Microwave dielectric properties of SnO-SnF2-P2O5 glass and its composite with alumina for ULTCC applications

Indira J. Induja, Mailadil T. Sebastian

Abstract

Ultralow-temperature sinterable alumina-45SnF2:25SnO:30P2O5 glass (Al2O3-SSP glass) composite has been developed for microelectronic applications. The 45SnF2:25SnO:30P2O5 glass prepared by melt quenching from 450°C has a low Tg of about 93°C. The SSP glass has εr and tanδ of 20 and 0.007, respectively, at 1 MHz. In the microwave frequency range, it has εr=16 and Quxf=9900 GHz at 6.2 GHz with coefficient of thermal expansion (CTE) value of 17.8 ppm/°C. A 30 wt.% Al2O3-70 wt.% SSP composite was prepared by sintering at different temperatures from 150°C to 400°C. The crystalline phases and dielectric properties vary with sintering temperature. The alumina-SSP composite sintered at 200°C has εr=5.41 with a tanδ of 0.01 (1 MHz) and at microwave frequencies it has εr=5.20 at 11 GHz with Quxf = 5500 GHz with temperature coefficient of resonant frequency (τf) = -18 ppm/°C. The CTE and room-temperature thermal conductivity of the composite sintered at 200°C are 8.7 ppm/°C and 0.47 W/m/K, respectively. The new composite has a low sintering temperature and is a possible candidate for ultralow-temperature cofired ceramics applications.

1. Introduction

There is an increased demand for new materials with attractive dielectric properties in the areas of wireless communication, satellite communication, electronic memory devices, and so on.1,2 Low-temperature cofired ceramic technology (LTCC) is a well-established multilayer technology having numerous applications.3 At present, extensive research is being carried out to develop new materials having sintering temperature less than 700°C.4 Several glass-ceramics, molybdates, vanadates, tungstates, tellurates based ceramics are reported in the literature as ultralow-temperature cofired ceramics (ULTCC) materials.2 Energy saving, reduction in processing time, as well as cost effectiveness, and cofiring with conductors such as nanosilver ink are the attractive features of ULTCC technology.2,4 For future applications, there is an urgent demand for the development of new ULTCC materials.5

Over the past several years, considerable efforts have been made by researchers to develop new glasses having low glass-transition temperature. Glasses having low glass-transition temperature (Tg) offers a wide variety of applications such as glass-metal sealing, IC packaging, and so on.6 Among them, fluorophosphate glasses are of significant interest. In general fluorophosphate glasses have low Tg compared to silicate and borate glasses.7 The optical properties of fluorophosphate glasses are comparable with that of fluoride glasses, and mechanical properties that of oxide glasses.8 Besides this, another attracting property of phosphate glasses is its ability to associate fluoride compounds without losing the tendency to form glass.9 Due to the nonlinear refractive index change, fluorophosphate glasses can be qualified as suitable candidates for high-power lasers.10 Fluorine-containing glasses find application in the field of laser windows, lenses, and filters.11 The introduction of network modifying cation tin (Sn) lowers the Tg of fluorophosphate glasses.12

Alumina (Al2O3) is considered as the gemstone of the electronic industry due to its excellent electrical and physical properties compared to other ceramics.13 The sintering temperature of Al2O3 is relatively high at about 1600°C. The main challenge behind making Al2O3 as LTCC/ULTCC material is its high sintering
temperature.\textsuperscript{14,15} Low melting and low-loss glasses are known to be effective sintering aids for reducing the sintering temperature of various ceramics without much affecting the microwave properties.\textsuperscript{3} The traditional method to lower the sintering temperature of the Al\textsubscript{2}O\textsubscript{3} is by glass addition. Several authors reported the effective role of glass in reducing the sintering temperature of Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{16-26}

Several research groups have reported the preparation of ternary glass SnO-SnF\textsubscript{2}-P\textsubscript{2}O\textsubscript{5}. The structure of SSP glass was studied by spectroscopic methods.\textsuperscript{6,27,28} Liu et al. prepared different compositions of SSP glass with xSnF\textsubscript{2}-(70-x) SnO-30P\textsubscript{2}O\textsubscript{5} glasses (x=40, 45, 50, 55, 60), and employed Fourier Transform Infrared and X-ray photoelectron spectroscopy (XPS) techniques to understand the SSP glass structure for the different compositions.\textsuperscript{6} From XPS analysis, they found that the change in glass network dimension was responsible for the variation in glass properties for different compositions. They reported that the T\textsubscript{g} value decreases and the coefficient of thermal expansion (CTE) value increases with increase in SnF\textsubscript{2} content.\textsuperscript{6} Although extensive work has been reported on the structure and properties of SSP glass, no attempt was done to study the dielectric properties. In this study, we report the radiofrequency and microwave dielectric properties of SSP glass and its composite with alumina.

2. Experimental procedure

2.1. Preparation of 45SnF\textsubscript{2}-25SnO:30P\textsubscript{2}O\textsubscript{5} glass

Tin-based fluorophosphate ternary glass having the composition 45SnF\textsubscript{2}-25SnO:30P\textsubscript{2}O\textsubscript{5} (SSP) was prepared by conventional melt quenching technique. A two-step melting process was adopted to minimize fluorine loss. Initially ammonium dihydrogen phosphate (NH\textsubscript{4}H\textsubscript{2}PO\textsubscript{4}, ≥98%, Sigma Aldrich, St. Louis, MO, USA) was first melted at 450°C for 30 minutes. Then stoichiometrically weighed tin oxide (SnO, 99%, Alfa Aesar, Tewksbury, MA, USA) and tin fluoride (SnF\textsubscript{2}, 99%, Sigma Aldrich) were added one by one to the melt and again heated in the furnace at 450°C for 30 minutes. The whole melt was quenched in distilled water. The molten glass was poured into moulds having different dimensions for dielectric and thermal studies.

2.2. Al\textsubscript{2}O\textsubscript{3}-SSP glass composite preparation

The aim of our work was to develop alumina-SSP glass composite suitable for ULTCC applications. Different weight % of alumina and SSP glasses had been prepared. Only 30 wt.% alumina and 70 wt.% SSP glass compositions can be sintered below 400°C with good dielectric properties suitable for ULTCC applications. The sintering temperature was found to increase to above the ULTCC range with increase in alumina content. Only the composition which contains 30 wt.% Al\textsubscript{2}O\textsubscript{3}-70 wt.% SSP glass yields the required ULTCC temperature range. The suitable composition between Al\textsubscript{2}O\textsubscript{3} and 45SnF\textsubscript{2}-25SnO:30P\textsubscript{2}O\textsubscript{5} glass having low sintering temperature was selected for further studies. The composite with 30 wt.% Al\textsubscript{2}O\textsubscript{3}-70 wt.% SnO-SnF\textsubscript{2}-P\textsubscript{2}O\textsubscript{5} glass was prepared by mixing the raw materials using acetone for 10 hours. The slurry was dried and ground well. The Al\textsubscript{2}O\textsubscript{3}-SSP composite was sintered at different temperatures from 150°C to 400°C.

2.3. Characterization techniques

The amorphous nature of the as-prepared glass as well as the phase composition of the 30 wt.% Al\textsubscript{2}O\textsubscript{3}-70 wt.% SnO-SnF\textsubscript{2}-P\textsubscript{2}O\textsubscript{5} glass composite was studied using XRay diffractometer (XRD) (CuKa radiation, PANanalytical X'Pert PRO dиффрактометр, Netherlands). The spectra of the powder glass were recorded using PerkinElmer Series FT-IR Spectrometer, USA. The glass-transition temperature of the powder glass sample was determined using differential scanning calorimeter (DSC) analysis (TA Instruments Q2000 DSC with Refrigerated Cooling System (RCS), New Castle, DE, USA). For DSC analysis, the glass powder was heated from 30°C to 300°C with a heating rate of 10°C/min. Thermo gravimetric/differential thermal analysis (TG/DTA) analysis was done for the glass powder (STA 7300, Thermal Analysis System, Hitachi, Japan) from 30°C to 700°C with a heating rate of 10°C/min under nitrogen atmosphere. The density of the SSP glass was measured using Archimedes method using distilled water medium and the density of Al\textsubscript{2}O\textsubscript{3}-SSP glass composite was
determined using dimensional method with the help of a digital screw gauge and weight measured using a semi-micron weighing balance (Shimadzu, AUW220D, Japan). The microstructure of the composite was studied using JOEL-JSM 5600 LV, Tokyo, Japan. The radio (low)-frequency dielectric properties of the glass powder having dimensions 8 mm diameter and 2 mm thickness were determined by parallel plate capacitor method using an inductance capacitance resistance (LCR) meter (Hioki 3532-50LCR Hi Tester, Japan). For the radiofrequency measurements of the bulk Al2O3-SSP composite, samples having 11 mm diameter and 1.5 mm thickness, electrode with copper on both sides were used. The thermal conductivity of the composite was measured using a laser flash thermal properties analyzer (Flash-Line2000, Anter Corporation, Pittsburgh, PA, USA). The thermal expansions of the glass pellet as well as the Al2O3-SSP glass composite were measured using thermo mechanical analyzer (Exstar-TMA/SS7300, SII Nano Technology, Inc., Tokyo, Japan). The microwave dielectric properties were measured using a network analyzer (Agilent E5071C ENA series, Agilent Technologies, Santa Clara, CA, USA) operating in the frequency region 300 kHz to 20 GHz. SSP glass samples having 14.2 mm diameter and 6.7 mm thickness were used for microwave measurements. In the case of Al2O3-SSP composites, samples having 11 mm diameter and 5.4 mm thickness were used. The dielectric constant was measured by Hakki-Coleman method.\(^9\) The unloaded quality factor was determined using resonant cavity method in the TE01d mode.\(^9\) The temperature coefficient of resonant frequency (\(\tau_f\)) of the SSP glass and the Al2O3-SSP glass composite was measured in the temperature range 25°C-60°C using the cavity method.\(^9\) \(\tau_f\) was determined using the formula:

\[
f = \frac{1}{f} \frac{\Delta f}{\Delta T}
\]

3. Results and discussions

3.1 Structural, dielectric, and thermal properties of SSP glass

Figure 1A shows the XRD pattern of the SSP glass indicating the amorphous nature. The absence of crystalline phase in the XRD confirms the formation of 45SnF2:25SnO:30P2O5 glass prepared by quenching method. Figure 1B shows the room-temperature FT-IR spectrum of 45SnF2:25SnO:30P2O5 glass powder in the range 4000 to 400 cm\(^{-1}\). The spectra indicate the presence of OH which might be due to the moisture absorption during the preparation of the sample using KBr. The band at 3438 cm\(^{-1}\) can be attributed to the stretching vibration of O–H bond, 1630 cm\(^{-1}\) due to the bending vibration of H–OH bond. The bands corresponding to 1100 to 930 cm\(^{-1}\) is due to the stretching vibration of P=O bond. The band around 630 cm\(^{-1}\) is attributed to the P–O bending vibration. The band at 1028 cm\(^{-1}\) corresponds to the P–F stretching vibration.\(^6\)

The glass-transition temperature of 45SnF2:25SnO:30P2O5 glass as determined by the DSC is found to be about ~93°C (see Figure 2A). Liu et al. reported that the glass-transition temperature of 45SnF2:25SnO:30P2O5 at about 135°C.\(^6\) The difference in the \(T_g\) value in the present study as compared to the reported value may be due to the difference in melting time duration, origin and purity of chemicals, furnace heating conditions, and so on. The TG/DTA of SSP glass is shown in Figure 2B. The exothermic peak in the DTA curve at 163°C is attributed to crystallization of SnF\(_2\) and SnO\(_2\) formed by the oxidation of SnO\(_2\) and the endothermic peak at ~343°C in the DTA curve corresponds to the onset of the melting of the individual components in the glass, particularly SnF\(_2\) as evident from XRD (Figure 5). The weight loss found in the TG curve can be attributed to the volatilization loss of fluorine and hydroxyl by forming hydrogen Fluoride during melting.\(^6\)

Table 1 gives the dielectric properties of SSP glass. In general, the density of the glasses depends on the atomic weight of the individual components used in the glass as well as the compactness of the structure units in the glass.\(^9\) The density of the SSP glass is obtained as 4.38 g cm\(^{-3}\). For most of the glasses, the
dielectric constant depends on ionic and electronic polarization, while the dielectric loss depends on relaxations. Dielectric loss in the glass is mainly due to conductance, ion relaxation, deformation, and vibration. At low frequencies, ion relaxation and conductance losses are predominant. The dielectric constant and dielectric loss at 1 MHz are 20 and 0.02, respectively. The dielectric constant for 45SnF$_2$:25SnO:30P$_2$O$_5$ glass at microwave frequency is found to be 16 (6.2 GHz). The quality factor ($Q_x \times f$) is obtained as 990 GHz. The $\varepsilon_r$ value for the thin sheet of 45SnF$_2$:25SnO:30P$_2$O$_5$ glass measured at 5 GHz is 17 with tanδ 0.006. The small variation in $\varepsilon_r$ of SSP glass in two methods (Hakki and split post dielectric resonator [SPDR]) is due to the difference in frequency used for measurement and the use of thin sheet and large bulk samples with slight variations in density. The density reported for the bulk SSP glass in the present study is 4.38 g cm$^{-3}$. However, the sample used for SPDR measurement is very thin compared to the bulk and has a lower density of 4.30 g cm$^{-3}$. The difference in density of the samples used for determining the dielectric constant using Hakki and SPDR method is the possible reason for the difference in dielectric constant. In the microwave frequency region, only ionic and electronic polarization contributes to dielectric constant. For practical applications, the resonant frequency should be independent of temperature variations. $\tau_r$ value of SSP glass is found to be -290 ppm/°C measured in the temperature range 25°C-60°C.

The knowledge about thermal expansion studies of the SSP glass is very crucial for practical applications. Figure 3 shows the linear expansion of SSP glass in the temperature range 30°C-100°C. The CTE value for the 45SnF$_2$:25SnO:30P$_2$O$_5$ is found to be 17.8 ppm/°C which is very close to that reported by Liu et al. The photograph of SSP glass is shown in the inset of Figure 3. It has been reported that low $T_g$ glasses would have higher CTE value. The $T_g$ value obtained for the SSP glass from CTE measurement is about ~95°C and is in agreement with that obtained from DSC analysis (Figure 2A).

3.2. Structural, dielectric, and thermal properties of Al$_2$O$_3$-SSP glass composite

The XRD patterns of the Al$_2$O$_3$-SSP glass composite sintered at different temperatures (150°C-400°C) are shown in Figure 4. It is found that SSP glass which has a low $T_g$ glass, recrystallizes to form the individual components of the glass and react to form secondary phases at higher temperatures. The XRD pattern shows the peaks of Al$_2$O$_3$ (JCPDS file no. 88-0107), SnO$_2$ (JCPDS file no. 88-0287), SnF$_2$ (JCPDS file no. 71-2018), and secondary phases of SnP$_2$O$_7$ (JCPDS file no. 75-1143) and Sn$_3$(PO$_4$)$_2$ (JCPDS file no. 70-0391) are also identified. The DSC and TG/DTA analysis of the SSP glass indicates that crystallization starts at about 150°C. The glass in the composite crystallizes into SnO$_2$, SnF$_2$ and is evident in the XRD of the sample sintered at 150°C. Above 200°C, the SnF$_2$ melts and peaks become very weak indicating that fluorine is escaping. The SnO$_2$ reacts with P$_2$O$_5$ to form SnP$_2$O$_7$ and Sn$_3$(PO$_4$)$_2$ and is supported by the DSC and TG/DTA curves.

Figure 5 shows the microstructure of the fractured surface of Al$_2$O$_3$-SSP glass composite in the temperature range 150°C-400°C. The SEM pictures show the presence of secondary phases. Al$_2$O$_3$ do not react with SSP glass in the entire sintering temperature range. The porosity of the composite increases above 200°C due to escape of fluorine. The deficiency of fluorine lead to the crystallization of SnP$_2$O$_7$ and Sn$_3$(PO$_4$)$_2$ at temperatures above 200°C.

Figure 6 shows the variation in dielectric properties of the Al$_2$O$_3$-SSP glass composite measured in the radiofrequency region for the samples sintered at different temperature range 150°C-400°C. The dielectric constant is found to increase with increase in sintering temperature and is attributed to the formation of secondary phases. The increased amount of secondary phase formation and phase transition of tin-based phosphates may be the possible reason for the increase in dielectric constant at higher temperatures. The formation of secondary phases during sintering at different temperatures and vaporization of fluorine may be responsible for the variations in dielectric properties. The contribution of extrinsic loss is more predominant in Al$_2$O$_3$-SSP glass composite. Impurities, microstructural defects, grain boundaries, porosity,
and so on, in the composite lead to high dielectric losses. It has been reported that SnP₂O₇ undergoes phase transitions at 287°C and 557°C which may affect the dielectric properties. The composite sintered at 200°C has εₓ=5.41 with a tanδ of 0.01 at 1 MHz. The composite sintered above 200°C, show an increase in dielectric loss with frequency due to the increased amount of porosity in the composite. At 200°C temperature, the dielectric properties of the composite are found to be good for ULTCC practical applications. The dielectric properties of the composite can be tailored according to the need by sintering at different temperatures. Figure 7 shows the variation of density with sintering temperature for Al₂O₃-SSP glass composite. The density of the composites drops after 200°C which in turn increases the porosity in the composite. The decrease in density after 200°C also supports the escape of fluorine from Al₂O₃-SSP composite. The dielectric properties of the secondary phase’s particularly tin phosphates are not known due to the difficulty in getting sintered pellets of these materials. Hibino et al. also observed the same difficulty in sintering SnP₂O₇ ceramic. The precise knowledge about the dielectric properties of these secondary phases are needed to account for the anomalous trend observed in dielectric properties over the range of sintering temperature.

Figure 8 shows the variation of εₓ, Q₀, x f, and τₓ for Al₂O₃-SSP glass composite as a function of sintering temperature at microwave frequency. In the microwave frequency, the dielectric constant varies between 4.6 and 17.0. The composite sintered at 200°C has dielectric constant of 5.20 (11 GHz). The microwave dielectric properties of the Al₂O₃-SSP glass composite revealed that with increase in sintering temperature, the Q₀, x f values increases up to 350°C and further increase in sintering temperature decreases the quality factor. However, the dielectric constant increases with increase in sintering temperature. It may be noted that the secondary phases are formed in the composite at different sintering temperatures. The τₓ value is small for the samples sintered at 200°C and 250°C. In the present study, the Al₂O₃-SSP glass composite sintered at 200°C (2 h) has Q₀, x f value 5500 GHz with τₓ of -18 ppm/°C. The possible error in the measurement of εₓ using Hakki-Coleman method is of the order of 0.3%. The increased glass content, secondary phase formation, and poor densification of the samples may be the reason for the relatively low quality factor. However, the material has a very low sintering temperature. The thermal expansion studies of the Al₂O₃-SSP glass composite is carried out in the temperature range 30°C-90°C and the linear dimensional change with temperature is shown as Figure 9. The bulk composite sintered at 200°C has a CTE value of 8.7 ppm/°C.

The thermal conductivity of the composite is very important for electronic applications. The room temperature thermal conductivity of the Al₂O₃-SSP glass composite is 0.47 W/m/K. It has been reported that phosphate glasses have low thermal conductivity as well as higher thermal expansion as compared to the silicate glasses.

4. Conclusions

A novel composition based on Al₂O₃-SSP glass has been developed for ULTCC applications. The 45SnF₂:25SnO:30P₂O₅ glass has good dielectric properties both in radio (εₓ of 20 and tanδ of 0.007 at 1 MHz) and microwave frequencies (εₓ of 16 [6.2 GHz], Q₀, x f=990 GHz with a τₓ value of -290 ppm/°C). The CTE value of 45SnF₂:25SnO:30P₂O₅ glass is found to be 17.8 ppm/°C. The Al₂O₃-SSP glass composite sintered below 200°C indicates the presence of Al₂O₃, SnF₂ and SnO₂ and above 200°C, SnP₂O₇, Sn₃(PO₄)₂ are identified from the XRD. The Al₂O₃-SSP glass composite sintered at 200°C (2 h) has εₓ =5.41 with a tanδ of 0.01 at 1 MHz and εₓ =5.20 (11 GHz) with Q₀, x f = 5500 GHz with temperature coefficient of resonant frequency (τₓ) = -18 ppm/°C at microwave frequency. The room-temperature thermal conductivity of the Al₂O₃-SSP glass composite is 0.47 W/m/K and CTE in the temperature range 30°C-90°C is found to be 8.7 ppm/°C.
ACKNOWLEDGMENTS

I. J. Induja is grateful to Kerala State Council for Science Technology and Environment (KSCSTE), Kerala, India for providing the research fellowship. The authors thank Dr. K. P. Surendran for the constant support; Dr. P. Prabhakar Rao, Mr. Prithviraj, and Mrs. Soumya for recording XRD and SEM facilities; Dr. E. Bhoje Gowd for DSC measurement; and Dr. T. P. D Rajan for TG/DTA measurements.

REFERENCES


Table and Figures

| TABLE 1 Dielectric properties of SSP glass having density 4.38 g cm\(^{-3}\) |
| --- | --- | --- | --- | --- | --- |
| **Dielectric properties at 1 MHz** | **Dielectric properties at 5 GHz using split post dielectric resonator** | **Dielectric properties at using Hakki-Coleman method** |
| \(\varepsilon_r\) | \(\tan\delta\) | \(\varepsilon_r\) | \(\tan\delta\) | \(\varepsilon_r\) (6.2 GHz) (Hakki) | \(Q_u \times f\) (GHz) (Cavity) | \(\tau_f\) (ppm/°C) |
| 20 | 0.02 | 17 | 0.006 | 16 | 990 | -290 |

SPDR, split post dielectric resonator

![XRD pattern (A) and room-temperature FT-IR spectrum (B) of 45SnF\(_2\):25SnO:30P\(_2\)O\(_5\) glass](image1)

**FIGURE 1** XRD pattern (A) and room-temperature FT-IR spectrum (B) of 45SnF\(_2\):25SnO:30P\(_2\)O\(_5\) glass

![DSC and TG/DTA curve of SSP glass powder](image2)

**FIGURE 2** DSC and TG/DTA curve of SSP glass powder
FIGURE 3  Variation in thermal expansion with temperature for SSP glass

FIGURE 4  XRD pattern of Al$_2$O$_3$-SSP glass composite sintered at different temperatures (150°C-400°C)
FIGURE 5 Microstructure of fractured surfaces of Al$_2$O$_3$-SSP glass composite sintered at (A) 150°C, (B) 175°C, (C) 200°C, (D) 250°C, (E) 300°C, (F) 350°C, and (G) 400°C
FIGURE 6 Variation in (A) dielectric constant and (B) dielectric loss with radiofrequency for Al₂O₃-SSP glass composites sintered at different temperatures (150°C-400°C)

FIGURE 7 Variation in density with sintering temperature for Al₂O₃-SSP glass
FIGURE 8 Variation in (A) $\epsilon_r$, (B) $Q \times f$, and $\tau_f$ for Al$_2$O$_3$-SSP glass composite at microwave frequency with sintering temperature (150°C-400°C).

FIGURE 9 Thermal expansion study of Al$_2$O$_3$-SSP glass composite sintered at 200°C.