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A reduced sintering temperature and improvement in the microwave dielectric properties of $\text{Li}_2\text{Mg}_3\text{TiO}_6$ through Ge substitution

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Abstract:

In this paper, we demonstrate a strategy to reduce the sintering temperature of titanates through an appropriate amount of Ge substitution for Ti. A series of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ($x = 0.04, 0.06, 0.08, 0.10, 0.12$) ceramics, prepared by a solid-state reaction method, are reported. By controlling the content of the Ge substitution, the sintering temperature of $\text{Li}_2\text{Mg}_3\text{TiO}_6$ was significantly reduced to 1140 °C. When $x = 0.10$, the $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics sintered at 1140 °C for 6 h displayed excellent values of $\varepsilon_r = 13.7$, $Q \times f = 131,500$ GHz and $\tau_f = -34.2$ ppm/°C. In addition, the temperature stability was successfully adjusted to be close to zero by adding CaTiO_3 to form a composite ceramic. A temperature stable ceramic $0.96\text{Li}_2\text{Mg}_3\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_6$ - 0.04CaTiO_3 with $\tau_f = -3.5$ ppm/°C, $\varepsilon_r = 14.9$ and $Q \times f = 68,900$ GHz was obtained

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when sintered at 1180 °C. The good dielectric performances of the CaTiO_3 -modified $\text{Li}_2\text{Mg}_3\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_6$ ceramics makes them possible candidates for substrates in microwave integrated circuits.

Keywords:

Ceramics; Dielectric properties; Rock-salt structure; Low loss

1. Introduction

The rapid advances in wireless communications from cellular phones and global position satellites (GPS) to intelligent transport system (ITS), the Internet of Things (IoTs) and military radar systems, have stimulated the enormous development of microwave dielectric ceramics. [1-3]. Practical applications require an appropriate relative permittivity (ϵ_r , high for miniaturization; low for signal propagation), a high quality factor ($Q \times f$) for better frequency selectivity and a near-zero temperature coefficient of frequency (τ_f) (for thermal stability) [4, 5]. However, most of the reported ceramics cannot satisfy all these requirements simultaneously. Consequently, a search for materials with sophisticated dielectric characteristics is still an urgent issue.

Unfortunately, the sintering temperatures of many of the developed microwave dielectrics such as CaTiO_3 , ZnAl_2O_4 , $\text{Ba}_8\text{MgTa}_6\text{O}_{24}$, and $\text{Ba}_4\text{LiNb}_3\text{TaO}_{12}$, are extremely high (> 1300 °C), [6-9]. Some approaches, such as the addition of sintering aids and wet-chemical synthesis, could effectively reduce the sintering temperature but these methods usually induce additional dielectric losses because of the introduction of secondary phases or alternatively can suffers from complicated internal processes [10, 11]. However, partial ionic substitution by low-melting constituents has been proved to be an effective method to lower sintering

temperatures while maintaining good dielectric performances. Examples of this are $\text{K}_{0.5}\text{Na}_{0.5}\text{NbO}_3$, $(\text{Ag}_{0.5}\text{Bi}_{0.5})(\text{Mo}_{0.5}\text{W}_{0.5})\text{O}_4$, and $\text{Na}_{2x}\text{Ba}_{1-x}\text{Li}_2\text{Ti}_6\text{O}_{14}$ [12-14].

More recently, the microwave dielectric properties of some rock-salt structured ceramics have been extensively investigated, especially those containing lithium. Among these, $\text{Li}_2\text{Mg}_3\text{BO}_6$ ($\text{B} = \text{Ti}, \text{Zr}, \text{Sn}$) compounds have attracted considerable attention due to their excellent dielectric properties with $Q \times f = 152,000$ GHz, $\varepsilon_r = 15.2$ and $\tau_f = -39$ ppm/ $^{\circ}\text{C}$ [15]. However, their high sintering temperature (1280 $^{\circ}\text{C}$) and large negative τ_f values limit their commercial applications to some extent. Consequently, in the present paper, an appropriate amount of Ge^{4+} substitution for the Ti^{4+} site was introduced in an attempt to reduce the sintering temperature of $\text{Li}_2\text{Mg}_3\text{TiO}_6$. The associated effects of the Ge substitution on the sintering behavior, crystal structure and microwave dielectric properties were also investigated. Additionally, CaTiO_3 ($\tau_f \sim +800$ ppm/ $^{\circ}\text{C}$) was utilized to form composite ceramics with $\text{Li}_2\text{Mg}_3\text{TiO}_6$ to compensate the thermal stability.

2. Experimental section

2.1. Preparation

$\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics with $x = 0.04, 0.06, 0.08, 0.10, 0.12$ were prepared by a traditional solid-state route. The high purity raw materials Li_2CO_3 , MgO , TiO_2 , and GeO_2 (> 99.9%, Guo-Yao Co., Ltd., Shanghai, China) were weighed according to the compositions and ball milled for 6 h in an ethanol medium. The mixture was then dried and calcined at 980 $^{\circ}\text{C}$ for 6 h after which the calcined powder was ball milled again for 6 h. The resultant calcined powder was granulated with polyvinyl alcohol (PVA, 10 vol%) as a binder and isostatically pressed into cylindrical pellets (diameter 10 mm, thickness 5-7 mm) under a pressure of 200 MPa. The pellets were fired at 550 $^{\circ}\text{C}$ in air for 2 h at a heating rate of 1.5 $^{\circ}\text{C}/\text{min}$ to expel the binder. Finally, the

samples were sintered over a temperature range of 1060–1220 °C for 6 h in air at a heating rate of 5 °C/min.

2.2 Characterization

The crystal structure and phase purity of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics were analyzed by X-ray diffractometer (XRD) (X'Pert PRO, PANalytical, Almelo, Holland) using $\text{Cu K}\alpha$ radiation, and a Raman Microscope (Thermo Fisher Scientific DXR, America). The microstructural analysis was performed using scanning electron microscopy (SEM, JSM6380-LV, Tokyo, Japan). The densities were determined using the Archimedes' method. The microwave dielectric properties (ϵ_r , $Q \times f$, and τ_f) were recorded by a network analyzer (N5230A, Agilent Co., Palo Alto, California) at 10 MHz–40 GHz and a temperature chamber (Delta 9039, Delta Design, San Diego, CA). The temperature coefficient of resonant frequency (τ_f) was calculated from the equation:

$$TCF(\tau_f) = \frac{f_{T_1} - f_{T_0}}{f_{T_0}(T_1 - T_0)} \quad (1)$$

where f_{T_1} and f_{T_0} are the resonant frequencies at 85 °C and room temperature, respectively.

3. Results and discussion

Fig. 1 shows the linear shrinkage characteristics of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics in the temperature range 25–1100 °C. Within the low temperature range 25–800 °C, the linear shrinkage was small but the value increased substantially after reaching a characteristic temperature, indicating the onset of the densification process. At $x = 0.06$ the onset temperature was around 920 °C with 1 % of linear shrinkage. As x increased to 0.08 and 0.10, the densification started around 900 and 880 °C with larger linear shrinkages of about 1.2 % and 1.4 %, respectively. This implied that the

Ge⁴⁺ substitution for Ti⁴⁺ could reduce the densification temperature of Li₂Mg₃TiO₆ ceramics.

Fig. 2 shows the powder X-ray diffraction patterns of Li₂Mg₃Ti_{1-x}Ge_xO₆ ($x = 0.04\text{--}0.14$) samples fired at 1120 °C for 6 h in air. When $x = 0.04\text{--}0.10$, only a single phase was detected according to the JCPDS#39-0932 for Li₂Mg₃SnO₆ (same structure with Li₂Mg₃TiO₆) with a space group *Fm-3m* (225). These results indicated that Ge⁴⁺ ions could dissolve into the crystal lattice of Li₂Mg₃TiO₆ to form a solid solution and that the samples with $x = 0.04\text{--}0.10$ exhibited the cubic phase with an ordered rock salt structure. However, a further increase in Ge substitution induced the appearance of a secondary phase, detected as Li₂MgGeO₄ phase (JCPDS #24-0627), in the $x = 0.12$ sample. As x increased, the intensity of the Li₂MgGeO₄ peaks became stronger, which indicated that the solid solubility of Ge in Li₂Mg₃TiO₆ was located between 10% and 12%.

Fig. 3 shows the Raman spectra of the Li₂Mg₃Ti_{1-x}Ge_xO₆ in the wavenumber range 100-1000 cm⁻¹. The Raman spectrum of Li₂MgGeO₄ is also presented for comparison. According to the literature, the observed main Raman bands at 185 cm⁻¹, 397 cm⁻¹ and 730 cm⁻¹ are the characteristic modes of a rock salt structure [16]. An additional band around 757 cm⁻¹ was observed in the $x = 0.12$ sample, which was the characteristic band of the Li₂MgGeO₄ phase. The Raman results further confirmed the formation of a secondary phase when $x \geq 0.12$. In addition, it was observed that with increasing x , the Raman modes of rock salt became broader and stronger, which was associated with a change in rigidity and symmetry in the structure due to the Ge substitution. A similar phenomenon has been previously reported in the Ba(Co_{1-x}Mg_x)₂(VO₄)₂ system [17].

SEM images of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics sintered at densification temperature are displayed in Fig. 4 (a-e). All samples exhibited a relatively dense microstructure in spite of some pores due to the loss of lithium at elevated temperatures ($\geq 1000\text{ }^\circ\text{C}$) [18]. But the densification was obviously enhanced as compared with un-doped $\text{Li}_2\text{Mg}_3\text{TiO}_6$ ceramics sintered at $1280\text{ }^\circ\text{C}$ [15, 19]. Thus one immediate conclusion is that Ge^{4+} substitution in $\text{Li}_2\text{Mg}_3\text{TiO}_6$ can effectively enhance the density and reduce the sintering temperature.

Changes in bulk density and microwave dielectric properties (ε_r , $Q \times f$, and τ_f) of the $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramic as a function of sintering temperature are shown in Fig. 5. In Fig. 5(a), with an increasing sintering temperature, the apparent density first increased, reached a maximum value and then decreased. The increase in the density could be due to the elimination of pores and to homogenous grain growth. Grain coarsening is the accepted reason for the reduction of density at higher sintering temperatures [20]. The densification temperature of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ decreased from $1200\text{ }^\circ\text{C}$ at $x = 0.04$ to $1120\text{ }^\circ\text{C}$ at $x = 0.10$. This was much lower than that of the parent $\text{Li}_2\text{Mg}_3\text{TiO}_6$ which had a value of $1280\text{ }^\circ\text{C}$. It should be noted that further increase in the Ge^{4+} content to 0.12 resulted in an increase in optimal densification temperature and bulk density. This phenomenon might be due to the presence of $\text{Li}_2\text{MgGeO}_4$ with its higher densification temperature ($1220\text{ }^\circ\text{C}$) and larger density (4.08 g/cm^3).

Fig. 5(b) and (c) shows the change in the relative permittivity (ε_r) and quality factor ($Q \times f$) of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics as a function of sintering temperature. It was found that both the relative permittivity and the quality factor changed with increasing sintering temperature in a manner similar to that of the density. For each composition, a saturated ε_r and $Q \times f$ value was achieved at the densification

temperature. As the Ge^{4+} content increased from 0.04 to 0.12, the ε_r value decreased from 15.5 to 11.6. This reduction can be explained by the lower dielectric polarizability of the Ge^{4+} (1.63 Å) ion compared with that of Ti^{4+} (1.93 Å). Meanwhile, the $Q \times f$ values increased from 115,500 GHz at $x = 0.04$ to 131,500 GHz at $x = 0.10$. However, the sample with $x = 0.12$ exhibited an extremely low $Q \times f$ value of 60,500 GHz. The reason for this sharp decrease in $Q \times f$ value was the lower $Q \times f$, ~ 28,500 GHz, of $\text{Li}_2\text{MgGeO}_4$ compared to that of $\text{Li}_2\text{Mg}_3\text{TiO}_6$. As shown in Fig.5 (d), the temperature coefficient of the resonance frequency exhibited a weak dependence on sintering temperature and composition. The τ_f value was in the range -36.6 to -34.2 ppm/°C except for the $x = 0.12$ sample which had a larger negative τ_f value of -41.5 ppm/°C.

For practical applications the thermal stability characterized by a near-zero τ_f value is required. In order to adjust the τ_f value of the $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics, CaTiO_3 with a positive τ_f of $+800$ ppm/°C [21] was added to form a composite ceramic with $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$. XRD patterns, a back scattered electron image and EDS analysis of the $0.96\text{Li}_2\text{Mg}_3\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_6-0.04\text{CaTiO}_3$ ceramics are shown in Fig. 6. Only the peaks of CaTiO_3 (JCPDS No. 76-2400) and the $\text{Li}_2\text{Mg}_3\text{TiO}_6$ phase were observed in the XRD profiles. Two types of grains could easily be detected in the back scattered electron image. EDS analysis identified that the smaller grains (marked as “C”) were rich in Ca, Ti and O, and the ratio of Ca:Ti in the grains was approximately 1:1. Thus the smaller grains were assigned to belong to the CaTiO_3 phase. All the above results indicated that CaTiO_3 and $\text{Li}_2\text{Mg}_3\text{TiO}_6$ can co-exist to form composite ceramics.

It is well-known that the theoretical permittivity (ε_r) and τ_f values of a two-phase composite ceramic can be obtained from the Lichtenecker empirical logarithmic rule [22, 23]:

$$\lg \varepsilon = y_1 \lg \varepsilon_1 + y_2 \lg \varepsilon_2 \quad (2)$$

$$\tau_f = y_1 \tau_{f1} + y_2 \tau_{f2} \quad (3)$$

where y_1 and y_2 are the volume fractions ($y_1 + y_2 = 1$), ε_1 , τ_{f1} and ε_2 , τ_{f2} are the relative permittivity and τ_f value of the two phases, respectively. In the present case, the calculated relative permittivity and τ_f values of $0.96\text{Li}_2\text{Mg}_3\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_6$ - 0.04CaTiO_3 composite ceramic were 15.15 and $-0.83 \text{ ppm}/^\circ\text{C}$, which were in good agreement with the measured values as shown in Table 1. A near-zero τ_f value of $-3.5 \text{ ppm}/^\circ\text{C}$ combined with a relative permittivity of 14.9 and a quality factor of 68,900 GHz (measured at 10.3 GHz) was obtained in the $0.96\text{Li}_2\text{Mg}_3\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_6$ - 0.04CaTiO_3 composite. The good thermal stability, together with the low permittivity and high quality factors, of the CaTiO_3 -modified $\text{Li}_2\text{Mg}_3\text{TiO}_6$ ceramics makes them possible candidates for substrates in microwave integrated circuits.

4. Conclusions

A series of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics was prepared via the solid state reaction route. The effects of Ge substitution on the crystal structure, sintering behavior, and microwave dielectric properties of $\text{Li}_2\text{Mg}_3\text{TiO}_6$ were studied in detail. XRD patterns, Raman, and EDS analysis indicated that a solid solution formed when $x = 0.04$ – 0.10 , while a secondary phase $\text{Li}_2\text{MgGeO}_4$ was detected at $x = 0.12$. Ge substitution effectively reduced the sintering temperature and improved the densification of $\text{Li}_2\text{Mg}_3\text{TiO}_6$. An excellent dielectric performance, with $\varepsilon_r \sim 13.7$, $Q \times f \sim 131,500 \text{ GHz}$ and $\tau_f \sim -34.2/^\circ\text{C}$, was obtained in the $x = 0.10$ sample. In addition, the thermal stability of $\text{Li}_2\text{Mg}_3\text{TiO}_6$ was successfully adjusted by forming a composite ceramic

with CaTiO_3 . A temperature stable ceramic $0.96\text{Li}_2\text{Mg}_3\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_6$ - 0.04CaTiO_3 with $\tau_f = -3.5 \text{ ppm}/^\circ\text{C}$, $\varepsilon_r = 14.9$ and $Q \times f = 68,900 \text{ GHz}$ was obtained. The good dielectric performance of CaTiO_3 -modified $\text{Li}_2\text{Mg}_3\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_6$ ceramics makes them possible candidates for substrates in microwave integrated circuits.

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References:

- [1]. J. Varghese, T. Joseph, K.P. Surendran, T.P.D. Rajana, M.T. Sebastian, A new microwave dielectric ceramic with low thermal expansivity, *Dalton Trans.* 44 (2015) 5146–5152.
- [2]. M. Valant, D. Suvorov, Glass-free low-temperature cofired ceramics: calcium germanates, silicates and tellurates, *J. Eur. Ceram. Soc.* 24 (2004) 1715–1719.
- [3]. N. Joseph, J. Varghese, T. Siponkoski, M. Teirikangas, M.T. Sebastian, H. Jantunen, Glass-free CuMoO_4 ceramic with excellent dielectric and thermal properties for ultralow temperature cofired ceramic applications, *Acs Sustain. Chem. Eng.* 4 (2016) 5632–5639.

- [4]. W. Lei, Ran An, X.C. Wang, W.Z. Lu, Phase evolution and near-zero shrinkage in $\text{BaAl}_2\text{Si}_2\text{O}_8$ low-permittivity microwave dielectric ceramics, *Mater. Res. Bull.* 50 (2014) 235–239.
- [5]. H.C. Xiang, C.C. Li, Y. Tang, L. Fang, Two novel ultralow temperature firing microwave dielectric ceramics LiMVO_6 ($\text{M} = \text{Mo}, \text{W}$) and their chemical compatibility with metal electrodes, *J. Eur. Ceram. Soc.* 37 (2017) 3959–3963.
- [6]. W.S. Kim, K.H. Yoon, E.S. Kim, Microwave dielectric properties and far-infrared reflectivity characteristics of the $\text{CaTiO}_3\text{--Li}_{(1/2)-3x}\text{Sm}_{(1/2)+x}\text{TiO}_3$ ceramics, *J. Am. Ceram. Soc.* 83 (2000) 2327–2329.
- [7]. K.P. Surendran, N. Santha, P. Mohanan, M.T. Sebastian, Temperature stable low loss ceramic dielectrics in $(1-x)\text{ZnAl}_2\text{O}_4\text{--}x\text{TiO}_2$ system for microwave substrate applications, *Eur. Phys. J. B* 41 (2004) 301–306.
- [8]. S. Kawaguchi, H. Ogawa, A. Kan, S. Ishihara, Microwave dielectric properties of $\text{Ba}_8\text{Ta}_6(\text{Ni}_{1-x}\text{M}_x)\text{O}_{24}$ ($\text{M} = \text{Zn}$ and Mg) ceramics, *J. Eur. Ceram. Soc.* 26 (2006) 2045–2049.
- [9]. L. Fang, C.C. Li, X.Y. Peng, C.Z. Hu, B.L. Wu, H.F. Zhou, $\text{Ba}_4\text{LiNb}_{3-x}\text{Ta}_x\text{O}_{12}$ ($x = 0\text{--}3$): a series of high-Q microwave dielectrics from the twinned 8H hexagonal perovskites, *J. Am. Ceram. Soc.* 93 (2010) 1229–1231.
- [10]. X.P. Lu, Y. Zheng, B. Zhou, Effect of B_2O_3 addition on the microwave dielectric properties of $\text{Li}_2\text{ZnTi}_3\text{O}_8$ ceramic, *J. Electroceram.* 31 (2013) 360–363.
- [11]. J. Guo, H.Z. Guo, A.L. Baker, M.T. Lanagan, E.R. Kupp, G.L. Messing, C.A. Randall, Cold sintering: a paradigm shift for processing and integration of ceramics, *Angew. Chem. Int. Ed.* 55 (2016) 11457–11461.

- [12]. S.S. Wu, W.F. Zhu, L.J. Liu, D.P. Shi, S.Y. Zheng, Y.M. Huang, L. Fang, Dielectric properties and defect chemistry of WO₃-doped K_{0.5}Na_{0.5}NbO₃ ceramics, *J. Electron. Mater.* 43 (2014) 1055–1061.
- [13]. D. Zhou, W.B. Li, J. Guo, L.X. Pang, Z.M. Qi, T. Shao, H.D. Xie, Z.X. Yue, X. Yao, Structure, phase evolution, and microwave dielectric properties of (Ag_{0.5}Bi_{0.5})(Mo_{0.5}W_{0.5})O₄ ceramic with ultralow sintering temperature, *Inorg. Chem.* 53 (2014) 5712–5716.
- [14]. H.C. Xiang, L. Fang, M.Y. Xu, Y. Tang, C.C. Li, Microwave dielectric properties of Na_{2x}Ba_{1-x}Li₂Ti₆O₁₄ ceramics and their chemical compatibility with silver, *Mater. Chem. Phys.* 195 (2017) 275–282.
- [15]. Z. Fu, P. Liu, J. Ma, X. Zhao, H. Zhang, Novel series of ultra-low loss microwave dielectric ceramics: Li₂Mg₃BO₆ (B = Ti, Sn, Zr), *J. Eur. Ceram. Soc.* 36 (2016) 625–629.
- [16]. J.L. Ma, Z.F. Fu, P. Liu, B. Wang, Y. Li, Microwave dielectric properties of low-fired Li₂TiO₃–MgO ceramics for LTCC applications, *Mater. Sci. Eng., B* 204 (2016) 15–19.
- [17]. C.H. Su, F.C. Lin, T.M. Chu, C.L. Huang, Structural characteristics and microwave dielectric properties of low-firing Ba(Co_{1-x}Mg_x)₂(VO₄)₂ ($x = 0-1$) ceramics, *J. Alloys Compd.* 686 (2016) 608–615.
- [18]. Z. Fang, B. Tang, F. Si, S. Zhang, Temperature stable and high-Q microwave dielectric ceramics in the Li₂Mg_{3-x}Ca_xTiO₆ system ($x = 0.00-0.18$), *Ceram. Int.* 43 (2017) 1682–1687.
- [19]. Z. Fu, P. Liu, J. Ma, X. Chen, H. Zhang, New high Q low-fired Li₂Mg₃TiO₆ microwave dielectric ceramics with rock salt structure, *Mater. Lett.* 164 (2016) 436–439.

- [20]. X.Q. Sha, Z. Lü, X.Q. Huang, J.P. Miao, Z.G. Liu, X.S. Xin, Y.H. Zhang, W.H. Su, Influence of the sintering temperature on electrical property of the $\text{Ce}_{0.8}\text{Sm}_{0.1}\text{Y}_{0.1}\text{O}_{1.9}$ electrolyte, *J. Alloys Compd.* 433 (2007) 274–278.
- [21]. B. Jančar, D. Suvorov, M. Valant, Microwave dielectric properties of CaTiO_3 – NdAlO_3 ceramics, *J. Mater. Sci. Lett.* 20 (2001) 71–72.
- [22]. Y. Wu, D. Zhou, J. Guo, L.X. Pang, H. Wang, X. Yao, Temperature stable microwave dielectric ceramic $0.3\text{Li}_2\text{TiO}_3$ – $0.7\text{Li}(\text{Zn}_{0.5}\text{Ti}_{1.5})\text{O}_4$ with ultra-low dielectric loss, *Mater. Lett.* 65 (2011) 2680–2682.
- [23]. W. Li, L. Fang, Y. Tang, Y.H. Sun, C.C. Li, Microwave dielectric properties in the $\text{Li}_{4+x}\text{Ti}_5\text{O}_{12}$ ($0 \leq x \leq 1.2$) ceramics, *J. Alloys Compd.* 701 (2017) 295–300.

Table 1 Microwave dielectric properties of $(1-y)\text{Li}_2\text{Mg}_3\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_6$ – $y\text{CaTiO}_3$ ceramics sintered at optimum temperature.

y values	S.T. (°C)	ϵ_r	$Q \times f$ (GHz)	τ_f (ppm/°C)	References
0	1140	13.7	131,500	-34.2	This work
0.02	1160	14.4	97,500	-18.5	This work
0.04	1180	14.9	68,900	-3.5	This work
0.06	1200	15.7	46,000	+16.2	This work
1	1300	170	3,500	+800	[21]

Fig. 1 The linear shrinkage characteristics of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics.

Fig. 2 XRD patterns of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ($x = 0.04$ – 0.14) samples sintered at 1120 °C for 6 h.

Fig. 3 Raman spectra of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ($x = 0.04, 0.06, 0.08, 0.1, 0.12$) ceramics.

Fig. 4 SEM images of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics sintered at different temperatures for 6h: (a) $x = 0.04$ at 1200 °C, (b) $x = 0.06$ at 1160 °C, (c) $x = 0.08$ at 1140 °C, (d) $x = 0.1$ at 1120 °C, (e) $x = 0.12$ at 1180 °C.

Fig. 5 The (a) density, (b) permittivity, (c) quality factor, and (d) temperature coefficient of frequency of $\text{Li}_2\text{Mg}_3\text{Ti}_{1-x}\text{Ge}_x\text{O}_6$ ceramics as a function of sintering temperature.

Fig. 6 The XRD patterns, SEM image and EDS analysis of the $0.96\text{Li}_2\text{Mg}_3\text{Ti}_{0.9}\text{Ge}_{0.1}\text{O}_6-0.04\text{CaTiO}_3$ ceramics sintered at 1180°C .