

Sintering behavior and microwave dielectric properties of Li_2O and In_2O_3 doped zinc orthosilicate

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Sintering behavior and microwave dielectric properties of Li_2O and In_2O_3 doped zinc orthosilicate having the composition of $\text{Zn}_{1.9}\text{Si}_{1.05}\text{O}_4$, i.e. the $\text{Zn}_{1.9-2x}\text{Li}_x\text{In}_x\text{Si}_{1.05}\text{O}_4$ system where $x = 0.01\sim0.06$, were investigated. The liquid phase occurred by sintering contributed to the densification. As the amount of Li_2O and In_2O_3 increased, the temperature indicating the maximum value of bulk density in each composition decreased from 1250 °C to 1050 °C. And the value of dielectric constant against sintering temperature showed a similar tendency. Also, the value of quality factor decreased as the amount of Li_2O and In_2O_3 increased. The dielectric constant and the quality factor of the composition of $x = 0.02$ sintered at 1150 °C were 6.49 and 55,437 GHz, respectively.

Key words: Zinc orthosilicate, Li_2O , In_2O_3 , Liquid phase sintering, Dielectric constant, Quality factor.

Introduction

Microwave and millimeter-wave dielectric ceramics have been developed for a wide range of applications in telecommunication, such as cellular phone, wireless LAN, global position satellite (GPS), military radar system, intelligent transport system (ITS), and direct broadcast satellite [1, 2]. Dielectric ceramics with low loss can be classified into three categories according to their applications. One of them with low dielectric constant and high Q is for millimeter-wave and substrate applications [2]. For these applications, silicates are proposed to be good candidates because of their low dielectric constant [2]. Zinc orthosilicate (Zn_2SiO_4) ceramics which is the only stable compound at atmospheric pressure in the ZnO-SiO_2 binary system [3, 4] having the willemite structure showed excellent millimeter-wave dielectric properties when the sintering were carried out from 1280 to 1340 °C; the dielectric constant value of 6.6 and the quality factor ($Q \times f$) value of 219,000 GHz [5]. To apply zinc orthosilicate as the material for low temperature co-fired ceramics (LTCC) with the electrodes such as Ag or Cu, on the other hand, many efforts have been made to reduce the sintering temperature below 900 ~ 950 °C. The addition of various sintering aids, such as Li_2CO_3 , B_2O_3 , V_2O_5 , Bi_2O_3 , and glasses, allows to lower the sintering

temperature of zinc orthosilicate based ceramics [6-18]. In this work, microstructure, phase evolution, and microwave dielectric properties of Li_2O and In_2O_3 doped zinc orthosilicate having the composition of $\text{Zn}_{1.9}\text{Si}_{1.05}\text{O}_4$ which was exhibited the best microwave dielectric properties within the $\text{Zn}_{2-2x}\text{Si}_{1+x}\text{O}_4$ system in the previous study are investigated [19].

Experimental Procedure

Li_2O and In_2O_3 doped zinc orthosilicate ceramics were prepared by a conventional solid-state reaction. ZnO , SiO_2 with a quartz form, Li_2CO_3 , and In_2O_3 were used as starting powders. All of the powders with the purity of 3 N were manufactured by High Purity Chemicals Co. Ltd, Japan. The proper ratio of starting powders in the $\text{Zn}_{1.9-2x}\text{Li}_x\text{In}_x\text{Si}_{1.05}\text{O}_4$ system where $x = 0.01 \sim 0.06$ was ball-milled using zirconia balls and ethanol as the medium in a polyethylene container for 12 hrs. After the drying process, powder mixtures were calcined at 900 °C for 10 hrs using an alumina crucible. The disk-type specimens were obtained by a sintering process between 1000 °C and 1250 °C for 2 hrs after a uniaxial pressing at 50 MPa. The microstructure of the sintered specimen was characterized by a field emission scanning electron microscope (FE-SEM, S-4200, Hitachi, Japan) after a thermal etching. 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 bulk density of the sintered specimens was

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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

Powder X-ray diffraction patterns of Li_2O and In_2O_3 doped zinc orthosilicate sintered at 1150°C for 2 hrs are shown in Fig. 1. Willemite structure with a rhombohedral (ICDD file number 70-1235) is identified as the main phase in all of the compositions. ZnO and SiO_2 , which were respectively reported as the secondary phases formed in the stoichiometric composition of zinc orthosilicate or SiO_2 -rich one, are not observed [20]. For the compositions of $x \geq 0.02$ (Fig. 1(b)), additional diffraction peaks marked by a closed diamond are observed whereas any additional peaks are not detected for the composition of $x = 0.01$. These peaks are identified by $\text{In}_2\text{Si}_2\text{O}_7$ with a monoclinic structure (ICDD file number 82-0847) as shown in Fig. 1(e). An unidentified peak is also observed at $2\theta \approx 30.6$ in Fig. 1(d); it is in accord with the strongest peak of cubic In_2O_3 (ICDD file number 06-0416). From the results that $\text{In}_2\text{Si}_2\text{O}_7$ is formed at least as the secondary phase and the obvious shift of diffracted peaks for zinc orthosilicate is not observed, the introduction effect of Li^+ and In^{3+} ions on zinc orthosilicate may be negligible.

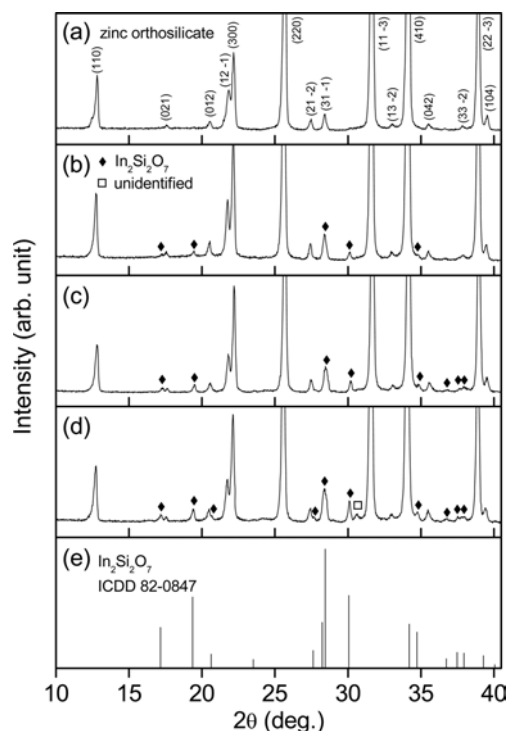


Fig. 1. Powder X-ray diffraction patterns of $\text{Zn}_{1.9-2x}\text{Li}_x\text{In}_x\text{Si}_{1.05}\text{O}_4$; (a) $x = 0.01$, (b) 0.02 , (c) 0.04 , (d) 0.06 , and (e) $\text{In}_2\text{Si}_2\text{O}_7$ (ICDD file number 82-0847).

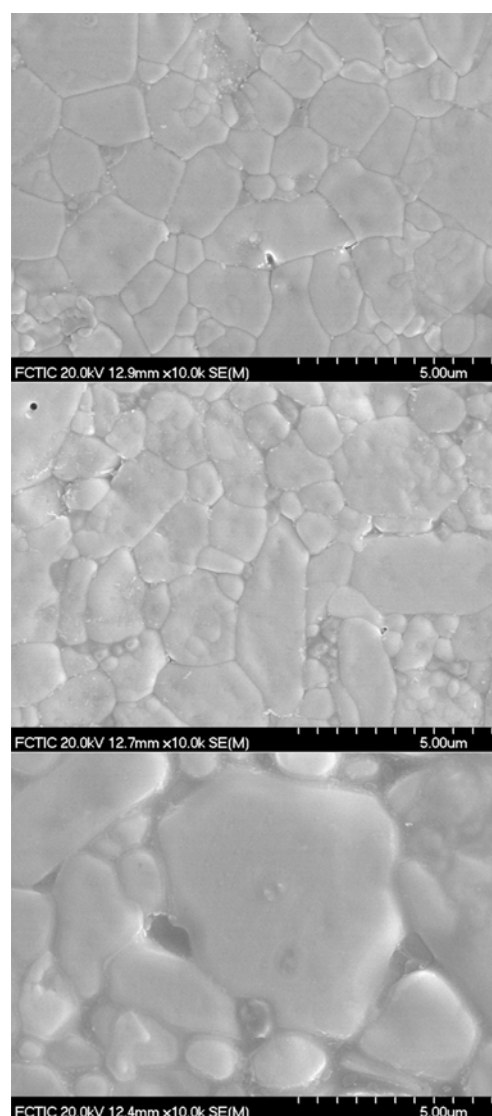


Fig. 2. FE-SEM micrographs of $\text{Zn}_{1.9-2x}\text{Li}_x\text{In}_x\text{Si}_{1.05}\text{O}_4$; (a) $x = 0.01$, (b) $x = 0.02$, and (c) $x = 0.04$.

The typical microstructures of Li_2O and In_2O_3 doped zinc orthosilicate are shown in Fig. 2. The photographs show a dense microstructure. The flat-faced grains for the compositions of $x = 0.01$ and 0.02 and the very large grain for the composition of $x = 0.04$ imply that the liquid phase contribute to the densification of this system. It has been reported that the densification of zinc orthosilicate proceeded with the presence of the liquid phase likewise this system [19, 20]. For the compositions of $x = 0.01$ and 0.02 , the dark-colored grains are observed. In the SE mode of FE-SEM, the grains with dark color, which are composed of lighter elements, are identified; the observed dark-colored grains may at least contain Li^+ and Si^{4+} ions which are lighter than Zn^{2+} and In^{3+} ions in this work. It is suggested that the dark-colored grains containing Li_2O and SiO_2 may be correlated with the liquid phase; at least Li_2O , In_2O_3 , and SiO_2 may form the liquid phase

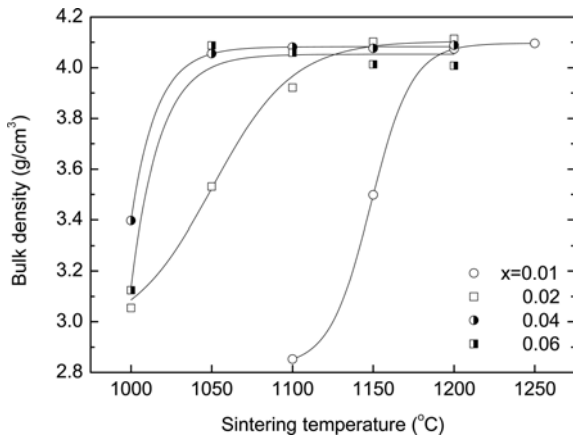


Fig. 3. Bulk density of $\text{Zn}_{1.9-2x}\text{Li}_x\text{In}_x\text{Si}_{1.05}\text{O}_4$ as a function of the sintering temperature.

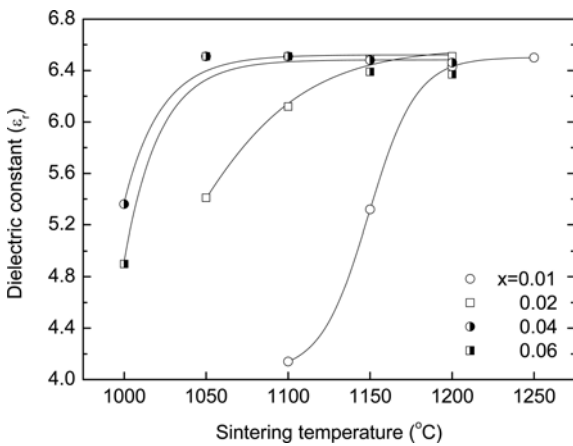


Fig. 4. Dielectric constant of $\text{Zn}_{1.9-2x}\text{Li}_x\text{In}_x\text{Si}_{1.05}\text{O}_4$ as a function of the sintering temperature.

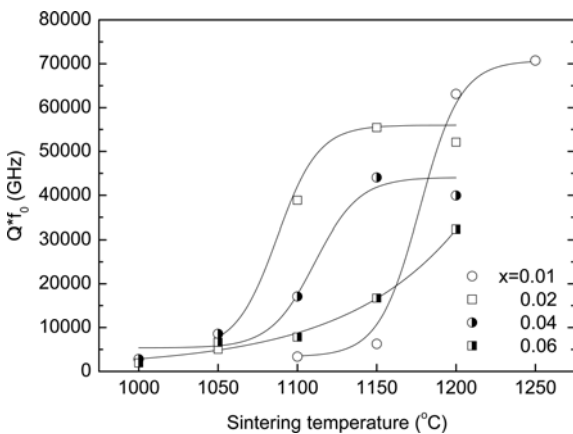


Fig. 5. Quality factor of $\text{Zn}_{1.9-2x}\text{Li}_x\text{In}_x\text{Si}_{1.05}\text{O}_4$ as a function of the sintering temperature.

at the sintering temperature and contribute to the densification. The observed $\text{In}_2\text{Si}_2\text{O}_7$ may be precipitated from the liquid during the cooling process after the sintering.

In our previous studies, on the other hand, the secondary phase of β -spodumene solid solution having

a composition close to $\text{LiAlSi}_3\text{O}_8$ was formed in the Li_2O and Al_2O_3 doped zinc orthosilicate system [21]. It is interesting that other compounds in Li_2O , Al_2O_3 , and Li_2O , Ga_2O_3 doped system are detected as the secondary phase regardless of Al^{3+} and Ga^{3+} doping elements which are included in the 3A group in the periodic table.

Bulk density of all specimens as a function of the sintering temperature is shown in Fig. 3. All of the densification curves show a sigmoidal shape. As the amount of Li_2O and In_2O_3 increases, the temperature indicating the maximum value of bulk density in each composition decreases from 1250 °C to 1050 °C, implying that the densification is influenced by the amount of the liquid. The variation of the dielectric constant against the sintering temperature shows almost similar behavior of the bulk density. This result indicates that the dielectric constant may mainly depend on the density, i.e. porosity. Penn et al. stated that the dependence of the real part of the dielectric constant (ϵ') of polycrystalline alumina on porosity can be described by some mixture models [22]. The dielectric constant and quality factor of Li_2O and In_2O_3 doped zinc orthosilicate versus the sintering temperature is shown in Fig. 4. and Fig. 5. The value of the quality factor decreases as the amount of Li_2O and In_2O_3 increases. The presence of the liquid phase as shown in Fig. 2. may cause the deterioration of the quality factor. Moreover, the increase of Zn/Si in the grains resulted from the formation of the liquid containing SiO_2 may also cause the deterioration; in the study of the $\text{Zn}_{2-2x}\text{Si}_{1+x}\text{O}_4$ system, the quality factor apparently decreased with increasing Zn/Si from at 1.81 (i.e. $\text{Zn}_{1.9}\text{Si}_{1.05}\text{O}_4$) to 2.0 (i.e. the stoichiometric zinc orthosilicate) [19]. The dielectric constant and the quality factor of the composition of $x = 0.02$ sintered at 1150 °C were 6.49 and 55,437 GHz, respectively.

Conclusions

Microstructure, phase evolution, and microwave dielectric properties of Li_2O and In_2O_3 doped zinc orthosilicate having the composition of $\text{Zn}_{1.9}\text{Si}_{1.05}\text{O}_4$, i.e. the $\text{Zn}_{1.9-2x}\text{Li}_x\text{In}_x\text{Si}_{1.05}\text{O}_4$ system where $x = 0.01 \sim 0.06$, were investigated. For the composition of $x \geq 0.02$, $\text{In}_2\text{Si}_2\text{O}_7$ was observed as the secondary phase. The densification occurred by the liquid phase sintering in all specimens. As the amount of Li_2O and In_2O_3 increased, the temperature indicating the maximum value of bulk density in each composition decreased from 1250 °C to 1050 °C, implying that doped Li_2O and In_2O_3 participate in the formation of the liquid and bulk density is influenced by the amount of the liquid. The value of dielectric constant against the sintering temperature showed a similar tendency as that of the bulk density. The value of the quality factor decreased as the amount of Li_2O and In_2O_3 increased. The presence of the liquid phase may cause the deterioration of the quality factor.

The dielectric constant and the quality factor of the specimen of $x = 0.02$ sintered at 1150°C were 6.49, and 55,437 GHz, respectively.

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