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Short communication

Thermal conductivity of low-temperature sintered calcium aluminosilicate glass–silicon nitride whisker composites

Mingsheng Ma[a,c], Zhifu Liu[a,*], Yongxiang Li[a,*], Yuping Zeng[b], Dongxu Yao[b]

[a]*CAS Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*

[b]*Structural Ceramics Engineering Research Center, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China*

[c]*The University of Chinese Academy of Sciences, Beijing 100049, PR China*

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Abstract

A new type of low temperature co-fired ceramic (LTCC) composite, comprising β-Si_3N_4 whiskers and calcium aluminosilicate (CAS) glass, is introduced in this paper. We show that the CAS–Si_3N_4 composite can be densified at 775–850 °C in air. The effect of β-Si_3N_4 whiskers incorporation on the thermal conductivity of this relatively low-temperature sintered CAS–Si_3N_4 composite is investigated. The thermal conductivity of the CAS glass is increased from 1.6 to 7.9 W/mK after adding 35 vol% of β-Si_3N_4 whiskers. Microstructure characterization and percolation model analysis indicate that the likely cause of increased thermal conductivity of the ceramic composites is the formation of thermal percolation networks. The crystallization of the CAS glass also contributes to the enhancement of thermal conductivity. The sample with the highest thermal conductivity shows a low relative dielectric constant of 7.1 and a dielectric loss of 0.006 at 1 MHz. Such a ceramic composite with excellent thermal and dielectric properties is a promising LTCC substrate material.

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1. Introduction

Low temperature co-fired ceramics (LTCC) are nowadays extensively utilized to make substrates for microelectronic packaging [1,2]. Compared to the high temperature co-fired ceramics, the low processing temperature (<950 °C) of LTCC enables the use of highly conductive and cheaper metals, such as silver and copper, for the circuit lines [3,4]. LTCC materials usually consist of glass and ceramic fillers, and exhibit low dielectric constants (4–9), which advantageously increase the signal speed and also ensure coefficients of temperature expansion (CTE, in a range of 4.5–7.5 ppm/K), matching that of silicon chips [5–7]. However, the thermal conductivity of many commercial LTCC materials in their glass phase is only in the range of 2–4 W/mK [8], which makes the thermal management of LTCC-based electronic packages a great challenge.

One approach to increase the thermal conductivity of LTCC materials is to add ceramic fillers with high thermal conductivity into the glass matrix. Compared with the common choice of metal oxide fillers (Al_2O_3), AlN and Si_3N_4 are excellent filler candidates for high performance electronic device packaging due to their suitable thermal, mechanical, and electrical properties [9–11]. To date, there has been very limited number of reports on the use of nitride fillers in LTCC materials [12,13]. Zhang et al. reported that the thermal conductivity of lead borosilicate glass–AlN composites can reach values as high as 10 W/mK [12], but the high loading of AlN (>70 vol%) and special sintering processing (hot-press sintered in vacuum) increase the cost and hinder the practical application for LTCC processes. One must pay attention that it is generally challenging to improve the thermal conductivity

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*Corresponding authors. Tel.: +86 21 52411066; fax: +86 21 52413122.
E-mail addresses: liuzf@mail.sic.ac.cn (Z. Liu), yxli@mail.sic.ac.cn (Y. Li).

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of glass-based LTCC materials, because the high thermal conductivity fillers are easily insulated by the glass phase and cannot effectively contribute to the thermal conductivity of composites. The formation of thermally conducting networks in the composite that has a strong influence on its overall thermal conductivity [14,15]. One-dimensional materials with high thermal conductivity, such as AlN, β-Si_3N_4, and SiC whiskers and carbon nanotubes, can readily construct thermally conducting paths on account of their large aspect ratios [16]. Several studies based on polymer composites have also demonstrated the feasibility of forming thermally conducting paths embedded in the polymers, using the aforementioned one-dimensional materials [17–19].

In this study, we introduce a new type of LTCC system using β-Si_3N_4 whiskers instead of conventional oxide fillers to build thermally conducting networks in a calcium aluminosilicate (CAS) glass matrix. The effects of whiskers content on the thermal conductivity and the sintering behavior of CAS–Si_3N_4 composites are investigated, and the dielectric properties of CAS–Si_3N_4 composites are studied. The developed material unveils a great potential for high performance electronic packaging applications.

2. Experimental procedure

The composition of the CAS glass is 25 wt% CaO, 15 wt% Al_2O_3, 20 wt% B_2O_3 and 40 wt% SiO_2. The starting materials, including $CaCO_3$ (99.6%), Al_2O_3 (99.5%), H_3BO_3 (99.5%), and SiO_2 (99.0%) (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China), were first mixed according to the given proportion, then melted at 1400 °C and kept at the melting temperature for 2 h. The molten glass was quenched into de-ionized water and then ball-milled to about 1 μm in mean particle size. β-Si_3N_4 whiskers (synthesized by researchers in the Structural Ceramics Engineering Research Center of SICCAS) with the mean diameter of 0.1–0.5 μm and an aspect ratio of ~10 were used as the filler. The CAS glass powders with different amounts of β-Si_3N_4 whiskers were mixed using rolling ball mill for 6 h in ethanol. The dried mixtures were then pressed into green disks with a diameter of 15 mm, under 2 MPa pressure, and sintered in air at 750–875 °C for 30 min, with a heating rate of 5 °C/min. Table 1 shows the sample codes of CAS–Si_3N_4 composites, in which the numbers stand for the proportion of β-Si_3N_4 whiskers.

Table 1
Coding of the prepared samples.

Sample code	CAS glass (vol%)	β-Si_3N_4 whisker (vol%)
SN0	100	0
SN8	92	8
SN17	83	17
SN26	74	26
SN35	65	35
SN45	55	45

Table 2
The measured thermal diffusivity and specific heat of the samples sintered at the optimal temperature.

Sample	Sintered temperature (°C)	Thermal diffusivity (mm^2/s)	Specific heat (J/gK)
SN0	775	0.76	0.78
SN8	775	1.05	0.79
SN17	800	1.62	0.79
SN26	825	2.36	0.80
SN35	850	3.37	0.79
SN45	850	2.61	0.78

Phase identification for the ceramics was performed using the X-ray diffraction analysis (XRD, Rigaku D/MAX 2550 V, Japan) and the microstructures were characterized by scanning electron microscope (SEM, JEOL JSM6700F, Japan). Density (ρ) of the samples was measured using the Archimedes method. Thermal diffusivity (α) was determined by a laser flash apparatus (Netzsch LFA427, Germany) and specific heat (C_p) was determined by a differential scanning calorimeter (Perkin–Elmer DSC-2C, USA). The thermal conductivity (λ) was obtained by multiplying the thermal diffusivity with the density and specific heat ($\lambda = \alpha \rho C_p$). Table 2 shows the measured thermal diffusivity and specific heat of the samples sintered at optimal temperatures. The dielectric properties were measured by an impedance analyzer (Wayne-Kerr, 6500B, UK) at 1 MHz.

3. Results and discussion

Fig. 1 shows the densities of the CAS–Si_3N_4 composites with different volume fractions of β-Si_3N_4 whisker sintered at 750–875 °C for 30 min. It is obvious that the sintering temperature and whisker volume fraction are two important factors in the densifying process of the composites. The samples with different whisker contents show their maximum densities at different sintering temperatures. The maximum density of the samples increases as the whisker content increased from 0 to 35 vol%. It can be also seen that the sample SN45 shows a lower maximum density than that of SN35. As such, it is suggested that at least 65 vol% of glass content is needed in the CAS–Si_3N_4 composites to achieve densification during the sintering process. In all CAS–Si_3N_4 composites, the sample SN35 can achieve the highest density (2.98 g/cm^3) at 850 °C. It is worth mentioning that the CAS glass (SN0) can be densified at 775 °C. The CAS glass matrix with such a low densification temperature is favorable for the sintering CAS–Si_3N_4 composites at low temperatures.

According to the densification behavior shown in Fig. 1, the samples sintered at the optimal temperatures were used for property characterizations. The results of the

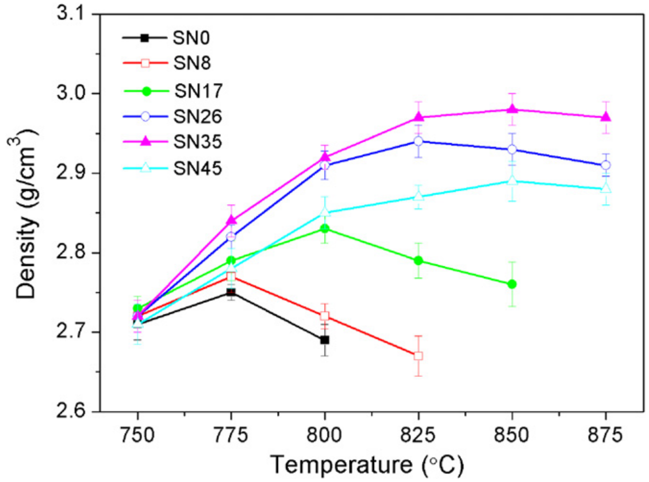

Fig. 1. Sample density as a function of sintering temperature for CAS–Si_3N_4 composites with different β-Si_3N_4 whisker contents.

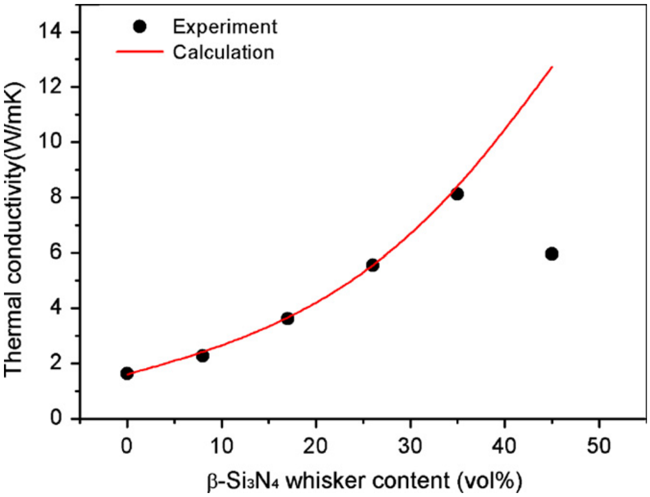

Fig. 2. Experimental data and theoretical curve of the thermal conductivity of CAS–Si_3N_4 composites as a function of β-Si_3N_4 whisker contents.

experimental and calculated thermal conductivities are presented in Fig. 2. As expected, the thermal conductivities of the CAS–Si_3N_4 composites increase with the loading of β-Si_3N_4 whiskers. The measured thermal conductivity of the composites can reach as high as 7.9 W/mK, when filled with 35 vol% whisker (SN35). This thermal conductivity is nearly five times higher than that of CAS glass and also much higher than that of the commercial LTCC materials [8]. The substantial enhancement may be attributed to the formation of thermally conducting paths in the glass matrix due to the interconnecting β-Si_3N_4 whiskers. However, the thermal conductivity of the CAS–Si_3N_4 composites cannot further increase by increasing the whisker content. When the whisker loading exceeds 35 vol%, the thermal conductivity of the composites decreases. This phenomenon may be related to the reduction of the density, resulting from the shortage of glass phase.

The thermal conductivity enhancements by introducing one-dimensional whiskers are normally related to the occurrence of percolation behavior, because one-dimensional fillers are most likely to be in contact with each other and then form percolation networks throughout the material system [16,20]. Thus, for further understanding the significant thermal conductivity increase in the CAS–Si_3N_4 composites, we compared our experimental data with calculations using a percolation model by Agari et al. [21]:

$$\log\lambda = VC_2 \log\lambda_s + (1-V)\log(C_1\lambda_m) \quad (1)$$

where λ is the thermal conductivity of CAS–Si_3N_4 composites, λ_s is the thermal conductivity of β-Si_3N_4 whisker, λ_m is the thermal conductivity of CAS glass matrix, and V is the volume fraction of β-Si_3N_4 whisker. The values of C_1 and C_2 should be between 0 and 1. C_1 is a factor relating to the matrix of the composite, and usually the values of C_1 are approximately 1 [22]. C_2 is a factor relating to the possibility of forming conductive chains of the filler. The closer C_2 values are to 1, the easier conductive chains are formed in the composite [21]. Here, we found that when $C_2=0.92$, as shown in Fig. 2, the calculated thermal conductivity values from Eq. (1) have a rather good match with the experimental data when the β-Si_3N_4 whisker content is less than 35 vol%. This result demonstrates the formation of thermal percolation networks in the CAS–Si_3N_4 composites. The deviation between experiment and calculation can be observed when the contents of β-Si_3N_4 whiskers are increased from 35 vol% to 45 vol%. The decrease in the thermal conductivity may be caused by the increase in voids and pores in the composites [18].

To confirm the formation of thermal percolation networks, the microstructural characterizations are carried out using electron microscopy. Fig. 3 shows the SEM images of the fracture surface of CAS–Si_3N_4 composites with different compositions sintered at optimal temperatures. The CAS glass exhibits a well-densified sample at 775 °C as shown in Fig. 3(a), and the inset shows the microstructure of β-Si_3N_4 whiskers in more details. In the case of the composites filled with whisker lower than 17 vol%, only a few whiskers could be seen from the SEM images, marked with circles in Fig. 3(b) and (c). This suggests that low volume fractions of whiskers are insulated by the glass matrix, which prevents the formation of thermally conducting paths. When the whiskers content are increased, as shown in Fig. 3(d) and (e), more whiskers can be observed and the possibility of establishing thermally conducting paths are therefore enhanced significantly. In general, percolation heat transfer within composites results from direct inclusion-to-inclusion contact. Heat conduction bypasses the matrix, and depending on the volume fraction of the dispersed phase, can make a significant contribution to the overall composite thermal conductivity [23]. The high thermal conductivity value for SN35 is probably attributed to the heat conduction by percolation of direct whisker-to-whisker contacts, as shown in Fig. 3(e). Fig. 3(f), demonstrating poor densification with evidence of considerable porosities due to insufficient glass content, which is consistent with the reduction of the density observed in Fig. 1.

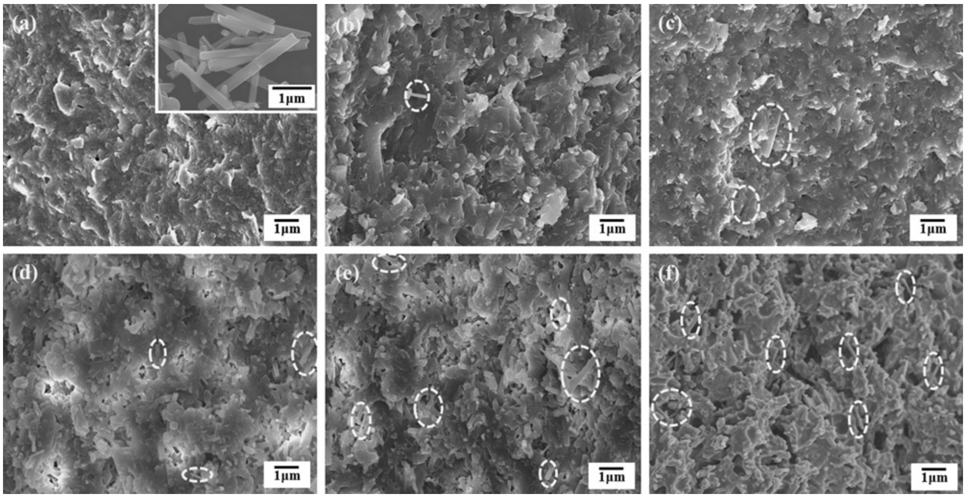

Fig. 3. The fracture surface SEM images of CAS–Si_3N_4 composites filled with different volume of whiskers and sintered at optimal temperatures: (a) SN0, 775 °C. The inset shows the microstructure of β-Si_3N_4 whiskers: (b) SN8, 775 °C; (c) SN17, 800 °C; (d) SN26, 825 °C; (e) SN35, 850 °C and (f) SN45, 850 °C.

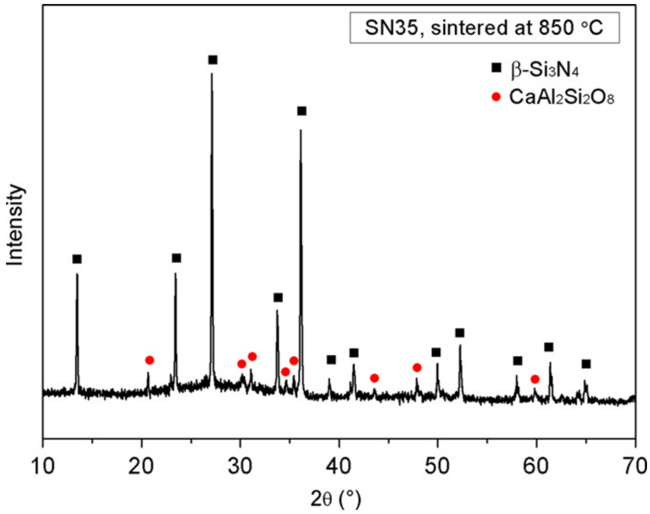

Fig. 4. X-ray diffraction pattern of the sample SN35 sintered at 850 °C.

Fig. 4 shows the XRD pattern of the sample SN35 sintered at 850 °C. Hexagonal β-Si_3N_4 can be confirmed from the XRD pattern, which is accompanied with the crystal phase of $CaAl_2Si_2O_8$ in the CAS glass matrix. This result demonstrates that there is no obvious chemical reaction between β-Si_3N_4 and CAS glass. As a highly covalent compound, Si_3N_4 transports heat primarily by phonons at room temperature and below [10]. Due to the long-range disorder of the glass phase, the phonon thermal conduction is retarded and the thermal conductivity of glass materials usually presents a very low value [24]. The crystallization of the glass phase is considered to be helpful for obtaining a larger phonon mean free path, and therefore facilitating the thermal conductivity [25].

Obtaining low relative dielectric constant is another important parameter for electronic device packaging. Low dielectric constant and low dielectric loss are both required for high speed signal propagation [1,4]. Fig. 5 shows the relative dielectric constant and dielectric loss as a function of the volume fraction of β-Si_3N_4 whiskers. Unlike the thermal conductivity, the percolation behavior is absent in the dielectric properties of the CAS–Si_3N_4 composites. It is may be due to the fact that the dielectric constant of CAS glass are comparable to that of Si_3N_4 [26,27]. It can be seen that the dielectric constant slightly waves with the increase of whisker loading and has a peak value of 7.2 when the whisker loading reaches 26 vol%. The dielectric loss increases with the increase of β-Si_3N_4 whisker loading. Since the sintering temperature is different for the samples with different whisker loadings, the composition of the CAS–Si_3N_4 composites and the crystalline phase content in the glass matrix have important effect on the dielectric properties. In addition, pores in the composites may also have strong influence on the dielectric constant and dielectric loss [28]. Nonetheless, the sample SN35 that showed the highest thermal conductivity exhibited a relative dielectric constant of 7.1 and low dielectric loss

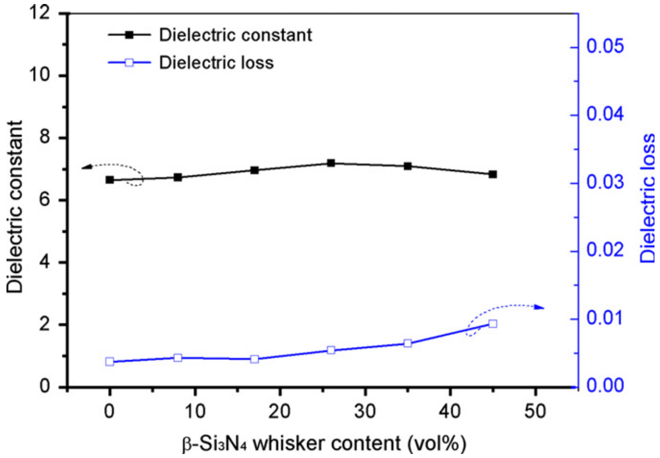

Fig. 5. Relative dielectric constant and dielectric loss of CAS–Si_3N_4 composites as a function of β-Si_3N_4 whisker volume fraction.

of 0.006 at 1 MHz, which indicates the potential of this CAS–Si_3N_4 optimum composite for LTCC packaging substrates application.

4. Conclusions

A novel LTCC system, incorporating β-Si_3N_4 whiskers, was proposed in order to improve the thermal conductivity of LTCC materials. The enhancement of the thermal conductivity can be attributed to the formation of thermal percolation networks in the matrix as a result of the β-Si_3N_4 whiskers loading. Moreover, the crystalline phases in the glass matrix can also promote the efficient phonon conduction. The high thermal conductivity, along with low dielectric constant and low loss, make the low-temperature sintered ceramics composite a promising material for high speed and high power device packaging applications.

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