

Phase evolution, microstructure, and microwave dielectric properties of $Zn_{2-2x}Si_{1+x}O_4$

Sang-Ok Yoon^a, Shin Kim^b, Yun-Han Kim^a, So-Jung Kim^c and Seong-Min Jeong^{d,*}

^aDepartment of Materials Engineering, Graduate School, Gangneung-Wonju National University, Gangneung 210-702, Korea

^bHasla Co., Ltd, Gangneung 210-340, Korea

^cDepartment of Electrical and Electronic Engineering, Hanzhong University, Donghae 240-713, Korea

^dEnergy & Environmental Division, Korea Institute of Ceramic Engineering and Technology(KICET), Jinju 606-031, Korea

Phase evolution, microstructure, and dielectric properties of zinc orthosilicate, $Zn_{2-2x}Si_{1+x}O_4$, sintered at 1350 °C were investigated. All sintered specimen in the composition of $0 \leq x \leq 0.1$ showed dense microstructures. For the specimen of $x = 0$, low quality factor was obtained due to the insufficient grain growth. The grain boundaries in the specimens of $x \geq 0.05$ were observed clear, which indicates that the grain growths in these compositions were well developed. From these results, the composition of the synthesized zinc orthosilicate was assumed to be $x = \sim 0.02$, $Zn_{1.96}Si_{1.02}O_4$, where Zn/Si is 1.922. The dark-colored grains having 0.52 of Zn/Si ratio were assumed to be the liquid phase in the sintering which promoted the liquid phase sintering. The specimens of $x = 0.05$, $Zn_{1.9}Si_{1.05}O_4$, exhibited improved microwave dielectric characteristic of 6.27 in the dielectric constant and 104,323 GHz in the quality factor. The value of the quality factor for $Zn_{1.9}Si_{1.05}O_4$ was much higher than other specimens with different compositions, probably due to the effect of the grain boundaries.

Key words: Zinc orthosilicate, Grain growth, Liquid phase sintering, Dielectric constant, Quality factor.

Introduction

Zinc orthosilicate (Zn_2SiO_4) with the mineralogical name of willemite has been reported as the only stable compound in the ZnO-SiO₂ binary system and applied as phosphor hosts [1, 2]. Zn_2SiO_4 belongs to a phenacite (beryllium silicate) structure, a rhombohedral one where all cations are tetrahedrally coordinated with oxygen ions and each oxygen is bonded to three tetrahedral cations, i.e. two divalent and one tetravalent, resulting in a much more rigid tetrahedral network [3]. Recently, Zn_2SiO_4 has been reported as one of the low-loss dielectric materials in the microwave band [4,5]; Zn_2SiO_4 synthesized by a conventional solid-state reaction exhibited an extremely high quality factor ($Q \times f$) of 219,000 GHz and a low dielectric constant of 6.6 when it was sintered at 1340 °C after calcination at 1150 °C and cold-isostatic pressing and Zn_2SiO_4 prepared through a sol-gel process also exhibited a high quality factor of 198,400 GHz, indicating that Zn_2SiO_4 is a candidate material for millimeter-wave communication with ultra-high Q and low dielectric constant. The high Q of Zn_2SiO_4 may be related to the rigid network. Microwave and millimeter-wave dielectric ceramics can be used for a wide range of applications in telecommunication, such as cellular phone, wireless network, global position satellite (GPS), military radar system, intelligent transport system (ITS), and direct broadcast satellite [6].

Nguyen et al. reported that the stoichiometric Zn_2SiO_4 synthesized by a solid-state method exhibited a relatively low quality factor due to the formation of the secondary phase (ZnO) and the ZnO-deficient Zn_2SiO_4 , particularly $Zn_{1.8}SiO_{3.8}$ composition, had a large grain and exhibited an improved quality factor of 147,000 GHz.⁷ In this work, by substituting two Zn with one Si for the charge compensation, a series of zinc orthosilicate with deficient Zn-site and excess Si-site were synthesized and their characteristics were analyzed.

Experimental procedure

$Zn_{2-2x}Si_{1+x}O_4$ ($0 \leq x \leq 0.1$) were synthesized through a conventional solid-state reaction. ZnO (purity 99.9%, High Purity Chemicals Co. Ltd, Japan) and SiO₂ with a quartz form (purity 99.9%, High Purity Chemicals Co. Ltd, Japan) were used as starting powders. The compositions of $x = 0, 0.02, 0.05, 0.08,$ and 0.1 were prepared. The proper ratio of starting powders was ball-milled by ZrO₂ balls under ethanol medium in a polyethylene-based container for 24 hrs. After drying in an oven, the powder mixture was calcined at 1150 °C for 10 hrs using an alumina crucible. The disk-type specimens were obtained by a sintering process at 1350 °C for 2 hrs after a uniaxial pressing at 50 MPa. The crystalline phases of the sintered specimen were identified by a powder X-ray diffractometer (D/MAX-2500V/PC, Rigaku, Japan) using pulverized powder. The microstructure of the sintered specimen was characterized by a field emission scanning electron

*Corresponding author:
Tel : +82-55-792-2570
Fax: +82-55-792-2580
E-mail: smjeong@kicet.re.kr

microscope (FE-SEM, S-4200, Hitachi, Japan) after a thermal etching at 1250 °C. The compositional analysis was performed by an energy dispersive spectroscopy (EDS, 7200-H, Horiba, Japan). The bulk density of the sintered specimens was measured by the Archimedes method. The microwave dielectric properties of the disk-type specimens were measured by a network analyzer (HP8720ES, Agilent, USA) using a Hakki-Coleman fixture configuration.

Results and Discussion

Figs. 1(a-e) show the powder X-ray diffraction patterns of $Zn_{2-2x}Si_{1+x}O_4$ ($0 \leq x \leq 0.1$) sintered at 1350 °C. Zinc orthosilicate with a rhombohedral structure (ICDD file number 70-1235) is identified as the main phase in the all compositions. A small quantity of ZnO (ICDD file number 36-1451) marked by a diamond symbol in Fig. 1(a) ($2\theta \approx 36.2^\circ$) is observed in the specimen of $x = 0$ whereas it disappears in the specimens of $x \geq 0.02$. The residual ZnO in the Zn_2SiO_4 composition was observed in the $ZnO-B_2O_3-SiO_2$ at 950 °C by Eldem et al. [2]. The existence of ZnO in this composition is also supported by the experimental findings of Nguyen et al [7]. In the specimen of $x = 0.02$, unidentified peak with a broad shape marked by a square symbol in Fig. 1(b) appears about $35.6 \sim 36.0^\circ$. SiO_2 with a low-quartz form (ICDD file number 46-1045) is observed in the specimens of $x \geq 0.05$ (marked by inverted triangles in Figs. 1(c-e)). From the results that (1) ZnO as the secondary phase is

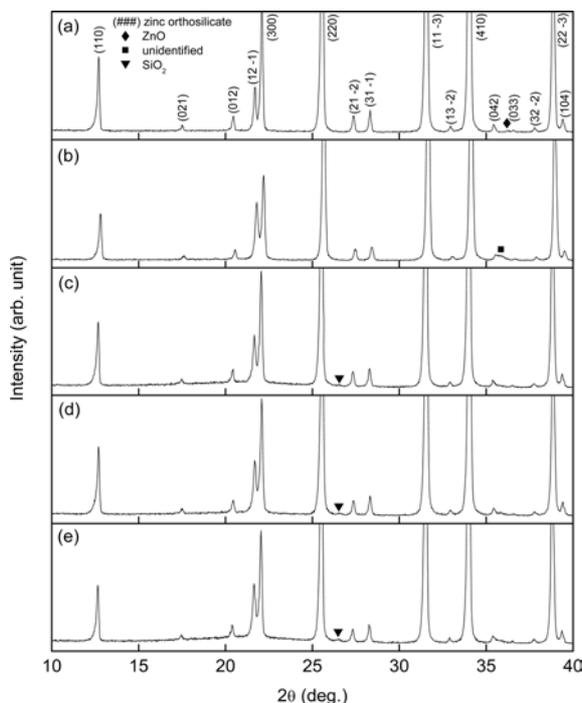


Fig. 1. Powder XRD patterns of $Zn_{2-2x}Si_{1+x}O_4$ sintered at 1350 °C; (a) $x = 0$, (b) 0.02, (c) 0.05, (d) 0.08, and (e) 0.10 (diamond, square, and inverted triangle symbols are ZnO, unidentified phase, and SiO_2 with a low-quartz form, respectively).

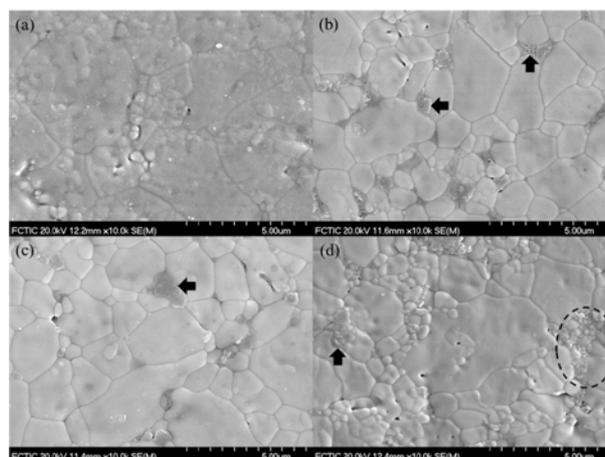


Fig. 2. FE-SEM images of $Zn_{2-2x}Si_{1+x}O_4$ sintered at 1350 °C; (a) $x = 0$, (b) 0.05, (c) 0.08, and (d) 0.10.

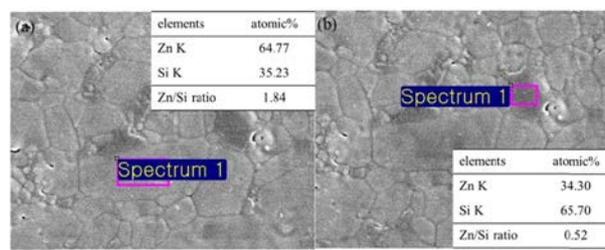


Fig. 3. The EDS results for the specimen of $x = 0.05$; (a) matrix and (b) dark-colored grain.

detected in the specimen of $x = 0$ and it disappears in the specimens of $x \geq 0.02$ and (2) the low-quartz form as another secondary phase is observed in the specimens of $x \geq 0.05$, the composition of the synthesized zinc orthosilicate is assumed to be $x \sim 0.02$, $Zn_{1.96}Si_{1.02}O_4$, where Zn/Si is 1.922.

The surface morphology of the specimens sintered at 1350 °C for 2 hrs is observed by the secondary electron (SE) mode of FE-SEM. The FE-SEM images of the specimens for $Zn_{2-2x}Si_{1+x}O_4$ ($x = 0, 0.05, 0.08, \text{ and } 0.1$) in Fig. 2 show dense microstructures with the absence of pores except some pin holes. The grain boundary for the specimen of $x = 0$ (Fig. 2(a)) is observed unclearly, implying that the grain growth may be insufficient. For the specimens of $x \geq 0.05$, however, the grain boundary is clearly observed although the specimens have different grain sizes. Grains with sizes of $0.5 \sim 3 \mu\text{m}$ are generally observed in the specimens of $x = 0.05$ and 0.08 , whereas abnormally grown grains mixed with very small grains are frequently observed in the specimen of $x = 0.1$, as represented as the ellipse of Fig. 2(d).

In addition, dark-colored grains marked by arrows in Figs. 2(b-d) are detected for the specimens of $x \geq 0.05$ whereas those are not observed for the specimen of $x = 0$. In the SE mode of FE-SEM, the dark color indicates that grains are composed of lighter elements. Because cations other than zinc and silicon are not included in this work, therefore, dark-colored grains may contain

more silicon which is lighter than zinc. As shown in Fig. 3, the EDS results for the specimen of $x = 0.05$ support the suggestion; the ratio of Zn/Si at the spot marked by small cross in the grain (Fig. 3(a)) is 1.84 whereas it in the dark-colored grain is 0.52, i.e. SiO₂-rich composition (Fig. 3(b)). Because any secondary crystalline phases except a little amount of low-quartz are not observed in the composition of $x = 0.05$ as shown in Fig. 1, the dark-colored grains are assumed to exist as glassy phases at the room temperature. Therefore, this phase should be in the liquid state at the sintering temperature of 1350 °C which promote the liquid phase sintering. The creation of the low-quartz may be caused by the precipitation from the SiO₂-rich liquid during the cooling process. Therefore the grain growth in the specimens of $x \geq 0.05$ and the large grains in the specimen of $x = 0.1$ may be related to the presence of the liquid phase. The insufficient grain growth in the specimen of $x = 0$ could be explained by the lack of the liquid phase; the dark-colored grains in this composition are not observed as mentioned above.

The presence of the liquid phase in zinc orthosilicate sintered at 1300 °C has been reported by Nguyen et al. [7]. It is interesting to note that two eutectic temperatures in the ZnO-SiO₂ binary system have been reported as 1507 °C and 1432 °C [8], indicating that a liquid in this system could form at least above 1432 °C which is higher than the sintering temperatures of this work and Nguyen's work. From the reinvestigation of the phase equilibria in the ZnO-SiO₂ system, Hansson et al. have suggested that the eutectic temperature between zincite (ZnO) and Zn₂SiO₄ exists at 1505 ± 5 °C and that between Zn₂SiO₄ and tridymite (SiO₂) exists at 1448 ± 5 °C [9]. In the study about ZnGa₂O₄ spinel ceramics, Xue et al. suggested that Zn element volatilized at high temperatures (above 1360 °C) and captured by ZnGa₂O₄ to form Zn liquid droplets, which functioned as catalysts during the growth process [10]. Further study for the formation of the liquid phase in the above binary system is necessary.

Figs. 4 and 5 represent linear shrinkage, bulk density, dielectric constant, and quality factor ($Q \times f$) of Zn_{2-2x}Si_{1+x}O₄ sintered at 1350 °C. The linear shrinkage of the specimen of $x = 0.05$, i.e. Zn_{1.9}Si_{1.05}O₄, is 19.73% whereas that of $x = 0$ is 17.13%, implying that the liquid phase enhances the sinterability of Zn_{2-2x}Si_{1+x}O₄. The bulk density apparently increases with increasing x to a maximum value at $x = 0.05$ and then declined thereafter; the bulk density of $x = 0.05$ is 4.034 g/cm³, 95% of the theoretical density for Zn₂SiO₄ (4.25 g/cm³) [11]. The decrease of the bulk density after the maximum value is assumed to be related to a large quantity of SiO₂. The dielectric constant against the sintering temperature represents a similar tendency with the bulk density; as increasing x , the dielectric constant increases until $x = 0.05$ and then decreases. The value of the dielectric constant for $x = 0.05$ is 6.27 which is lower than that of

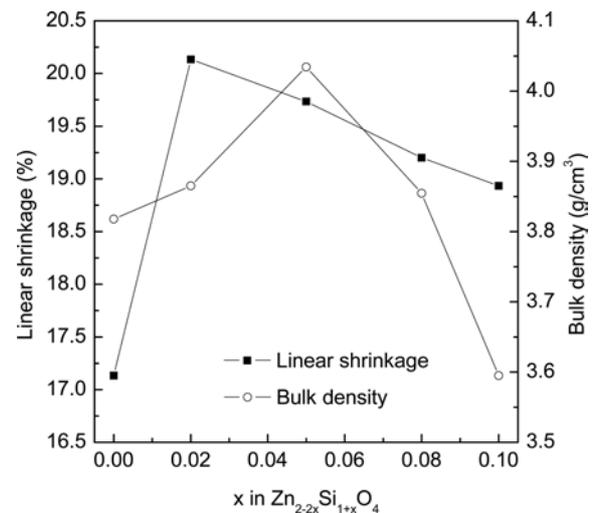


Fig. 4. Linear shrinkage and bulk density of Zn_{2-2x}Si_{1+x}O₄ sintered at 1350 °C.

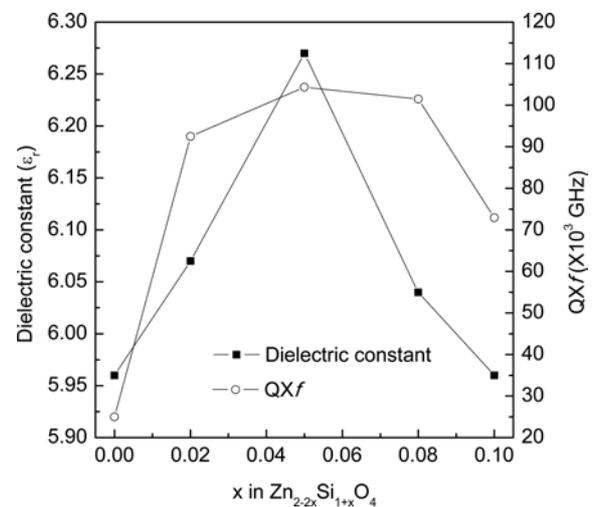


Fig. 5. Dielectric constant and quality factor ($Q \times f$) of Zn_{2-2x}Si_{1+x}O₄ sintered at 1350 °C.

Zn₂SiO₄ (6.6). It is considered that the presence of the glassy phase results in the relatively low dielectric constant in this work. The value of the quality factor for Zn_{1.9}Si_{1.05}O₄ is 104,323 GHz whereas that of $x = 0$ is as low as 24,959 GHz, probably due to the insufficient grain growth, i.e. a large quantity of the grain boundary as shown in Fig. 2(a). The relatively low value for $x = 0.1$ (72,889 GHz) may also be explained by the term of the large grain-size distribution as shown in Fig. 2(d).

Conclusions

Phase evolution, microstructure, and dielectric properties of zinc orthosilicate, Zn_{2-2x}Si_{1+x}O₄, sintered at 1350 °C for 2 hrs were investigated. The composition of the synthesized zinc orthosilicate is assumed to be close to $x = 0.02$, Zn_{1.96}Si_{1.02}O₄. Microstructure analysis using FE-SEM showed that the SiO₂-rich liquid phase enhanced the grain growth of the sintered body via liquid phase

sintering. The composition of $x = 0.05$, i.e. $Zn_{1.9}Si_{1.05}O_4$, showed best microwave dielectric properties of 6.27 with the dielectric constant and 104,323 GHz with the quality factor in the given compositions.

References

1. M. Takesue, H. Hayashi, and R.L. Smith Jr., *Prog. Cryst. Growth Ch.* 55 (2009) 98-124.
2. M.A. Eldem, B.R. Orton, and A. Whitaker, *J. Mater. Sci.* 22 (1987) 4139-4143.
3. J.R. Smith, S.D. Jacobsen, and R.M. Hazen, *Rev. Mineral. Geochem.* 41 (2000) 187-209.
4. Y. Guo, H. Ohsato, and K.-I. Kakimoto, *J. Eur. Ceram. Soc.* 26 (2006) 1827-1830.
5. M. Dong, Z. Yue, H. Zhuang, S. Meng, and L. Li, *J. Am. Ceram. Soc.* 91 (2008) 3981-3985.
6. S.B. Narang and S. Bahel, *J. Ceram. Process Res.* 11 (2010) 316-321.
7. N.H. Nguyen, J.B. Lim, S. Nahm, J.H. Paik, and J.H. Kim, *J. Am. Ceram. Soc.* 90 (2007) 3127-3130.
8. E.M. Levin, C.R. Robbins, H.F. McMurdie, M.K. Reser, *Phase Diagrams for Ceramists*, Revised edn. (The American Ceramic Society, 1964), Figure No. 302.
9. R. Hansson, B. Zhao, P.C. Hayes, and E. Jak, *Metall. Mater. Trans. B* 36B 187-193 (2005).
10. J. Xue, S. Wu, and J. Li, *J. Am. Ceram. Soc.* 96 (2013) 2481-2485.
11. J.-L. Zou, Q.-L. Zhang, H. Yang, and H.-P. Sun, *Jpn. J. Appl. Phys.* 45 (2006) 4143-4145.