

## Phase Evolution, Microstructure and Microwave Dielectric Properties of $Zn_{1.9-2x}Li_xAl_xSi_{1.05}O_4$ Ceramics

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### ABSTRACT

Phase evolution, microstructure, and microwave dielectric properties of  $Li_2O$  and  $Al_2O_3$  doped  $Zn_{1.9}Si_{1.05}O_4$ , i.e.,  $Zn_{1.9-2x}Li_xAl_xSi_{1.05}O_4$ , ceramics ( $x = 0.02 \sim 0.10$ ) were investigated. The ceramics were densified by  $SiO_2$ -rich liquid phase composed of the Li-Al-Si-O system, indicating that doped Li and Al contributed to the formation of the liquid. As the secondary phase,  $\beta$ -spodumene solid solution with the composition of  $LiAlSi_3O_8$  was precipitated from the liquid during the cooling process. The dense ceramics were obtained for the specimens of  $x \geq 0.06$  showing the rapid densification above  $1000^\circ C$ , implying that a certain amount of liquid is necessary to densify. The specimen of  $x = 0.06$  sintered at  $1050^\circ C$  exhibited good microwave dielectric properties; the dielectric constant and the quality factor ( $Q \times f_0$ ) were 6.4 and 11,213 GHz, respectively.

**Key words :**  $Zn_2SiO_4$ , Liquid-phase sintering,  $LiAlSi_3O_8$ , Dielectric constant, Quality factor

### 1. Introduction

As a result of drastic recent development of wireless communication industry, studies and development of microwave dielectric ceramics used for mobile phones, wireless LAN (Local Area Network), GPS (Global Position Satellite), military radar system, Intelligent Transport System (ITS), etc. are being actively conducted.<sup>1-3)</sup> Dielectric properties of microwave dielectric ceramics are specified by dielectric constant ( $\epsilon_r$ ), quality factor(Q), temperature coefficient of resonance frequency ( $\tau_f$ ), while the quality factor, i.e., the inverse of dielectric loss, is varied with frequency so as to be generally expressed as a product with resonance frequency ( $f_0$ ), i.e., ( $Q \times f_0$ ).<sup>3)</sup>

For substrate materials applied to Microwave Integrated Circuit (MIC) among dielectric ceramics employed in the microwave domain, a low dielectric constant, a high quality factor (low dielectric loss) and a temperature coefficient of resonance frequency approaching 0 are required.<sup>4)</sup> As the ceramics showing a low dielectric constant and a high quality factor,  $Al_2O_3$ ,  $Mg_2SiO_4$  (fosterite),  $Zn_2SiO_4$  (willemite), etc. have been reported<sup>2-4)</sup> Guo *et al.* stated that dielectric constant and quality factor of  $Zn_2SiO_4$  synthesized by a solid phase reaction method and sintered at  $1340^\circ C$  were 6.6 and 219,000 GHz, respectively, while a specimen with doping of  $TiO_2$  showed a temperature coefficient of resonance fre-

quency close to 0 although its dielectric constant was increased to 9.3, and the quality factor decreased to 113,000 GHz.<sup>4)</sup> Dong *et al.* also reported that  $Zn_2SiO_4$ - $TiO_2$  ceramics prepared by sol-gel method exhibited similar dielectric properties and its application to a millimeter wave domain was possible.<sup>5)</sup>

In the meanwhile, studies are being reported where sintering temperature may be lowered by adding sintering aids such as  $Li_2CO_3$ ,  $Li_2CO_3 + Bi_2O_3$ ,  $Bi_2O_3$ ,  $V_2O_5$ ,  $B_2O_3$ ,  $BaO + B_2O_3$ , glasses based on  $ZnO$ - $B_2O_3$ - $SiO_2$ , etc. to enable co-firing of  $Zn_2SiO_4$  with metal electrodes.<sup>6-13)</sup> Kim *et al.* have reported a study where sintering temperature of  $Zn_{1.8}Si_{0.8}O_4$  was lowered to  $900^\circ C$  in a composition with doping of 25.0 mol%  $B_2O_3$  while maintaining excellent microwave dielectric properties.<sup>11)</sup> However, Li *et al.* have reported in a study on water-system tape casting that viscosities of slurry were drastically increased with contents of  $B_2O_3$  doped to lower sintering temperature of the ceramics based on  $Li_2O$ - $Nb_2O_5$ - $TiO_2$ , which was attributed to the fact that  $B(OH)_4^-$  was produced by dissolution of  $B_2O_3$  in the aqueous solution.<sup>14)</sup> Also, tensile strength and density of the tape were decreased with an increase in the doped amounts of  $B_2O_3$ , which was attributed to a decrease in dispersibility of particles and an increase in viscosity of the slurry due to the doped  $B_2O_3$ . Therefore, attention needs to be paid when moisture or water is included in a manufacturing process, although doping of  $B_2O_3$  allows a reduction in sintering temperature for  $Zn_2SiO_4$ .

In the meanwhile, Nguyen *et al.* have reported results where grain growth due to evolution of a liquid phase in a

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composition of  $Zn_2SiO_4$  with insufficient Zn, i.e.,  $Zn_{1.8}Si_{0.8}$ , along with excellent microwave dielectric properties were manifested.<sup>15</sup> Also, Kim has reported in a study on  $Zn_{2-2y}Si_{1+y}O_4$  system that  $Zn_{1.9}Si_{1.05}O_4$  composition showed the most excellent microwave dielectric properties.<sup>16</sup> In the present study, phase evolution, microstructure, sintering behavior and microwave dielectric properties of  $Zn_{1.9-2x}Li_xAl_xSi_{1.05}O_4$  with doping of  $Li_2O$  and  $Al_2O_3$  to  $Zn_{1.9}Si_{1.05}O_4$  have been evaluated and the results been discussed.

## 2. Experimental Procedure

In the present study, powders of ZnO (99.9% in purity),  $SiO_2$  (99.9% in purity),  $Li_2CO_3$  (99.9% in purity),  $Al_2O_3$  (99.9% in purity) produced by Kojundo Chem. Lab. Co., Ltd. of Japan have been used as a starting raw material. Powders of  $Zn_{1.9-2x}Li_xAl_xSi_{1.05}O_4$  corresponding to  $x = 0.02, 0.04, 0.06, 0.08, 0.10$ , zirconia balls and ethyl alcohol were placed in a polyethylene container to be ball-milled for 24 h. Mixed powders were calcined after drying, under the calcination conditions of  $900^\circ C$  for 10 h. No grain growth was observed in the calcined powders. Calcined powders ground by dry method were placed in a metallic mold of 15mm in diameter for uniaxial pressure-forming under a pressure of 50 MPa. A green body was then sintered at  $1000 \sim 1200^\circ C$  for 2 h. The heating rate was  $10^\circ C/min$ , followed by natural cooling.

Bulk density was measured by Archimedes method, and X-ray diffraction analysis (D/MAX-2500V/PC, Rigaku, Japan) was conducted for powders obtained by grinding a specimen. Also, surfaces of a specimen were polished, and microstructures observed with S-4200 (Hitachi, Japan) at a lower temperature than the sintering temperature by  $50 \sim 100^\circ C$  for 10 ~ 30 minutes. Microwave dielectric properties were measured by Hakki-Coleman method using a network analyzer (HP8720ES, Agilent, U.S.A.).

## 3. Results and Discussion

Powder X-ray diffraction patterns of  $Zn_{1.9-2x}Li_xAl_xSi_{1.05}O_4$  ( $x=0.02 \sim 0.10$ ) which was sintered at  $1050^\circ C$  for 2 h is shown in Fig. 1. Diffraction peaks of all compositions excluding a minor amount of secondary phase were in agreement with diffraction patterns of rhombohedral  $Zn_2SiO_4$  (ICDD (International Centre for Diffraction Data) File 70-1235). Diffraction peaks of ZnO or  $SiO_2$  reported to be produced as the secondary phases in calcined powders or sintered specimens of  $Zn_2SiO_4$  were not observed.<sup>13,15</sup> While diffraction peaks of the secondary phase were not observed in the composition of  $x = 0.02$  (Fig. 1(a)), these ( $\blacktriangledown$ ) were observed in the compositions above  $x=0.04$  (Figs. 1(b) ~ (e)) where diffraction intensities of the secondary phase were increased with an increase in  $x$  values, i.e., the contents of  $Li_2O$  and  $Al_2O_3$ . This result suggests that the produced secondary phase is a compound including  $Li_2O$  and  $Al_2O_3$ . While intensities of diffraction peaks for the secondary phase are relatively low and there exist peaks overlapping

with the diffraction peaks of  $Zn_2SiO_4$ , the second phase has very similar diffraction peaks to those of lithium orthoclase ( $LiAlSi_3O_8$ , ICDD File 35-0794,  $a=7.505 \text{ \AA}$ ,  $c=9.070 \text{ \AA}$ ) or  $\beta$ -spodumene ( $\beta$ - $LiAlSi_2O_6$ , ICDD File 35-0797,  $a=7.539 \text{ \AA}$ ,  $c=9.148 \text{ \AA}$ ) of orthorhombic structure in the ternary component system of  $Li_2O-Al_2O_3-SiO_2$ . Included in the pseudo binary system of  $Li_2O \cdot Al_2O_3-nSiO_2$  among the above ternary system are  $\beta$ -eucryptite ( $n=2$ ,  $\beta$ - $LiAlSiO_4$ ),  $\beta$ -spodumene ( $n=4$ ,  $\beta$ - $LiAlSi_2O_6$ ), lithium orthoclase ( $n=6$ ,  $LiAlSi_3O_8$ ) and petalite ( $n=8$ ,  $LiAlSi_4O_{10}$ ),<sup>17,18</sup> where  $LiAlSi_3O_8$  is reported as the solid solution of  $\beta$ - $LiAlSi_2O_6$ .<sup>19,20</sup> Based on the result where diffraction peaks of the second phase were observed at higher angles than the diffraction peaks of  $\beta$ - $LiAlSi_2O_6$ , the second phase is considered to be close to  $LiAlSi_3O_8$  having smaller lattice constants than  $\beta$ - $LiAlSi_2O_6$ . In Fig. 2, intensity ratio for the diffraction peaks at  $2\theta \approx 27.3^\circ$  and  $28.3^\circ$  ( $I_{28.3^\circ}/I_{27.3^\circ}$ ) obtained as a Gaussian function is shown as a function of  $x$  values. Diffraction peaks at  $2\theta \approx 27.3^\circ$  and  $28.3^\circ$  correspond to  $(21\bar{2})$  and  $(31\bar{1})$  diffraction planes of  $Zn_2SiO_4$ , respectively. As  $x$  values were increased, the resulting increase in intensity ratios was indicated, which appears to be due to the fact that  $(211)$  diffraction peak of  $LiAlSi_3O_8$  in the neighborhood of  $28.3^\circ$  is added to  $(31\bar{1})$  diffraction peak of  $Zn_2SiO_4$ . Meanwhile, an

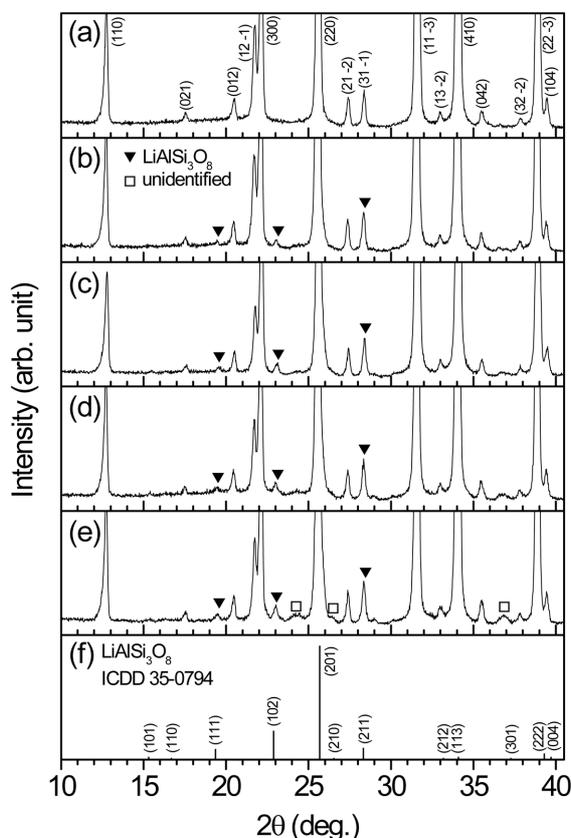


Fig. 1. Powder X-ray diffraction patterns of  $Zn_{1.9-2x}Li_xAl_xSi_{1.05}O_4$  sintered at  $1050^\circ C$  for 2 h; (a)  $x = 0.02$ , (b) 0.04, (c) 0.06, (d) 0.08, (e) 0.10, and (f)  $LiAlSi_3O_8$  (ICDD File 35-0794).

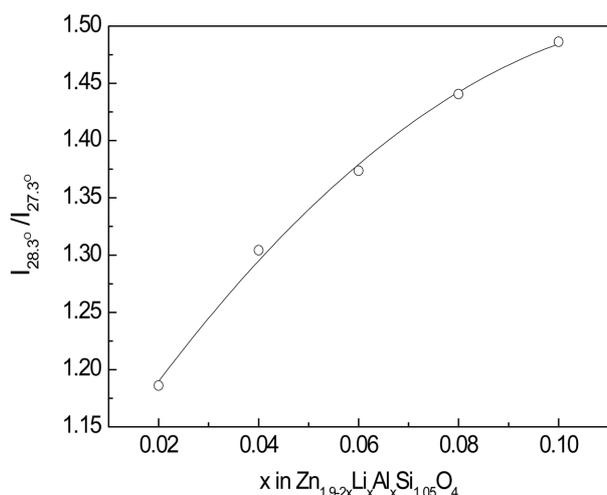


Fig. 2. Intensity ratio of X-ray diffraction peaks for  $2\theta \approx 28.3^\circ$  and  $27.3^\circ$  as a function of  $x$  in  $\text{Zn}_{1.9-2x}\text{Li}_x\text{Al}_x\text{Si}_{1.05}\text{O}_4$ .

unidentified diffraction peak ( $\square$ ) was also observed, for which additional studies are needed.

Bulk density as a function of sintering temperature are given in Fig. 3, showing different results depending on  $x$  values. Namely, whereas bulk density of  $x = 0.02$  and  $0.04$  compositions are gradually increased up to  $1200^\circ\text{C}$ , bulk density of compositions above  $x = 0.06$  are rapidly increased after  $1000^\circ\text{C}$ , leading to completion of densification at  $1050^\circ\text{C}$ . Sintering mechanism of  $\text{Zn}_2\text{SiO}_4$  is known to be liquid-phase sintering, and sintering aids such as  $\text{Li}_2\text{CO}_3$ ,  $\text{Li}_2\text{CO}_3 + \text{Bi}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3$ ,  $\text{V}_2\text{O}_5$ ,  $\text{B}_2\text{O}_3$ ,  $\text{BaO} + \text{B}_2\text{O}_3$ , glasses based on  $\text{ZnO} - \text{B}_2\text{O}_3 - \text{SiO}_2$  are reported to produce a liquid phase for contribution to densification of  $\text{Zn}_2\text{SiO}_4$  as mentioned in the introduction.<sup>6-13</sup> Meanwhile, in the pseudo ternary system of  $\text{SiO}_2 - \text{Li}_2\text{SiO}_3 - \text{LiAlSi}_2\text{O}_6$ , eutectic points exist at  $975^\circ\text{C}$  and  $980^\circ\text{C}$ , which correspond to a  $\text{SiO}_2$ -rich domain in the ternary system of  $\text{SiO}_2 - \text{Li}_2\text{O} - \text{Al}_2\text{O}_3$ .<sup>21</sup> Hence, in the present system, compositions near the above eutectic points are considered to form a liquid phase above  $975^\circ\text{C} \sim 980^\circ\text{C}$  for contribution to densification and for precipitation as  $\text{LiAlSi}_3\text{O}_8$  in the cooling process. This suggestion is substantiated by the result where bulk density for the compositions above  $x = 0.06$  are drastically increased above  $1000^\circ\text{C}$ . Also, based on the fact that bulk density show different results

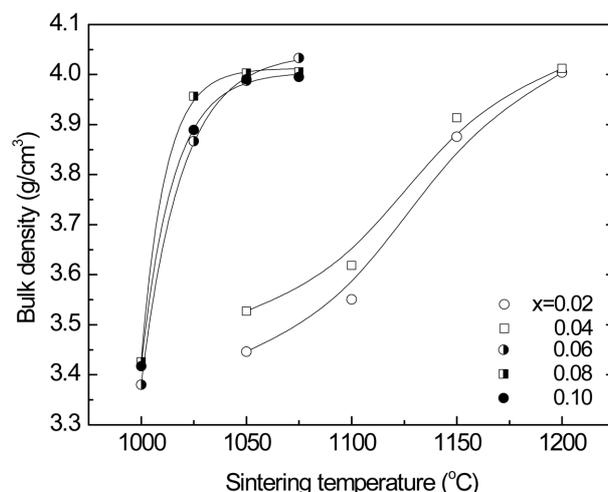


Fig. 3. Bulk density of  $\text{Zn}_{1.9-2x}\text{Li}_x\text{Al}_x\text{Si}_{1.05}\text{O}_4$  as a function of sintering temperature.

depending on  $x$  values, it is presumed that the amount of liquid phase should be more than a given amount for effective densification. To obtain a dense  $\text{Zn}_2\text{SiO}_4$ , sintering at high temperatures above  $1350^\circ\text{C}$  is reported to be required, and it may be seen that a dense specimen can be obtained at about  $1000^\circ\text{C}$  by doping of  $\text{Li}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ . Meanwhile, Mn substituted  $\text{Zn}_2\text{SiO}_4$  is widely applied as a fluorescent substance, where Mn has been reported to be substituted in  $\text{Zn}^{2+}$  sites,<sup>22</sup> and luminous colors from purple color to infrared radiation are exhibited, which is due to the fact that doping of diversified ions is possible. The only stable phase of  $\text{Zn}_2\text{SiO}_4$  in the binary system of  $\text{ZnO} - \text{SiO}_2$  under atmospheric pressure shows a phenacite structure (space group:  $R\bar{3}$ ) with the coordination number for both  $\text{Zn}^{2+}$  and  $\text{Si}^{4+}$  ions being 4.<sup>23</sup> However, based on the results of the present study, the doped  $\text{Li}^+$  and  $\text{Al}^{3+}$  ions are considered to contribute to evolution of a liquid phase rather than being substituted in  $\text{Zn}^{2+}$  sites. Ionic radius of  $\text{Zn}^{2+}$  in the case of the coordination number of 4 is  $0.6 \text{ \AA}$ , and that of  $\text{Li}^+$  is similar at  $0.59 \text{ \AA}$ , while that of  $\text{Al}^{3+}$  is smaller at  $0.39 \text{ \AA}$ .<sup>24</sup> Therefore, substitution is considered not to have been easily realized due to size differences between  $\text{Al}^{3+}$  ions and  $\text{Zn}^{2+}$  ions.

Shown in Fig. 4(a), (b), and (c) are microstructures for the compositions of  $x = 0.02$ ,  $0.06$  and  $0.10$ , respectively. Sinter-

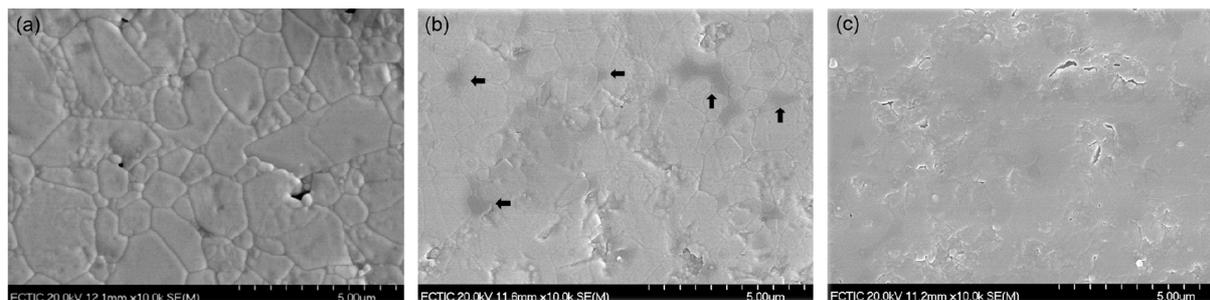


Fig. 4. FE-SEM photographs of  $\text{Zn}_{1.9-2x}\text{Li}_x\text{Al}_x\text{Si}_{1.05}\text{O}_4$ ; (a)  $x = 0.02$ , (b)  $0.06$ , and (c)  $x = 0.10$ .  $x = 0.02$  was sintered at  $1200^\circ\text{C}$  for 2 h whereas  $x = 0.06$  and  $0.10$  were sintered at  $1050^\circ\text{C}$  for 2 h.

ing temperature for the composition of  $x = 0.02$  was  $1200^{\circ}\text{C}$ , while that for the compositions of  $x = 0.06$  and  $0.10$  was  $1050^{\circ}\text{C}$ . Excluding some pores observed for the composition of  $x = 0.10$ , a dense microstructure was observed for all compositions. Grains shown by an arrow in the composition of  $x = 0.06$  are shown to be relatively dark, which imply their being composed of light elements. Therefore, these grains are considered to be  $\text{LiAlSi}_3\text{O}_8$  rather than  $\text{Zn}_2\text{SiO}_4$ , and to exist as a liquid phase at a sintering temperature of  $1050^{\circ}\text{C}$  contributing to densification, followed by crystallization during cooling as mentioned earlier. In the composition of  $x = 0.02$ , it is difficult to observe  $\text{LiAlSi}_3\text{O}_8$  grains, which is in agreement with the X-ray diffraction analysis result where no second phases were observed as shown in Fig. 1(a). However, based on the results where grains grown to more than  $2 \sim 3 \mu\text{m}$  were also observed for this composition and flat grain boundaries existed, densification appears to have been realized by liquid-phase sintering as in the composition of  $x = 0.06$ . German *et al.* stated that liquid-phase sintering occurred when a solid was dissolved in a liquid phase, and solid grains were mutually attracted due to wetting of liquid phase for solid grains and capillary tube forces produced thereby.<sup>25,26</sup> It was also stated that contact points of solid-phase grains were subjected to a compressive stress due to capillary force, and dissolution preferentially occurred at contact points as a result, while contact flattening of grains was realized due to matter transport to grain necks and precipitation. Also, the results were observed where grain size for the composition of  $x = 0.02$  with a little doping of  $\text{Li}_2\text{O}$  and  $\text{Al}_2\text{O}_3$  were larger than those for the composition of  $x = 0.06$ , and such results are considered attributable to the higher sintering temperature. Therefore, because of the relatively low sintering temperature, it is considered to be in dissolution-precipitation process following grain rearrangement one in the compositions above  $x = 0.06$ . Grain boundaries in the composition of  $x = 0.10$  are not clear as compared with the compositions of  $x = 0.02$  and  $0.06$  (Fig. 3(c)), which is considered to be caused by excessive evolution of a liquid phase as the result of an increase in the doped amounts of  $\text{Li}_2\text{O}$  and  $\text{Al}_2\text{O}_3$ .

Dielectric constant and quality factor ( $Q \times f_0$ ) as a function of sintering temperature are shown in Figs. 5 and 6, respectively. Dielectric constant showed similar results to the behavior of bulk density, and appear to be greatly affected by density, i.e., porosity. Penn *et al.* also reported in a study on dielectric properties of alumina ceramics in a microwave domain that porosity had an effect on dielectric constant although impurities or grain size did not have a great effect on the dielectric constant.<sup>27</sup> Also, as shown in Fig. 3 and Fig. 5, while bulk density sintered above  $1050^{\circ}\text{C}$  are somewhat higher for the compositions of  $x = 0.06 \sim 0.08$  than for the composition of  $x = 0.10$ , dielectric constant for the composition of  $x = 0.10$  showed a higher value, and this is considered to be related to evolution of  $\text{LiAlSi}_3\text{O}_8$  as the second phase. Dielectric constant (7.7) of  $\beta$ -spodumene ( $\beta$ - $\text{LiAlSi}_2\text{O}_6$ ) with the same structure as that of  $\text{LiAlSi}_3\text{O}_8$  has been

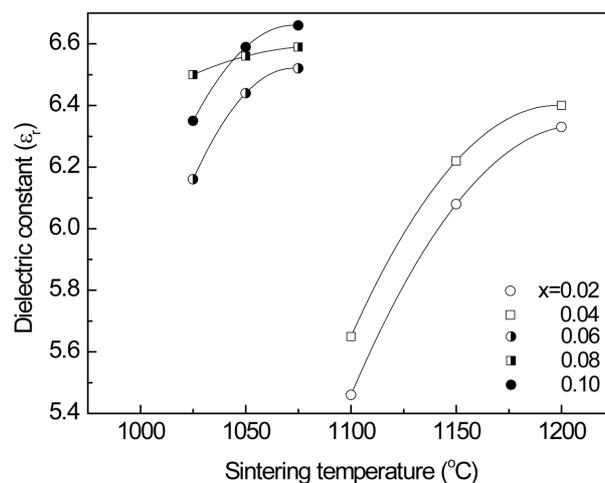


Fig. 5. Dielectric constant of  $\text{Zn}_{1.9-2x}\text{Li}_x\text{Al}_x\text{Si}_{1.05}\text{O}_4$  as a function of sintering temperature.

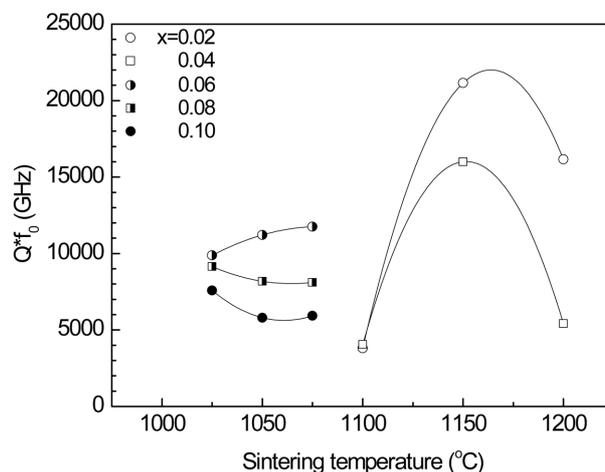


Fig. 6. Quality factor of  $\text{Zn}_{1.9-2x}\text{Li}_x\text{Al}_x\text{Si}_{1.05}\text{O}_4$  as a function of sintering temperature.

reported to be higher than the value of  $\text{Zn}_2\text{SiO}_4$ .<sup>28</sup> Whereas dielectric constant as a function of sintering temperature showed similar results to the behavior of bulk density, quality factor showed different results. This implies that quality factor is affected by several factors in addition to the effect of porosity (density). In general, reports are also being made that external factors such as impurities, defects, grain boundaries, porosity, microcracks, grain size, electrical conductivity, stress have a greater effect than internal factors caused by phonon interactions.<sup>29,30</sup> Quality factor of the compositions of  $x = 0.02$  and  $0.04$  fired at  $1100^{\circ}\text{C} \sim 1200^{\circ}\text{C}$  were increased from 3,809 and 4,049 GHz, and showed 21,149 and 16,005 GHz, respectively at  $1150^{\circ}\text{C}$ , after which a tendency of decrease at  $1200^{\circ}\text{C}$  was again exhibited. Quality factor of the compositions above  $x = 0.06$  fired at  $1025^{\circ}\text{C} \sim 1075^{\circ}\text{C}$  showed 5,803  $\sim$  11,755 GHz, and were decreased with an increase in  $x$  values. The decrease in the quality factor is attributed to evolution of the secondary phase, evolution of a liquid phase based on  $\text{Li}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$  of  $\text{SiO}_2$ -rich composition, and an increase in  $\text{Zn}/\text{Si}$  of grains

as a result of evolution of the liquid phase. In a study on microwave properties of  $Zn_{2-2y}Si_{1+y}O_4$ , Kim has reported that quality factor of the composition of  $Zn_{1.9}Si_{1.05}O_4$  with Zn/Si = 1.81 showed a very high value of 115,166 GHz whereas that of Zn/Si = 2 sintered at 1400°C, i.e.,  $Zn_2SiO_4$  with the stoichiometric composition was 51,634 GHz.<sup>16)</sup> In the future, studies are deemed necessary for improvement of quality factor while maintaining low-temperature sinterability.

#### 4. Conclusions

Phase evolution, microstructure, sintering behavior and microwave properties have been studied for  $Zn_{1.9}Si_{1.05}O_4$  doped with  $Li_2O$  and  $Al_2O_3$ , i.e.,  $Zn_{1.9-2x}Li_xAl_xSi_{1.05}O_4$  ( $x = 0.02 \sim 0.10$ ). While only  $Zn_2SiO_4$  was observed as a crystalline phase in the composition of  $x = 0.02$ ,  $LiAlSi_3O_8$  as  $\beta$ -spodumene ( $\beta$ - $LiAlSi_2O_6$ ) solid solution has been produced as the secondary phase in addition to  $Zn_2SiO_4$  in the compositions above  $x = 0.04$ . Based on the microstructure of specimens, densification by a liquid phase is considered to have occurred. Bulk density as a function of sintering temperature showed different results depending on the compositions. Whereas the compositions of  $x = 0.02$  and  $0.04$  showed a gradual increase in bulk density up to 1200°C, the compositions above  $x = 0.06$  showed a drastic increase after 1000°C leading to completion of densification at 1050°C. Based on such results, densification is presumed to occur effectively when a liquid phase exists by more than a given amount. Doped  $Li_2O$  and  $Al_2O_3$  are considered to contribute to evolution of a liquid phase based on  $Li_2O-Al_2O_3-SiO_2$  of  $SiO_2$ -rich composition together with  $SiO_2$  rather than being substituted in  $Zn^{2+}$  sites, and to be precipitated as  $LiAlSi_3O_8$  in the cooling process.

Dielectric constant in microwave domain as a function of sintering temperature are shown to be greatly affected by porosity. Quality factor showed lower values than those for  $Zn_{1.9}Si_{1.05}O_4$  sintered at 1350°C without doping of Li and Al. Causes for the low quality factor are attributed to evolution of a liquid phase with  $SiO_2$ -rich composition, precipitation of  $LiAlSi_3O_8$  as the secondary phase, and the corresponding changes in Zn/Si of grains. Dielectric constant and quality factor of the composition of  $x = 0.06$  fired at 1050°C were shown to be 6.4 and 11,213 GHz, respectively.

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