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Synthesis and microwave characterization of $2(MgO,CaO)\text{-}2Al_2O_3\text{-}5SiO_2$ glass ceramics from the sol-gel process

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The synthesis and microwave characterization of glass ceramic in the quaternary phase field of the $MgO\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2$ system synthesized by sol-gel method have been investigated in this paper. The glass powder was obtained by calcining the $MgO\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2$ xerogel, which was prepared from Magnesium nitrate hexahydrate ($Mg(NO_3)_2{\cdot}6H_2O$), Aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), Calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$), and tetraethylortho silicate (TEOS). The powder was characterized by differential thermal analysis, thermogravimety and X-ray diffraction. The calcined powder was pressed, sintered at different temperatures, and then the sintered sample was studied with scanning electron microscope, X-ray diffraction patterns, and microwave properties measurement. © *2003 Kluwer Academic Publishers*

1. Introduction

Cordierite ($Mg_2Al_4Si_5O_{18}$) and cordierite-based glass ceramics possess many excellent physical properties in microelectronic application, such as substrates in hybrid circuits as packaging material for electronic packing. Because cordierite and cordierite-based glass ceramics have a low dielectric constant (5–6 at 1 MHz) and a low thermal expansion coefficient (2.5–3.2×10^{-6}/°C, 20–125°C) close to that of silicon [1, 2], they are quite attractive to the electronics industry especially for high frequency circuits. There are several approaches to obtain glass ceramics including glass processing (crystallized glass) [3, 4], multiphase ceramics(glass + ceramic) [5], and sol-gel method. According to the conventional melting method, it requires a very high temperature of at least 1400°C; however, the glass processing produces major problems of chemical stoichiometry loss on ignition and phase separation [6, 7]. For the multiphase ceramics, a low-softening temperature glass used as sintering flux is added to crystalline ceramics and then fired at elevated temperature. Preparation of these low-softening glasses requires high temperature. However, through traditional solid–state sintering technique it is difficult to obtain dense material without any sintering aid, because the sintering temperature range is very narrow and lies close to its incongruent melting temperature [8]. Recently, pure and homogenous crystalline cordierite powder has been widely investigated by sol-gel process, because it synthesizes at lower temperature than the material used in the conventional melting method [9–11]. The sol-gel method has the advantage of an excellent control of chemical composition and the possibility of reducing the temperature of ceramic processing [12].

In this paper, the cordierite glass-based ceramic powder containing calcium is prepared by sol-gel method. Doping B_2O_3 is chosen for its low melting point and less harmful effect on the insulating characteristic than the other sintering aid [13]. The dielectric characteristic of the sintered $2(Mg,Ca)O\text{-}2Al_2O_3\text{-}5SiO_2$ glass ceramic are also described in this study.

2. Experiment procedure

In the present investigation, the following composition were prepared (in mol%): $2(Mg_{1-x}Ca_x)O\text{-}2Al_2O_3\text{-}5SiO_2$ with $x = 0$, 2%, 4%, 6%, 8%, 10%. Aluminum nitrate nonahydrate ($Al(NO_3)_3{\cdot}9H_2O$), magnesium nitrate hexahydrate ($Mg(NO_3)_3{\cdot}6H_2O$), calcium nitrate tetrahydrate ($Ca(NO_3)_2{\cdot}4H_2O$) and H_3BO_3 were dissolved in deionized water, and tetraethylortho silane (TEOS) was dissolved into ethanol. The composition of $2(Mg,Ca)O\text{-}2Al_2O_3\text{-}5SiO_2$ glass powder containing 2 wt% B_2O_3 were prepared by sol-gel method. The volume ratio of TEOS to ethanol was 1:2.5, and the volume ratio of TEOS to water was 1:5. Two solutions were mixed and stirred for 2-hrs at room temperature to form a mix solution. The mixed solution was poured into a dish and dried at 80°C for 24-hrs to transform into dried gel, and then heated at 700°C for 4-hrs. The powder was milled, granulated, and pressed into pellet under a uniaxial pressure of 1000 kgf/cm^2. Pellets

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were sintered in air from room temperature at a rate of 5°C/min 1100°C for 4-hrs.

A computer-interface X-ray powder diffractometer (XRD, Rigaku D/Max-II) with Cu K_α radiation was used to identify the crystalline phase of sintered 2(Mg,Ca)O-2Al_2O_3-5SiO_2 glass ceramics. The microstructure of the sintered specimens was observed by scanning electron microscopy (SEM, JEOL JSM-5410) with an accelerating voltage of 20 kV. The polish samples were etched with 2.5 M HF for 30 s. The density of sintered glass ceramics was measured by Archimendean method. Differential thermal analysis and thermogravimetry (TG/DTA, Rigaku Thermalplus TG 8120) were used to study the exo-endo temperature of as-prepared 2(Mg,Ca)O-2Al_2O_3-5SiO_2 gel. A heating rate of 10°C/min was used in both the TGA and TG measurements up to 1000°C in air. Dielectric characteristics in the microwave frequency range were measured by the Hakki-Coleman dielectric resonator method, as modified and improved by Courtney [14, 15]. The microwave properties were calculated by the resonant frequency of the TE_{011} resonant mode. Linear thermal expansion coefficient from room temperature to 300°C was measured in air at a heating rate of 10°C/min by using a thermal mechanical analyzer (TMA, Seiko Instrument TMA 320).

3. Results and discussion

The DTA results are very important in defining the sintering temperatures of the sample. Phase transformations of the cordierite gel were studied using a differential thermal analyzer. Fig. 1 shows the differential thermal analysis curve of cordierite gel. The endothermic peak appears in the temperature range 130–160°C, which is due to the remove of un-reacted OR groups. The exothermic peak appears around 1050°C, which is attributed to the crystallization of glass and is confirmed by the XRD analysis.

XRD studies reveal some important information regarding phase evolution and texture of the specimens. Fig. 2 shows the XRD patterns of all specimens heated at 1100°C for 4-hrs. Cordierite was observed in all the samples, the α-cordierite was developed as the single phase. Doping Ca in MgO lattice will induce uniform

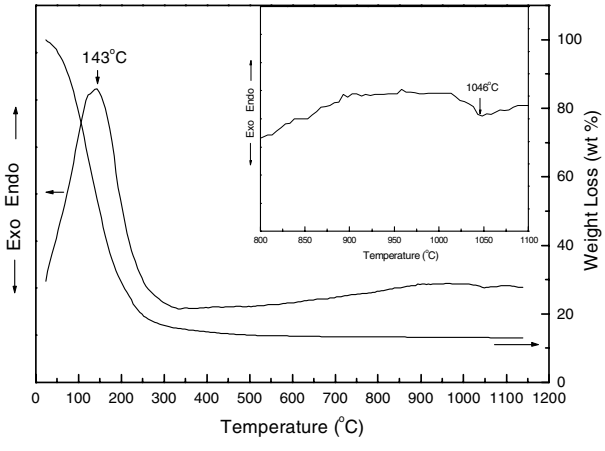

Figure 1 TG/DTA records of 2MgO-2Al_2O_3-5SiO_2 gel containing 2 wt% B_2O_3 and heated at 80°C for 24-hrs.

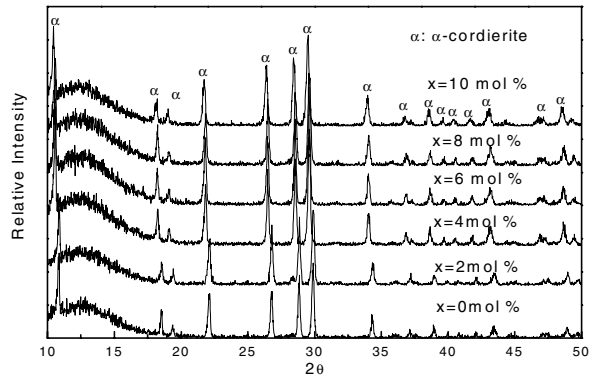

Figure 2 XRD patterns the 2($Mg_{1-x}Ca_x$)O-2Al_2O_3-5SiO_2 samples with different CaO addition heated at 1100°C for 4-hrs.

strain in the lattice as the material is elastically deformed. This effect causes the lattice plane spacing to change and the diffraction peaks to shift to new 2θ position.

Fig. 3 shows the SEM photographs of the etched samples. From the micrograph, it is clear that the sample with the higher CaO content ($x = 10$ mol%) shows a much denser material than the one with the lower CaO content ($x = 2$ mol%). This indicates that CaO can stuff into the crystalline phase, which would lead to higher relative density and increase the thermal expansion coefficient of the samples.

The thermal expansion coefficient (TCE) of densified glass ceramic vs. the different CaO content are shown in Fig. 4. The thermal expansion coefficient of material depends on its crystalline phases, and additives. The TEC values of glass ceramics without CaO addition and sintered at 1100°C for 4-hrs was 1.52×10^{-6}/°C. The TEC values of glass ceramics with 2 mol%, 4 mol%, 6 mol%, 8 mol%, and 10 mol% CaO addition were 1.53×10^{-6}/°C, 1.56×10^{-6}/°C, 1.57×10^{-6}/°C, 1.60×10^{-6}/°C, and 1.61×10^{-6}/°C, respectively. It is noticed that the higher thermal expansion coefficient (TEC) value may be cause by the addition of calcium oxide.

Fig. 5 shows the bulk density of the samples sintered at 1100°C for 4-hrs. The bulk density values of all specimens were more than 2.41 g/cm^3. As the sample increased with amount of CaO addition, the bulk density increased. It is shown that the addition of CaO may cause the bulk density to increase because the atomic weight of Ca is weighter than Mg.

The microwave properties of the samples with different CaO contents are shown in Fig. 6. For a glass ceramic material, many factors will affect the microwave properties, including the content of the individual crystalline, glass phases, and the degree of densification. The dielectric constant of the samples with different CaO contents is in the range 5–6. It shows slight increase with the increase of CaO addition from 0 mol% to 10 mol%. This result is attributed to addition of CaO cause the density increase. The microwave property of $Q * f$ value have maximum (~3500 GHz) at the sample with CaO 8 mol% addition.

From the above results, it is noticed that dielectric constant of the samples closely correspond to bulk density of the samples as shown in Figs 5 and 6. This

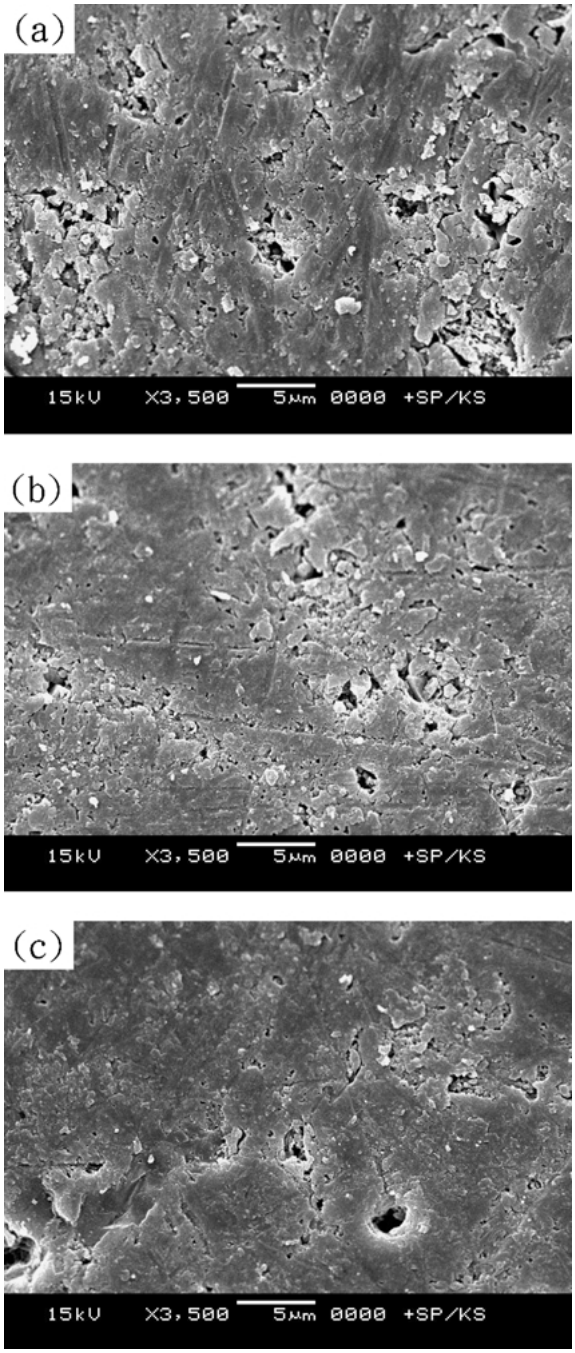

Figure 3 SEM photographs of the etched sample with different CaO contents heated at 1100°C for 4-hrs: (a) $x = 2$ mol%, (b) $x = 6$ mol%, and (c) $x = 10$ mol%.

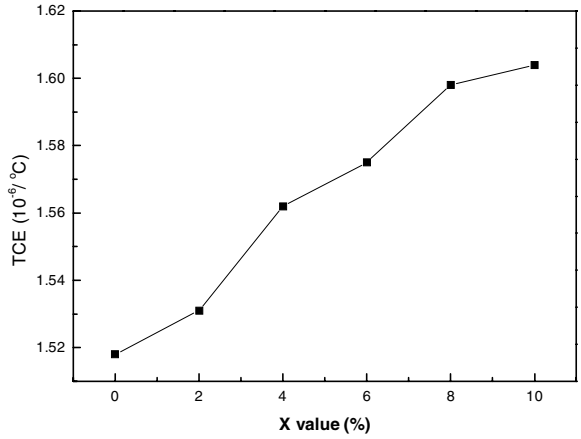

Figure 4 Thermal expansion coefficient of the samples with different CaO contents heated at 1100°C for 4-hrs.

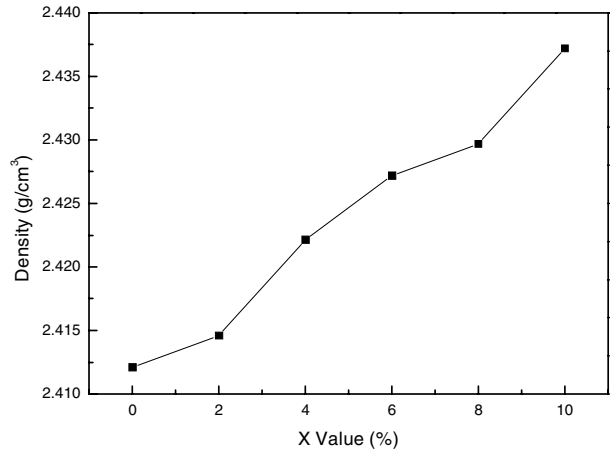

Figure 5 Relative density of the samples with different CaO contents heated at 1100°C for 4-hrs.

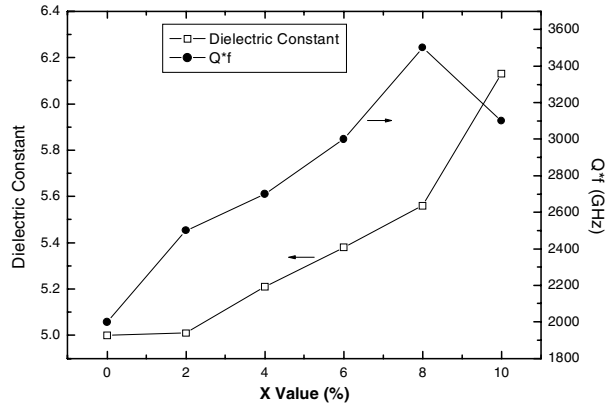

Figure 6 Dielectric properties of the samples with different CaO contents heated 1100°C for 4-hrs.

indicates that the degree of densification is an important factor affecting dielectric constant of the samples.

4. Conclusions

The glass ceramics with the composition of $2(Mg,Ca)O\text{-}2Al_2O_3\text{-}5SiO_2$, doped with 2 wt% B_2O_3 have been successfully synthesized by sol-gel method. The addition of CaO increases relative density, thermal expansion coefficient, and dielectric constant of the $MgO\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2$ glass ceramics. Dielectric constant and thermal expansion coefficient of the sintered bulk samples closely followed their relative densities. The amount of CaO addition will affect greatly in the densification of the $MgO\text{-}CaO\text{-}Al_2O_3\text{-}SiO_2$ glass ceramics.

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