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Microwave dielectric properties of low loss $Li_2(Mg_{0.95}A_{0.05})_3TiO_6(A = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+})$ ceramics system

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A B S T R A C T

Ultra low loss microwave dielectric materials of $Li_2(Mg_{0.95}A_{0.05})_3TiO_6(A = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+})$ ceramics were investigated through conventional solid-state reaction method. The effects of different bivalent $A^{2+}(A^{2+} = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+})$ substitution for Mg on the phase composition, microstructure and microwave dielectric properties were systematically discussed. The XRD patterns indicated that the main peaks belonged to $Li_2Mg_3TiO_6$, and little impurities were formed. We have found that Zn-substitution for Mg, which could increase its $Q \times f$ value and lower the $|\tau_f|$ compared to that of pure $Li_2Mg_3TiO_6$, had a significant effect on the $Q \times f$ and τ_f of the ceramics. $Li_2(Mg_{0.95}A_{0.05})_3TiO_6$ ceramics specimens with $A = Zn^{2+}$ sintered at 1275 °C for 6h exhibited excellent microwave dielectric properties of ε_r~14.6, $Q \times f$~158,000GHz (at 9.11GHz) and a near-zero τ_f~+3.2 ppm/°C.

1. Introduction

With the rapid development of mobile communications, microwave dielectric ceramics play an important role in multilayer or chip devices and attract much attention. These ceramics must fulfil a high quality factor ($Q \times f$), an appropriate dielectric constant (ε_r) and a near-zero temperature coefficient of resonant frequency (τ_f) [1,2]. However, many ceramics cannot meet these requirements simultaneously. Therefore, new material with excellent properties is still a hot issue for modern industry.

In previous works, the lithium based oxide ceramics such as $Li_2MgTi_3O_8$, Li_2MgTiO_4 and $Li_2Mg_3BO_6$(B= Ti, Sn, Zr) possess excellent microwave dielectric properties [3–5]. George and Sebastian firstly reported that the $Li_2MgTi_3O_8$ ceramics was produced by reaction-sintering method and had a good microwave dielectric properties of ε_r ~27.2, $Q \times f$~ 42000GHz and τ_f ~3.2 ppm/°C [3]. According to Su et al. [6], with the partial replacement of Mg^{2+} by Zn^{2+}, the $Li_2(Mg_{0.94}Zn_{0.06})Ti_3O_8$ ceramics exhibited good microwave dielectric properties of ε_r ~27.1, $Q \times f$~ 44,800 GHz and τ_f ~1.9 ppm/°C. $Li_2Mg_3TiO_6$ ceramics was reported to exhibit excellent microwave dielectric properties (ε_r ~15.2, $Q \times f$ ~152,000GHz, τ_f~ −39 ppm/°C) when sintered at 1280 °C for 6h [5]. Afterwards, in order to meet the requirements for LTCC, the 4 wt% LiF addition was used to lower the sintering temperature of $Li_2Mg_3TiO_6$ ceramics and achieved a good dielectric properties of ε_r ~16.2, $Q \times f$ ~131,000 GHz and τ_f~−44 ppm/°C when sintered at 950 °C [7]. However, there were few work about the effects of different divalent ions substitution on microwave dielectric properties of $Li_2(Mg_{0.95}A_{0.05})_3TiO_6$ $(A = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+})$ ceramics.

In this paper, the effect on the microwave dielectric properties of $Li_2Mg_3TiO_6$ ceramics resulting from isovalent substitution of A $(A = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+})$ at the Mg site was firstly investigated. In addition, the X-ray diffraction (XRD) pattern and the scanning electron microscopy (SEM) analysis were used to analyze the microstructures.

2. Experimental procedure

$Li_2(Mg_{0.95}A_{0.05})_3TiO_6(A = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+})$ ceramics were prepared using high-purity oxide powders of Li_2CO_3(99%), MgO(99.9%), $CaCO_3$(99.9%), ZnO(99.9%), NiO(99%), $MnCO_3$(99%) and TiO_2(99.9%). The raw materials were mixed according to the formula of $Li_2(Mg_{0.95}A_{0.05})_3TiO_6$ $(A = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+})$. The mixed powders were milled with ZrO_2 balls for 8h in distilled water. All mixtures were dried and calcined at 1000 °C for 4h. The calcined powders were remilled with ZrO_2 balls for 8h in distilled water, and then dried. These mixtures were mixed together with 6 wt% paraffin as a binder. Afterwards, the granulated powders were pressed into disks with 10mm in diameter and about 5 mm in height. Finally, these cylinder were sintered at 1225–1300 °C for 6 h in air.

The crystalline phases of the sintered samples were investigated by X-ray diffraction (XRD, Rigaku D/max 2550 PC, Tokyo, Japan) with Cu Ka radiation generated at 40kV and 40mA. The microstructure of the ceramic surfaces were performed and analyzed by a scanning electron microscopy (SEM, ZEISS MERLIN Compact, Germany). The microwave dielectric properties of sintered specimen were measured by a network analyzer (N5234A, Agilent Co, America) in the frequency range of 8–13 GHz. The dielectric constants were measured by exciting the TE_{01} resonant mode of dielectric resonator as suggested by Hakki-Coleman [8]. The unload quality factors were measured using TE_{01} mode by the cavity method [9].

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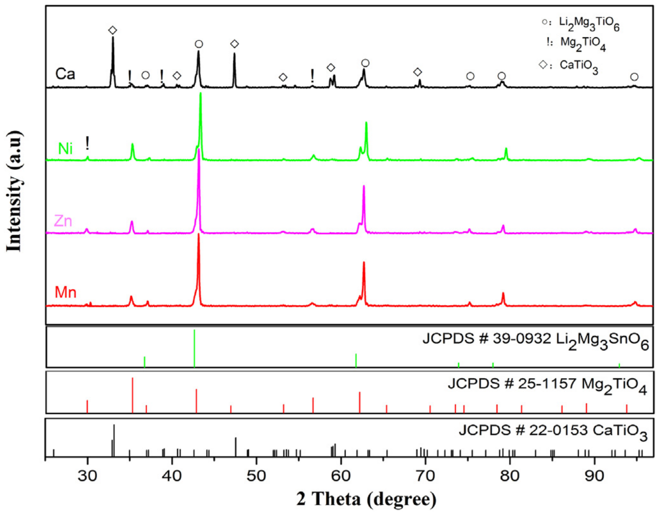

Fig. 1. The X-ray diffraction patterns of $Li_2(Mg_{0.95}A_{0.05})_3TiO_6$ (A = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}) ceramics sintered at 1275 °C.

The temperature coefficient of resonant frequency (τ_f) was measured in the temperature range from 25 °C to 85 °C and was calculated by the following formula:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25}(85 - 25)} \times 10^6 (ppm/°C) \quad (1)$$

where f_{85} and f_{25} were the resonant frequencies at 85 °C and 25 °C.

3. Results and discussions

The XRD patterns of $Li_2(Mg_{0.95}A_{0.05})_3TiO_6$(A = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}) ceramics sintered at 1275 °C for 6h are shown in Fig. 1. All samples exhibited the $Li_2Mg_3SnO_6$-like (JCPDS#39-0932) cubic phase with ordered rock salt structure. The main peaks of $Li_2Mg_3TiO_6$ shifted slightly to the higher angle than $Li_2Mg_3SnO_6$ phase due to the smaller ionic radius of Ti^{4+} (R = 0.605 Å, CN = 6) than that of Sn^{4+} (R = 0.69 Å, CN = 6) [5]. Besides, little impurity peaks defined as Mg_2TiO_4 were formed because lithium was easily volatile when the sintering temperature was higher than 1000 °C [10]. Specially, the peaks of $CaTiO_3$ were found in $Li_2(Mg_{0.95}Ca_{0.05})_3TiO_6$. Similar phenomena were reported in $CaCO_3$-doped $Li_2MgTi_3O_8$ and $Li_2ZnTi_3O_8$ ceramics systems [11].

Fig. 2 presents the SEM photographs of $Li_2(Mg_{0.95}A_{0.05})_3TiO_6$-

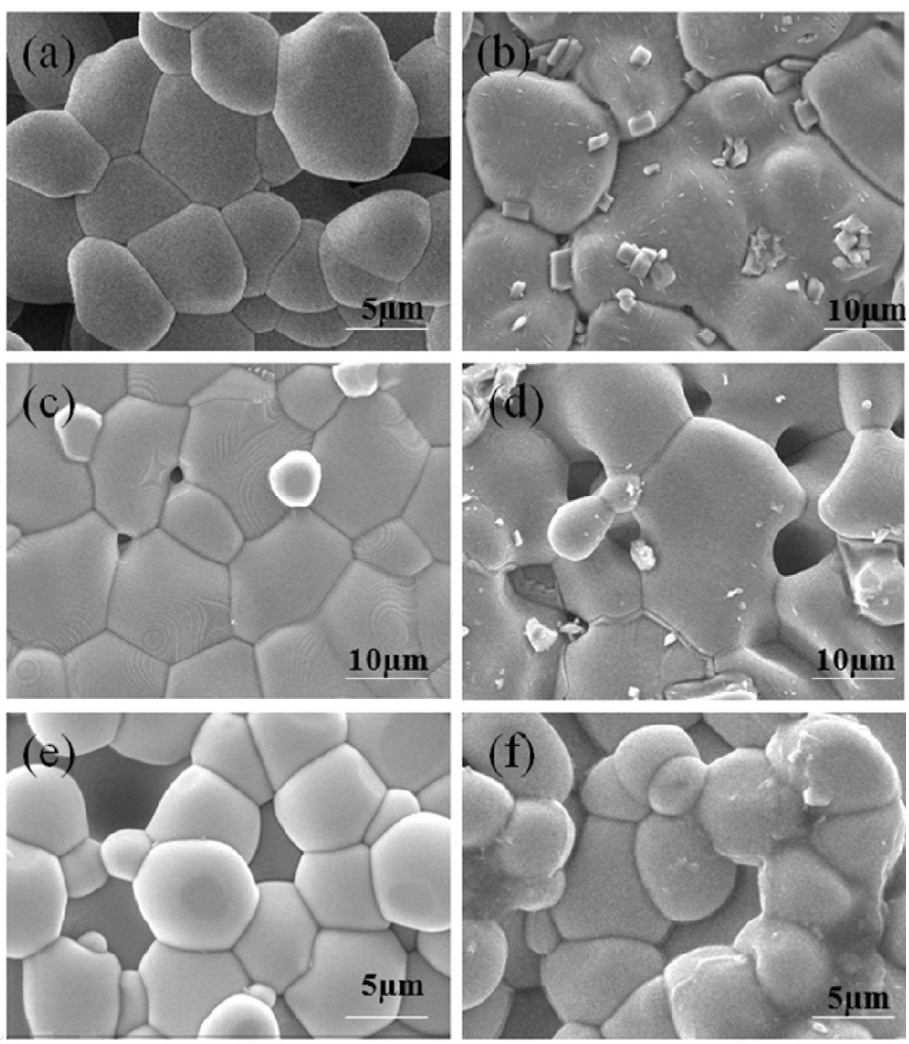

Fig. 2. The surface microstructural photographs of $Li_2(Mg_{0.95}A_{0.05})_3TiO_6$ (A = Ca^{2+}, Ni^{2+}, Zn^{2+}, Mn^{2+}) ceramics: (a)A = Ca, (b)A = Ni, (c)A = Zn, (d)A = Mn sintered at 1275 °C, and $Li_2(Mg_{0.95}Ca_{0.05})_3TiO_6$ ceramics sintered at (e) 1250 °C and (f) 1300 °C.