

Microstructure and microwave dielectric properties of $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ ceramics

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Abstract. $(\text{ZnMg})_2\text{SiO}_4$ powders was prepared by the sol–gel process, and the microstructure and dielectric properties of $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ microwave materials were investigated systematically. TG-DSC and XRD analyzes for gels indicate that the $(\text{ZnMg})_2\text{SiO}_4$ with pure willemite phase could be obtained at low temperature of 850°C. Further, XRD illustrates that just small amounts of Mg can be incorporated into Zn_2SiO_4 lattice, and the solid solution limit of Mg in Zn_2SiO_4 is about $x = 0.1$. By appropriate Mg substitution for Zn, the sintering range is widened and the sintering temperature of Zn_2SiO_4 ceramics can be lowered effectively. SEM shows that Mg-substitution for Zn can promote the grain growth of Zn_2SiO_4 . Moreover, the microwave dielectric properties strongly depended on the substitution content of Mg and sintering temperatures. $(\text{Zn}_{0.8}\text{Mg}_{0.2})_2\text{SiO}_4$ dielectrics sintered at 1170°C show the condense microstructure with small uniform grains and best microwave properties: $\epsilon_r = 6.3$, $Q \times f = 189800$ GHz and $\tau_f = -63$ ppm/°C.

Keywords. Willemite (Zn_2SiO_4); forsterite (Mg_2SiO_4); microwave ceramics; dielectric property; microstructure; millimetre-wave frequency.

1. Introduction

With the rapid development of mobile communication and radar systems, the utilized frequency has also correspondingly increased to millimetre-wave, where large quantity of information could be transported with rapid speed. The resonators and filters for such high-band microwave applications strongly require the microwave dielectrics with a very low dielectric constant (ϵ_r), a high-quality factor (Q), and a near-zero temperature coefficient of resonant frequency (τ_f). In recent years, several material systems with low ϵ_r and high- Q value such as Al_2O_3 , Mg_2SiO_4 and CaWO_4 have been investigated (Park *et al* 2001; Ohsato *et al* 2003; Tsunooka *et al* 2003). In addition, a newly developed Zn_2SiO_4 ceramics is considered to be good candidate material for high performance millimetre-wave devices.

Guo *et al* (2006) first reported that Zn_2SiO_4 ceramics prepared by solid-state method sintered at 1340°C exhibited excellent dielectric properties: $\epsilon_r = 6.6$, $Q \times f = 219,000$ GHz. However, Zn_2SiO_4 showed a high τ_f of -61 ppm/°C. The 11 wt% TiO_2 modified Zn_2SiO_4 ceramics sintered at 1250°C showed a near-zero τ_f value of 1.0 ppm/°C with ϵ_r of 9.3, $Q \times f$ value of 113,000 GHz. Nguyen *et al* (2007) studied the effect of Zn/Si ratio on

the microstructure and microwave properties of Zn_2SiO_4 ceramics, and found that the ceramics with nominal composition $\text{Zn}_{1.8}\text{SiO}_{3.8}$ sintered at 1300°C exhibited improved microwave dielectric properties of $\epsilon_r = 6.6$, $Q \times f = 147,000$ GHz, and $\tau_f = -22$ ppm/°C. Besides, Song *et al* (2008) improved the $Q \times f$ value of Zn_2SiO_4 ceramics by Mg^{2+} substituting for Zn^{2+} and $(\text{Zn}_{0.6}\text{Mg}_{0.4})_2\text{SiO}_4$ ceramics sintered at 1250°C achieved the dielectric properties: $\epsilon_r = 6.6$, $Q \times f = 95,650$ GHz and $\tau_f = -60$ ppm/°C. Accordingly, the high sintering temperature and large negative τ_f value of Zn_2SiO_4 -based ceramics put constraints on its application as microwave materials. However, Mg_2SiO_4 dielectrics recently have been lowered by the addition of suitable low melting glasses for possible LTCC applications (Sasikala *et al* 2008, 2010).

It is well known that sol–gel process is an efficient technique for the produce of the ceramics, due to the good mixing of starting materials and relatively low reaction temperature resulting in more homogeneous products than those obtained by direct solid state reactions. Dong *et al* (2008) reported that the sol–gel-prepared Zn_2SiO_4 ceramics sintered at 1325°C showed dielectric properties: $\epsilon_r = 6.6$, $Q \times f = 198,400$ GHz, and $\tau_f = -41.6$ ppm/°C. In this work, $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ ceramics with good microwave performance were synthesized by sol–gel procedure at such lower temperature of 1170°C. Moreover, the influence of Mg-substituting content on the structural and microwave dielectric properties of $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ system was investigated systematically.

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2. Experimental

2.1 Sample preparation

$(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ ($x = 0.1, 0.2, 0.3, 0.4$) was prepared with sol-gel method. According to the designed composition, ZnO and MgCO_3 were dissolved in HNO_3 and deionized water, and then poured into ethanol and ethyl silicate ($(\text{C}_2\text{H}_5)_4\text{SiO}_4$, TEOS). The volume ratio of $\text{C}_2\text{H}_5\text{OH}$ to TEOS was 1 : 1 and the pH value was adjusted to near 2. Highly transparent sols were obtained after vigorous stirring, and transparent gels could be formed at 90°C for 3 h. Dried gels were achieved by heating the wet gels at 100°C for 24 h. Then the xerogels were calcined at 700 – 1000°C for 2 h. The calcined powders were ball milled in alcohol for 24 h with zirconia balls. The dried powders with 10 wt% PVA were granulated and pressed into pellets (10 mm in diameter and 7 mm in height), and then sintered at temperatures of 1130 – 1190°C for 2 h.

2.2 Characteristics analysis

Thermoanalysis of dry gels was carried out using a TG-DSC thermoanalyzer (Netzsch STA 449C) from 29 to 1350°C at heating rate of $10^\circ\text{C}/\text{min}$. The crystalline phases of the calcined powders and sintered ceramics were identified by X-ray diffraction analysis (XRD, Philips X'Pert-MPD) using $\text{Cu-K}\alpha$ radiation. Microstructural observation of the sintered ceramics was performed by scanning electron microscopy (SEM, Hitachi S-530) equipped with energy dispersive spectroscopy (EDS). The dielectric characteristics at microwave frequencies were measured by the Hakki-Coleman dielectric resonator method. A system combined with an Agilent network analyzer E8363A was employed in the measurement. The $Q \times f$ factor was used to evaluate the loss quality, where f is the resonant frequency. The temperature coefficient of resonant frequency (τ_f) was measured by the open cavity method in the temperature range from 25 to 75°C and was defined as

$$\tau_f = \frac{f_{75} - f_{25}}{50 \cdot f_{25}},$$

where f_{25} and f_{75} are the resonant frequency at 25 and 75°C , respectively.

3. Results and discussion

TG and DSC curves of the $(\text{Zn}_{0.8}\text{Mg}_{0.2})_2\text{SiO}_4$ dried gel are drawn in figure 1. A 56.1% weight loss is observed in the thermogravimetric curve of the $(\text{Zn}_{0.8}\text{Mg}_{0.2})_2\text{SiO}_4$ gel in the temperature range between 29 and 600°C . This is due to the removal of hydration water and the decomposition of the nitrate and $\text{Si}(\text{OH})_4$. Moreover, there is no weight

change when the temperature is higher than 700°C . From DSC pattern, there are two endothermic peaks at about 152.1 and 322.8°C , respectively, and one exothermic peak around 777.9°C . The first endothermic peak at 152.1°C indicates the dehydration of $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$ and hydrated silica. The next endothermic peak around 322.8°C is connected to the decomposition of nitrate radical $(\text{NO}_3)^\cdot$. The exothermic peak located at 777.9°C may be caused by the crystallization of ZnO as well as the phase formation of Zn_2SiO_4 .

XRD was used to investigate the change in crystalline phase during the preparation of $(\text{Zn}_{0.8}\text{Mg}_{0.2})_2\text{SiO}_4$. According to DSC curve, the obtained gel was treated at $700, 800, 850$ and 1000°C , and their XRD patterns are shown in figure 2. The XRD pattern of gel at 700°C shows no obvious diffraction peaks, which indicates that the composite is amorphous. At 800°C , the diffraction peaks almost belong to Zn_2SiO_4 main phase, while a few ZnO second phase appears. This demonstrates that the exothermic peak at 777.9°C is caused by the phase formation of Zn_2SiO_4 together with ZnO. It could be seen that the pure $(\text{ZnMg})_2\text{SiO}_4$ phase is formed at low temperature of about 850°C , but the secondary phase ZnO disappears. The intensity of diffraction peaks of Zn_2SiO_4 became stronger as the calcining temperature increases to 1000°C . Thus, the dry gel for $(\text{Zn}_{0.8}\text{Mg}_{0.2})_2\text{SiO}_4$ should be heat-treated at 850°C to obtain the pure $(\text{ZnMg})_2\text{SiO}_4$ phase and produce the active fine powders used in the following experiments.

Figure 3 shows the XRD patterns of $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ ($x = 0$ – 0.4) ceramics sintered at 1170°C for 2 h. Only diffraction peaks of willemite phase are observed for specimens with $x = 0$ – 0.1 , which can be indexed as a trigonal structure. Nguyen *et al* (2007) reported that the ZnO secondary phase was formed in the Zn_2SiO_4 ceramics, which would result in the low $Q \times f$ value. But the unwanted ZnO phase is not found for all the present specimens. A few diffraction peaks of the secondary

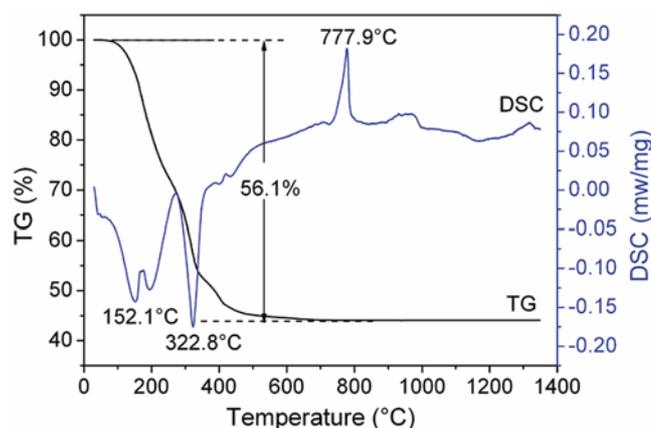


Figure 1. TG–DSC curves of $(\text{Zn}_{0.8}\text{Mg}_{0.2})_2\text{SiO}_4$ gel from 29 to 1350°C .

phase Mg_2SiO_4 appear accompanying the main phase Zn_2SiO_4 with the increase of Mg content ($x = 0.2\text{--}0.3$), and the obvious co-presence of two such crystal phases is determined at $x = 0.4$. At the same time, the peak intensity of Zn_2SiO_4 phase is weakened and that of Mg_2SiO_4 phase is enhanced significantly. Therefore, the solid solution limit of Mg ions in Zn_2SiO_4 is about $x = 0.1$ on the basis of XRD results here. However, Song *et al* (2008) previously found that the Mg_2SiO_4 secondary phase disappears at $x = 0.95$ for $(\text{Mg}_{1-x}\text{Zn}_x)_2\text{SiO}_4$, which agrees well with that reported by Segnit and Holland (1965). This result indicates that the solubility limit of Mg ions in the Zn_2SiO_4 lattice could be somewhat influenced by the preparation method used as well.

In fact, the small solid solution limit of Mg in Zn_2SiO_4 is because of the large difference between the crystal structure of Zn_2SiO_4 and Mg_2SiO_4 . Though Zn_2SiO_4 and

Mg_2SiO_4 are both island silicate compounds with similar formula, the former generally known as willemite, has a rhombohedral structure belonging to space group $R\bar{3}$, and the latter, known as forsterite, has an orthorhombic structure belonging to space group Pmnb (Chang *et al* 1999; Horiuchi and Sawamoto 1981). Zn_2SiO_4 is built on connection of Zn–O tetrahedron with Si–O tetrahedron by sharing vertex, and Mg_2SiO_4 is composed of connection of Mg–O octahedron with Si–O tetrahedron by sharing vertex and edge. Accordingly, just small amount of Mg can be incorporated into Zn_2SiO_4 lattice and substitute zinc ions. That is, the solid solution $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ without any other phases could be formed at $x < 0.2$.

In the previous literatures, it has been reported that the preparation temperature of Zn_2SiO_4 and $(\text{ZnMg})_2\text{SiO}_4$ via the solid state reaction is usually higher than 1280°C (Guo *et al* 2006; Nguyen *et al* 2007; Song *et al* 2008). But in the case of the sol–gel processing method, the $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ ceramics can be sintered at the temperatures lower than 1200°C due to the fine powders with high activity. Figure 4 shows the SEM photographs of $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ ceramics sintered at 1170°C . It is clearly seen that the microstructures of the $(\text{ZnMg})_2\text{SiO}_4$ materials change markedly with the doping content of Mg. The spheroidic grains are small ($1\text{--}3\ \mu\text{m}$) and uniformly distributed for samples with $x = 0.1\text{--}0.2$. However, the presence of white spots shown in figures 4b–d is confirmed by EDS analysis to be Mg_2SiO_4 , which is consistent with the result from XRD. Moreover, with Mg content up to 0.3 , the grains grew rapidly and two kinds of grains including spheroidic grains and stick grains are observed clearly. These phenomena indicate that the introduction of Mg in Zn_2SiO_4 could accelerate the grain growth of Zn_2SiO_4 , and elongate the grains at the same time.

Figure 5 shows the dielectric constant (ε_r) of specimens with different Mg content as a function of sintering temperature. For samples with $x \leq 0.3$, the ε_r value slightly increases at first with increasing the firing temperature from 1130 to 1150°C . A large increase in ε_r value is observed at a temperature between 1150 and 1170°C , and then only small change occurs with further increase in the sintering temperature. It is understood that higher density will lead to higher dielectric constant owing to lower porosity in willemite-based ceramics (Guo *et al* 2006; Nguyen *et al* 2007). This suggests that the rapid densification for $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ ceramics x with ≤ 0.3 occurred at a temperature above 1150°C , and then density nearly saturated at above 1170°C . For sample with $x = 0.4$, the variation of ε_r value versus temperature is not significant ($6.1\text{--}6.2$), suggesting that the firing temperature range is wide, that is, it can be sintered at a lower temperature. It is found that Mg-substitution for Zn can decrease the sintering temperature of Zn_2SiO_4 ceramics. Moreover, it can be seen that ε_r values increase greatly with

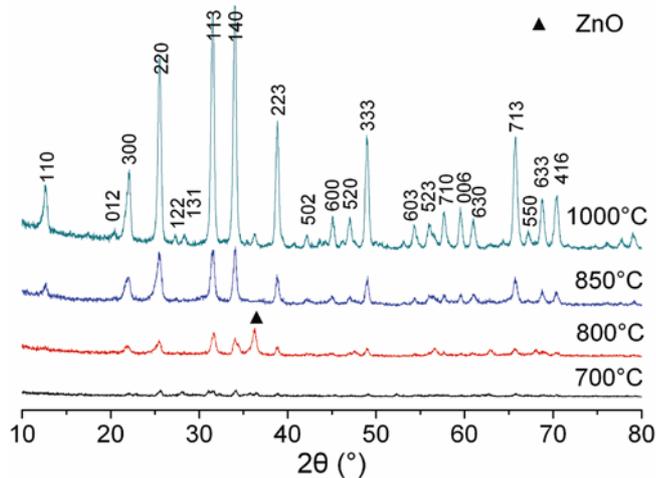


Figure 2. XRD patterns of $(\text{Zn}_{0.8}\text{Mg}_{0.2})_2\text{SiO}_4$ gel calcined at different temperature.

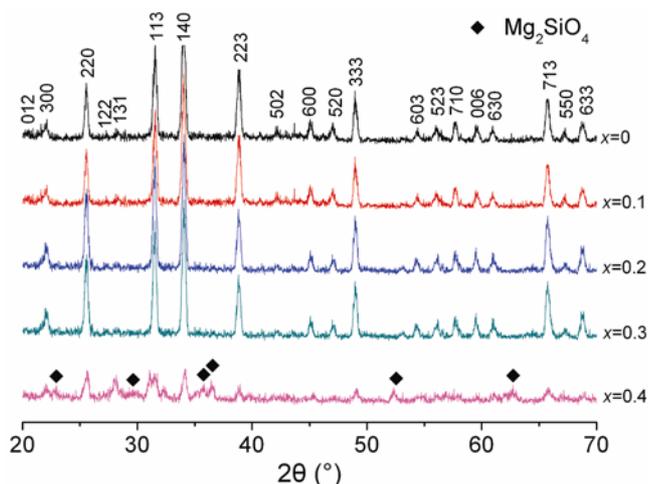


Figure 3. XRD patterns of $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ ceramics sintered at 1170°C .

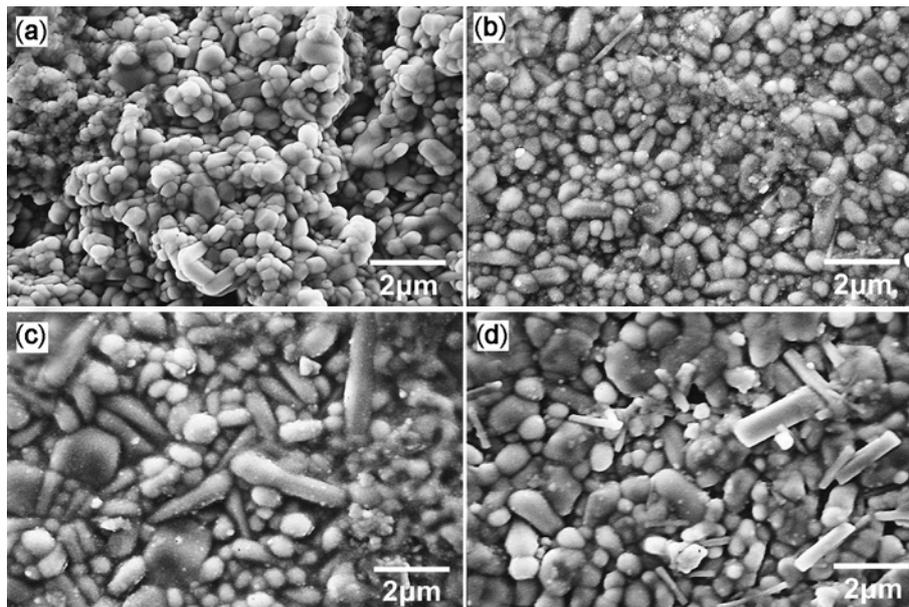


Figure 4. SEM photographs of $(Zn_{1-x}Mg_x)_2SiO_4$ ceramics sintered at $1170^\circ C$: (a) $x = 0.1$; (b) $x = 0.2$; (c) $x = 0.3$; (d) $x = 0.4$.

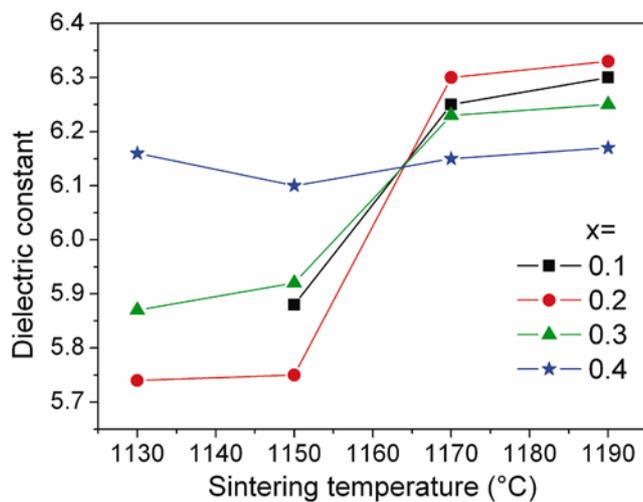


Figure 5. Sintering temperature dependence of dielectric constant for $(Zn_{1-x}Mg_x)_2SiO_4$ ceramics.

increasing x for samples fired at such low temperature range (1130 – $1150^\circ C$). When specimens sintered at the temperature higher than $1170^\circ C$, firstly, the ϵ_r increases to the maximum value at $x = 0.2$, and then turns to decrease steady with increasing x . It implies that the densification temperature of $(Zn_{1-x}Mg_x)_2SiO_4$ ceramics decreases from 1190 to $1130^\circ C$ with increasing x up to 0.4 . Therefore, it suggests that it is difficult for Zn_2SiO_4 ceramics to obtain a dense microstructure and its sintering range is very narrow. By appropriate Mg^{2+} substituting for Zn^{2+} , the sintering range is widened and the sintering temperature of Zn_2SiO_4 ceramics can be lowered from 1190 to $1130^\circ C$.

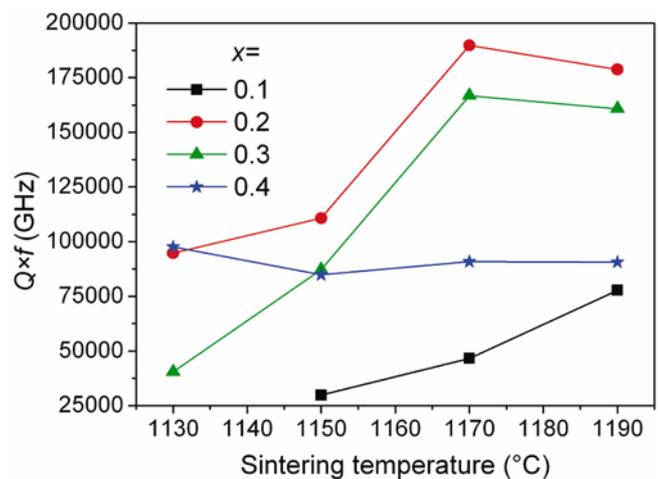


Figure 6. $Q \times f$ of $(Zn_{1-x}Mg_x)_2SiO_4$ ceramics as a function of sintering temperature.

Figure 6 illustrates the sintering temperature dependence of $Q \times f$ value for $(Zn_{1-x}Mg_x)_2SiO_4$ ceramics. It can be observed that the $Q \times f$ value increases gradually with increasing temperature for the sample with $x = 0.1$. For samples with $x = 0.2$ – 0.3 , with the increase of firing temperature, $Q \times f$ values also increase and reach the maximum (about $189,800$ GHz) at $1170^\circ C$, then decrease slightly. For the sample with $x = 0.4$, the $Q \times f$ shows insignificant variation as a function of temperature between $85,000$ and $100,000$ GHz. It is found that the $Q \times f$ value approximately shows the same tendency of the dielectric constant, but there is still some difference between them. In fact, quality factor (Q) is affected by

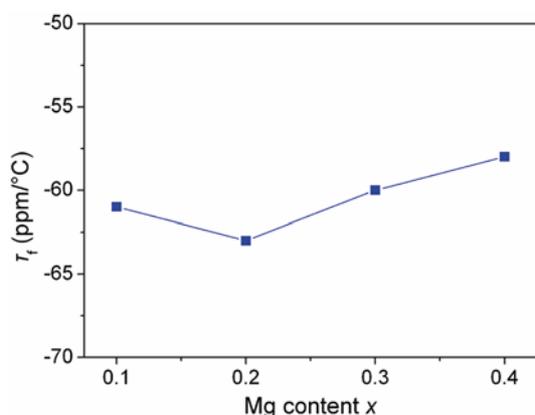


Figure 7. The dependence of the τ_f value of $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ on Mg content sintered 1170°C.

impurities, secondary phases, porosity and oxygen vacancy etc, although density plays an important role in controlling the dielectric loss. Furthermore, Huang *et al* (2001) reported that the $Q \times f$ is independent of density or porosity as the density is higher than 90% of theoretical density. Thus, the $Q \times f$ shows relative lower value at $x = 0.4$, possibly due to the increase of the secondary phase Mg_2SiO_4 ($Q \times f = 50,000\text{--}60,000$). In addition, the specimen containing $x = 0.2$ Mg exhibits higher $Q \times f$ value than other specimens in the temperature range from 1130 to 1190°C, which is ascribed to the high density and minor amount of the secondary phase Mg_2SiO_4 in the $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ as $x = 0.2$.

The variation of τ_f value with the Mg-substituting content in $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ sintered 1170°C is shown in figure 7. It can be seen clearly that τ_f values vary slightly (-63 to -58 ppm/°C) as the substituting content of Mg increases. But τ_f value initially decreases with increasing x , and then turns to increase when x exceeds 0.2, which is attributed to the increase of Mg_2SiO_4 with comparatively higher τ_f (-50 ppm/°C) than Zn_2SiO_4 ($\tau_f = -61$ ppm/°C). From the above experimental data, it can be concluded that $(\text{Zn}_{0.8}\text{Mg}_{0.2})_2\text{SiO}_4$ dielectrics via sol-gel process sintered at lower temperature of 1170°C has the condense microstructure and shows better microwave properties: $\epsilon_r = 6.3$, $Q \times f = 189,800$ GHz and $\tau_f = -63$ ppm/°C, compared with the higher temperature sintered samples prepared by solid state method. Therefore, it is much easier to lower the sintering temperature of $(\text{ZnMg})_2\text{SiO}_4$

ceramics below 960°C based on the sol-gel preparation above, and further investigation is required.

4. Conclusions

$(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ powders was prepared by the sol-gel process, and the thermal behaviour and phase transformation of the gels were investigated by the TG-DSC and XRD analyses, which indicated that pure $(\text{ZnMg})_2\text{SiO}_4$ phase could be formed at low temperature of 850°C. Further, the structural and microwave dielectric properties of $(\text{Zn}_{1-x}\text{Mg}_x)_2\text{SiO}_4$ system was investigated. XRD indicated that the solid solution limit of Mg ions in Zn_2SiO_4 is small (about $x = 0.1$), because of the differing crystal structure between Zn_2SiO_4 and Mg_2SiO_4 . SEM showed that the introduction of Mg in Zn_2SiO_4 could accelerate the grain growth of Zn_2SiO_4 , and decrease the sintering temperature of Zn_2SiO_4 ceramics. The microwave dielectric properties changes markedly with the chemical composition (Mg content) and sintering conditions. $(\text{Zn}_{0.8}\text{Mg}_{0.2})_2\text{SiO}_4$ ceramics sintered at 1170°C exhibited the condense microstructure with fine grains and the good microwave dielectric properties of $\epsilon_r = 6.3$, $Q \times f = 189,800$ GHz and $\tau_f = -63$ ppm/°C.

References

- Chang H J *et al* 1999 *J. Kore. Phys. Soc.* **34** 545
- Dong M, Yue Z, Zhuang H, Meng S and Li L 2008 *J. Am. Ceram. Soc.* **91** 3981
- Guo Y, Ohsato H and Kakimoto K -I 2006 *J. Eur. Ceram. Soc.* **26** 1827
- Horiuchi H and Sawamoto H 1981 *Am. Miner.* **66** 568
- Huang C -L and Weng M -H 2001 *Mater. Res. Bull.* **36** 2741
- Nguyen N -H, Lim J -B, Nahmw S, Paik J -H and Kim J -H 2007 *J. Am. Ceram. Soc.* **90** 3127
- Ohsato H, Tsunooka T, Ohishi Y, Miyauchi Y, Ando M and Kakimoto K 2003 *J. Korean Ceram. Soc.* **40** 350
- Park I -H, Kim B -S, Kim K -Y and Kim B -H 2001 *Jpn. J. Appl. Phys.* **40** 4956
- Sasikala T S, Suma M N, Mohananb P, Pavithran C and Sebastian M T 2008 *J. Alloys Compd.* **461** 555
- Sasikala T S, Pavithran C and Sebastian M T 2010 *J. Mater. Sci.: Mater. Electron.* **21** 141
- Segnit E R and Holland A E 1965 *J. Am. Ceram. Soc.* **48** 409
- Song K X, Chen X M and Zheng C W 2008 *Ceram. Int.* **34** 917
- Tsunooka T, Andou M, Higashida Y, Sugiura H and Ohsato H 2003 *J. Eur. Ceram. Soc.* **23** 2573