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Short communication

Properties of glasses based on the CaO–MgO–SiO_2 system for low-temperature co-fired ceramic

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Abstract

Glass compositions based on the CaO–MgO–SiO_2 system are investigated with an aim to increase the coefficient of thermal expansion (CTE) in a low-dielectric constant layer material for low-temperature co-fired ceramics (LTCC). The effect of changing the glass composition on the CTE is examined by the addition of ZnO, Al_2O_3, BaO, and SrO. X-ray diffraction (XRD) results show that $CaMgSi_2O_6$ is the major crystalline phase of all sintered samples except for one composition. According to the experimental results, the substitution of BaO and SrO for CaO plays an important role in increasing the CTE.

Keywords: C. Thermal expansion; D. Glass-ceramic; $CaMgSi_2O_6$

1. Introduction

Low-temperature co-fired ceramic (LTCC) is a promising technology and it has become increasingly attractive for high frequency applications. In recent years, much attention has been paid to the development of LTCC technology due to the increased demand for microwave and millimeter-wave applications, such as the front-end module for mobile phones, 3G cellular, wireless local-area networks and radar for automobiles [1,2]. In order to meet the demands for LTCC in high frequency applications, glass plus ceramics and glass-ceramics have been investigated. The glass-ceramics have several suitable properties that can be controlled for LTCC substrates, such as a low-dielectric constant, good chemical durability, an appropriate coefficient of thermal expansion (CTE), and the advantage of mass production [3]. The main glass-ceramic systems for LTCC applications that have been reported are based on CaO–B_2O_3–SiO_2, Li_2O–Al_2O_3–SiO_2, MgO–Al_2O_3–SiO_2, CaO–Al_2O_3–SiO_2, and CaO–MgO–SiO_2 [4–7]. Among these popular glass-ceramics, the CaO–MgO–SiO_2-based system has a higher CTE and lower loss tangent than the conventional CaO–Al_2O_3–SiO_2-based system. Moreover, it is an important material for LTCC due to its excellent durability and mechanical property [8–10].

In this work, eight new glasses with compositions based on the CaO–MgO–SiO_2 system are investigated in order to attain high CTE glass-ceramics. Table 1 summarizes the chemical compositions of the batches of the eight glasses. The compositions are designed according to the following guidelines. The basic composition of the parent glass with a molar ratio of CaO, MgO, and SiO_2 of 2:1:1 is maintained. All compositions are doped with different amounts of ZnO and Al_2O_3. Some compositions involve the replacement of CaO by BaO and SrO, with an aim to increase the CTE. Considering the compositions of each total batch to be 100 wt%, 20 wt% of alumina is added to the mixture of the glass frits as a filler. In addition, the crystalline phases of each composition, the physical properties, such as dielectric properties, and the thermal properties, such as glass transition temperature, crystallization temperature, and characteristics of the thermal expansion behavior are also evaluated.

2. Experimental procedure

The eight glass samples of homogeneous mixture reported in Table 1 are prepared by ball milling. Melting is performed in Pt crucibles at 1500 °C for 1 h. Glasses in frit form are obtained by

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Table 1
Chemical compositions of the investigated glasses in molar ratio.

Sample	SiO_2	CaO	MgO	ZnO	Al_2O_3	SrO	BaO
DOE1	2	1	1	0.1	0.1	–	–
DOE2	2	0.85	1	0.1	0.3	–	0.15
DOE3	2	0.85	1	0.2	0.1	–	0.15
DOE4	2	1	1	0.2	0.3	–	–
DOE5	2	0.7	1	0.1	0.1	0.15	0.15
DOE6	2	0.85	1	0.1	0.3	0.15	–
DOE7	2	0.85	1	0.2	0.1	0.15	–
DOE8	2	0.7	1	0.2	0.3	0.15	0.15

Table 2
DTA characteristic data for glass samples (T_g: glass transition temperature; T_{p1}, T_{p2}, and T_{p3}: crystallization peak temperature).

Sample	T_g (°C)	T_{p1} (°C)	T_{p2} (°C)	T_{p3} (°C)
DOE1	734.4	872.5	–	–
DOE2	730.4	853.4	950.9	–
DOE3	727.6	839.9	897.8	–
DOE4	736.1	848.5	941.6	–
DOE5	730.3	844.3	921.6	–
DOE6	738.1	856.6	950.6	–
DOE7	729.1	834.6	887.5	–
DOE8	749.7	845.1	905.1	942.5

quenching the melts in a quenching roller. The frits are milled in a planetary ball mill (Pulverisette 5, Fritsch, Germany) up to a median particle size of 4–6 μm. These powders are pressed into pellets that are 12 mm in diameter and 3 mm thick. Pellets are sintered in air at 870 °C for 1 h at a heating rate of 5 °C/min with a view to making glass-ceramics. Phase evolution in each crystallized sample is identified by a high resolution X-ray diffractomer (D8 Discover, Bruker, Germany) with a wavelength of Cu Kα ($\lambda = 1.5406$ Å), in the 2θ range from 20° to 60°, at a scanning speed of 0.02°/min. Differential thermal analysis (DTA) (STA 409 EP, Netzsch, Germany) is used to determine the temperature of the glass transition (T_g) and crystallization peak (T_p). The analysis is made in the range of 25–1000 °C using powdered samples, at a heating rate of 5 °C/min. The CTE is measured with the sintered pellets in air at a heating rate of 5 °C/min using a dilatometer (DIL402C, Netzsch, Germany). The CTE is determined from the slope of the expansion curve in the temperature range of 25–300 °C and represents an average value over this temperature range. The dielectric characteristics, including dielectric constant and dissipation factor at 1 MHz, are measured using an In–Ga electrode in an LCR meter (4288A, Agilent, USA).

3. Results and discussion

Table 3
Crystalline phases in samples identified by XRD analysis.

Sample	Crystalline phases
DOE1	$CaMgSi_2O_6$, Al_2O_3
DOE2	$CaMgSi_2O_6$, $Ca_2MgSi_2O_7$, Al_2O_3
DOE3	$CaMgSi_2O_6$, $Ca_2MgSi_2O_7$, Al_2O_3
DOE4	$CaMgSi_2O_6$, Al_2O_3
DOE5	$CaMgSi_2O_6$, $BaAl_2Si_2O_8$, Al_2O_3
DOE6	$CaMgSi_2O_6$, $Ca_2MgSi_2O_7$, Mg_2SiO_4, Al_2O_3
DOE7	$CaMgSi_2O_6$, Al_2O_3
DOE8	$CaAl_2Si_2O_8$, $Ca_2MgSi_2O_7$, Mg_2SiO_4, $BaAl_2Si_2O_8$, Al_2O_3

The DTA traces of the different investigated compositions of glasses (DOE1–DOE8) are carried out to determine the glass transition temperature (T_g) and the crystallization peak temperature (T_p). Several different exothermic peaks that are attributed to the formation of the crystalline phase are detected and their values for different glass compositions are listed in Table 2. Almost all of the samples have T_g in the range of 730–740 °C. With respect to this fact, comparison between the T_g value and each glass composition reveals that increasing the Al_2O_3 content leads to a higher glass transition temperature. In addition, 2 or 3 crystallization peaks are observed in all samples except DOE1. Based on this result, it can be expected that more than one crystalline phase is generated, including $CaMgSi_2O_6$. A broad exothermic peak, as seen in the sample of DOE8, indicates a sluggish crystallization propensity and a low crystallization rate; whereas, a sharp exothermic peak, such as in DOE1, DOE4, and DOE7, indicates a high crystallizability and a high crystallization velocity [11]. The existing phases in various samples from the X-ray diffraction (XRD) results are summarized in Table 3. From the experimental results, several facts are noted. Firstly, all eight samples possess the Al_2O_3 phase due to the effect of the additional filler. Secondly, with increasing the amount of BaO and/or SrO substituting for CaO, the number of glass-ceramic phases is clearly increased. Thirdly, the main phase of all samples, except DOE8, is $CaMgSi_2O_6$. The result of qualitative XRD analysis is consistent with the trend shown by a comparison with the DTA result. The physical properties including CTE, dielectric constant, and dielectric loss at 1 MHz of samples sintered at 870 °C are listed in Table 4. It is observed that the CTE value of samples clearly increases with an increasing amount of substitution of both BaO and SrO for CaO. Thus, samples with DOE5 and DOE8 have relatively high CTEs. The dielectric constant at 1 MHz of all the samples is in the range of 7.2–8.1. For all samples measured, the dissipation factor at

Table 4
Properties of glass samples heat-treated at 870 °C for 1 h.

Property	DOE1	DOE2	DOE3	DOE4	DOE5	DOE6	DOE7	DOE8
Coefficient of thermal expansion (10^{-6} K^{-1})	8.9	8.5	9.4	8.9	9.9	9.2	9.6	10.9
Dielectric constant at 1 MHz	7.2	7.7	8.1	7.6	7.8	7.6	7.8	7.5
Dissipation factor at 1 MHz (10^{-3})	0.68	0.95	0.93	0.96	0.86	1.18	0.91	3.51

1 MHz is always $<0.15\%$, except the sample of DOE8. These results are thought to be obtained because $CaMgSi_2O_6$-based glass-ceramic has a low-dielectric loss at 1 MHz.

4. Conclusion

Eight glass compositions based on the ternary CaO–MgO–SiO_2 system containing small amounts of ZnO, Al_2O_3, BaO, and SrO are investigated with respect to increasing the CTE. XRD results show that $CaMgSi_2O_6$ is the major phase of all samples heat-treated at 870 °C, except for DOE8. Although the composition of DOE8 has the highest CTE among the investigated glass compositions, the sample of DOE5 with the CTE of $9.9 \times 10^{-6}\ K^{-1}$ is the most suitable glass composition due to its thermal and physical properties. The improvement of CTE is attributed to the replacement of CaO with BaO and SrO.

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