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Part II: Phase transformation-induced bloating behavior in diopside glass-ceramics for microwave dielectrics

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ABSTRACT

Phase transformation and bloating behavior of $CaMgSi_2O_6$ glass-ceramics with ZrO_2 nucleating agent using two-stage heat treatments were investigated as functions of annealing temperature. The specimens annealed below critical nucleation temperature (T_{cn}) and sintered at 950 °C exhibit significant bloating phenomena. Kinetic study of CaO-MgO-SiO_2-ZrO_2 (CMSZ) glasses annealed below T_{cn} reveals high activation energy of crystallization for the ZrO_2 nucleation, and XRD refinement results show the least ZrO_2 contents. The formations of fleeing oxygen and bloating are likely associated with high energy barrier of ZrO_2 phase and zirconia dissolution in the CMSZ glass. Specimens annealed above the T_{cn} and sintered at 950 °C show significant reduction of activation energy of ZrO_2 and enhanced densities. This work demonstrates that the bloating behavior of diopside glass-ceramics is attributed to the activation energy of nucleating agents.

1. Introduction

Low temperature co-fired ceramic (LTCC) is a novel branch in the ceramic field due to many advantages of mechanical, thermal and microwave dielectric properties [1]. For example, the apatite–wollastonite glass-ceramics are important materials for biomaterial applications due to their high strength, especially in the replacement of nature bond [2,3]. The cordierite and diopside glass-ceramics have excellent thermal and mechanical properties and are promising compositions for LED packaging materials [4–6]. The glass-ceramics can be used as a substrate for wireless communication elements such as capacitors, filters and inductors. The CaO-SiO_2-B_2O_3 (CSB), wollastonite, cordierite and diopside glass-ceramics have much lower tangent losses [7–12].

However, coarse pores appear easily in glass-ceramic systems and the tangent loss depends strongly on pore volume fraction with a small degree of porosity having a significant effect on the loss [13]. The bloating phenomena in glass-ceramics have been reported in several studies [14–17]. At elevated temperature, Alizadeh et al. [14] reported that Fe_2O_3 is a possible nucleating agent for CaO-SiO_2-MgO-P_2O_5 glass-ceramics. However, it partially reduces the FeO phase and the bloating gaseous phase (oxygen), generating large pores within the fired body to reduce densities of materials. Moreover FeO is an unstable phase and therefore the oxidation from Fe^{II} to Fe^{III} can cause non-stoichiometry of iron oxide phases [18]. It is a difficult transformation from Fe_2O_3 to FeO at high sintering temperature. Karamanov and Pelino [16,17] investigated the formation of induced crystallization porosity in diopside-albite glass-ceramics with different percentages of Cr_2O_3 as the nucleating agent. It was shown that kinetics of crystallization for the diopside-albite phase was not influenced by the formation of induced-crystallization porosity. However, kinetics of crystallization for nucleating agent and the origin of bloating have not been well revealed.

In our pre-study [19], it was revealed that specimens with two-stage heat treatment show significant variation of density, and some specimens show bloating phenomena with huge pores in

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materials leading to degraded electrical properties. Pores in the specimens are considered as negative factors for mechanical and electrical properties. There are other glass-ceramics revealing huge pores in materials during sintering [14–17], but the reason why bloating occurs is still unclear. In the part II of this study, kinetics in the bloating phenomena is investigated.

2. Experimental procedure

The diopside glass-ceramics were prepared using an oxide mixing method. A mixture of $Mg(OH)_2$ (>99%, Ube, Japan), $CaCO_3$ (>99%, Komoshina, Japan) and SiO_2 (>99%, Sibelco, Taiwan) powders were weighted in a specific molar ratio of 1:1:2, and 5 mol.% ZrO_2 (>99.5%, Daiichi, Japan) was added as a nucleating agent. The mixtures were ball-milled and then vacuum-dried at 60 °C. The CMSZ powders were melted at 1500 °C for 2 h. Then, the furnace-cooled, pulverized, and ball milled processes were used to form glass frits with an average particle size of 1 μm. CMSZ glasses were then annealed at 770 °C–830 °C (close to a nucleation temperature) for 5 min as the first-stage of heat treatment. After the heat treatment, powders were milled again and pressed at a loading of 100 MPa into thin circular pellets and rods (φ15 mm), and sintered at 950 °C for 2 h for crystallization as the second-stage of heat treatment. The crystallization temperature, kinetic parameters and nucleation behavior were determined using differential thermal analysis (DTA). The DTA was performed using an alumina crucible in a flowing air with ramping rates of 5, 10, 15 and 20 °C/min up to 1100 °C. Phase identification of the annealed glass frits and sintered pellets was carried out using an X-ray diffractometer (D2 Phaser, Bruker, Germany). The Rietveld refinements (TOPAS 2.1 code) of the XRD patterns were used to determine structures.

3. Results and discussion

3.1. Kinetics analysis of crystal nucleation and growth

In our pre-study of Part I: Effects of two-stage heat treatment on densification, microstructural features and dielectric properties of CaO-MgO-SiO_2 glass-ceramics with ZrO_2 agents [19]. Fig. 1 shows densities of CMSZ glasses annealed at temperatures from 780 to 830 °C for 5 min and then sintered at 950 °C for 2 h. The densities decreased down to 2.21 g/cm^3 as CMSZ glasses were annealed from 780 °C to 806 °C. The densities raised up to 3 g/cm^3 at annealed temperatures from 814 °C to 830 °C.

In our pre-study [19], it was found that T_{cn} occurs at 812 °C from the DTA and XRD results. The specimens annealed below T_{cn} showed alternation of nucleation behavior and an induced bloating phenomenon. To resolve this problem, we consider fundamentals of nucleation and crystal growth [20]. In order to achieve a successful nucleation, the critical activation energy of nucleation ΔG^* needs to be taken into account. To obtain the critical activation energy of nucleation, a non-isothermal DTA study was undertaken and was used to determine the crystallization kinetics. The CMSZ glass was heated at various rates to determine the activation energy of crystallization. Fig. 2 shows the evolution of crystallization exotherms as a function of heating rate for the CMSZ glass annealed at 806 °C. It was found that crystallization temperature (T_m) increases with increasing heating rates (ϕ), indicating an activation-controlled crystallization.

As shown in Fig. 2, the DTA results can be analyzed using the Kissinger [21,22] equation to determine the kinetic parameters of the diopside glass-ceramics;

$$\ln\frac{\phi}{T_m^2} = \frac{-E_a}{R}\frac{1}{T_m} + \ln\frac{A}{E_a/R} \quad (1)$$

where E_a, R and A represent activation energy of crystallization, universal gas constant and pre-exponential frequency factor, respectively. The slope of the plot of $\ln[\phi/T^2_m]$ versus $1/T_m$ in Fig. 3(a) & (b) gives the activation energy of crystallization for t-ZrO_2 and diopside phases. Table 1 shows that activation energy of crystallization for diopside varies from 468 to 515 kJ/mole, indicating that the CMSZ glass with the first-stage heat treatment doesn't exhibit obvious alterations of E_a for the diopside phase. The activation energy of nucleation for zirconia reveals a value of 463 kJ/mol for the CMSZ glass annealed at 780 °C. Specimens with higher annealing temperatures reveal enhanced activation energies of crystallization of zirconia. The highest E_a for zirconia (745 kJ/mole) appears in the CMSZ glass annealed at 806 °C. It indicates that sluggish crystallization and high energy barrier of zirconia nucleating agent are observed when the annealing temperatures of CMSZ glass are below the critical nucleation temperature. The CMSZ glass annealed at 814 °C shows significant decrease of E_a (468 kJ/mole) for zirconia, indicating that the specimens with annealing temperature above T_{cn} have a low energy barrier of the zirconia phase. These results can be correlated with the mechanism proposed by Porter et al. [20].

Furthermore, glass-ceramics generally crystallizes by either surface or internal (volume) mechanism. Both crystallization mechanisms can occur simultaneously and competitively, but in most cases one mechanism usually dominates over the other. The

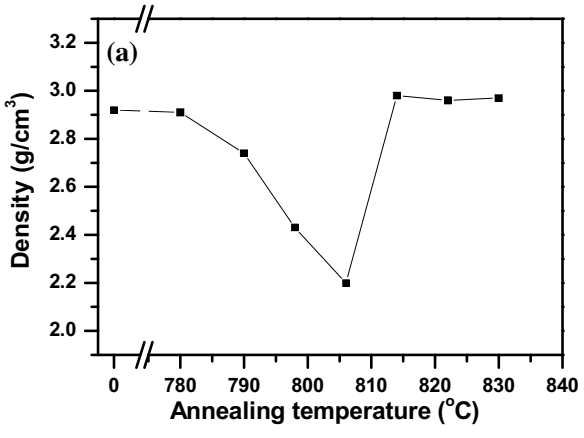

Fig. 1. Effects of the first-stage annealing temperature on densities of $CaMgSi_2O_6$ specimens sintered at 950 °C for 2 h.

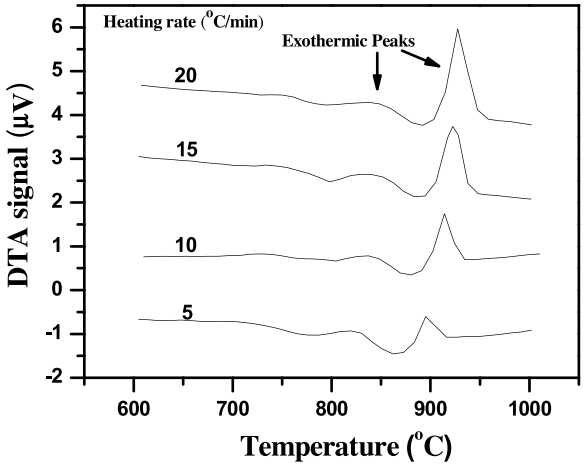

Fig. 2. DTA patterns of CMSZ glasses annealed at 806 °C with different heating rates.

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