Low κ, low loss alumina-glass composite with low CTE for LTCC microelectronic applications

I.J. Induja, K.P. Surendran, M.R. Varma, M.T. Sebastian

Abstract

Alumina based low κ LTCC composite has been prepared with the use of AGC commercial glass (DL828). The 30 wt% Al₂O₃–70 wt% AGC glass composite was sintered at 875 °C (2 h). X-ray diffraction study indicated the presence of BaSi₂O₅, BaAl₂Si₂O₈ and Ba₂Si₂O₆ secondary phases in addition to Al₂O₃ in the composite. The bulk ceramic sintered at 875 °C has κ of 4.80 and tan δ of 0.007 at 1 MHz. The composite shows good microwave dielectric properties: κ of 4.52, tan δ of 0.004 and τκ close to zero. The composite has a low CTE of 4.38 ppm/°C which is close to that of silicon used in microelectronic industry and thermal conductivity of 1.41 W m⁻¹ K⁻¹ at room temperature. The results indicate that the Al₂O₃ - AGC glass composite has good dielectric, thermal properties and is chemically compatible with Ag electrode indicating it as a promising candidate for low κ LTCC substrate applications.

1. Introduction

The recent advances in microwave wireless communication industry, demands light weight, compact, small, low cost microwave communication devices [1,2]. Low temperature cofired ceramic (LTCC) technology, which is considered as the backbone of Multi Chip Module (MCM) technology has attracted considerable attention over the past decades [3]. LTCC technology offers a variety of applications mainly in wireless communication, automotive, medical electronics etc. The most important advantage of LTCC technology is the integration of passive elements resulting in 3D circuits saving production cost and time [4]. The important requirements for an LTCC material are low sintering temperature less than 950 °C, low dielectric constant (κ), low dielectric loss (tan δ), temperature coefficient of dielectric constant (τκ) close to zero, good thermal properties and chemical compatibility with the electrode material [5]. Most of the low loss dielectric ceramics have high sintering temperatures. The most effective and low cost method to reduce the sintering temperature of ceramics is through liquid phase sintering by glass addition [6,7]. In general glass addition degrades the dielectric properties [8]. Hence the most challenging aspect of the microelectronic industry is to develop new low loss, low dielectric constant materials in order to increase the signal propagation speed in communication systems. Presently glass + ceramic and glass – ceramic routes are extensively used to formulate LTCC materials [5].

Alumina (Al₂O₃) based glass - ceramic composites are extensively used in LTCC applications due to their unique combination of excellent electrical and physical properties [9]. In Al₂O₃ - glass composites, the main role of Al₂O₃ is to maintain the physical dimensions and mechanical strength, in addition to good electrical properties, while the glass plays the role of lowering the sintering temperature [10]. The commonly used glasses for Al₂O₃ based LTCC materials are BaO-B₂O₃-SiO₂, BaO-Al₂O₃-B₂O₃-SiO₂, PbO-B₂O₃-SiO₂, CaO-Al₂O₃-SiO₂, CaOZnO-B₂O₃-SiO₂, Bi₂O₃-ZnO-B₂O₃-SiO₂, ZnO-Bi₂O₃-B₂O₃, La₂O₃-B₂O₃, SiO₂-B₂O₃-CaO-MgO, Li₂O-B₂O₃-SiO₂-CaO-Al₂O₃ etc [11–17]. Several people reported [18,23] that addition of alumina inhibited the formation of cristobalite in borosilicate glass. The amount of alumina content required to inhibit cristobalite formation
increases with increase in alumina particle size [18]. Jean et al. obtained cristobalite free glass composite with \( \kappa \) of 4.5–5.5 at 1 MHz [18]. Shin et al. studied the physical and dielectric properties of alumino borosilicate based dielectrics containing different divalent oxides (CaO, MgO, BaO, SrO and ZnO). They found that, with 35 wt% Al\(_2\)O\(_3\) filler into CaO modified alumino borosilicate glass, showed promising properties with \( \kappa = 8.05, \tan \delta = 0.0018 \) [19]. Hsing et al. reported the effect of alumina on the crystallization behavior, densification and dielectric properties of BaOZnO-SrO-CaO-Nd\(_2\)O\(_3\)-TiO\(_2\)-B\(_2\)O\(_3\)-SiO\(_2\) glass-ceramics. The addition of 30 vol\% Al\(_2\)O\(_3\) in BaO-ZnO-SrO-CaO-Nd\(_2\)O\(_3\)-TiO\(_2\)-B\(_2\)O\(_3\)-SiO\(_2\) glass has lowered the sintering temperature to 900 °C and the sintered composite has \( \kappa \) of 17 and quality factor (Q) of 820 [20]. Seo et al. investigated the effect of La\(_2\)O\(_3\)-B\(_2\)O\(_3\) glass on Al\(_2\)O\(_3\) and reported that 30 wt% Al\(_2\)O\(_3\) – glass composite has \( \kappa \) of 8.4 and Q\( x f = 12,400 \) GHz [21]. Byeon et al. studied the thermal expansion and dielectric properties of CaO-ZnO-B\(_2\)O\(_3\)-SiO\(_2\) glass added Al\(_2\)O\(_3\) composites for LTCC applications. They have achieved \( \kappa, \tan \delta \) and coefficient of thermal expansion as 6.4, 0.009, and 8.5 ppm/°C, respectively for 60 wt% glass added composite [14]. Chen et al. reported 50 wt% SiO\(_2\)-B\(_2\)O\(_3\)-CaO-MgO glass added Al\(_2\)O\(_3\) ceramics sintered at 875 °C has \( \kappa \) of 7.3 with \( \tan \delta = 0.0115 \) at 1 MHz [16]. Chen et al. also investigated the effect of BaO-B\(_2\)O\(_3\)-SiO\(_2\) and Al\(_2\)O\(_3\) ceramics prepared through aqueous suspension route 900–940 °C and has \( \kappa \) of 7.1 – 7.4 with \( \tan \delta = 0.0005–0.0007 \) [22]. Li et al. reported that 15 wt% nano Al\(_2\)O\(_3\) added glass-Al\(_2\)O\(_3\) sintered at 900 °C has better dielectric properties [24]. Recently Ren et al. studied the effect of glass former SiO\(_2\) and glass network amender Na\(_2\)O in CaOAl\(_2\)O\(_3\)-B\(_2\)O\(_3\)-SiO\(_2\)/Al\(_2\)O\(_3\) composites [25]. It was found that decreasing SiO\(_2\) content or increasing Na\(_2\)O content appropriately could both promote sintering densification, formation of anorthite phase and lower the dielectric loss. The signal transmission speed in communication systems depends on the dielectric constant: the smaller the dielectric constant, the higher the signal speed. Most of the reported LTCC materials have a dielectric constant in the range 5–20. In the present paper, we report the dielectric properties of a new Al\(_2\)O\(_3\)-AGC glass based LTCC composite with low dielectric constant useful for high speed communication devices.

2. Experimental

For synthesizing Al\(_2\)O\(_3\) glass composite, Al\(_2\)O\(_3\) (> 98%, Sigma Aldrich) and commercially available glass with brand name DL828 were used, (AGC, Japan). 30 wt% of Al\(_2\)O\(_3\) was mixed with 70 wt% commercial glass and ball milled for 24 h in distilled water medium. The slurry was dried and ground well. The composition of the composite for LTCC applications was optimized after several trials and error experiments. The composite was mixed with 5% polyvinyl alcohol (PVA) and pressed into pellets having different dimensions using a uniaxial press. The composite was sintered at 875 °C (2 h) with a heating rate of 5 °C/min. The sintered samples were used for different characterizations. The elemental analysis of the commercial glass was done using X-ray fluorescence (XRF) spectrometer (PANalytical-Epsilon 3, Netherlands) using Omnian software. The phase purity of the developed composite was studied using X-ray diffraction (XRD) CuK\(_\alpha\) radiation, PANalyticalX'Pert PRO diffractometer, Netherlands). The microstructure study of the fractured surface of sintered samples was studied using JOEL-JSM 5600 LV, Tokyo, Japan. The coefficient of thermal expansion (CTE) was determined using a thermo mechanical analyzer (Exstar-TMA/SS7300, SII Nano Technology Inc). The density of the composites sintered at different temperatures were measured using Archimedes method. The thermal conductivity of the composite was measured using a laser flash thermal properties analyzer (FlashLine2000, Anter Corporation, Pittsburgh, USA) with Al\(_2\)O\(_3\) as the reference. The variation of dielectric constant with frequency in the radio frequency range for the bulk composites of dimensions 11 mm diameter and 1 mm thickness were measured at room temperature using LCR meter (Hioki 3532-50LCR Hi Tester, Japan). For this sintered pellets having 11 mm diameter and 1 mm thickness was coated with Ag paste on the two surfaces. The microwave dielectric properties of the sintered samples (sheets) having dimensions 40 mm×40 mm and 1.2 mm thickness was measured using split post dielectric resonator (SPDR) operating at 5.155 GHz with the help of a vector network analyzer (Agilent E5071C ENA series, Agilent Technologies, Santa
The temperature variation of the dielectric constant was measured using LCR meter at 1 MHz and SPDR method at 5 GHz in the temperature range 30–60 °C.

3. Results and discussions

3.1. Phase compositions

The XRF analysis of the starting DL828 AGC glass indicated that it is rich in silica. The composition of the glass powder obtained from XRF analysis is given in Table 1. Fig. 1(a) shows the XRD pattern of the AGC commercial glass. The XRD pattern for the DL828 glass confirmed its amorphous nature. Fig. 1(b) shows the XRD of 70 wt% glass−30 wt% alumina composite sintered at 875 °C (2 h). The XRD of the composite contain crystalline peaks of Al₂O₃ (JCPDS file no. 88-0107), BaSi₂O₅ (JCPDS file no. 71-1441), BaAl₂Si₂O₈ (JCPDS file no.86-1794) and Ba₂Si₃O₈ (JCPDS file no. 12–0694). The corresponding (h k l) planes of different phases are marked in Fig. 1(b). Lim et al. reported the formation of crystallization of BaSi₂O₅ from the barium based silica rich glass [12] whereas Borhan et al. reported the presence of BaAl₂Si₂O₈ and Ba₂Si₃O₈ in BaO-Al₂O₃-SiO₂ glass–ceramic [26]. It is known that the formation of secondary phases is common in commercial LTCC tapes [27]. These secondary phases are unavoidable and often improve the electrical and physical properties of the LTCC material.

3.2. Microstructure analysis

Fig. 2 shows the microstructure of the fractured surface of the AGC glass–alumina composite sintered at 875 °C (2 h). The composite shows a homogenous, dense microstructure and the crystalline grains can be observed embedded within the melted glass.

3.3. Dielectric properties

It is well known that dielectric properties of the ceramics are related to the densification of the samples [8]. For the design of advanced packaging and passive elements in integrated circuits, a low dielectric constant is an essential prerequisite [28]. Fig. 3(a) shows the variation of dielectric constant at 1 MHz and density as a function of sintering temperature. It is obvious from the figure that the dielectric constant reaches a maximum for the well densified sample. The highest density (2.16 g/cm³) is obtained for the sample sintered at 875 °C (2 h). The sintering temperature of the 30 wt% Al₂O₃–70 wt% AGC glass composite is optimized based on dielectric constant as well as density. The variation of dielectric properties for the optimized sample with frequency at room temperature is shown in Fig. 3(b). The dielectric constant and dielectric loss at 1 MHz for the sample sintered at 875 °C (2 h) is 4.80 and 0.007 respectively. Fig. 4(a) shows the variation of dielectric properties (κ and tan δ) for the 30 wt% Al₂O₃–70 wt% AGC glass composite as a function of sintering temperature measured at 5 GHz by the SPDR method. The dielectric constant value varies from 3.68–4.52 within the sintering temperature range 800–900 °C. With the increase in the sintering temperature, the dielectric constant increases up to 875 °C and thereafter it decreases. The decrease in dielectric constant of the composite after 875 °C is due to the decrease in density and increase in porosity. This may be due to the escape of low melting volatile constituent in the glass and or abnormal grain growth. At 875 °C, the dielectric constant is 4.52 with a dielectric loss of 0.004. The dielectric constant obtained at microwave frequency is less as compared to that obtained at 1 MHz and this is due to the difference in polarization mechanisms. According to the literature reports, silica rich glasses usually have low dielectric constant because of the low dielectric constant of silica [26]. The dielectric properties of the composite are influenced by densification and the constituent phases in the composite [29]. The effect of the increased silica content as well as the influence of secondary phases may be the reason for the low dielectric constant of the composite. Among the low loss dielectric materials silica and AlPO₄ have the lowest dielectric constants which are about 4 [30]. The present alumina-AGC glass composite LTCC has a dielectric constant of 4.52 at 5 GHz and is suitable for low κ applications.
For practical applications, the variation of dielectric constant with temperature should be small in order to maintain thermal stability [5]. The variation of dielectric constant for 30 wt% $\text{Al}_2\text{O}_3$–70 wt% AGC glass composite with temperature in the range 30–60 °C measured using SPDR at 5 GHz and LCR meter at 1 MHz is shown in Fig. 4(b). The variation of dielectric constant with temperature is negligible within the measured temperature range. The $\tau_\kappa$ value for the 30 wt% $\text{Al}_2\text{O}_3$–70 wt% AGC glass composite sintered at 875 °C is found to be very close to zero, which is one of the necessary criterions for LTCC device applications. The observation of near to zero is more significant considering the fact that majority of the reported LTCC compositions are not thermostable [5].

3.4. Thermal properties

Fig. 5 shows the CTE, thermal diffusivity and thermal conductivity of 30 wt% $\text{Al}_2\text{O}_3$–70 wt% AGC glass composite sintered at 875 °C (2 h). The thermal expansion of the glass-ceramic composite is very important for microwave substrate applications [10]. The CTE of the composite was measured in the temperature range 30–300 °C. The AGC, glass DL828 has a CTE 3.7 ppm/°C in the temperature range 50–350 °C. The coefficient of thermal expansion of the 30 wt% $\text{Al}_2\text{O}_3$–70 wt% AGC glass composite is found to be 4.38 ppm/°C. The CTE value of the present glass composite is comparable with the CTE value of silicon (3.1 ppm/°C) which indicates that the composite can be used in microelectronic applications. In general the CTE of glass-ceramic composites are in the range 3.5–9.7 ppm/°C [31]. As compared to the commercially available LTCC material, the present glass – ceramic composite has a low thermal expansion coefficient. The variation of thermal diffusivity and thermal conductivity for 30 wt% $\text{Al}_2\text{O}_3$–70 wt% AGC glass composite is shown in Fig. 5(b). It is obvious that the thermal diffusivity and thermal conductivity decreases with increase in temperature. This may be due to the decrease of phonon pathway [32]. Thermal diffusivity, which is an intrinsic material property, depends on microstructure, density, crystal structure of the phase and grain size of the material [33]. Most of the LTCC materials have low thermal conductivity due to the poor thermal conductivity of the glassy phase [15]. Since 30 wt% $\text{Al}_2\text{O}_3$–70 wt% AGC glass composite contains large amount of glass, the thermal conductivity of the composite is relatively low. The thermal conductivity of the composite at room temperature is 1.41 W m$^{-1}$ K$^{-1}$.

3.5. Reactivity with silver

The AGC glass-alumina LTCC composite is chemically compatible with silver, which is a common electrode material. Fig. 6. (a) shows the XRD pattern and Fig. 6(b), the SEM of the fractured surface of 30 wt% $\text{Al}_2\text{O}_3$–70 wt% AGC glass composite +20 wt% Ag sintered at 875 °C(2 h). The XRD peaks corresponding to metallic Ag is indexed based on the JCPDS file no. 03-0921. The corresponding (h k l) planes of $\text{Al}_2\text{O}_3$, secondary phases and Ag are marked in Fig. 6(a). The XRD and SEM micrographs of 30 wt% $\text{Al}_2\text{O}_3$–70 wt% AGC glass composite show that the composite is cofireable with Ag electrode.

4. Conclusions

The AGC glass (DL828) - alumina LTCC composite was prepared by sintering at 875 °C. The sintered composites contain secondary phases of $\text{BaSi}_2\text{O}_5$, $\text{BaAl}_2\text{Si}_2\text{O}_8$ and $\text{Ba}_2\text{Si}_3\text{O}_8$. The composite has 4.52 and tan $\delta$ of the order of 10$^{-3}$ at 5 GHz. It has a $\tau_\kappa$ close to zero, CTE of 4.38 ppm/°C and thermal conductivity of 1.41 W m$^{-1}$ K$^{-1}$. The low $\kappa$ composite is chemically compatible with the silver electrode and is suggested as a suitable material for increasing the signal speed in communication systems.

Acknowledgements

Induja. I. J is grateful to the Kerala State Council for Science, Technology and Environment (KSCSTE), Kerala, India (Grant no. 001/FSHO/2012/KSCSTE) for the award of Research Fellowship. The authors are thankful to Dr. Prabhakar Rao, Mr. Prithviraj, Mrs. Soumya for XRD and SEM facility and also to Harikrishna.
References


Table 1. Chemical analysis of the glass powder obtained from XRF analysis.

<table>
<thead>
<tr>
<th>Component</th>
<th>Percentage</th>
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<tr>
<td>BaO</td>
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<tr>
<td>Al₂O₃</td>
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<tr>
<td>K₂O</td>
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</tr>
<tr>
<td>P₂O₅</td>
<td>0.480</td>
</tr>
<tr>
<td>ZnO, SrO, Bi₂O₃, ZrO₂, Fe₂O₃</td>
<td>0.097ᵃ</td>
</tr>
</tbody>
</table>

ᵃ Each component in ppm units

Fig. 1. XRD pattern of (a) commercial DL828 AGC glass powder (b) 30 wt% Al₂O₃–70 wt% AGC glass composite sintered at 875 °C (2 h).

Fig. 2. Microstructure of fractured surface of 30 wt% Al₂O₃–70 wt% AGC glass composite sintered at 875 °C (2 h) with different magnifications.
Fig. 3. (a) Variation of dielectric constant at 1 MHz and density with sintering temperature and (b) variation of dielectric properties of 70 wt% glass-30 wt% Al$_2$O$_3$ with frequency at room temperature for the composite sintered at 875 °C (2 h).

Fig. 4. (a) Variation of dielectric properties with sintering temperature at 5 GHz and (b) temperature dependence of dielectric constant for 30 wt% Al$_2$O$_3$–70 wt% AGC glass composite at 5 GHz and 1 MHz.

Fig. 5. (a) CTE,(b) thermal diffusivity and thermal conductivity of 30 wt% Al$_2$O$_3$–70 wt% AGC glass composite sintered at 875 °C (2 h).
Fig. 6. (a) XRD and (b) microstructure of the fractured surface of 30 wt% Al$_2$O$_3$–70 wt% AGC glass composite +20 wt% Ag sintered at 875 °C.