J Mater Sci (2007) 42:7239–7244
DOI 10.1007/s10853-007-1548-3

Effect of replacement of MgO by CaO on sintering, crystallization and properties of $MgO–Al_2O_3–SiO_2$ system glass-ceramics

Guo-Hua Chen

Received: 3 September 2006 / Accepted: 24 January 2007 / Published online: 10 May 2007

Abstract The effects of replacement of MgO by CaO on the sintering and crystallization behavior of $MgO–Al_2O_3–SiO_2$ system glass-ceramics were investigated. The results show that with increasing CaO content, the glass transition temperature firstly increased and then decreased, the melting temperature was lowered and the crystallization temperature of the glass-ceramics shifted clearly towards higher temperatures. With the replacement of MgO by less than 3 wt.% CaO, the predominant crystalline phase in the glass-ceramics fired at 900 °C was found to be α-cordierite and the secondary crystalline phase to be μ-cordierite. When the replacement was increased to 10 wt.%, the predominant crystalline phase was found to be anorthite and the secondary phase to be α-cordierite. Both thermal expansion coefficient (TCE) and dielectric constant of samples increases with the replacement of MgO by CaO. The dielectric loss of sample with 5 wt.% CaO fired at 900 °C has the lowest value of 0.08%. Only the sample containing 5 wt.% and10 wt.% CaO (abbreviated as sample C5 and C10) can be fully sintered before 900 °C. Therefore, a dense and low dielectric loss glass-ceramic with predominant crystal phase of α-cordierite and some amount of anorthite was achieved by using fine glass powders ($D_{50} = 3$ μm) fired at 875–900 °C. The as-sintered density approaches 98% theoretical density. The flexural strength of sample C5 firstly increases and then decreases with sintering temperature, which closely corresponds to its relative density. The TCE of sample C5 increases with increasing temperature. The dielectric property of sample C5 sintered at different temperatures depends on not only its relative density but also its crystalline phases. The dense and crystallized glass-ceramic C5 exhibits a low sintering temperature ($\leq$ 900 °C), a fairly low dielectric constant (5.2–5.3), a low dielectric loss ($\leq 10^{-3}$) at 1 MHz, a low TCE ($4.0–4.25 \times 10^{-6}$ K^{-1}), very close to that of Si (~3.5×10^{-6} K^{-1}), and a higher flexural strength (≥134 MPa), suggesting that it would be a promising material in the electronic packaging field.

Introduction

Due to the high frequency transportation for wide applications in the wireless communications and computer fields, low dielectric constant, low temperature co-fired ceramics (LTCCs) package have been developed to achieve the requirements of high signal propagation speed, good reliability and low cost [1–3]. ''Low temperature'' means that ceramic substrates should be sintered at less than 1,000 °C in order to be co-fired with copper (1,083 °C), silver (961 °C), or gold (1,061 °C). Several material systems such as glass plus ceramics [4, 5] and glass-ceramics have been developed to meet the requirements in applications for LTCCs. Glass-ceramics formed by controlled crystallization of glass, are materials of high crystalline grade. Properties such as low dielectric constant, appropriate thermal expansion coefficient (TCE) and cofirability with other materials, make glass-ceramic compatible with the high performance multiplayer ceramic substrates [6, 7].

Cordierite ($2MgO \cdot 2Al_2O_3 \cdot 5SiO_2$) based glass-ceramics are attractive materials for preparing low firing temperature

---

G.-H. Chen (✉)
Department of Information Materials Science and Engineering,
Guilin University of Electronic Technology, Guilin 541004,
P.R. China
e-mail: cgh1682002@163.com

substrates due to their low dielectric constant and matching TCE of single crystal silicon [1, 6, 7]. However, cordierite glass has a high melting temperature (≥1,600 °C).It is difficult to obtain dense glass-ceramics below 1,000 °C because the cordierite-based glasses have high viscosity and narrow sintering temperature range [3]. Because glass powder sintering proceeds by viscous flow [8], the decreasing glass viscosity shows good effect on its sinterability. In order to fabricate dense glass-ceramics, it may be a critical factor to select adequate glass composition and flux, which reduces glass viscosity.

Several studies have been conducted on the nucleation and crystallization of cordierite glass-ceramics, and some are related to the low-temperature sintering behavior of cordierite-based glass-ceramics [9–13]. It was found that an addition of CaO in the $MgO–CaO–Al_2O_3–SiO_2–TiO_2$ and $ZnO–Al_2O_3–SiO_2$ system glass-ceramics can lower the melting temperature and glass transition temperature and decrease dielectric loss as well as adjust the TCE and of glass-ceramics [14, 15]. Hu et al. [16] have found that the replacement of MgO by BaO in the $MgO–Al_2O_3–SiO_2$ system glass-ceramics can improve the sintering densification, decrease dielectric loss and adjust the TCE of glass-ceramics. According to our knowledge, both Ca^{2+} ion and Ba^{2+} ion have a similar characteristic, it is expected that the replacement of MgO by CaO in the $MgO–Al_2O_3–SiO_2$ system glass-ceramics has a helpful effect on low temperature sintering and some properties.

The aim of the present study was to investigate the effect of replacement of MgO by CaO on sintering and crystallization behavior of $MgO–Al_2O_3–SiO_2$ system glass-ceramics. The physical properties such as dielectric properties and thermal expansion characteristics were also evaluated.

Experimental

In the present investigation, the following composition was prepared (in wt.%): $(21 - x)$ MgO-xCaO-$26Al_2O_3$-$53SiO_2$-5 ($B_2O_3 + P_2O_5$) with x = 0, 1 wt.%, 3 wt.%, 5 wt.%, 10 wt.%. The starting materials were analytical grade: SiO_2, Al_2O_3, MgO, $CaCO_3$, H_3BO_3, $NH_4H_2PO_4$ and $Sb_2O_3 \cdot Sb_2O_3$ was added due to its promising clarifying effect. The powder batches were mixed with alcohol medium in a ball mill for 6 h, dried with infrared lamp, and then melted in corundum crucibles. The powder batches were first held at 900 °C for 1 h for reaction, followed by heating to 1,520–1,540 °C for 4 h in an electric furnace, and then quenched in distilled water to form frits, which were crushed and wet-milled for 48 h. The mean particle sizes of the glass powders were measured with a particle size analyzer to be about 3 μm. Non-isothermal reaction analysis of the glass powders was investigated using a thermoanalyzer with a heating rate of 10 °C/min in air.

To prepare the bulk samples, the obtained glass powders were granulated with 3% poly (vinyl alcohol) (PVA) and then were pressed into disks and rectangle strips under a uniaxial pressure of 100 MPa. Glass-ceramics were obtained by isothermal heat treatment of the samples between room temperature and 900 °C at a heating rate of 3–5 °C/min in air. Phase evolution in the samples was identified by X-ray powder diffraction (D8-Advance, Bruker) using Cu-Kα radiation. Density of the bulk samples was measured by the Archimedean method using distilled water as medium. Dielectric properties were measured by a LCR meter (HP4292A, Aglient) at 1 MHz and at room temperature. Average liner TCE from room temperature to 300 °C was measured in air at a heating rate of 10 °C/min using a dilatometer (DIL 402C, NETZSCH). The flexural strength was measured using a 3-point bending strength with a span of 30 mm at a crosshead speed of 0.5 mm/min. The micrographs of the glass samples were examined by scanning electron microscopy (JSM-5610LV, JOEL).

Results and discussion

Crystallization behavior

Figure 1 shows the DTA traces of glasses under a non-isothermal heat-treatment at a constant heating rate of 10 °C/min. From Fig. 1, it is observed that all glass powders exhibit a transition of glass between 880 °C and

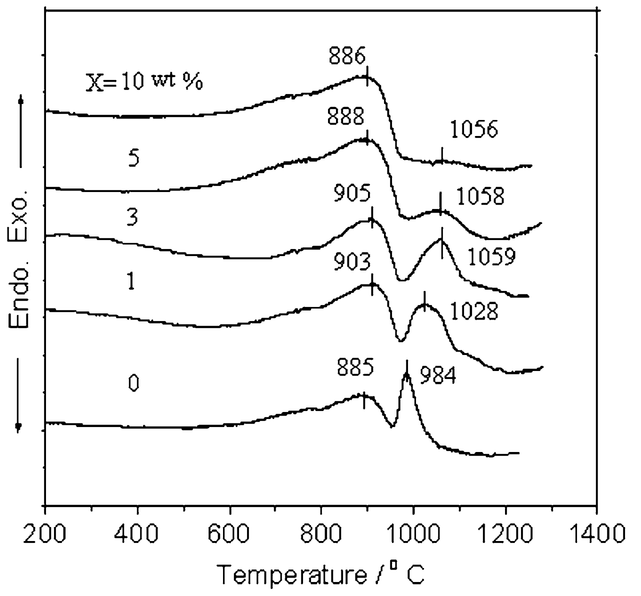
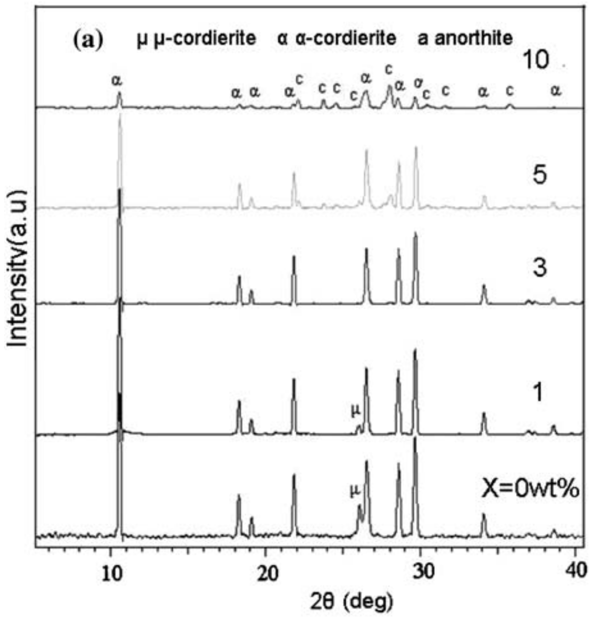


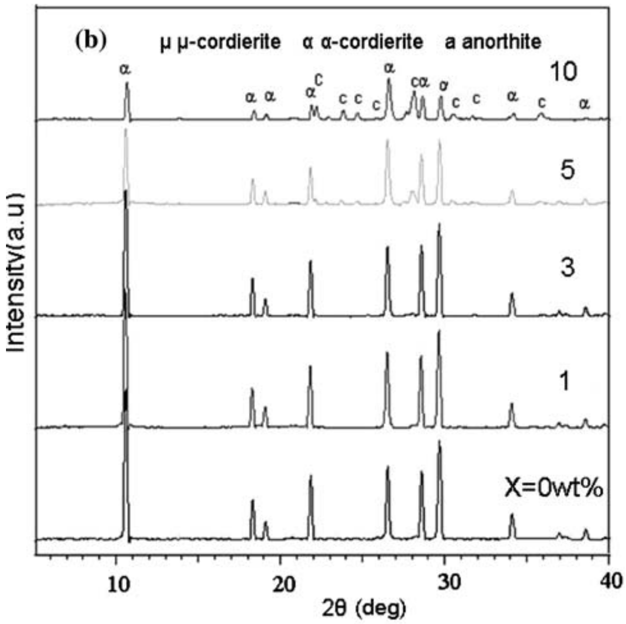
Fig. 1 DTA traces of the glass powders with various CaO content at a heating rate of 10 K/min

905 °C, followed by one exothermic transformations, corresponding to crystallization of α-cordierite from the glass. With increasing CaO content from 0 to 3 wt.%, both glass transition temperature (T_g) and crystallization peak temperature (T_p) of glass samples increase as shown in Fig. 1. As increasing CaO content from 5 wt.% to 10 wt.%, the glass transition temperature (T_g) decreases from 888 °C to 886 °C and the crystallization peak temperatures (T_p) also decrease and its intensity steps down. It is clear that the crystallization peak gets to broadening with an increase content of CaO. The above results indicate that the replacement of MgO by CaO influences the crystallization process of the glasses. It was believed that 5 wt.% CaO substituting for MgO can reduce transition temperature of the glass, retard the crystallization of the glass, increase a range between T_g and T_p and improve the sintering densification of glass-ceramics. Whereas, overfull CaO (10 wt.%) will greatly inhibit the crystallization of glasses and finally increase the TCE of samples as well as decrease the flexural strength of samples. On the other hand, addition of a small amount of CaO (less than 5 wt.%) will increase the glass viscosity and finally restrain the sintering densification of glass-ceramics. This is attributed to the stuffing effect of the Ca element on the glass network.

Calcium ion is one of the larger ions and its effective radius is close to those of Ba^{2+} and Pb^{2+}, which show a very limited mobility in the glass network and thus blocking the jumping of alkali ions [10]. Such a blocking effect would hinder the jumping of Mg ions and the formation of α-cordierite. This results in the increase of the glass transition temperature and the crystallization peak temperature with an increase in the CaO content (0 ~ 3 wt.%). However, Ca is a modifying cation and the number of non-bridging oxygens (NBO) in the glass structure would increase with increasing the CaO content. The glass network, therefore, would become looser with increasing the number of NBO, and thus decreasing its viscosity. This would result in the decrease in glass transition temperature with increasing the CaO content (more than 3 wt.%), as seen in Fig. 1. The stuffing effect of Ca ions on the glass network would be degraded in the looser glass structure by increasing the number of NBO. The variation in the glass structure would act upon the formation of the predominant phase which is controlled by the diffusion process.



Heated at 900 °C for 2 h



Heated at 950 °C for 2 h

Fig. 2 XRD patterns of the samples after heat treatment (**a**) Heated at 900 °C for 2 h (**b**) Heated at 950 °C for 2 h

Figure 2 shows the XRD patterns of each glass powders after heat treatment. From Fig. 2a, it was found that the predominant crystalline phase in sample with 0 wt.% and 1 wt.% CaO was α-cordierite and the minor crystalline phase was *μ*-cordierite. In sample with 3 wt.% CaO, the phase was only α-cordierite. In sample with 5 wt.% CaO, α-cordierite still as the main phase, anorthite occurred here. In sample containing 10 wt.% CaO, the main phase had become anorthite, α-cordierite obviously decreased. When the glass powders heated at 950 °C for 2 h as shown in Fig. 2b, the main phase was α-cordierite in sample with 0–3 wt.% CaO. With increasing CaO content substituting for MgO (from 5 wt.% to 10 wt.%), anorthite evidently increased, and α-cordierite clearly decreased. It means that addition of CaO would impede the formation of α-cordierite. On the other hand, addition of CaO would promote the formation of anorthite in the Mg deficient region. The reaction in the crystallization process can be expressed as follows:

$$MgO + Al_2O_3 + SiO_2 \rightarrow Mg_2Al_4Si_5O_{18}(\mu\text{ - cordierite}) \quad (1)$$

$$Mg_2Al_4Si_5O_{18}\,(\mu\text{ - cordierite}) \rightarrow Mg_2Al_4Si_5O_{18}\,(\alpha\text{ - cordierite}) \quad \text{For lower CaO content} \quad (2)$$

$$CaO + Al_2O_3 + SiO_2 \rightarrow CaAl_2Si_2O_8(\text{anorthite}) \quad \text{For higher CaO content} \quad (3)$$

The crystallization of cordierite is usually though surface crystallization between glass particles and is retarded by CaO addition. It is clear from the above reactions that the type of phase formation in the crystallization process depends on the kind of coordinated elements for SiO_2. This result is in agreement with the report by Hu [16].

Sintering behavior

The relative density for the fired samples in the temperature range between 750 °C and 950 °C is illustrated in Fig. 3. The relative density equals the theoretical density of a sample divided by its apparent density. The relative density for the samples increased as the CaO content increased. It was found that high densification rate in all samples took place between 850 °C and 900 °C. It is interesting that both sample with 5 wt.% CaO and sample with 10 wt.% CaO have better sintering behavior. At 875 °C, the relative density of both of the samples has reached 98.0%, which indicates that the samples get to almost full densification. Such a high rate of densification for two samples is thought to be attributed to the larger gaps between glass transition temperature and crystallization onset temperature (as seen in Fig. 1) and the viscous glass phase during the firing process [7, 13]. With increasing temperature to 900 °C, the relative density of the sample with 5 wt.% CaO has reached a maximum value of 98.5%, and the relative density of the sample with 10 wt.% CaO slightly decreases. When sintering temperature exceeds 900 °C, the relative density of samples with 5 wt.% and 10 wt.% CaO obviously decrease. This might be due to the fact that overheat results in an increase in the ringent pores derived from inner close pores in the dense samples, which is agreement with the result reported by Wang et al. [17]. It was observed that other samples had not become full densification though the sintering temperature reached 950 °C.

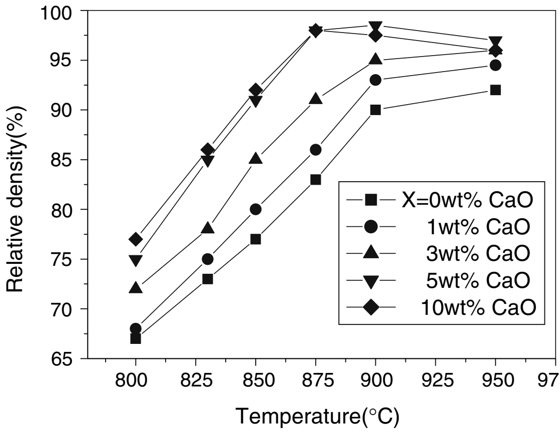


Fig. 3 Relative densities of the samples heated at various temperatures

The optimum heat-treatment procedures for a dense and crystallized glass-ceramic could be developed by considering the following factors. (1) Transition temperature of glass, T_g: It determines the starting sintering temperature. In forming useful LTCC substrates, it is important that no sintering occurs before the complete binder burnout [16]. The binder decomposition temperature is usually in the range of 400–700 °C. (2) Crystallization temperature (T_p): It determines the temperature that the crystal phase starts to grow. When crystallization occurs, it would decrease the densification. Usually the crystallization temperature must be below 950 °C for LTCC application. (3) Sintering rate: Whether glass-ceramic powders can be fully sintered before densification stops depends on the sintering rate. It is revealed that both factors (1) and (2) contributes the temperature region for efficient densification.

In present study, both samples with 5 wt.% and 10 wt.% CaO have been evaluated in an efficient densification before 900 °C. This meets the requirements of factors discussed above and is suitable for using in LTCC substrates fabrication. Full densification specimens can be achieved before the occurrence of crystallization in this work using micron-scale glass powders. A completely sintered sample with α-cordierite and some amount of anorthite phases is obtained at 900 °C. Figure 4 shows the SEM of fractured surface of samples with different CaO content sintered at 900 °C. It can be seen that the porosity decreased with increasing CaO content and the sample with 5 wt.% CaO has the lowest porosity than the others. This result corresponds to the relative density of samples as shown in Fig. 3.

Physical properties

The thermal expansion coefficients (TCE, 25–300 °C) of samples sintered at 900 °C for 2 h are shown in Fig. 5. The

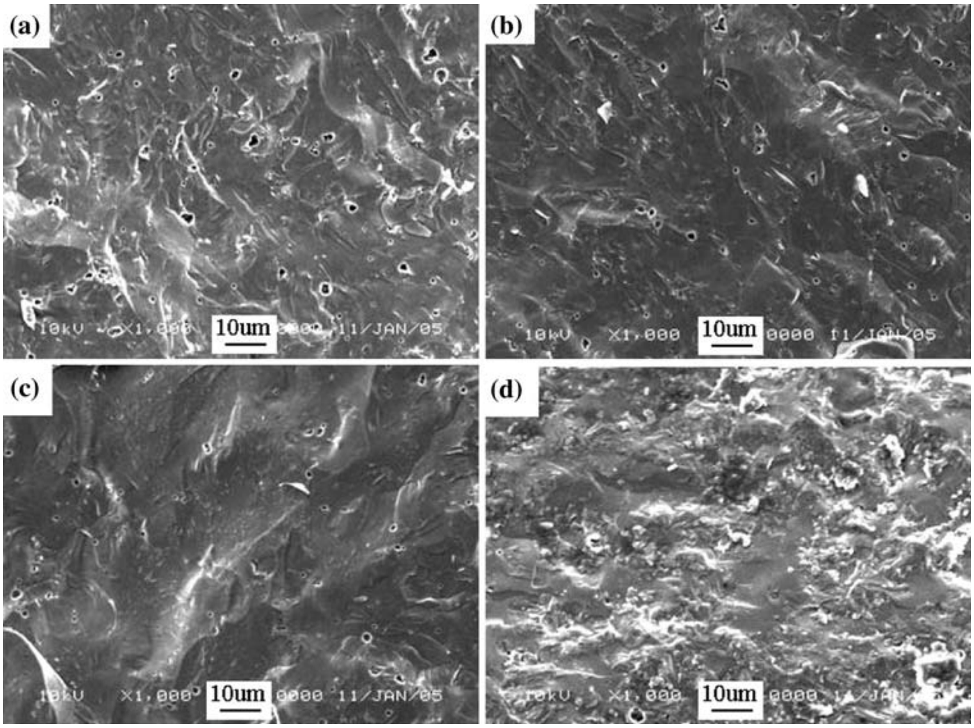


Fig. 4 SEM photographs of fresh fractured surface of sample with different CaO contents sintered at 900 °C for 2 h: (**a**) X = 0 wt.%, (**b**) X = 3 wt.%, (**c**) X = 5 wt.%, (**d**) X = 10 wt.%

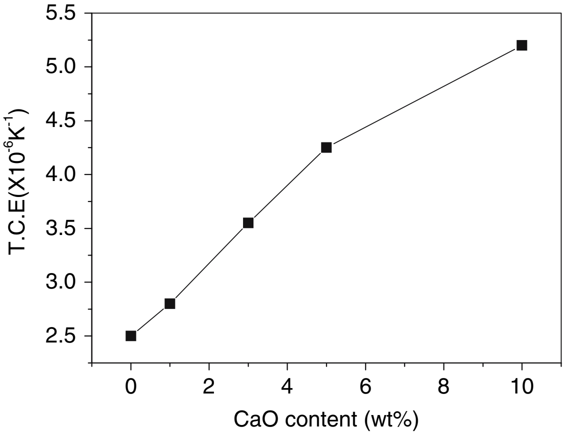


Fig. 5 Thermal expansion coefficient of samples with CaO contents

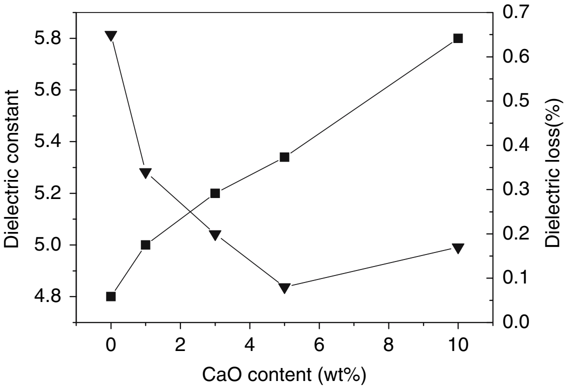


Fig. 6 Dielectric properties of the samples with CaO contents sintered at 900 °C for 2 h

TCE value of glass-ceramics obviously increases with the addition of CaO content. Since TCE of crystalline cordierite has a lower value (~1–2 × 10^{-6} K^{-1}) [6, 7] and TCE of crystalline anorthite has a higher value (~4.8 × 10^{-6} K^{-1}) [18], residual glass phase and anorthite would be responsible for the variation in TCE, as shown in Fig. 5.

Figure 6 shows the dielectric properties of the samples with different CaO contents. For a glass-ceramic material, many factors will affect the dielectric properties, including the content of the individual crystalline, glass phases, and the degree of densification. With an increase of CaO content, the dielectric constant of samples increases. As both anorthite and residual glass have a higher dielectric constant(anorthite, ~6 [18]; residual glass, ~5 [16, 19]), the increase in density and in residual glass phase and the formation of anorthite would be responsible for the variation in dielectric constant of samples, as shown in Fig. 6. It was found that the dielectric loss of samples with low CaO content (≤ 5 wt.%) obviously decreased, which may be attributed to the porosity decrease and the increase of anorthite having the lower dielectric loss [16] and the dielectric loss of the sample with 10 wt.% CaO content slightly increased, which may be due to the increase in the residual glass phase and pores which contribute to the sites

Table 1 Some properties of the sample with 5 wt.% CaO sintered at different temperatures for 2 h

Sintering temperature (°C)	Linear shrinkage (%)	Dielectric constant 25 °C, 1 MHz	Dielectric loss (%) 25 °C, 1 MHz	TCE ($\times 10^{-6}$ K^{-1}) (25–300 °C)	Flexural strength (MPa)
850	11.2	4.87	0.36	5.00	86
875	18.5	5.25	0.14	4.07	134
900	18.7	5.34	0.08	4.25	145
950	18.4	5.36	0.16	5.04	128

for carriers to move. The samples with 5 wt.% CaO have the lowest dielectric loss of 0.08%. The dielectric constant of all the samples is in the range 4.8–5.8.

Some of the other important properties of the sample with 5 wt.% CaO are listed in Table 1. It is observed that the dielectric constant increases with increasing sintering temperature. The dielectric loss of the sample with 5 wt.% CaO sintered at 875–900 °Creaches the lower value. Dielectric properties were found to be depended upon the relative density, the type of crystalline phases and residual glass phase [16, 20]. The TCE of glass-ceramics chiefly depends on its crystalline phase and residual glass phase. The flexural strength of glass-ceramics mainly depends on its relative density [21]. The flexural strength of the sample with 5 wt.% CaO firstly increases and then slightly decreases with sintering temperatures as shown in Table 1, which closely corresponds to the relative density as seen in Fig. 3. It is clear that the sample with 5 wt.% CaO sintered at 875–900 °C has the best dielectric property, and is preferred as the material for LTCCs. Firstly, it possesses the lowest dielectric loss lower than 0.001 at 1 MHz, which is desirable for reducing heat generation at high frequency; Secondly, its low dielectric constant (5.25–5.34), which is lower than that of alumina (~9), is absolutely necessary to reduce the propagation delay and parasitic capacitance (C_p) between internal conductor patterns of LTCCs and to achieve the requirements of high signal propagation speed. Thirdly, it possesses a low thermal expansion coefficient (TCE, 4.0–4.25 × 10^{-6} K^{-1}), very close to that of Si (3.0–3.5 × 10^{-6} K^{-1}) and a higher flexural strength; Lastly, its low sintering temperature (≤ 900 °Cenables the usage of Ag and Cu electrodes.

Conclusions

The sintering and crystallization behaviors for MgO–Al_2O_3–SiO_2 system glass-ceramics containing CaO were investigated. The replacement of MgO by CaO can lower the melting temperature and glass transition temperature of the glass-ceramics as well as promote sintering densification. An optimized sintering profile for glass powder with 5 wt.% CaO was established. The fully dense glass-ceramic with crystallized α-cordierite and a small amount of anorthite was successfully fabricated at relative low temperature (≤ 900 °C) Superior and reliable properties such as low temperature sinterability, thermal expansion coefficient, dielectric properties, and flexural strength were successfully derived in the dense specimen prepared from MgO–Al_2O_3–SiO_2 system glass-ceramic powder with the replacement of 5 wt.% CaO.

Acknowledgement This work was supported by Natural Science Foundation of Guangxi Province (No.0339066).

References

1. Tummala RR (1991) J Am Ceram Soc 74(5):895
2. Sarah HK, Ananda HK, Herron LW (1993) Am Ceram Soc Bull 72:90
3. Kumar AH, Mcmillan PW, Tummala RR (1981) US Pat 4301324
4. Jean JH, Gupta TK (1992) J Mater Sci 27:1575
5. Ei-Kheshen AA, Zawrah MF (2003) Ceram Int 29(3):251
6. Bridged DR, Mcmillan PW (1985) Glass Technol 26:286
7. Chen GH, Liu XY (2004) J Mater Sci: Mater Elect 15(9):595
8. Jean JH, Gupta TK (1992) J Mater Res 7(12):3342
9. Sohn SB, Young CS (2001) J Non-Cryst Solids 282:221
10. Hu Y, Tsai HT (1998) Mater Chem Phys 52(2):184
11. Wu JM, Huang HL (2000) J Mater Res 15:222
12. Chen LS, Fu SL (1992) Jpn, J Appl Phys 31(12A):3917
13. Yang CF, Cheng CM (1999) Ceram Int 25:383
14. Torres FJ, Alarcon LJ (2003) J Euro Ceram Soc 23(6):817
15. Mcmillan PW, Patridge G (1972) J Mater Sci 7(8):847
16. Hu Y, Tsai HT (2001) J Non-Cryst Solids 286:51
17. Wang SH, Zhou HP, Luo LH (2003) Mat Res Bull 38:1367
18. Mergena A, Aslanoglub VZ (2003) Ceram Int 29:667
19. Lo CH, Duh JG, Chiou BS (2003) J Mater Sci 38(4):693
20. Camerucci MA, Urretavizcaya G, Castro MS (2001) J Euro Ceram Soc 21(16):2917
21. Shi ZM, Liu Y, Yang WY (2002) J Euro Ceram Soc 22(8):1251