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A novel temperature stable and high Q microwave dielectric ceramic in $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ system

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Abstract The compositions of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics were prepared by the conventional solid state reaction method. The effects of Mn^{2+} substitution on the microstructure, sintering behavior and microwave dielectric properties of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics were investigated systematically. The XRD patterns revealed that all the specimens sintered at 1075–1200 °C remained a single phase with orthorhombic structure. The obtained microwave dielectric properties indicated that appropriate amount of Mn^{2+} substitution for Mg^{2+} could significantly promote the grain growth and densify $Li_3Mg_2NbO_6$ ceramics. The permittivity and $Q\times f$ values were strongly dependent on the bulk density and grain size, respectively. And near zero τ_f values could be realized in the $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ $(0.02 \leqq x \leqq 0.08)$ compounds sintered at 1125 °C. To sum up, the $x=0.02$ sample sintered at 1125 °C for 4 h exhibited excellent microwave dielectric properties of $\varepsilon_r \sim 15.22$, $Q\times f$~110,582 GHz, τ_f ~−4.57 ppm/°C which demonstrated that the $Li_3(Mg_{0.98}Mn_{0.02})_2NbO_6$ ceramic would be a novel temperature stable and high Q material for microwave device.

1 Introduction

Microwave dielectric materials are all-pervasive in modern society with a wide range of applications from wireless communication to microwave device [1–3]. Compared with bulk metallic cavities used in the early microwave systems, microwave dielectric ceramics have distinct advantages in terms of cost, dimension, mass, stability, efficiency, tenability, ruggedness and ease of use in practical applications [4, 5]. With the recent revolution in mobile phone and satellite communication systems using microwaves as the carrier, the research and development of novel low loss microwave dielectric ceramics has been one of the biggest challenges in contemporary materials science [1]. Some materials which possess high quality factors and have been developed for commercial applications [6–8], while the high sintering temperature (>1300 °C) is indispensable for achieving excellent microwave dielectric properties. Otherwise, many microwave materials have superior dielectric properties [9–11], but the large negative τ_f values tremendously degrade the stability of operating frequency and limit their further applications in microwave circuit. Therefore, searching for new temperature stable and high Q microwave materials is still an urgent project nowadays.

As one of the rock salt structure compounds, $Li_3Mg_2NbO_6$ ceramics [12] sintered at 1250 °C showed fairly good microwave dielectric properties of ε_r ~16.8, $Q\times f$~79,643 GHz, τ_f ~−27.2 ppm/°C. And to the best of our knowledge, the most studies of $Li_3Mg_2NbO_6$ ceramics were about lowering sintering temperature for LTCC applications. For instance, Zuo et al [13, 14] used 0.5wt% $0.17Li_2O–0.83V_2O_5$ compositions to decrease the sintering temperature of $Li_3(Mg_{0.92}Zn_{0.08})_2NbO_6$ ceramics to 925 °C and the ceramic possessed excellent microwave dielectric properties of ε_r ~14, Q × f ~83,395 GHz, τ_f ~−37.2 ppm/°C. Later, they successfully adjusted the temperature coefficient of resonant frequency of $Li_3(Mg_{0.92}Zn_{0.08})_2NbO_6$ ceramics to a near zero value (τ_f~+1.5 ppm/°C) and reduced the sintering temperature to 950 °C by adding 30 wt% $Ba_3(VO_4)_2$ additives. Recently,

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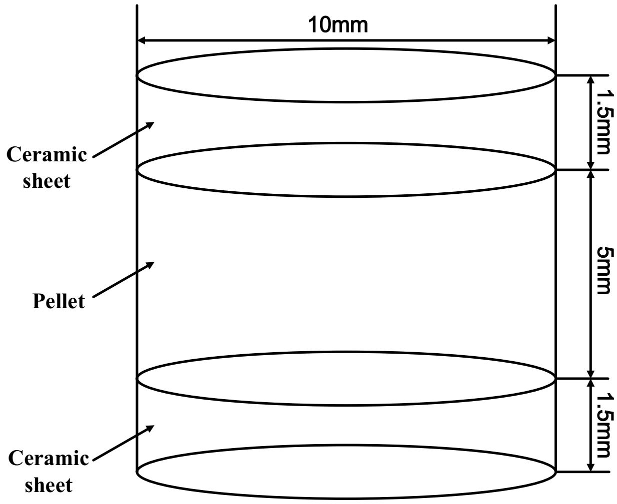
Zhang et al [15] also did some research works about low temperature sintering of $Li_3Mg_2NbO_6$ ceramics and found that 0.5 wt% $MgO–B_2O_3–SiO_2$(MBS) glass additives could lower the sintering temperature to 925 °C and the ceramic had preferable microwave dielectric properties of ε_r ~14.5, Q × f ~80,759 GHz, τ_f ~−20.7 ppm/°C. In addition, Wu et al [16] investigated the correlation between properties and structures of $Li_3Mg_2NbO_6$ ceramics based on chemical bond theory and certified that the sample sintered at 1225 °C presented excellent microwave properties of ε_r ~14.94, Q×f~100,965 GHz and τ_f ~−21.96 ppm/°C. Meanwhile, Zhang et al [17] reported the dielectric properties of $Li_3(Mg_{0.95}A_{0.05})_2NbO_6$($A=Ca^{2+}$, Ni^{2+}, Zn^{2+}, Mn^{2+}) ceramics and found that the Q×f value could be increased to 96,160 GHz as 0.05 mol Ca^{2+} was used. Unfortunately, the specimen had a large negative τ_f value (−18.49 ppm/°C) which might seriously damage the reliability of microwave system.

Until now, there are few reports about altering the dielectric properties of $Li_3Mg_2NbO_6$ ceramics by Mg-site substitution. And it has been reported that substitution always alters the dielectric properties depending on the solid solubility of substituting element with the parent composition [18]. Moreover, the compatibility of ionic radius, ionic charge and structure are the conditions required for the formation of solid solution without much degradation of the required properties. Therefore, in this paper, we manage to alter the dielectric properties by using various amount of Mn^{2+}, since the shannon effective ionic radii [19] of Mg^{2+} (0.72 A CN = 6) is similar to that of Mn^{2+} (0.83 A CN = 6), and the ionic charge of Mg^{2+} is equal to that of Mn^{2+}. Furthermore, we have seen that Mn^{2+} acts as a good substituent in the composition of $(Mg_{1-x}Mn_x)_2TiO_4$ [20], the Q×f values of $(Mg_{0.95}Mn_{0.05})_2TiO_4$ ceramics could be easily improved to a ultrahigh value over 250,000 GHz and own a compatible dielectric constant and τ_f value. Hence, it is worthwhile to investigate whether $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics may reveal equivalent or superior properties compare to above $Li_3Mg_2NbO_6$-based ceramics [12–17]. The present paper discusses the microstructure, phase constitution and sintering behavior of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) ceramics and the effects of Mn^{2+} substitution for Mg^{2+} on the microwave dielectric properties of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics are also investigated in detail.

2 Experimental procedure

The $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics were synthesized through the conventional solid state reaction method from high purity oxide powders of Li_2CO_3(97%), MgO(99.9%), Nb_2O_5(99.9%), $MnCO_3$(99%). These raw powders were weighed based on the formula of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$). Then, they were mixed and milled with deionized water for 8 h in a nylon container. The obtained slurry was dried, sieved and calcined at 950 °C for 4 h. The calcined powders were re-milled for 8 h, then dried and mixed with 8 wt% paraffin as a binder. Subsequently, the granulated powders were axially pressed into cylindrical disks with dimension of 10 mm in diameter and 5 mm in height. The pellets of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics were sintered at 1075–1200 °C for 4 h in the air with the heating rate of 5 °C/min. And in order to reduce the lithium evaporation, we pressed the granulated powders into ceramic sheet with dimension of 10 mm in diameter and 1.5 mm in height. Then the pellets were placed between two ceramic sheets during the whole sintering process.



The method of reducing the lithium evaporation

The phase composition of sintered samples were identified by X-ray diffraction (XRD, Rigaku D/max 2550 PC, Tokyo, Japan). The natural surface morphology was examined by a scanning electron microscope (SEM, ZEISS MERLIN Compact, Germany). While microwave dielectric properties [21] of sintered specimens were measured by a network analyzer (N5234A, Agilent Co, America) in the frequency range of 7–13 GHz. The temperature coefficients of resonant frequency were measured in the temperature range from 25 to 85 °C. It was calculated by the following formula:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \times 10^6 (ppm/^oC)$$

where f_1 and f_2 represented the resonant frequency at T_1 (25 °C) and T_2 (85 °C), respectively.

Table 1 The lattice parameters and unit cell volume of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) ceramics sintered at 1125 °C for 4 h

Composition	ST (°C)	a (Å)	b (Å)	c (Å)	V_{unit} (Å ^{3})
0.02	1125	8.56985	5.89987	17.73383	896.64
0.04	1125	8.57979	5.90546	17.72174	898.07
0.06	1125	8.58662	5.91152	17.71652	899.29
0.08	1125	8.59148	5.91413	17.71957	900.35

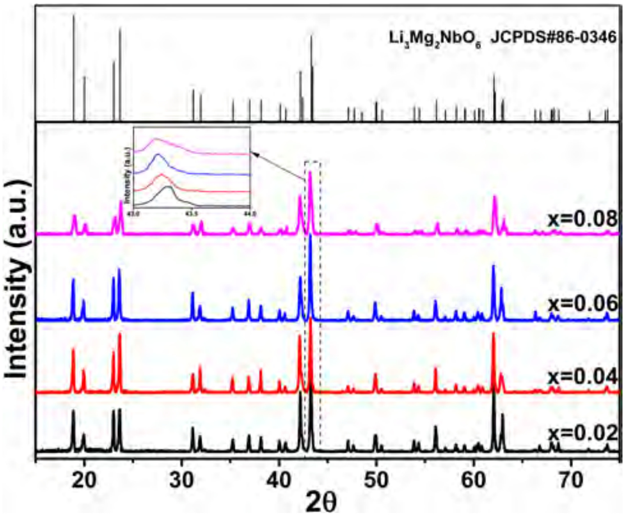


Fig. 1 The XRD patterns of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) ceramics sintered at 1125 °C for 4 h

3 Results and discussion

Figure 1 shows the XRD patterns of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) ceramics sintered at 1125 °C for 4 h. Table 1 reveals the lattice parameters and unit cell volume of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) ceramics sintered at 1125 °C for 4 h. We can see that all the main peaks could be indexed based on JCPDS file number 86–0346 for $Li_3Mg_2NbO_6$ phase with orthorhombic structure, which belongs to the space group Fddd (70). In particular, the strongest diffraction peak gradually shifts toward a lower angle direction as x value increases, indicating that the unit cell volume increases slightly with increasing x value, which is in accordance with the results as shown in Table 1. We can observe that the cell volume gradually increases from 896.64 Å^3 at $x=0.02$ to 900.35 Å^3 at $x=0.08$ due to the bigger radius of Mn^{2+} ($r=0.83$ A, $CN=6$) than that of Mg^{2+} ($r=0.72$ A, $CN=6$). All these conclusions confirm that the $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ solid solutions could be formed during the whole substitution range.

Figure 2 illustrates the SEM images of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) ceramics sintered at various temperatures. We can clearly detect that the $x=0.02$ sample sintered at 1100 °C has a densified microstructure but with relatively uneven grain size (6–20 μm) as shown in Fig. 2a. And as the temperature increases, small grains grow rapidly and became bigger, well homogeneous morphology with the grain size of 20 μm can be obtained in the sample at 1125 °C (Fig. 2b). While further rising the temperature would significantly decrease the grain size. Some grains begin to melt, leading to the smaller grains and ambiguous gain boundaries as shown in Fig. 2c. It might be an indication of over sintering. Above results suggest that micro-morphologies of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics are sensitive to the sintering conditions. And proper sintering temperature could effectively promote the grain growth and benefit the uniform distribution of grain particles. Whereas higher temperature would result in an inferior microstructure. Some grains exhibit the indistinct grain boundaries and comparatively smaller grain size, which might severely deteriorate the microwave dielectric properties.

Moreover, to clarify the effects of Mn^{2+} substitution on the microstructure of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics, the natural surface micrographs of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.04 \leqq x \leqq 0.08$) compounds sintered at 1125 °C are revealed (Fig. 2d–f). We can notice that the grains present a densified and uniform distribution as 0.02 and 0.04 mol Mn^{2+} are used. Especially the $x=0.02$ sample shows a more uniform and smooth surface morphology with bigger grain size of 20 μm (Fig. 2b). Whereas continue increasing the substitution content would give rise to an obvious decline in grain size as shown in Fig. 2e, f. As a result, we conclude that small amount of Mn^{2+} substitution for Mg^{2+} has a significant role in raising the grain size and contributing to the homogeneous distribution of ceramic grains. Whereas excessive amounts of Mn^{2+} would inhibit the grain growth, causing smaller grain size in the compounds.

Figure 3 presents the bulk density and permittivity of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) ceramics sintered at various temperatures. For $x=0.02$ sample, it can be clearly observed that the density exhibits a rising variation trend with increasing sintering temperature. Whereas densities of other specimens initially increase and reach the maximum value at 1125 °C, while subsequent raising the temperature would decrease the density slightly. The highest density (3.615 g/cm^3) is achieved in the $x=0.06$ sample when sintered at 1125 °C for 4 h. And we find that densities of the compounds increase steadily as the substitution content increase from 0.02 to 0.06 mol, but decrease rapidly as x value exceed to 0.08. According to the above results, we can make a conclusion that 0.06 mol Mn^{2+} could effectively promote the densification of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics and reduce the optimum sintering temperature to 1125 °C to some extent, while excessive amount of Mn^{2+} would decrease the density of ceramics. It is generally

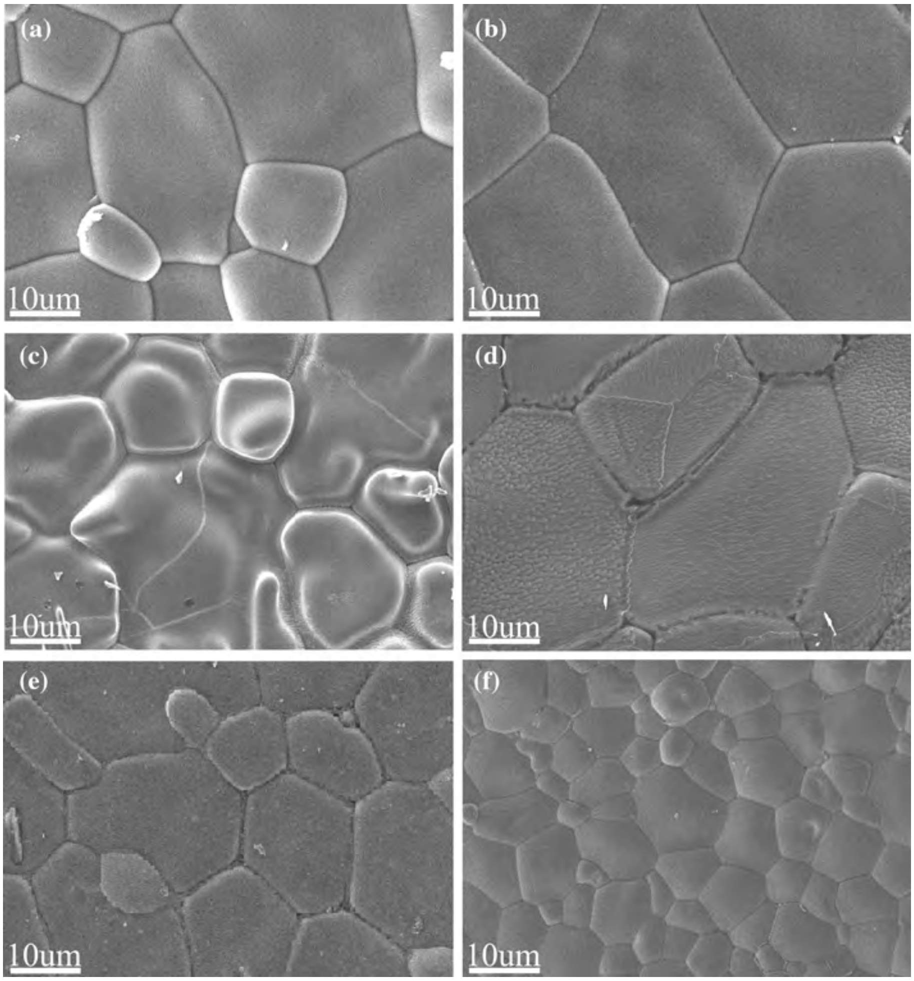


Fig. 2 The SEM images of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) ceramics sintered at various temperatures for 4 h: **a** x = 0.02, 1100 °C; **b** x = 0.02, 1125 °C; **c** x = 0.02, 1150 °C; **d** x = 0.04, 1125 °C; **e** x = 0.06, 1125 °C; **f** x = 0.08, 1125 °C

known that the permittivity is mainly related to the density, ionic polarizabilities, porosity, second phase or structural characteristics of the ceramics [22, 23]. In present study, the permittivity of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics is mainly controlled by the density of compositions. The variation of permittivity is consistent with that of bulk density. The maximum permittivity (15.97) is obtained in the x = 0.06 specimen sintered at 1125 °C for 4 h.

Figure 4 exhibits the Q×*f* values of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) ceramics sintered at various temperatures. It can be clearly detected that the Q×*f* values of specimens reveal a similar variation trend, they all firstly increase slightly with increasing sintering temperature and reach the maximum value of 110,582 GHz, 100,139 GHz, 78,469 GHz, 59,522 GHz for $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics at 1125 °C, respectively. Further raising the temperature would lead to an abrupt decline in Q×*f* values. Generally, the dielectric loss of microwave ceramics is influenced by two primary factors, extrinsic factor and intrinsic factor. The extrinsic factor usually consists of the density, grain size, porosity, impurities, and second phase. While the intrinsic factor is mainly correlated with cation ordering or lattice anharmonicity [24–26]. But it is extremely difficult to make a crucial conclusion on the correlation between above two factors and dielectric loss in the polycrystalline microwave dielectric ceramic [27, 28]. In this paper, the dielectric loss is mainly controlled by the extrinsic factors. The increment of Q×*f* values ($0.04 \leqq x \leqq 0.08$) can be mainly attributed to the promotion of densification while the decrement of Q×*f* values may be relevant to the low density caused by high temperature. Of particular note is that Q×*f* values of the x = 0.02 sample gradually increase when temperature increase from 1075 to 1125 °C, but decrease rapidly when temperature exceed to 1150 °C although the density keep an increasing tendency. It has been reported [4] that reducing the grain boundaries might be expected to reduce the dielectric loss, thus larger grains exhibit more preferable microwave dielectric properties compare to the inherent properties. Hence, this unusual behavior might due to the abnormal grain growth at 1150 °C, causing the relatively smaller grain size and ambiguous grain boundaries, as shown in Fig. 2c. Beside of these, we can detect that Q×*f* values of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics

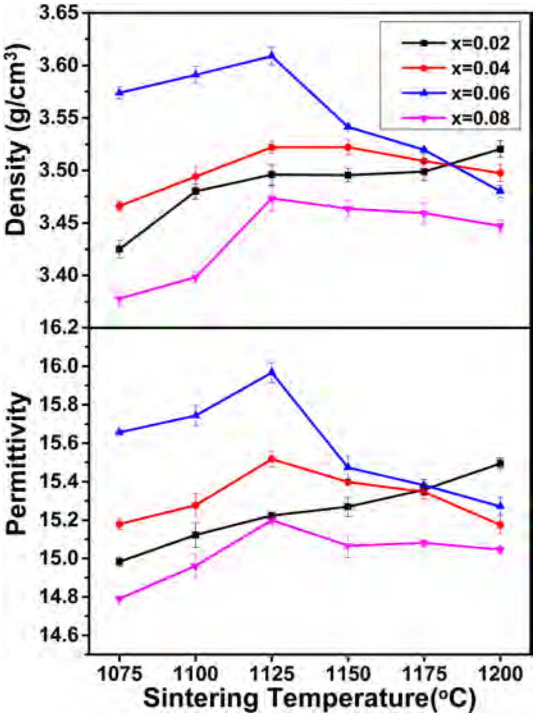


Fig. 3 The bulk density and permittivity of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ $(0.02 \leqq x \leqq 0.08)$ ceramics sintered at various temperatures for 4 h

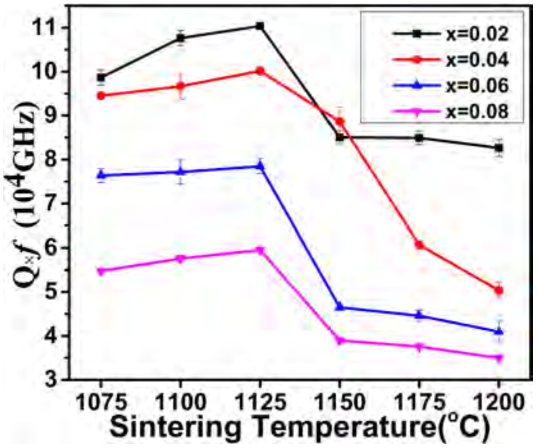


Fig. 4 The $Q\times f$ values of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ $(0.02 \leqq x \leqq 0.08)$ ceramics sintered at various temperatures for 4 h

sintered at 1125 °C gradually decrease as x value rises from 0.02 to 0.06 mol while the densities display an increasing variation tendency. According to the SEM images, uniform and smooth grains with bigger grain size of 20um appear in the x = 0.02 compound at 1125 °C as shown in Fig. 2b, while further increasing the x value would damage the homogeneous microstructure of ceramics, resulting in the smaller grain size as shown in Fig. 2e, f. Thus, the higher $Q\times f$ value with comparatively lower density could be associated with the bigger and uniform grains, while the high density specimen possess a lower $Q\times f$ value which might be correlated with the inferior grain morphology. In addition, all these samples present a densified micro-morphology, implying that high densities are realized in these compounds. Consequently, the grain morphology factors have a more significant influence on the quality factor of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics while the density factors may be weakened.

Figure 5 shows the τ_f values of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ $(0.02 \leqq x \leqq 0.08)$ ceramics sintered at 1125 °C for 4 h. We can see that the τ_f values vary in a narrow range from −3.14 to −5.93 ppm/°C which are favorable to the stability of operating frequency for microwave components. It has been reported that the τ_f value is mainly affected by the composition, additives or second phase of the materials [10, 29]. Based on the XRD patterns, no second phases arise in the sample and no additives are added into the compositions. Therefore, the obtained near zero τ_f values could be attributed to the small amount of Mn^{2+} substitution for Mg^{2+}. In general, the optimum microwave dielectric properties of ε_r ~15.22, $Q\times f$~110,582 GHz, τ_f ~−4.57 ppm/°C can be achieved in the $Li_3(Mg_{0.98}Mn_{0.02})_2NbO_6$ sample when sintered at 1125 °C for 4 h.

4 Conclusion

The $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ $(0.02 \leqq x \leqq 0.08)$ ceramics are prepared by the conventional solid state reaction route. Effects of Mn^{2+} substitution on the microstructure, sintering behavior and microwave dielectric properties of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics are studied in detail. The XRD patterns indicate that all these compositions present a single phase. We conclude that small amount of Mn^{2+}

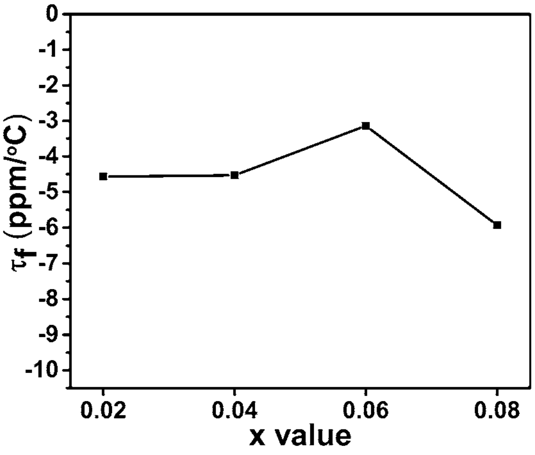


Fig. 5 The τ_f values of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ $(0.02 \leqq x \leqq 0.08)$ ceramics sintered at 1125 °C for 4 h

substitution for Mg^{2+} has a significant role in promoting the densification and improving the microwave dielectric properties of $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ceramics. The permittivity and Q×*f* values are immensely determined by bulk density and grain size, respectively. Furthermore, near zero τ_f values can be obtained in the $Li_3(Mg_{1-x}Mn_x)_2NbO_6$ ($0.02 \leqq x \leqq 0.08$) compounds sintered at 1125 °C. In summary, the $Li_3(Mg_{0.98}Mn_{0.02})_2NbO_6$ specimen sintered at 1125 °C for 4 h exhibits excellent microwave dielectric properties of ε_r ~15.22, Q×*f*~ 110,582 GHz, τ_f ~−4.57 ppm/°C which prove that it would be a promising temperature stable and high Q material for microwave circuit.

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