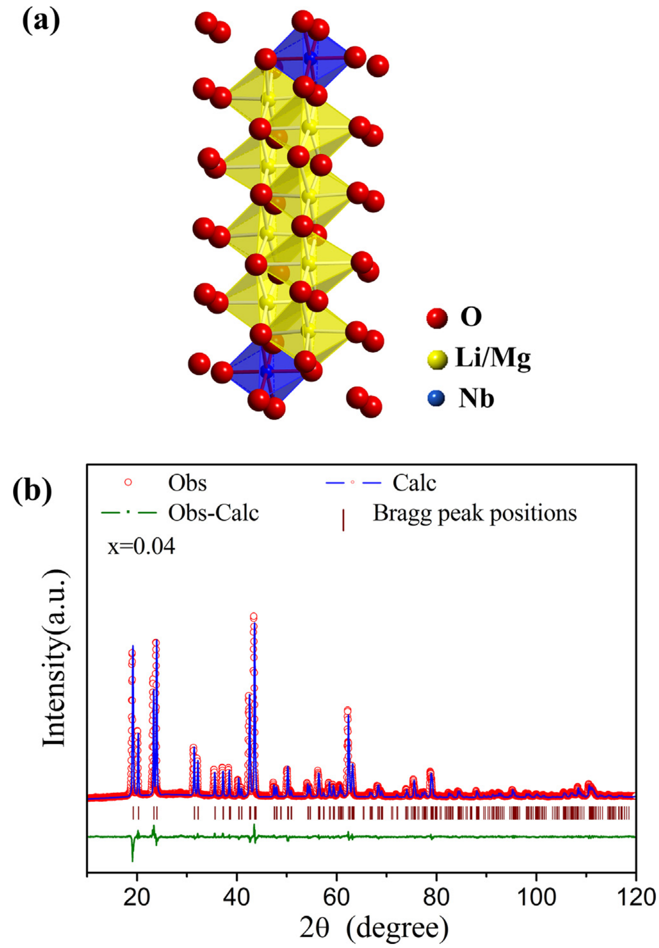

Fig. 2. Schematic diagram of the crystal structure and Rietveld refinement of the $Li_3Mg_{2+x}NbO_6$ ceramics with x = 0.04.

Table 1
The lattice parameters, unit cell volume and the reliability factors of $Li_{3+x}Mg_2NbO_6$ ceramics sintered at 1100 °C.

x	0	0.02	0.04	0.06	0.08
a(Å)	5.89685	5.90043	5.90571	5.90217	5.89906
b(Å)	8.54166	8.54722	8.55031	8.53905	8.53876
c(Å)	17.72513	17.723522	17.75068	17.7401	17.73115
V(Å^3)	892.795	894.427	896.333	894.080	893.130
R_p(%)	5.2	5.1	5.5	6.3	6.2
R_{wp}(%)	7.0	6.7	7.5	7.9	8.3
χ^2	2.2	2.4	2.9	3.3	3.6

visible pores could be observed. Particularly, the samples for x = 0.04 possessed a more dense and considerably homogeneous microstructures with larger grain size, indicating a higher $Q \times f$ values. As 006 ≤ x ≤ 0.08, nonuniform microstructures with abnormal grain growth and with pores were observed, thus deteriorating the microwave dielectric characteristics. In addition, the microstructures of x = 0.04 sintered at 1125 °C exhibited a nonuniform morphology with some relatively smaller grains as displayed in Fig. 3(f). These results indicate moderate amount of non-stoichiometric Li addition can promote the grain growth.

Fig. 4 displays the apparent density and microwave dielectric properties of the $Li_3Mg_{2+x}NbO_6$ ceramics. As shown in Fig. 4(a)–(b), Since the sintering temperature increased from 1050 °C to 1150 °C, the apparent density and dielectric constant (ε_r) first increased reaching a maximum approximately 1100 °C and then