FULL PAPER

Microwave dielectric properties of $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass-ceramics ($x = 30-50 \text{ wt.}\%$)Linshan XIE^{1,2,†}, Chaowei ZHONG^{1,2}, Zixuan FANG^{1,2}, Yu ZHAO^{1,2}, Bin TANG^{1,2} and Shuren ZHANG^{1,2}¹School of Microelectronics and Solid State Electronics, University of Electronic Science and Technology of China, Chengdu 610054, People's Republic of China²National Engineering Center of Electromagnetic Radiation Control Materials, University of Electronic Science and Technology of China, Jianshe Road, Chengdu 610054, People's Republic of China

High crystallization, low-dielectric-loss $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($x = 30, 35, 40, 45$ and $50 \text{ wt.}\%$) (LMZBS) glass-ceramics were prepared with different MgO contents using the solid-state method in this study. The effects of the MgO content on the microstructures, flexural strength and microwave dielectric properties of LMZBS were investigated. X-ray diffractometer results, for samples sintered at 920°C , for $30 \text{ wt.}\% \leq x \leq 35 \text{ wt.}\%$, showed that the main phase was $\text{Mg}_2\text{B}_2\text{O}_5$ and the secondary phase was $\text{Li}_2\text{ZnSiO}_4$. But a new $\text{Mg}_3\text{B}_2\text{O}_6$ phase appeared when the MgO content exceeded $35 \text{ wt.}\%$, becoming the main phase at $x = 50 \text{ wt.}\%$. Scanning electron microscopy showed that the average grain size decreased with increases in MgO and that a compact, homogeneous microstructure could be obtained at $x = 40 \text{ wt.}\%$. The $Q \times f$ value (product of quality factor and resonant frequency) increased at first due to increases in the theoretical Q (quality factor) value and relative density, and then decreased due to a decrease in the average grain size and the appearance of large amounts of the liquid phase. Finally, the $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass-ceramics with $40 \text{ wt.}\%$ MgO exhibited excellent microwave properties and mechanical properties in terms of dielectric constants ($\epsilon_r = 6.66$), $Q \times f = 54600 \text{ GHz}$, temperature coefficient of resonant frequency ($\tau_f = -35 \text{ ppm}/^\circ\text{C}$) and flexural strength ($\sigma = 160 \text{ MPa}$) after the samples were sintered at 920°C for 2 h in air, indicating their suitability as low-temperature co-fired ceramics.

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1. Introduction

Microwave dielectric materials and devices have been widely investigated and used in the rapidly progressing microwave telecommunication industry, particularly in satellite communications and global positioning systems. Low-temperature co-fired ceramics (LTCC) technology is required to miniaturize and integrate microwave components for wireless communications.^{1,2)} And LTCC materials are being studied and widely applied in microelectronic substrate packages, such as glass-ceramics or glass + ceramic. $\text{Li}_2\text{O}-\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ (LMZBS), for example, is a type of glass material, that becomes highly crystallized during the sintering process, which is the source of the term glass-ceramics. Sebastian, et al.³⁾ also reported that glass-ceramics are polycrystalline materials that start at a glassy system but devitrify almost completely during the sintering process. The important parameters of glass-ceramics are their low dielectric constants (ϵ_r) for reducing the signal propagation delay, low dielectric loss⁴⁾ for

good microwave selectivity, and low sintering temperature (T_s) permitting co-firing with low-melting-point metals such as Cu and Ag.⁵⁻⁷⁾ The $Q \times f$ value (product of quality factor and resonant frequency) is more important than other parameters, moreover, for high-frequency ($> 13 \text{ GHz}$) applications.⁸⁾ Among microwave materials, glass-ceramics systems have been widely researched and used as sintering aids because of their low temperature sintering behavior, such as $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($\epsilon_r = 8.5$, $Q \times f = 1800 \text{ GHz}$, $T_s < 800^\circ\text{C}$), $\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($\epsilon_r = 6.91$, $Q \times f = 1717 \text{ GHz}$, $T_s = 640^\circ\text{C}$) and $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ ($\epsilon_r = 6.8$, $Q \times f = 4100 \text{ GHz}$, $T_s = 800^\circ\text{C}$).⁹⁻¹¹⁾ Their low $Q \times f$ values are not sufficient, however, to meet the demands of commercial devices. Duan, S., et al.,¹²⁾ for example, studied the influence of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass on the microwave dielectric properties of $\text{BaO}-0.15\text{ZnO}-4\text{TiO}_2$ (BZT) ceramics. Although they reduced the sintering temperature to 900°C , the $Q \times f$ of BZT deteriorated seriously from 38,410 to 14,795 GHz because of the low $Q \times f$ value of $\text{Li}_2\text{O}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass ($\epsilon_r = 8.5$, $Q \times f = 1800 \text{ GHz}$, $T_s < 800^\circ\text{C}$), which limits the utilization in devices for high-frequency ($> 13 \text{ GHz}$) applications. Thus, it became essential to develop a glass-ceramic system with

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a high $Q \times f$ value, and LMZBS glass-ceramics with high $Q \times f$ values were therefore investigated. To date, LMZBS glass-ceramics have been widely used as sintering aids in many reports.^{8),13)-16)} Mori, N., et al.⁸⁾ reported that the sintering temperature of MgAl_2O_4 ceramics was effectively reduced from 1350 to 940°C by doping LMZBS, and that the MgAl_2O_4 ceramics showed good microwave dielectric properties of $\epsilon_r = 7.4$, $Q \times f = 52800$ GHz. Du, et al.¹³⁾ studied the influence of LMZBS glass on the sintering temperature and microwave dielectric properties of $\text{Li}(\text{Zn}_{0.95}\text{Co}_{0.05})_{1.5}\text{SiO}_4$ ceramics, and the sintering temperature of the ceramics was effectively reduced from 1340 to 900°C, at the same time, excellent microwave dielectric properties: $\epsilon_r = 6.12$, $Q \times f = 83,600$ GHz were achieved. To reduce the sintering temperature of $\text{Mg}_3\text{B}_2\text{O}_6$,¹⁴⁾ $\text{SrCuSi}_4\text{O}_{10}$ ¹⁵⁾ and $\text{Li}_2\text{MgSiO}_4$,¹⁶⁾ LMZBS was also employed, moreover, and the microwave dielectric properties were greatly improved.

According to the previous reports, the MgO content was beneficial for improving the microwave dielectric properties of $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{CeO}_2$ glass-ceramics, and Wang, et al.¹⁷⁾ found that a high $Q \times f$ value could be obtained in $\text{MgO}-\text{Al}_2\text{O}_3-\text{SiO}_2-\text{TiO}_2-\text{CeO}_2$ glass-ceramics when the MgO content was appropriate. Currently, LMZBS systems have been widely used as sintering aids. To date, however, there is no study on the effects of MgO content on the microstructures and dielectric properties of LMZBS glass-ceramics. Thus, in this study, the effects of MgO on the microstructures, flexural strength (σ) and microwave dielectric properties of LMZBS glass-ceramic system were investigated systematically.

2. Experimental procedures

The raw materials Li_2CO_3 , MgO, ZnO, H_3BO_3 and SiO_2 with at least 99% purity were used to prepare an LMZBS glass-ceramic system. Five glass-ceramic samples were weighed according to the weight percentage of $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($x = 30, 35, 40, 45$ and 50 wt.%) ($x = 36, 40, 43, 46$ and 48 mol %). The raw ingredients were mixed by ball milling in a polyethylene jar with zirconium balls and deionized water for 6 h, and then dried at 100°C and calcined at 800°C for 2 h in air. The calcined powders were then reground. After drying, the obtained powders were granulated after mixing with acrylic emulsion, after which they were uniaxially pressed under a pressure of 20 MPa to obtain green cylinders ($\Phi 15$ mm $\times$ 7.5 mm) and bars ($\Phi 50$ mm $\times$ 4 mm $\times$ 4 mm). The green samples were fired in air at a temperature of 920°C for 2 h and cooled at a controlled rate of 2°C/min.

The microstructure of the glass-ceramic specimens were observed by scanning electron microscopy (SEM, FEI Inspect F50, U.S.A.). The compositions of different phases were examined by Energy Dispersive X-ray Spectroscopy (EDS). An X-ray diffractometer (XRD, PANalytical PW3040/60, Netherlands) using Cu-K α radiation in the 2θ range of 10–70° in steps of 0.02° was employed to detect the crystal phases. For the experiments employing thermomechanical analyses (TMA) (NETZSCH,

Germany), samples were fired at a heating rate of 5°C/min in flowing air. The flexural strength was determined by an electromechanical Universal testing machine (MTS CMT6104, China). The theoretical density (D) of the glass-ceramics was calculated using the equation:¹⁸⁾

$$D = \frac{\sum_{i=1}^n W_i}{\sum_{i=1}^n W_i/D_i}, \quad (1)$$

where W_i is the weight of different components with density D_i , and n is the amount of phases in sample.

The dielectric characteristics at various microwave frequencies were measured by the Hakkie-Coleman dielectric resonator method in the TE_{011} mode using a network analyzer¹⁹⁾⁻²⁵⁾ (Agilent Technologies E5071C, U.S.A.) and a temperature chamber (DELTA 9023, Delta Design, U.S.A.). The permittivity and dielectric losses ($\tan \delta$) were calculated at the resonant conditions. The resonant peak frequency ranged from 13–15 GHz. The $Q \times f$ values were calculated from the $\tan \delta$ and f (resonant frequency) in accordance with the equation $Q \times f = f/\tan \delta$. The temperature coefficient of the resonant frequency (τ_f) was measured by following the drift of f as the temperature was varied slowly from 25 to 85°C and calculated from the below equation:

$$\tau_f = \frac{f_{85} - f_{25}}{f_{25} \times 60} \times 10^6 \text{ (ppm/}^\circ\text{C)}, \quad (2)$$

where f_{25} and f_{85} are the resonant frequencies measured at 25 and 85°C, respectively.

3. Results and discussion

XRD patterns of LMZBS with different MgO contents sintered at 920°C for 2 h are illustrated in Fig. 1(a). For low-content MgO from 30 to 35 wt.%, the main phase was $\text{Mg}_2\text{B}_2\text{O}_5$ (JCPDS Card No. 15-0537), and $\text{Li}_2\text{ZnSiO}_4$ (JCPDS Card No. 15-0056) was also observed as the secondary phase. When the MgO content was 35 wt.%, the main crystal phase $\text{Mg}_2\text{B}_2\text{O}_5$ showed the strongest intensity, and this result indicated that $\text{Mg}_2\text{B}_2\text{O}_5$ crystals grew better than other compositions. But a new $\text{Mg}_3\text{B}_2\text{O}_6$ phase (JCPDS Card No. 38-1475) appeared when the MgO content exceeded 35 wt.%. The intensities of diffraction peaks of $\text{Mg}_3\text{B}_2\text{O}_6$ increased and the formation of $\text{Mg}_2\text{B}_2\text{O}_5$ was suppressed, moreover, as the amount of MgO content increased further. For 50 wt.%, especially, the diffraction intensity of the $\text{Mg}_2\text{B}_2\text{O}_5$ phase was nearly one-fourth that for 30 wt.%. As the Mg content exceeded 45 wt.%, the main phase of the glass-ceramics was $\text{Mg}_3\text{B}_2\text{O}_6$, and the second phases were $\text{Li}_2\text{ZnSiO}_4$ and $\text{Mg}_2\text{B}_2\text{O}_5$. To clarify the peaks of the secondary phase, the amplified profiles (a) of the strongest characteristic peak (around the 2θ angle of 35°) for the $\text{Mg}_2\text{B}_2\text{O}_5$ phase of the corresponding specimens are shown in Fig. 1(b). As displayed in Fig. 1(b), it is clear that the amount of $\text{Mg}_3\text{B}_2\text{O}_6$ phase increased sharply with increases in MgO content at the cost of a decreasing intensity of the $\text{Mg}_2\text{B}_2\text{O}_5$ phase. A possible reason is that the $\text{Mg}_2\text{B}_2\text{O}_5$ phase reacted with MgO from the glassy matrix during crystallization of the glass-ceramics

Fig. 1. (a) XRD patterns of $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ samples with different x values sintered at 920°C for 2 h in air; (b) the strongest peak (around the 2θ angle of 35°) for the $\text{Mg}_2\text{B}_2\text{O}_5$ phase of the corresponding specimens.

Fig. 2. SEM surface images of $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($x = 30\text{--}50$ wt.%) glass-ceramics sintered at 920°C for 2 h with (a) $x = 30$ wt.%, (b) $x = 35$ wt.%, (c) $x = 40$ wt.%, (d) $x = 45$ wt.% and (e) $x = 50$ wt.%.

to form the $\text{Mg}_3\text{B}_2\text{O}_6$ phase. The chemical reaction can be expressed as:

Figure 2 shows SEM surface images of $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($x = 30\text{--}50$ wt.%) glass-ceramics sintered at 920°C for 2 h in air with (a) $x = 30$ wt.%, (b) $x = 35$ wt.%, (c) $x = 40$ wt.%, (d) $x = 45$ wt.% and (e) $x = 50$ wt.%. The sample shown in Fig. 2(a) presented two kinds of grains with clear boundaries. The matrix grain A and stick-like grain B were observed, and the ceramics had an average grain size of $7\text{--}8\text{ }\mu\text{m}$. For $35\text{ wt.}\% \leq x \leq$

$50\text{ wt.}\%$, the average grain sizes were in the range of 2 to $6\text{ }\mu\text{m}$, and it was clear that the grains were much smaller than those at $x = 30\text{ wt.}\%$, because MgO can inhibit the growth of grain.²⁶⁾ Large amounts of the liquid phase were observed for $40\text{ wt.}\% \leq x \leq 50\text{ wt.}\%$, moreover, which would also inhibit the growth of grains.²⁷⁾ As shown in Fig. 2(c), a small circular grain (grain C) was detected for the first time. When the content of MgO reached $40\text{ wt.}\%$, the sample showed a compact, homogeneous microstructure. The stick-like grains finally disappeared, however, when the MgO content exceeded $45\text{ wt.}\%$.

EDS was employed to identify the chemical composi-

Table 1. Energy dispersion X-ray analysis (EDS) data for LMZBS glass-ceramics

Spot	Atoms(%)				
	Li	Mg	Zn	B	O
A	—	6.92	19.13	—	20.73
B	—	38.30	3.92	—	3.14
C	—	34.50	2.93	—	3.89
D	—	41.31	7.74	—	5.96
E	—	43.41	5.24	—	2.07

Fig. 3. Linear shrinkage curves and onset temperatures of shrinking for $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($x = 40\text{ wt.}\%$) glass-ceramics fired at a heating rate of $5^\circ\text{C}/\text{min}$ in flowing air.

tions of the differently shaped grains shown in Fig. 2. **Table 1** presents the results of EDS testing for the marked areas (A–E) of LMZBS glass-ceramics corresponding to Fig. 2. As shown in Table 1, all points contained Mg, Zn, Si and O. The matrix grain A contained large amounts of Zn and Si, however, its ratios were about 1:1. Thus, the matrix grains should be $\text{Li}_2\text{ZnSiO}_4$. Large amounts of Mg were found in stick-like grains B and C. Small circular grains D and E had different Mg and O atom percentages, moreover, from those of grains B and C. According to Table 1, the ratios of Mg:O were close to 6:10 in grains B and C, and the ratios of Mg:O were approximately 9:10 at points D and E. We found that Mg:O in the $\text{Mg}_2\text{B}_2\text{O}_5$ phase was 4:10, which was lower than the Mg:O (5:10) in $\text{Mg}_3\text{B}_2\text{O}_6$. XRD and SEM analyses revealed that the $\text{Mg}_2\text{B}_2\text{O}_5$ content was decreasing, and the stick-like grains disappeared with the increase in MgO content. Thus, the stick-like grains are thought to represent the $\text{Mg}_2\text{B}_2\text{O}_5$ phase, and small circular grains the $\text{Mg}_3\text{B}_2\text{O}_6$ phase.

Figure 3 presents the shrinkage curve and onset temperatures of shrinking for $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($x = 40\text{ wt.}\%$) glass-ceramics with a heating rate $5^\circ\text{C}/\text{min}$. For $x = 40\text{ wt.}\%$, the shrinkage of $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass-ceramics occurred at very low sintering temperatures of $800\text{--}930^\circ\text{C}$. The onset temperature of shrinking for the samples was 821°C , and the temperature of maximum shrinkage was around 910°C . Thus, LMZBS is applicable to LTCC devices.

Fig. 4. Relative density, dielectric constant, temperature coefficient of resonant frequency and flexural strength of $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ samples with different MgO contents sintered at 920°C for 2 h.

Figure 4 shows the changes in the dielectric constant, relative density, temperature coefficient of resonant frequency and flexural strength of LMZBS with different MgO contents, with the samples sintered at 920°C for 2 h in air. As shown in Fig. 4(a), the relative density increased from 92% at $x = 30\text{ wt.}\%$ to 97.8% at $x = 40\text{ wt.}\%$, after which it decreased to 94% at $x = 50\text{ wt.}\%$. It is clear, furthermore, that the relative density is in agreement with the research results of Zhou, et al.¹⁴⁾ Figures 4(b) and 4(c) show the changes in the dielectric constant and the temperature coefficient at the resonant frequency with increases in MgO content increased. There were clearly no major changes in ε_r or τ_f . The ε_r was improved slightly from 5.8 to 6.8, and the τ_f increased from -36 to $-30\text{ ppm}/^\circ\text{C}$. This finding was mainly attributable to a change of the main crystal phase from $\text{Mg}_2\text{B}_2\text{O}_5$ ($\varepsilon_r = 7.2$ and $\tau_f = -46\text{ ppm}/^\circ\text{C}$) to $\text{Mg}_3\text{B}_2\text{O}_6$ ($\varepsilon_r = 7.4$ and $\tau_f = -36\text{ ppm}/^\circ\text{C}$)²⁸⁾ according to the analysis of XRD results.

Figure 4(d) shows the changes in LMZBS's flexural strength with changes in the MgO content. The flexural strength increased at first from 132 MPa at $x = 30\text{ wt.}\%$ to 160 MPa at $x = 40\text{ wt.}\%$, but it then went down to 145 MPa at $x = 50\text{ wt.}\%$. The flexural strength of the material was related to the material's internal structure and the relative density of the sintered sample. When the MgO content increased to 40 wt.%, it was apparent that the densification of the microstructure⁷⁾ and stick-like grains increased. Thus, the flexural strength of the sample ($x = 40\text{ wt.}\%$) reached the maximum. The flexural strength then deteriorated due to a decrease in relative density and porosity.

Figure 5 shows the changes in the $Q \times f$ value, the theoretical Q (quality factor) value and the average grain size for LMZBS with different MgO contents, and with the samples sintered at 920°C for 2 h in air. As shown in Fig. 5(a), the $Q \times f$ value improved at first from 6,700 GHz at $x = 30\text{ wt.}\%$ to 54,000 GHz at $x = 40\text{ wt.}\%$, and then went down to 39,000 GHz at $x = 50\text{ wt.}\%$. As mentioned, the $Q \times f$ value was affected by the combination of intrinsic and external losses. Intrinsic loss can be reflected by the

Fig. 5. $Q \times f$ value, theoretical Q value, and average grain size of LMZBS with different MgO contents sintered at 920°C for 2 h in air.

packing fraction, but since there are three phases, it is difficult to obtain the lattice parameters by whole-pattern fitting; thus, we mainly discuss the influence coming from external loss, such as the relative density, average grain size, secondary phase and grain boundary. First, we calculated average grain size and the grain size distribution by Nano measurer 1.2 software, and calculated the influence of each phase on the total quality factor by the mixture rule^{29)–32)} (quality value of $\text{Mg}_2\text{B}_2\text{O}_5$, $\text{Li}_2\text{ZnSiO}_4$, and $\text{Mg}_3\text{B}_2\text{O}_6$ are 2547.6, 2450, and 19567.8,^{28),33)} respectively), combined with the measured $Q \times f$ value, shown in Figs. 5 and 6. As mentioned above, there is an increase in relative density from 30 to 40 wt.% MgO content, and the smaller the porosity, the higher the $Q \times f$ value. In addition, grain size decreases with increases in MgO

Fig. 6. Grain size distribution of LMZBS with different MgO contents sintered at 920°C for 2 h in air.

Fig. 7. Interfacial morphology between $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($x = 40 \text{ wt.}\%$) glass-ceramics and Ag metallization sintered at 920°C for 2 h.

content from 2.44 to $1.59 \mu\text{m}$, which causes corresponding increase in the number of grain boundaries. The increase in grain boundaries produces more grain defects, which exerts a negative impact on the $Q \times f$ value. The effects of each phase should also be considered by the mixture rule, moreover, and the theoretical Q value was calculated using the equation:³⁰⁾

$$\frac{1}{Q} = \sum_{i=0}^n \frac{V_i}{Q_i}, \quad (4)$$

where Q_i is the Q value of different components, V_i is the volume fraction, and n is the number of phases in the sample. Here, we use the ratio of the strongest peaks in each phase, which was shown to be an effective method by Kim.³⁴⁾ The calculated results are also shown in Fig. 5(b), and it is found that the variations in the calculated Q value increase. Thus, we inferred that the larger dielectric loss at low MgO content ($30 \text{ wt.}\% \leq x \leq 35 \text{ wt.}\%$) was caused mainly by the secondary phase and lower relative density, since the large grain size produces fewer grain defects. With increases in the MgO content, moreover, the relative densities of the sintered samples are higher than 95%, and the relative density will thus not affect the $Q \times f$ value dramatically.³⁵⁾ The grain size effect becomes the dominant factor, and the large dielectric loss is mainly caused by grain size. As the MgO content increased to 40 and 50 wt.%, the appearance of large amounts of the liquid phase was another cause for the decline in $Q \times f$ value. The $Q \times f$ value of glass is much lower than that of pure microwave dielectric ceramics,³⁶⁾ because network formers contained in the liquid phase may absorb a significant volume of microwave power in the high-frequency region so as to degrade the $Q \times f$ value of the material.³⁷⁾ Hence, the above reasons could explain the sharp decrease in the

$Q \times f$ value from 54,000 to 39,000 GHz when the MgO content was raised from 40 to 50 wt.%.

To test in the chemical compatibility with silver electrodes, $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($x = 40 \text{ wt.}\%$) glass-ceramics with Ag coating were co-fired at 920°C for 2 h and analyzed to detect interactions between the low-fired samples and the electrodes. **Figure 7** presents an SEM image of a cross-section and an EDS analysis of the $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ ($x = 40 \text{ wt.}\%$) glass-ceramics with Ag coating. There was clearly no chemical reaction between the sample and the Ag electrode, as shown in the Fig. 7(b). A good contact between the glass-ceramics and Ag was observed in the SEM image. LMZBS ($x = 40 \text{ wt.}\%$) can therefore be considered a promising candidate for LTCC applications because of its low sintering temperature, good microwave dielectric properties, and chemical compatibility with Ag electrodes.

4. Conclusions

The effects of MgO content on microstructure, microwave dielectric properties and flexural strength of $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass-ceramics were systematically investigated in this study. With sintering at 920°C , $\text{Mg}_2\text{B}_2\text{O}_5$ was identified as the main phase and a small amount of $\text{Li}_2\text{ZnSiO}_4$ was detected with low MgO content ($x = 30$ and $35 \text{ wt.}\%$) in LMZBS glass-ceramics. With increases in the content of MgO, a remarkable chemical reaction took place between the MgO and $\text{Mg}_2\text{B}_2\text{O}_5$ phases, leading to generation of $\text{Mg}_3\text{B}_2\text{O}_6$ phase at $x = 40 \text{ wt.}\%$. Most notably the $\text{Mg}_3\text{B}_2\text{O}_6$ phase became the main phase at $x = 50 \text{ wt.}\%$, and the second phases were $\text{Mg}_2\text{B}_2\text{O}_5$ and $\text{Li}_2\text{ZnSiO}_4$. SEM showed that the average grain sizes decreased with increases in MgO due to the appearance of large amounts of the liquid phase and the

influence of MgO, and the sample showed a compact, homogeneous microstructure at $x = 40$ wt.%. The microwave dielectric properties were strongly dependent on the MgO content. As x increased from 30 to 50 wt.%, the $Q \times f$ value increased significantly at first due to increases in the theoretical Q value and relative density, but it later decreased due to a decrease in the average grain size and the appearance of large amounts of the liquid phase. Flexural strength also increased initially, but it declined with $x > 40$ wt.%. At $x = 40$ wt.%, the $\text{Li}_2\text{O}-x\text{MgO}-\text{ZnO}-\text{B}_2\text{O}_3-\text{SiO}_2$ glass-ceramics sintered at 920°C for 2 h exhibited excellent comprehensive properties of $\epsilon_r = 6.66$, $Q \times f = 54600$ GHz, $\tau_f = -35$ ppm/ $^\circ\text{C}$ and $\sigma = 160$ MPa, indicating their suitability for LTCC.

References

- 1) W. Lei, W. Z. Lu, D. Liu and J. H. Zhu, *J. Am. Ceram. Soc.*, **92**, 105–109 (2009).
- 2) X. Bai, P. Liu, Z. Fu, Q. Feng and L. Zhao, *Mater. Lett.*, **178**, 68–70 (2016).
- 3) M. T. Sebastian, H. Wang and H. Jantunen, *Curr. Opin. Solid St. M.*, **20**, 151–170 (2016).
- 4) M. T. Sebastian and H. Jantunen, *Int. Mater. Rev.*, **53**, 57–90 (2008).
- 5) M. T. Sebastian, Dielectric materials for wireless communication, Elsevier, (2008).
- 6) Y. Imanaka, Multilayers low temperature cofired ceramics (LTCC) technology, Springer, (2005).
- 7) Z. X. Fang, B. Tang, F. Si and S. R. Zhang, *J. Alloy. Compd.*, **693**, 843–852 (2017).
- 8) N. Mori, Y. Sugimoto, J. Harada and Y. Higuchi, *J. Eur. Ceram. Soc.*, **26**, 1925–1928 (2006).
- 9) J. M. Wu and H. L. Huang, *J. Non-Cryst. Solids*, **260**, 116–124 (1999).
- 10) Y. J. Choi, J. H. Park, J. H. Park and J. G. Park, *Mater. Lett.*, **58**, 3102–3106 (2004).
- 11) B. Li, Z. Qing, Y. Li, H. Li and S. Zhang, *J. Mater. Sci.-Mater. El.*, **27**, 2455–2459 (2016).
- 12) S. Duan, E. Li, H. Chen, B. Tang, Y. Yuan and S. Zhang, *Ceram. Int.*, **42**, 7943–7949 (2016).
- 13) X. Du, H. Su, H. Zhang, Z. Zhou, Y. Jing, G. Gan and X. Tang, *Ceram. Int.*, **43**, 7636–7640 (2017).
- 14) D. X. Zhou, F. Sun, Y. X. Hu, Q. Y. Fu and G. Dou, *J. Mater. Sci.-Mater. El.*, **23**, 981–989 (2012).
- 15) K. M. Manu, P. S. Anjana and M. T. Sebastian, *Mater. Lett.*, **65**, 565–567 (2011).
- 16) S. George, P. S. Anjana, V. N. Deepu, P. Mohanan and M. T. Sebastian, *J. Am. Ceram. Soc.*, **92**, 1244–1249 (2009).
- 17) H. J. Wang, B. T. Li, H. X. Lin and L. Luo, *J. Mater. Sci.-Mater. El.*, **27**, 2860–2865 (2016).
- 18) T. Takahiro, S. F. Wang, Y. Shoko, J. S. Joo and R. E. Newnham, *J. Am. Ceram. Soc.*, **77**, 1909–1916 (1994).
- 19) J. J. Bian, D. W. Kim and K. S. Hong, *Jpn. J. Appl. Phys.*, **43**, 3521–3525 (2004).
- 20) J. Kim, J. Lee, C. Cheon and C. Lee, Proceedings of the Third International Conference on Microwave Materials and their Applications (MMA 2004), **108**, 25–28 (2004).
- 21) J. S. Kim, J. C. Lee, C. I. Cheon and H.-J. Kang, *Jpn. J. Appl. Phys.*, **45**, 7397–7400 (2006).
- 22) Y. J. Seo, D. J. Shin and Y. S. Cho, *J. Am. Ceram. Soc.*, **89**, 2352–2355 (2006).
- 23) M. Terada, K. Kawamura, I. Kagomiya, K. Kakimoto and H. Ohsato, *J. Eur. Ceram. Soc.*, **27**, 3045–3048 (2007).
- 24) H. P. Wang, Q. L. Zhang, H. Yang and H. P. Sun, *Ceram. Int.*, **34**, 1405–1408 (2008).
- 25) T. Honma and J. Tatami, *Mater. Chem. Phys.*, **171**, 1–5 (2016).
- 26) B. Tang, X. Guo, S. Q. Yu, Z. X. Fang and S. R. Zhang, *Mater. Res. Bull.*, **66**, 163–168 (2015).
- 27) U. Dosler, M. M. Krzmann and D. Suvorov, *J. Eur. Ceram. Soc.*, **30**, 413–418 (2010).
- 28) B. Li, S. L. Wang and Y. Fang, *J. Alloy. Compd.*, **693**, 9–15 (2017).
- 29) W. Lei, W. Z. Lu, X. H. Wang, F. Liang and J. Wang, *J. Am. Ceram. Soc.*, **94**, 20–23 (2011).
- 30) H. Y. Yang, E. Z. Li, S. X. Duan, H. C. He and S. R. Zhang, *Mater. Chem. Phys.*, **199**, 43–53 (2017).
- 31) C. L. Huang, J. J. Wang and Y. P. Chang, *J. Am. Ceram. Soc.*, **90**, 858–862 (2007).
- 32) Z. X. Fang, B. Tang, F. Si and S. R. Zhang, *Ceram. Int.*, **43**, 1682–1687 (2017).
- 33) G. Dou, D. X. Zhou, S. P. Gong and M. Guo, *J. Mater. Sci.-Mater. El.*, **24**, 1601–1607 (2013).
- 34) D. W. Kim, J. H. Kim, J. R. Kim and K. S. Hong, *Jpn. J. Appl. Phys.*, **40**, 5994–5998 (2001).
- 35) C. L. Huang, M. H. Weng and H. L. Chen, *Mater. Chem. Phys.*, **71**, 17–22 (2001).
- 36) J. B. Lim, S. Nahm, H. T. Kim, J. H. Kim, J. H. Paik and H. J. Lee, *J. Electroceram.*, **17**, 393–397 (2006).
- 37) L. Navias and F. Green, *J. Am. Ceram. Soc.*, **29**, 267–276 (1946).