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New high Q microwave dielectric ceramics with rock salt structures: $(1-x)Li_2TiO_3+xMgO$ system $(0 \leq x \leq 0.5)$

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Abstract

The structural evolution and microwave dielectric properties of $(1-x)Li_2TiO_3+xMgO$ system $(0 \leq x \leq 0.5)$ have been investigated in this paper. The ordering degree decreased with the increase of MgO content. The microcracks and cleavage on (0 0 1) due to the weak Li–O bonds disappeared with the increase of MgO content. The dielectric constant and temperature coefficient of resonant frequency decreased with the increase of MgO content. The $Q \times f$ value increased with x up to $x = 0.2$ and then decreases with the further increase of x. An excellent combined microwave dielectric properties could be obtained when $x = 0.24$, $\varepsilon_r = 19.2$, $Q \times f = 106{,}226$ GHz and $\tau_f = 3.56$ ppm/°C.

Keywords: Rock salt structure; Microwave dielectric properties

1. Introduction

With the development of wireless communication, low cost microwave dielectrics with high Q factor are strongly desired. Requirements for these dielectric materials must be the combined microwave dielectric properties of high dielectric constant ($\varepsilon_r > 20$), high unloaded quality factor ($Q \times f > 40{,}000$ GHz) and a temperature coefficient of the resonant frequency (τ_f) tunable through zero. For base station applications, ceramics are only used when high Q is paramount and low cost is achieved. Although several ultra low loss microwave dielectric systems such as $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT), $Ba(Zn_{1/3}Ta_{2/3})O_3$(BZT) and $Ba((ZnCo)_{1/3}Nb_{2/3})O_3$ (BZCN) have been developed,[1,2] the search for new low cost and high Q microwave dielectric ceramics is still continuing.

The NaCl or rock salt structure is one of the most common and well-known structure types. The regular octahedrons coordinated for both cations and anions are edge shared through three-dimensional network. Superstructure phases which display ordering among cation sites might form when two or three crystallographically distinct types of cations occupied the sodium sites in a non-random manner.[3] Li_2TiO_3, which belongs to the family of rock salt superstructure phases, undergoes an order–disorder phase transition at 1215 °C.[4] It formed complete solid solution with MgO and the temperature of order–disorder change decreased rapidly with increasing MgO content.[5] Most ultra-high Q microwave dielectric ceramics were found in complex perovskites. The high Q values of the complex perovskites were considered to be related to the high cation ordering degree. Tamura et al. showed that the $Q \times f$ value of $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) can also be enhanced through the substitution of small concentrations (~4 mol%) of $BaZrO_3$ (BZ).[1] The high Q values of these ceramics were attributed to the stabilization of the ordering-induced domain boundaries by the partial segregation of Zr.[6] The partial segregation of Zr to the boundaries is consistent with the observed decrease in the domain size and the associated increase in the volume of boundaries with higher level of $BaZrO_3$.[6] The charge and size of Zr^{4+} were considered to be critical in its ability to stabilize the boundary regions, because only charge balance substitution of larger cation could be beneficial providing a stable interfacial "buffer layer" at the otherwise elastically strained domain boundaries.[6] In the case of Li_2TiO_3–MgO solid solutions the replacement mechanism could be considered as $3Mg^{2+} \leftrightarrow 2Li^{2+} + Ti^{4+}$, where charge balance was maintained. Furthermore the ionic radii of Mg^{2+} are larger than that of Li^+/Ti^{4+}. Therefore whether is it same that the domain boundaries could be stabilized by partial segregation of Mg^{2+} in Li_2TiO_3 as in the complex perovskites? Is

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it also possible to obtain high Q value in Li_2TiO_3 with small concentration of MgO addition? In addition, the temperature coefficients of resonant frequency τ_f of perovskites are usually tuned by changing the tilting angle of oxygen octahedrons since the oxygen octahedrons are corner shared in perovskites. However the oxygen octahedrons should not tilt like in perovskites since oxygen octahedrons are edge shared in rock salt structure. Therefore compounds with rock salt structure may exhibit a different tuning mechanism of τ_f value.

Li_2TiO_3 ceramics have been extensively investigated as promising solid breeder materials in the blanket of future fusion reactors and ionic conductors.[7–9] However, to the best our knowledge, no microwave dielectric properties of the compounds with rock salt structure have been reported yet.

Based on the above considerations, Li_2TiO_3–MgO system with ordered–disordered rock salt structure is great interest for the generation of new high Q microwave dielectrics. Furthermore low cost could be expected due to the cheaper raw materials and relatively lower sintering temperature resulted from low melting lithium constituent. The sintering behavior, structural evolution and microwave dielectric properties of Li_2TiO_3–MgO system have been studied in this paper.

2. Experimental

$(1-x)Li_2TiO_3$–xMgO ($0 \le x \le 0.5$) ceramic samples were prepared by conventional solid-state reaction process from the starting materials including MgO (99.0%), Li_2CO_3 (99.9%), TiO_2 (99.7%). The raw materials were weighed according to the above formula and milled with ZrO_2 balls in ethanol for 24 h. The wet mixed powders were dried and calcined at a temperature of 700–1100 °C for 2 h in an alumina crucible. The calcining temperature increased with the increasing MgO content. The calcined powders were regrounded for 24 h, dried, mixed with 7 wt% PVA as binder and granulated. The granulated powders were uni-axially pressed into compacts with 10 mm in diameter and 4–5 mm in height under the pressure of 100 MPa. The compacts were sintered between 1200 and 1350 °C for 2 h. In order to prevent the lithium evaporation loss, the compacts were muffled with powders of the same composition.

The phase constituents of the sintered samples were identified by X-ray powder diffraction (XRD) with Ni-filtered Cu Kα radiation (40 kV and 20 mA, Model Dmax-RC, Japan). The unit cell parameters were refined by a least-squares procedure using Jade 5.0 software. Bulk densities of the sintered specimens were identified by the Archimedes' method. The microstructure of the sintered sample was characterized by scanning electron microscopy (SEM) (Model XL20, Philips Instruments, Netherlands). All samples were polished and thermally etched at a temperature which was 200 °C lower than its sintering temperature**.** Microwave dielectric properties of the sintered samples were measured between 8 and 10 GHz using network analyzer (Hewlett Packard, Model HP8720C, USA). The quality factor was measured by the transmission cavity method. The relative dielectric constant (ε_r) was measured according to the Hakki Coleman method using the TE_{011} resonant mode, and the temperature coefficient of the resonant frequency (τ_f) was measured using invar cavity at the temperature range from 20 to 80 °C.

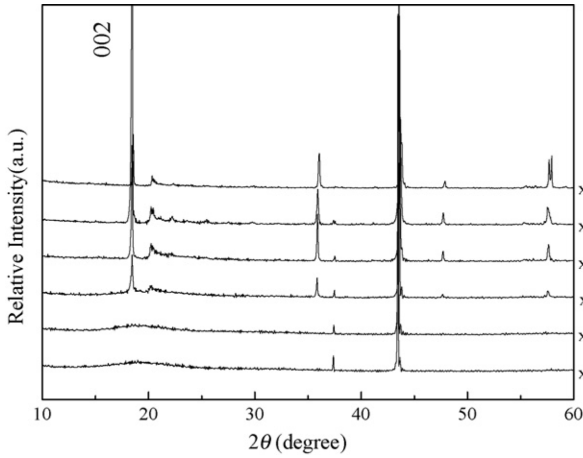

Fig. 1. XRD powder patterns of $(1-x)Li_2TiO_3 + x$MgO ($0 \le x \le 0.5$) ceramics sintered at 1300 °C/2 h.

3. Results and discussion

The powder XRD patterns of the sintered samples with different MgO contents are shown in Fig. 1. The examination of the patterns shown in Fig. 1 indicates that they are all single rock salt type phase, and continuous solid solutions were formed for $(1-x)Li_2TiO_3$–xMgO ($0 \le x \le 0.5$). The monoclinic type of rock salt phase of pure Li_2TiO_3 was transformed into cubic rock salt as $x \ge 0.4$. With increasing MgO content, the long range ordering (LRO) degree of cations indicated by the intensity of (0 0 2) peak decreased and became almost completely disorder when $x \ge 0.4$, which is in agreement with that reported previously.[5] It is noted that the peak position shifts to lower degree with increasing MgO content, which means the cell volume increases with increasing x due to the substitution of larger Mg^{2+} ($R = 0.72$ nm) for smaller Li^+ and Ti^{4+} ($R_{av} = 0.695$ nm). The variation of unit cell volume per oxygen as a function of x is shown Fig. 2. It indicates negative departure from Vegard's law in the lattice parameter of the single phase solid solutions, which

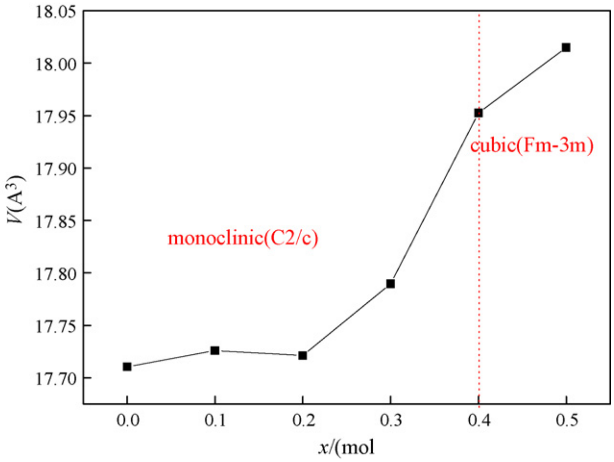

Fig. 2. Variation of unit cell volume per oxygen as a function of x value.

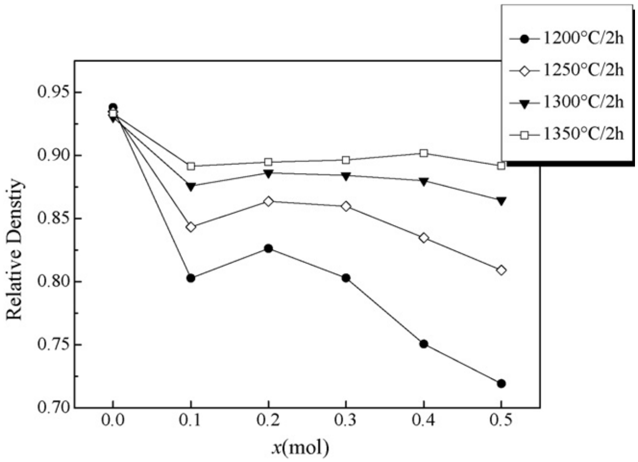

Fig. 3. Variation of relative bulk density as a function of MgO content for the samples sintered at different temperatures.

may be attributed to the cations ordering existed in the $x < 0.4$ samples.[10] Cations ordering generally causes lattice contraction due to the alleviation of electrostatic repulsion between the like cations by maximizing the cation distance.

Fig. 3 illustrates the variation of relative bulk densities as a function of MgO content for the samples sintered at different temperatures. The sintering temperature increases with MgO content. Highly densified samples seem to be difficult to obtain in our experiment. The relative densities for all samples are lower than 93%, which is probably due to the evaporation of Li during sintering process. The SEM images of sintered samples are shown in Fig. 4. All samples exhibit porous structure and the porosities of the MgO doped samples are larger than that of the un-doped sample, which is consistent with the results in Fig. 3. The $x = 0$ and $x = 0.1$ samples exhibit a plate like grain structure, and the grain shape changed into regular polygon when $x \geq 0.3$. It is noted that microcracks marked by arrow could be observed in the $x = 0$ sample. The phase of Li_2TiO_3 existed in three modifications, α, β and γ.[4,11,12] The α phase is metastable and transformed to β-Li_2TiO_3 at about 300 °C. The γ-Li_2TiO_3 is disordered with cubic structure. In ordered β-Li_2TiO_3 a layer accommodates one-third Li and two-thirds Ti with alternate layers occupied only by lithium atom, such that the formula may be written as $Li(Li_{1/3}Ti_{2/3})O_2$.[13] Li–Ti ordered with the mixed cation layer and its symmetry is reduced to monoclinic C2/c. The typical mean bond lengths, Li–O and Ti–O bond are 2.14 and 1.95 Å, respectively.[13] Therefore the plate like habit and microcracks are caused by the easy cleavage on (0 0 1) because of the weak Li–O bonds and phase transformation. With increasing x, the preferred orientation growth and cleavage diminished and disappeared as $x \geq 0.3$, which is in agreement with the variation trend of cations ordering with MgO content.

Variation of dielectric constant as a function of MgO content for the samples sintered at different temperatures is shown in Fig. 5. The dielectric constant decreases with the increase of MgO content. Dielectric constant increases with increasing sintering temperature except for Li_2TiO_3 ($x = 0$), which is consistent with the variation trend of bulk density with sintering temperature. According to the equation of Clausius–Mossotti (C–M), the dielectric constant decreases with decreasing total ion polarizability α_D and increasing molar volume (or unit cell volume). The total polarizability per unit volume decreased due to the

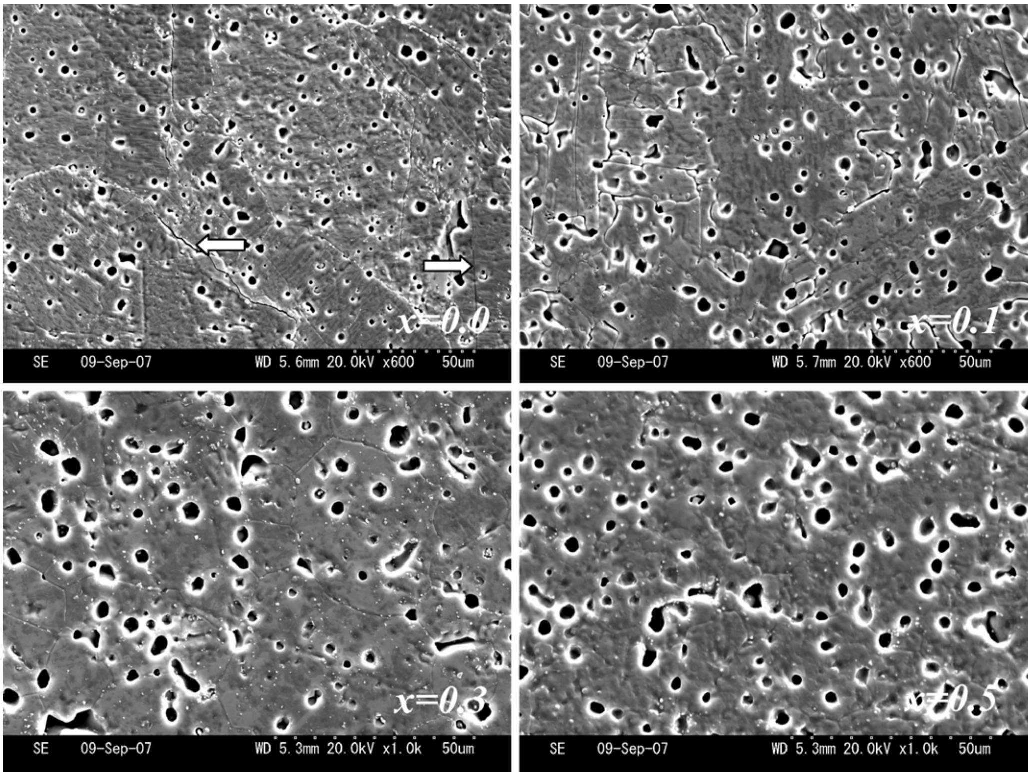

Fig. 4. SEM images of samples sintered at 1300 °C/2 h (microcracks are indicated by arrows).

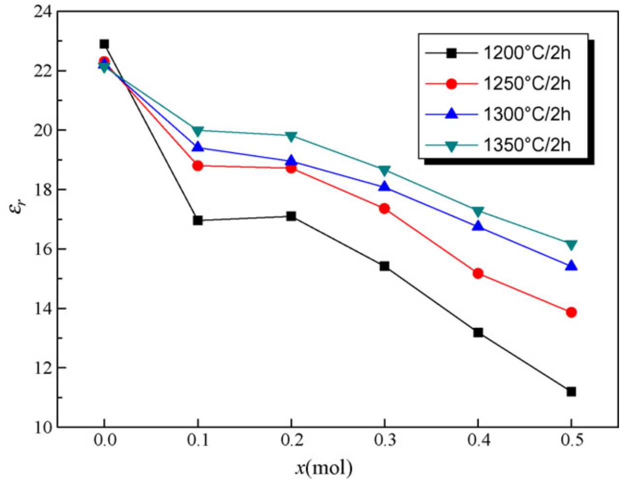

Fig. 5. Variation of dielectric constant as a function of x.

substitution of Mg^{2+} ($\alpha_{Mg}{}^{2+} = 1.32$ Å^3) for the $(Li_{2/3}Ti_{1/3})^{2+}$ ($\alpha_{AV} = 1.78$ Å^3)[14] and the increase of cell volume. We calculated the dielectric constant for $(1-x)Li_2TiO_3 + xMgO$ by using C–M equation (Fig. 6). The observed dielectric constants for the samples sintered at 1300 °C/2 h were corrected by considering the porosities.[15] The calculated and corrected dielectric constants exhibit same variation trend as a function of MgO content, and show good agreement when $x \geq 0.4$ (Fig. 6). Fig. 7 shows the variation of $Q \times f$ value as a function of x for the samples sintered at different temperatures. The $Q \times f$ value increases with the increasing x up to $x = 0.2$ and then decreases with the further increase of x. The great improvement of $Q \times f$ value with low concentration of MgO addition seems to contradict the observations of the beneficial effect of cations ordering on dielectric loss in pure complex perovskites. The alleviation and disappearance of cleavage on (0 0 1) should be responsible for the improvement of $Q \times f$ value. On the other hand, the size of the ordered domains for the samples sintered at 1300 °C, estimated from the peak width of superstructure diffraction by using Scherrer formula,

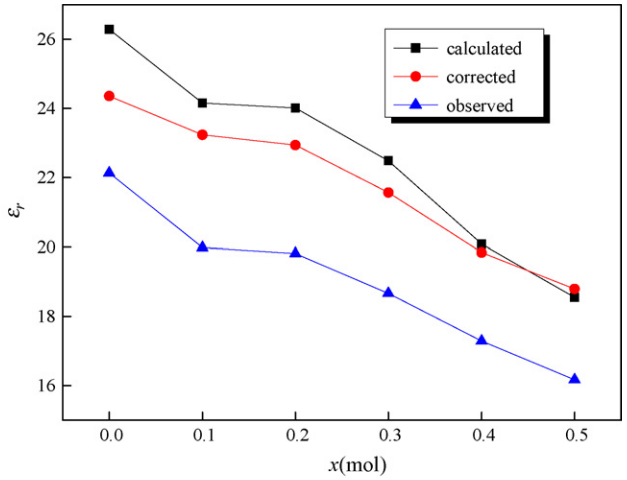

Fig. 6. Comparison between dielectric constant measured by Hakki Coleman method and calculated by C–M equation from the samples sintered at 1300 °C/2 h.

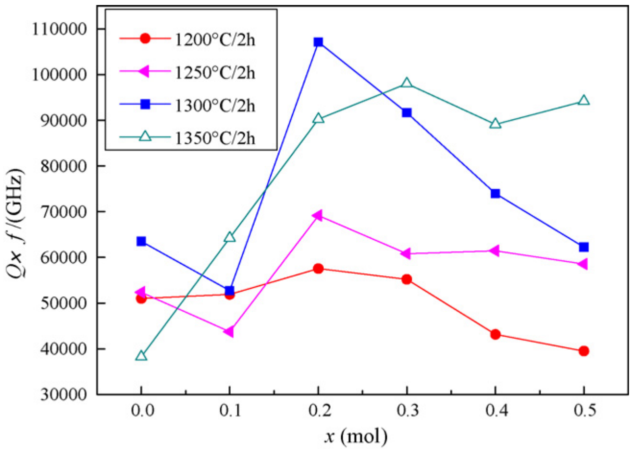

Fig. 7. Variation of $Q \times f$ value of xMgO–$(1-x)Li_2TiO_3$ as a function of x value.

is shown in Fig. 8. The ordering domain size decreases with increasing MgO content, which seems to indicate that a similar mechanism proposed by Davies and Tong[6] for BZT–BZ system also dominated in $(1-x)Li_2TiO_3 + xMgO$ system. Therefore the great improvement of $Q \times f$ value for Li_2TiO_3 with low level of MgO addition could also be ascribed to the stabilization of the ordering-induced domain boundaries by the partial segregation of Mg. The increase in $Q \times f$ value with increasing sintering temperature for the samples with $x \geq 0.3$ can be obviously attributed to the increase in bulk densities. For the samples with $x < 0.3$ the variation of $Q \times f$ value with sintering temperature is not monotonically, which might be due to the difficult controlling in lithium evaporation and cations ordering in these high lithium containing samples. Variation of temperature coefficient of resonant frequency τ_f for the samples sintered at 1300 °C/2 h as a function of x is shown in Fig. 9. τ_f value decreases monotonically from 20 to −26 ppm/°C with increasing x. Near zero τ_f value could be expected at $x = 0.24$ from the data fitting line. The measured τ_f value of the $x = 0.24$ sample is 3.56 ppm/°C, which is in good agreement with the expected value. The dielectric constant and $Q \times f$ value of the $x = 0.24$ sample sintered at

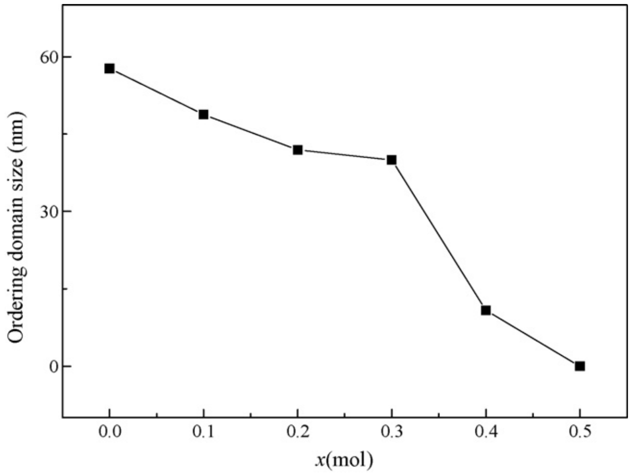

Fig. 8. Variation of ordered domain size for the samples sintered at 1300 °C/2 h as a function of x.

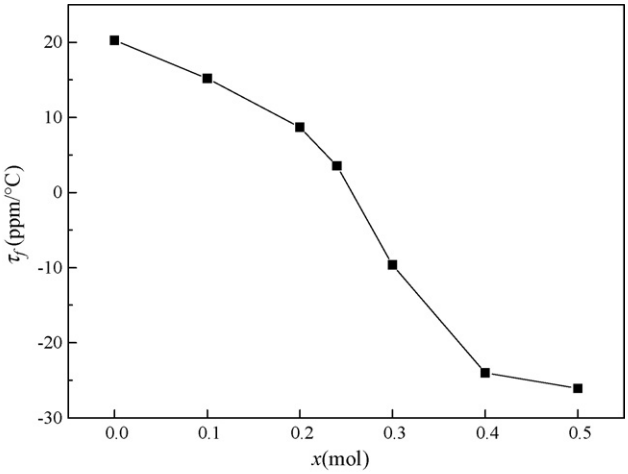

Fig. 9. Variation of τ_f as a function x.

1300 °C/2 h is 19.24 and 106,226 GHz, respectively. The temperature coefficients of resonant frequency τ_f of perovskites are usually tuned by changing the tilting angle of oxygen octahedrons. In rock salt structure oxygen octahedrons are edge shared and should not tilt like in perovskites. It is well known that the sign and magnitude of τ_f mainly depend on the temperature coefficient of dielectric permittivity τ_ε. Bosman and Havinga[16] suggested that the sign and magnitude of τ_ε are closely related to the dilution of dipoles and increase in dipole strength due to thermal expansion and to the direct dependence on temperature of the polarizabilities. The former two effects have very similar in magnitude but opposite in sign, therefore the resulting effect on τ_ε could be generally ignored. The third effect was suspected to be related to the restoring force acting on ions, which depends on the crystal structure and lattice parameter.[15] Yoon et al. found that τ_ε was proportional to the relative magnitude of cell volume in divalent metal tungstate compounds.[17] Fig. 10 shows the relation between temperature coefficient of resonant frequency and unit cell volume. As can be seen in Fig. 10 the τ_f decreases with increasing unit cell volume, which is in agreement with the results reported by Yoon et al.[17]

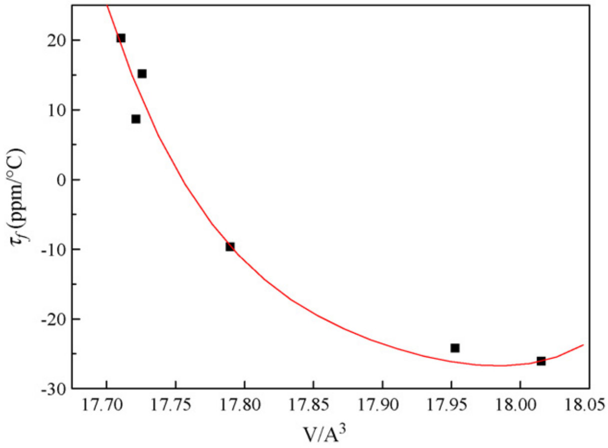

Fig. 10. Variation of τ_f as a function of V_m.

4. Conclusions

Microstructure and microwave dielectric properties of $(1-x)Li_2TiO_3+xMgO$ $(0\leq x\leq 0.5)$ system have been investigated in this paper. The cation ordering degree decreased with increasing MgO content. The cleavage on (0 0 1) due to weak Li–O bond disappeared with increasing MgO addition. The $Q\times f$ value was greatly improved by small level of MgO addition ($x\approx 0.2$) due to the disappearance of microcracks, cleavage on (0 0 1) and the stabilization of the ordering-induced domain boundaries by the partial segregation of Mg. The dielectric constant decreased with increasing MgO content mainly due to the dilution of polarizability per unit volume. Temperature coefficient of resonant frequency also decreased monotonically with the increase of MgO addition, which could be ascribed to the increase of unit cell volume with MgO addition. An excellent combined microwave dielectric properties could be obtained when $x=0.24$, $\varepsilon_r=19.2$, $Q\times f=106{,}226$ GHz and $\tau_f=3.56$ ppm/°C.

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