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Research Article

Microwave dielectric properties of $Ca_{0.7}Nd_{0.2}TiO_3$ ceramic-filled $CaO–B_2O_3–SiO_2$ glass for LTCC applications

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Abstract: The effects of the $Ca_{0.7}Nd_{0.2}TiO_3$ ceramic addition on the crystallization, densification, and dielectric properties of $CaO–B_2O_3–SiO_2–(Al_2O_3)$ glass (C1: $CaO–B_2O_3–SiO_2$ glass and C1A03: $CaO–B_2O_3–SiO_2–Al_2O_3$ glass) for low-temperature co-fired ceramic (LTCC) applications are investigated. The cristobalite phase crystallized from C1 glass was inhibited by adding Al_2O_3. During sintering, $Ca_{0.7}Nd_{0.2}TiO_3$ ceramic reacted with $CaO–B_2O_3–SiO_2–(Al_2O_3)$ glass to form the sphene ($CaTiSiO_5$) phase. The amount of sphene phase increases with increasing sintering temperature. By adding 50–60 wt% C1 or C1A03 glass, $Ca_{0.7}Nd_{0.2}TiO_3$ can be densified at 850–900 ℃. The relative dielectric constants for $Ca_{0.7}Nd_{0.2}TiO_3$ added with C1 and C1A03 glasses were all 20–23. $Ca_{0.7}Nd_{0.2}TiO_3$ added with C1 glass exhibited a lower dielectric constant than C1A03 glass due to cristobalite phase formation. For $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% glass, the variation in $Q \times f$ value presented the same trend as the sphene formation amount variation. The best $Q \times f$ value of 2380 GHz was achieved for $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% C1A03 glass sintered at 900 ℃ due to the dense structure and greater amount of sphene. $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% C1A03 glass sintered at 900 ℃ exhibited a dielectric constant of 22.8 and $Q \times f$ value of 2380 GHz, which are suitable for microwave LTCC applications.

Keywords: low-temperature co-fired ceramic (LTCC); $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics; microwave dielectric property; $CaO–B_2O_3–SiO_2$ glass

1 Introduction

Microwave dielectric ceramics are important for mobile telecommunication devices, such as dielectric resonators. The dielectric components must also be miniaturized to reduce the device size. For dielectric ceramic applications in microwave devices, a high dielectric constant (ε_r), high quality factor ($Q \times f$), and near-zero resonant frequency (τ_f) temperature coefficient are required. Low-temperature co-fired ceramic (LTCC) is a ceramic filled glass composite based on crystallizable glass or a mixture of glass and ceramics. In Refs. [1,2] for the LTCC system, the glass acts mainly as a low temperature sintering aid and ceramic fillers help in enhancing mechanical strength and minimizing distortion. High volume glass content is often detrimental to the LTCC materials dielectric constant (K) and quality factor ($Q \times f$) [3]. Crystallizable glass–ceramic is crystallized from the glass phase occurring after densification, presenting

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a distinct advantage for LTCC applications. Among several LTCC glass–ceramic systems, the $CaO–B_2O_3–SiO_2$ system was reported as a suitable candidate material for LTCC applications owing to its low firing temperature and low dielectric loss [4]. The LTCC properties with the crystallizable glass–ceramic filler system are controlled by the glass structure, crystallization behavior, and interaction between the glass and ceramic filler during firing. Therefore, a thorough understanding of the structure and crystallization behavior of glass–ceramic systems is needed before the processing parameters are optimized. $Ca_{1-x}Nd_{2x/3}TiO_3$ [5,6] exhibits high K (~100), high $Q \times f$ value (> 10,000 GHz), and much lower positive τ_f than that of $CaTiO_3$. Wei and Jean [7] reported that the $Ca_{1-x}Nd_{2x/3}TiO_3$ can be densified at temperatures below 900 ℃ by adding 20–40 vol% $3ZnO–2B_2O_3$ glass, which exhibited a dielectric constant of 30–60 and a quality factor of 200–550 at 1–10 GHz. The delamination and warpage in low-K and middle-K LTCC layer co-firing can be easily minimized by using common glass frits [8]. $CaO–B_2O_3–SiO_2$ (CBS) glass ceramics have been reported as a promising low-K LTCC material for use in the microelectronic field [9–12]. However, the addition effects of $Ca_{1-x}Nd_{2x/3}TiO_3$ ceramics into the $CaO–B_2O_3–SiO_2$ glass on the glass structure, crystallization behavior, and dielectric properties have never been studied in detail to our best knowledge. The addition effects of $Ca_{1-x}Nd_{2x/3}TiO_3$ ceramics on the crystallization, densification, and dielectric properties of $CaO–B_2O_3–SiO_2–(Al_2O_3)$ glass for LTCC applications are investigated in this study.

2 Experimental

The $CaO–B_2O_3–SiO_2–(Al_2O_3)$ glass chemical composition is shown in Table 1. 2.64 mol% Al_2O_3 was added into the $CaO–B_2O_3–SiO_2$ glass, while the ratios of other ingredients in $CaO–B_2O_3–SiO_2$ glass were kept constant. $CaO–B_2O_3–SiO_2$ and $CaO–B_2O_3–SiO_2–Al_2O_3$ glasses are denoted by C1 and C1A03 glass, respectively. The glasses were prepared by melting powders containing appropriate amounts of reagent grade CaO, Al_2O_3, MgO, $CaCO_3$, K_2CO_3, B_2O_3, and SiO_2, in a Pt crucible at 1450 ℃ for 1 h. The melt was rapidly quenched in distilled water and planetary ball milled with yttria tetragonally stabilized zirconia (Y-TZP) balls for 10 h. The glass powder had a mean particle size of 6.6 μm based on the scanning electron microscopy image analysis. The X-ray diffraction (XRD) analysis did not reveal any crystal phase for the glass powder.

Table 1 Glass compositions of C1 and C1A03

(Unit: mol%)

Glass	SiO_2	B_2O_3	CaO	Al_2O_3	MgO	Na_2O	K_2O
C1	63.44	18.12	9.06	—	3.01	3.17	3.17
C1A03	61.76	17.64	8.82	2.64	2.93	3.09	2.93

$Ca_{0.7}Nd_{0.2}TiO_3$ ceramic was prepared from reagent grade $BaCO_3$, Nd_2O_3, and TiO_2, which were mixed and then calcined at 1300 ℃ for 4 h. $Ca_{0.7}Nd_{0.2}TiO_3$ powder was planetary milled for 10 h in acetone using YTZ balls. The mean particle size of the planetary milled $Ca_{0.7}Nd_{0.2}TiO_3$ powder is about 3 μm based on the SEM image analysis.

The glass powder was mixed with different volume fractions of $Ca_{0.7}Nd_{0.2}TiO_3$ powder and then pressed uniaxially at about 90 MPa to make a pellet with 8 mm diameter and 2 mm in height. The samples were then sintered at temperatures in 800–900 ℃ for 1 h. The crystallization temperature (T_c) was determined using a differential thermal analyzer (DTA, Netzsch STA 409C, Germany). The DTA was performed at a heating rate of 10 ℃/min under flowing air. The glass transition temperature (T_g) and softening temperature (T_s) of the glasses were measured using a dilatometer (Netzsch, 402PC) at a heating rate of 10 ℃/min. The glass densities were measured using a helium gas pycnometer (Accupyc1340, Micromeretics Instrument Corporation, Norcross, GA, USA). The crystalline phase evolution was characterized using an X-ray diffractometer with a Cu Kα (Dandong Fangyuan, DX-2700, Shandong, China). The sintered sample microstructures were examined using scanning electron microscope (SEM) (Hitachi, S-4100). The microwave dielectric properties (relative dielectric constant, quality factor value) were measured using a vector network analyzer (Keysight Tech., E5071C ENA) at 9 kHz–20 GHz.

3 Results and discussion

The T_g and T_s of C1 and C1A03 are 585, 628, 600, and 640 ℃ based on the dilatometric measurements. In addition, C1 and C1A03 glasses exhibited T_c at around 740 and 780 ℃, respectively.

Figure 1 shows the XRD patterns of $Ca_{0.7}Nd_{0.2}TiO_3$ powders added with 40, 50, and 60 wt% C1 and C1A03

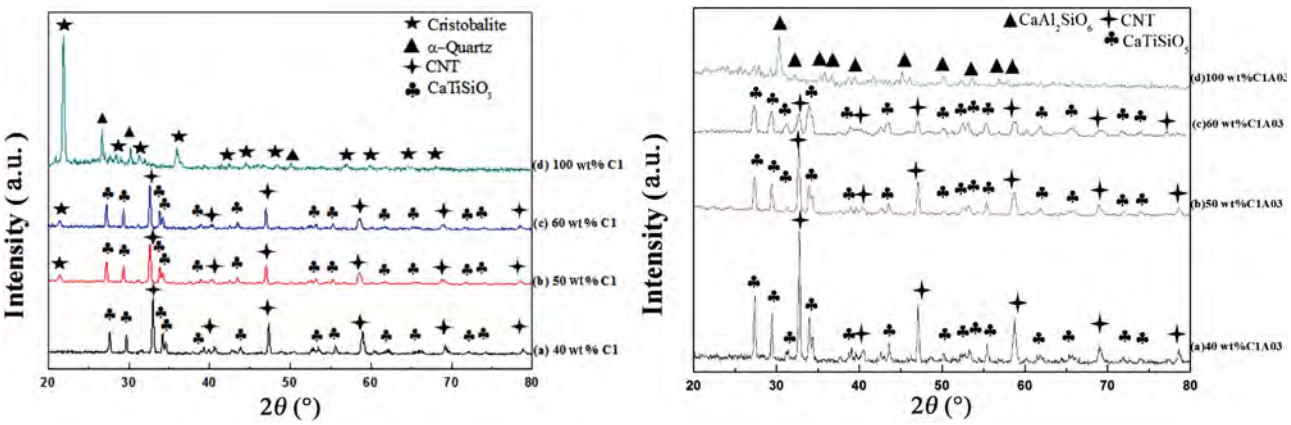

Fig. 1 XRD patterns of $Ca_{0.7}Nd_{0.2}TiO_3$ powders added with 40, 50, and 60 wt% C1 and C1A03 glass powders after sintering at 900 ℃ for 1 h.

glass powders after sintering at 900 ℃ for 1 h. The pure C1 glass crystalline phases after sintering are cristobalite accompanied with a minor amount of quartz. Only Ca-tschermakite ($CaAl_2SiO_6$) phase was observed for C1A03 glass. The main phases for the $Ca_{0.7}Nd_{0.2}TiO_3$ powders added with 40 wt% glass were $Ca_{0.7}Nd_{0.2}TiO_3$ phase and sphene ($CaTiSiO_5$). As the glass addition was increased above 50 wt%, cristobalite crystallized from C1 glass appeared. For $Ca_{0.7}Nd_{0.2}TiO_3$ powders added with C1A03 glass, the main crystalline phases were $Ca_{0.7}Nd_{0.2}TiO_3$ phase and sphene. The crystalline phases existed in the $Ca_{0.7}Nd_{0.2}TiO_3$ powders added with C1 and C1A03 glasses were different. This indicates that the addition of Al^{3+} ions into C1 glass modifies the glass structure and viscosity, which inhibit cristabalite crystallization [7].

Figure 2 shows the XRD patterns of $Ca_{0.7}Nd_{0.2}TiO_3$ powders added with 50 wt% C1 and C1A03 glass powders and sintered at various temperatures. The crystalline phase of $Ca_{0.7}Nd_{0.2}TiO_3$ powders added with 50 wt% C1 after sintering at 800 ℃ was $Ca_{0.7}Nd_{0.2}TiO_3$ phase only. As the sintering temperature was increased above 850 ℃, cristobalite and sphene crystalline phases formed. For the $Ca_{0.7}Nd_{0.2}TiO_3$ added with 50 wt% C1A03 glass and sintered at 800 ℃, no crystalline phase other than $Ca_{0.7}Nd_{0.2}TiO_3$ phase was observed. A new crystalline phase, sphene, appeared at temperatures above 850 ℃. The amounts of sphene for the samples sintered at various temperatures can be semi-quantitatively determined by calculating the ratio of integrated XRD intensities for sphene to that of the XRD peak sum for $Ca_{0.7}Nd_{0.2}TiO_3$ phase and sphene, as below:

$$\text{Amount of sphene} = \frac{I_{CaTiSiO_5}}{I_{CaTiSiO_5} + I_{CNT}}$$

where I_{CNT} and $I_{CaTiSiO_5}$ are the integrated XRD intensities of $Ca_{0.7}Nd_{0.2}TiO_3$ and sphene, respectively.

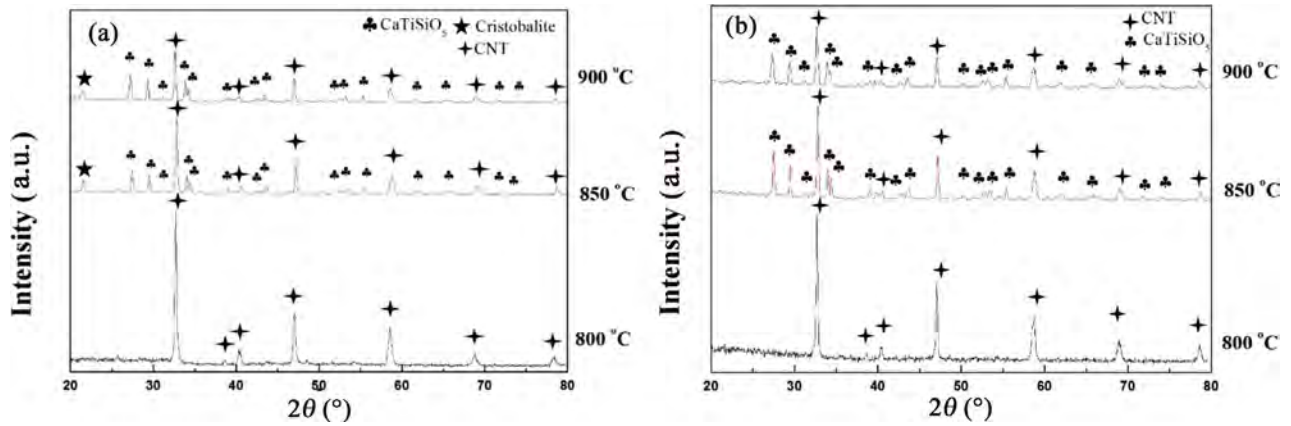

Fig. 2 XRD patterns of $Ca_{0.7}Nd_{0.2}TiO_3$ powders added with 50 wt% C1 (a) and C1A03 (b) glass powders and sintered at various temperatures.

Figure 3 shows the variation in the amount of sphene for the $Ca_{0.7}Nd_{0.2}TiO_3$ added with various amounts of C1 and C1A03 glasses and sintered at 850 and 900 ℃. As the temperature was raised from 850 to 900 ℃, the amount of sphene phase increased.

Figure 4 shows the SEM image and concentration profiles of the interface between $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics and C1A03 glass sintered at 900 ℃ for 1 h. This indicates that Nd^{3+} in $Ca_{0.7}Nd_{0.2}TiO_3$ ceramic dissolves into the glass, leaving CaO and TiO_2 behind, due to the solubility difference in the glass between CaO, Nd_2O_3, and TiO_2. Si^{4+} then diffuses from the glass to react with CaO and TiO_2 to form the $CaTiSiO_5$ phase.

Figure 5 shows the $Ca_{0.7}Nd_{0.2}TiO_3$ microstructures added with various amounts of C1 and C1A03 glasses after sintering at 900 ℃. $Ca_{0.7}Nd_{0.2}TiO_3$ added with 40 wt% C1 or C1A03 glass sintered at 900 ℃ did not result in comparable densification, which may be due to insufficient liquid phase. As the glass content increased, the sample became dense and the amount and size of the pores decreased. This suggests that densification can be achieved using the liquid phase sintering of glass and a dense microstructure with few and small pores can be obtained for $Ca_{0.7}Nd_{0.2}TiO_3$ added with 50–60 wt% C1 or C1A03 glass sintered at 900 ℃. Figure 6 shows the variation in porosities for $Ca_{0.7}Nd_{0.2}TiO_3$ added with various amounts of C1 and C1A03 glasses after sintering at 850 and 900 ℃. This indicates that the porosity decreased below 1% as the glass addition was above 50 wt% for the samples sintered at 850 or 900 ℃.

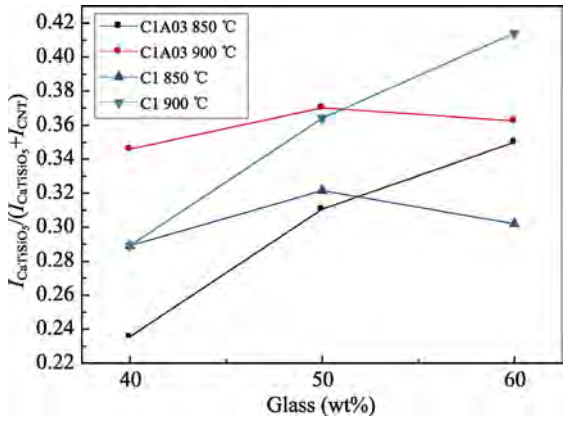

Fig. 3 Variation in the amount of sphene for the $Ca_{0.7}Nd_{0.2}TiO_3$ added with various amounts of C1 and C1A03 glasses and sintered at 850 and 900 ℃.

Figure 7 shows the dielectric constants of $Ca_{0.7}Nd_{0.2}TiO_3$ added with various amounts of C1 and C1A03 glasses after sintering at 900 ℃. The change in dielectric properties is attributed to the variation in density and phase constituents during sintering [13,14]. The relative dielectric constants were all 20–23. As the glass content was increased from 40 to 50 wt%, the size and amount of pores decreased, leading to increased dielectric constant. As the glass content was further increased to 60 wt%, the dielectric constant declined due to adding too much glass with low dielectric constant. $Ca_{0.7}Nd_{0.2}TiO_3$ added with C1 glass exhibited a lower dielectric constant than C1A03 glass, which may be due to cristobalite phase formation with lower dielectric constant (3.8).

The $Q \times f$ value of $Ca_{0.7}Nd_{0.2}TiO_3$ added with 60 wt% C1 or C1A03 glass cannot be determined due to the complete resonance peak disappearance during measurement. This may be explained by the addition of too much glass with lower $Q \times f$ value due to the larger ionic vibration loss [1]. The $Q \times f$ values of

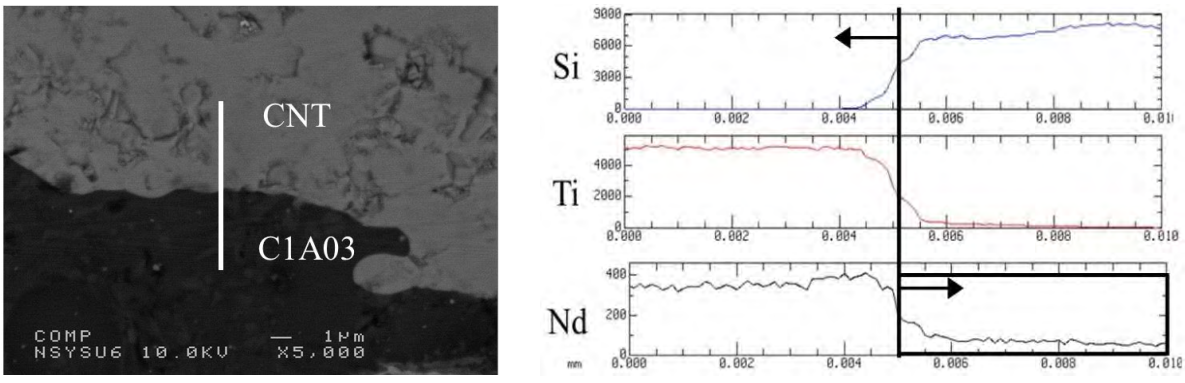

Fig. 4 (a) SEM image and (b) concentration profiles of the interface between $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics and C1A03 glass sintered at 900 ℃ for 1 h.

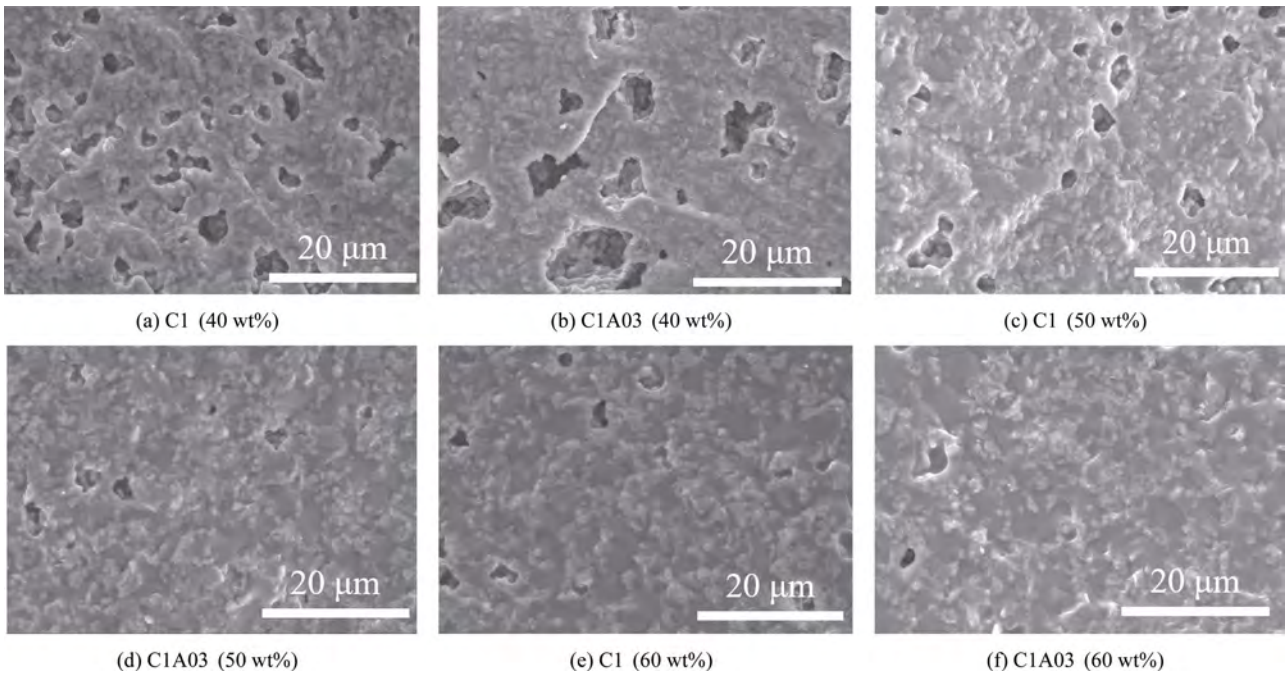

Fig. 5 Microstructures of $Ca_{0.7}Nd_{0.2}TiO_3$ added with various amounts of C1 and C1A03 glasses after sintering at 900 ℃.

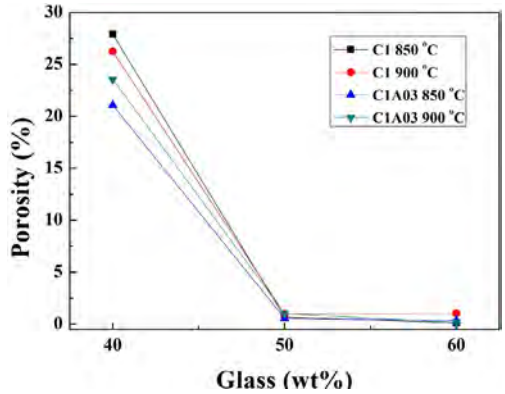

Fig. 6 Variation in porosities for $Ca_{0.7}Nd_{0.2}TiO_3$ added with various amounts of C1 and C1A03 glasses after sintering at 850 and 900 ℃.

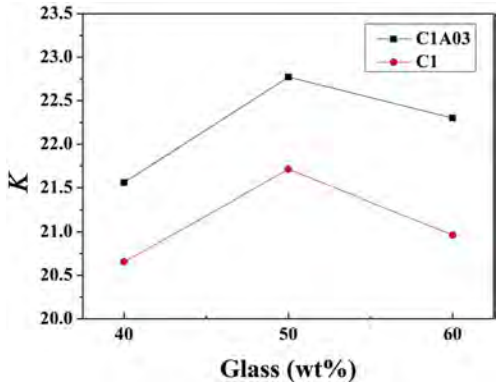

Fig. 7 Dielectric constants of $Ca_{0.7}Nd_{0.2}TiO_3$ added with various amounts of C1 and C1A03 glasses after sintering at 900 ℃.

$Ca_{0.7}Nd_{0.2}TiO_3$ added with C1 and C1A03 glasses after sintering at 850 and 900 ℃ are shown in Table 2. The $Q \times f$ value depends on the sintered density and crystalline phase [15,16]. The $Q \times f$ values of $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% glass were higher than those added with 40 wt% glass due to the higher densification. For $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% glass, the variation in $Q \times f$ value has the same trend as the variation in sphene formation amount. Sphene ($CaSiTiO_5$), which is known as titanite, exhibits low dielectric loss ($\tan\delta = 5 \times 10^{-4}$) [17]. The best $Q \times f$ value of 2380 GHz can be achieved for $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% C1A03 glass sintered at 900 ℃ due to the dense structure and

Table 2 $Q \times f$ values (at 7 GHz) of $Ca_{0.7}Nd_{0.2}TiO_3$ added with C1 and C1A03 glasses after sintering at 850 and 900 ℃

Glass	Glass addition (wt%)	Sintering temperature (℃)	$Q \times f$ (GHz)
C1	40	850	820
		900	610
C1A03	40	850	780
		900	775
C1	50	850	1800
		900	2100
C1A03	50	850	1700
		900	2380

greater amount of sphene. The $Q \times f$ value in this study is lower than that of the $Ca_{1-x}Nd_{2x/3}TiO_3$ added with 20–40 vol% $3ZnO–2B_2O_3$ glass and sintered at 900 ℃ glass reported by Wei and Jean [7]. This may be due to the dissolution of Nd^{3+} in $Ca_{0.7}Nd_{0.2}TiO_3$ ceramic into the glass increasing the dielectric loss. $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% C1A03 glass sintered at 900 ℃ exhibited a dielectric constant of 22.8 and $Q \times f$ value of 2380 GHz, which are suitable for microwave LTCC applications.

4 Conclusions

By adding 50–60 wt% C1 or C1A03 glass, $Ca_{0.7}Nd_{0.2}TiO_3$ can be densified at 850–900 ℃. The cristobalite phase crystallized from C1 glass was inhibited by adding Al_2O_3. During sintering, $Ca_{0.7}Nd_{0.2}TiO_3$ ceramic reacted with $CaO–B_2O_3–SiO_2–(Al_2O_3)$ glass to form the sphene phase. The amount of sphene phase increased with increasing sintering temperature. $Ca_{0.7}Nd_{0.2}TiO_3$ added with C1 glass exhibited lower dielectric constant than C1A03 glass due to cristobalite phase formation. For $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% glass, the variation in $Q \times f$ value presented the same trend as the variation in sphene amount formation. The best $Q \times f$ value of 2380 GHz can be achieved for $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% C1A03 glass sintered at 900 ℃ due to the dense structure and greater amount of sphene. $Ca_{0.7}Nd_{0.2}TiO_3$ ceramics added with 50 wt% C1A03 glass sintered at 900 ℃ exhibited dielectric constant of 22.8 and $Q \times f$ value of 2380 GHz, which are suitable for microwave LTCC applications.

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