CHAPTER 7

SYNTHESIS AND CHARACTERIZATION OF $MgO–B_2O_3–SiO_2$ GLASS-CERAMIC FOR LTCC APPLICATION

7.1 Introduction

Glass-ceramics are polycrystalline materials produced through controlled crystallization of the base glass. Glass-ceramic materials possess many properties of both the glasses and the ceramics. Many new glass-ceramic compositions especially low permittivity (ε_r) materials using alumina and suitable glass combinations have recently been developed for microwave devices. Frequency range of applications of low temperature co-fired ceramic (LTCC) materials is from several hundred MHz to 70+ GHz. The characteristic properties required for dielectric materials which are used in LTCC technology are low sintering temperature, low dielectric constant, low loss tangent value, matching coefficient of thermal expansion with that of silicon (or < 20 ppm/^oC), stable temperature coefficient of dielectric constant (τ_ε) and temperature coefficient of resonant frequency (τ_f) [Sebastian et al. (2015)]. The low sintering temperature provided by the LTCC technology is the key factor enabling its advantageous utilization for today's packaging concepts including low loss conductors like silver or copper in microwave modules [Joseph et al. (2010)]. The densification or sintering temperature of the LTCC should be less than 950 ^oC since the common electrode material Ag melts at 961 ^oC. In glass-ceramic, the main phase is a dielectric material having high sintering temperature. However, addition of a glass phase to the dielectric lowers the sintering temperature to a suitable level depending on the amount and type of the glass composition. The characterization of $SiO_2–B_2O_3–CaO–MgO$ glass/Al_2O_3 composites using lead free low melting glass was studied for LTCC application [Chenn et al. (2013)]. The sintering temperature of the glass-ceramics is reduced by doping P_2O_5+ZnO, ZrO_2+TiO_2, B_2O_3, ZnO, TiO_2 and low melting point glass [Zhu et al. (2009)]. Many researchers have studied CaO–B_2O_3–SiO_2 (CBS) based glass-ceramic systems previously and found it suitable for LTCC [Zhu et al. (2009); Shao et al. (2009); Chen et al. (2009); Wang et al. (2010); Wang et al. (2011); Chiang et al. (2008)]. CBS glass-ceramics possess excellent dielectric properties: ε_r is about 8 and tanδ is about 2 x 10^{-4} at 25 MHz [Zhu et al. (2009)].

In general, the silicate geometry mainly consists of covalent bonding which restricts the movement of atoms and results in the low dielectric loss. Also, the strong covalent bonding along with the low dielectric polarizability of silicon yield low dielectric constant [Sebastian et al. (2015)].

The primary requirement for the liquid phase sintering is that the grains of the ceramic should get best wet by the liquid phase. In general, the reaction between the ceramic and the sintering aids provides best wetting conditions along with the formation of secondary phases. Chen et al. (2003) reported that MgO–B_2O_3–SiO_2 is most susceptible for crystallization while BaO–B_2O_3–SiO_2 is the least.

The phase evolution and the crystallization behavior of MgO–B_2O_3–SiO_2 (MBS) based glass-ceramics have been studied. MBS glass ceramic sintered within the temperature range 850 – 950 ^{o}C exhibited Qxf values of 5000 – 8000 GHz (at ~12 GHz) which is comparable with the CBS based glass ceramic [Dosler et al. (2012)]. The effect of nucleating agents on the crystallization & microstructure of glass-ceramics has been reported previously [Das et al. (2012)]. TiO_2 has high permittivity of ~100 and Qxf ~ 40 000 GHz.

In the present chapter, the investigation on $MgO–B_2O_3–SiO_2$ (MBS) glass ceramic with TiO_2 addition (0 to 13 wt%) as nucleating agent is described. The effect of nucleating agent on thermal and dielectric properties of MBS glass-ceramics is also analysed. It should be noted here that for the material whose tan delta values is greater than 0.001, it is difficult to calculate its temperature coefficient of resonant frequency (τ_f) due to the reason that the monitoring of TE_{011} mode is not possible. The TE_{011} mode is not detected significantly for these type of ceramic materials with high dielectric loss [Sebastian et al. (2017)]. The temperature coefficient of dielectric constant is another important parameter for the dielectric substrates. This can be obtained by taking the dielectric constant using frequency analyser based on parallel plate capacitor method at lower frequencies (100 kHz – 1 MHz) with temperature controlled heating of the sample. Therefore, in the present investigation low frequency dielectric measurement is performed for temperature ranging from 30 – 400 ^oC and the temperature coefficient of dielectric constant is reported. The dielectric constant and loss tangent (tanδ) have also been reported for microwave frequency (X– Band). The measurement is performed by Network Analyser using waveguide method.

7.2 Material synthesis

High purity MgO, H_3BO_3, SiO_2 and TiO_2 were used as starting raw materials for MBS glass-ceramics preparation via melt-quench method. The synthesis steps from glass melting to glass ceramics formation is described in section 3.1.3 of Chapter 3. Five batches were prepared by adding 0, 3, 7, 11 and 13 wt.% of TiO_2 with MBS glass. The MBS glass composition and the nomenclature assigned to the different MBS glass-ceramic compositions are given in Table 7.1 and 7.2, respectively. The thermal behaviour, density, phase, microstructure and dielectric characterisation is performed for the MBS glass-ceramic samples.

Table 7.1 $MgO–B_2O_3–SiO_2$ (MBS) glass composition

Components	Weight %
SiO_2	20
B_2O_3	45
MgO	35

Table 7.2 Batch compositions for MBS glass-ceramics.

Composition	Nomenclature Assigned
MBS Glass + 0 wt% TiO_2	MBS0Ti
MBS Glass + 3 wt% TiO_2	MBS3Ti
MBS Glass + 7 wt% TiO_2	MBS7Ti
MBS Glass + 11 wt% TiO_2	MBS11Ti
MBS Glass + 13 wt% TiO_2	MBS13Ti

7.3 Experimental results

7.3.1 Differential thermal analysis (DTA)

Figure 7.1 shows DTA curve of MBS glass powder with different concentrations of TiO_2 in it (0 – 13 wt%). The DTA curve of the typical glass ceramics distinctly indicates the three significant parameters i.e. the glass transition temperature (T_g), followed by the exothermic peak representing the crystallization temperature (T_c) and the endothermic peak for the melting temperature (T_m). The glass transition temperature for MBS0Ti was found to be 652 ^oC (T_g) with the well-defined crystallization peak at 758 ^oC (T_c) followed by an endothermic peak at 1151 ^oC (T_m). No significant variation is seen in the glass transition temperature T_g of all the glass-ceramic compositions. The well-defined exothermic crystallization peak at 758 ^oC indicates the formation of MBS glass ceramic. On the addition of TiO_2, the crystallization temperature and melting temperature were found to be shifted to the lower temperature. This indicates that TiO_2 acting as a nucleating agent enhances the crystallization of the MBS glass ceramics by decreasing the crystallization temperature by around 13 ^oC. The beginning of crystallization and the crystallization peak of the bulk sample occurs at ~100^oC higher temperature than that of the powder [Krzmanc et al. (2011)]. In the present study the sintering temperature of 900 ^oC is opted for the better crystallization of the MBS glass ceramics.

7.3.2 Density

The bulk density of MBS glass ceramic compositions is measured using archimedes priciple. The bulk density lies in the range of 2.61 – 2.70 (Figure 7.2) . It was observed that the density increases with the addition of TiO_2 content in the glass-ceramic samples. Maximum bulk density of 2.7 g/cm^3 was observed for the MBS13Ti. The density and dielectric constant has the direct correlation. So, if the density is higher, its corresponding dielectric constant will also be higher (Figures 7.9 and 7.11).

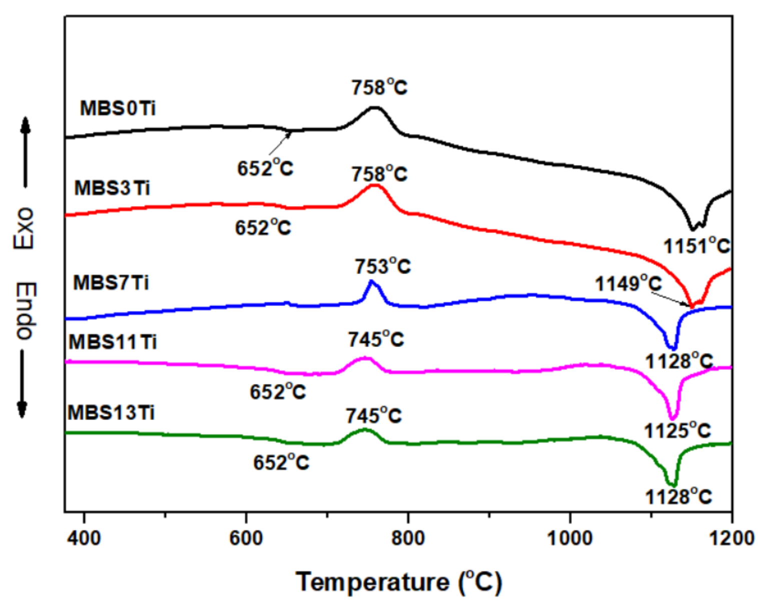


Figure 7.1 DTA curve of MBS glass added with different TiO_2 concentrations (0 – 13 wt%).

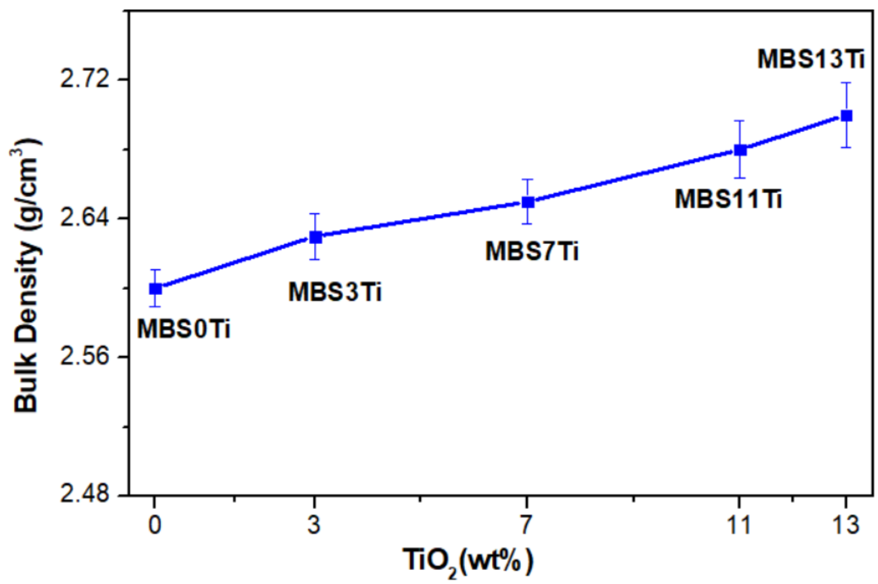


Figure 7.2 Bulk density of MBS glass-ceramic.

7.3.3 Phase analysis

XRD pattern of the MBS quenched glass powder shows that there is not any peak found for a crystalline phase which indicates the formation of glass (Figure 7.3).

Figure 7.4 shows powder XRD patterns of sintered MBS glass-ceramic samples. Isothermal heat treatment is done at 900 ^oC which led to crystallization of $Mg_2B_2O_5$ (JCPDS No. 16-0168) and $MgSiO_3$ (JCPDS No. 47-1750) phases [PCPDFWIN (1997)]. The sharp and the increased intensity of the most of the diffraction lines point out the growth of magnesium borate and magnesium silicate ($MgSiO_3$) crystallites. To promote the crystallization of the MBS glass, TiO_2 is added as a nucleating agent. The small addition of TiO_2 did not change the phase constitution of MBS glass. Dosler et al. (2012) have already reported the effect of 1 – 10 wt. % of TiO_2 to MBS glass ceramics on the resulting dielectric properties. As the amount of TiO_2 increases above 7 wt%, some more distinct peaks of TiO_2 (JCPDS No. 21–1276) were identified.

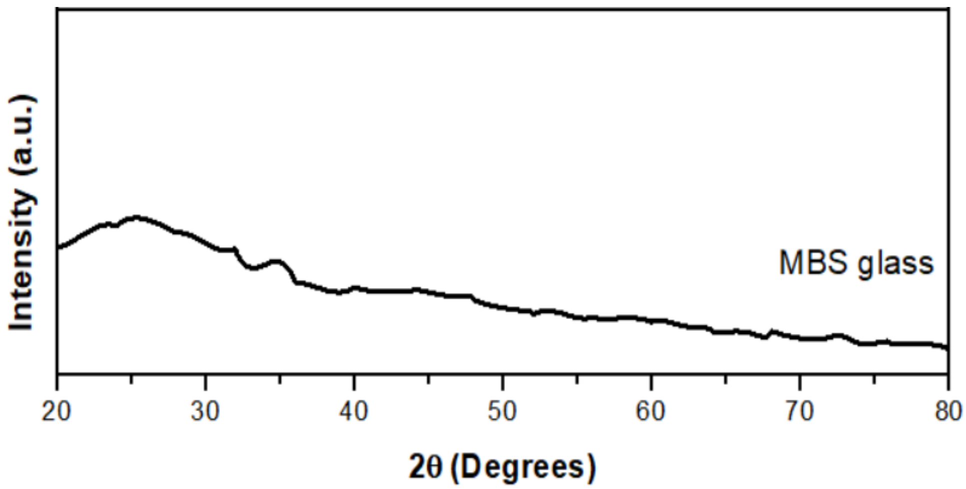


Figure 7.3 Powder X–ray diffraction pattern of MBS quenched glass powder sample.

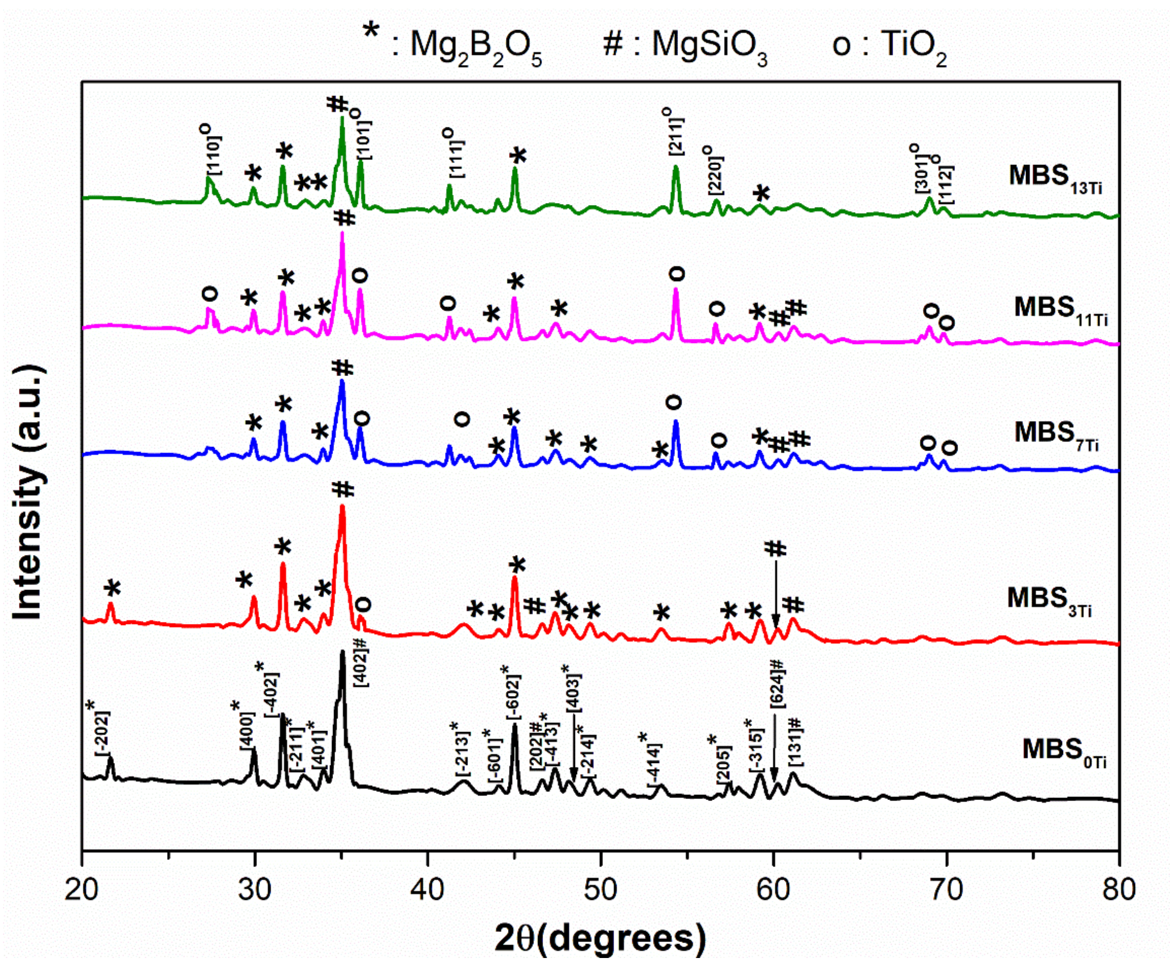


Figure 7.4 Powder X–ray diffraction patterns of the different MBS glass-ceramic powder samples with 0 – 13 wt% TiO_2 after sintering at 900 ^oC.

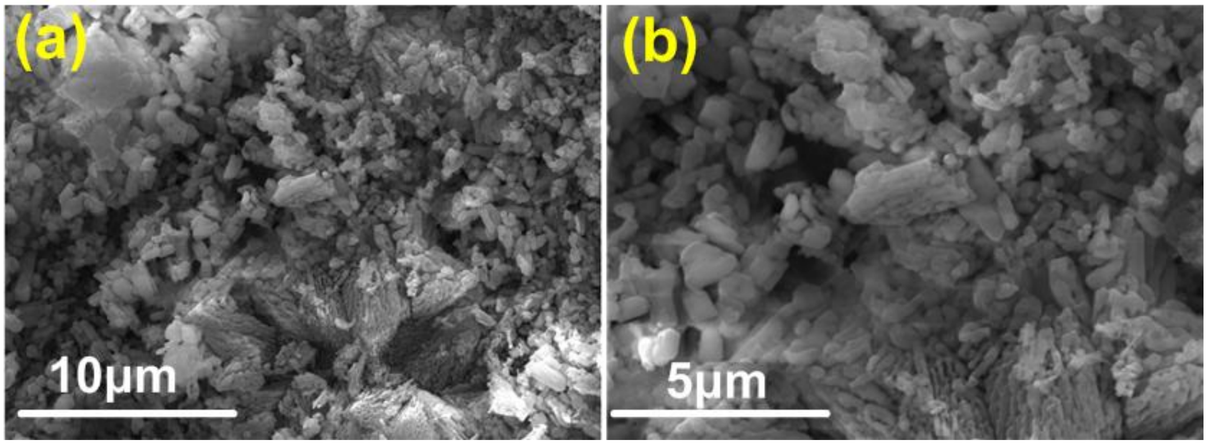


Figure 7.5 SEM micrographs of MBS0Ti sample at magnification of (a) 10K (b) 20K.

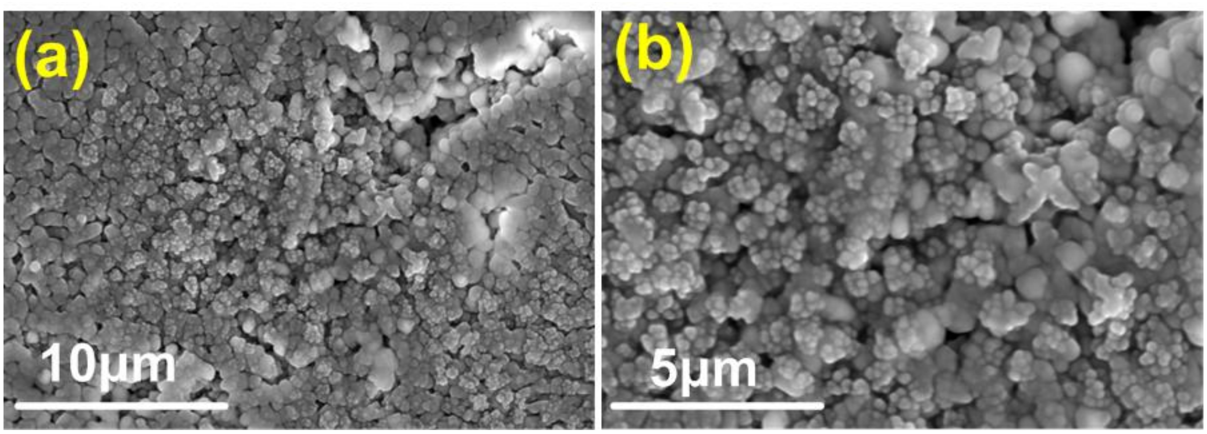


Figure 7.6 SEM Micrographs of MBS7Ti sample at magnification of (a)10K (b) 20K.

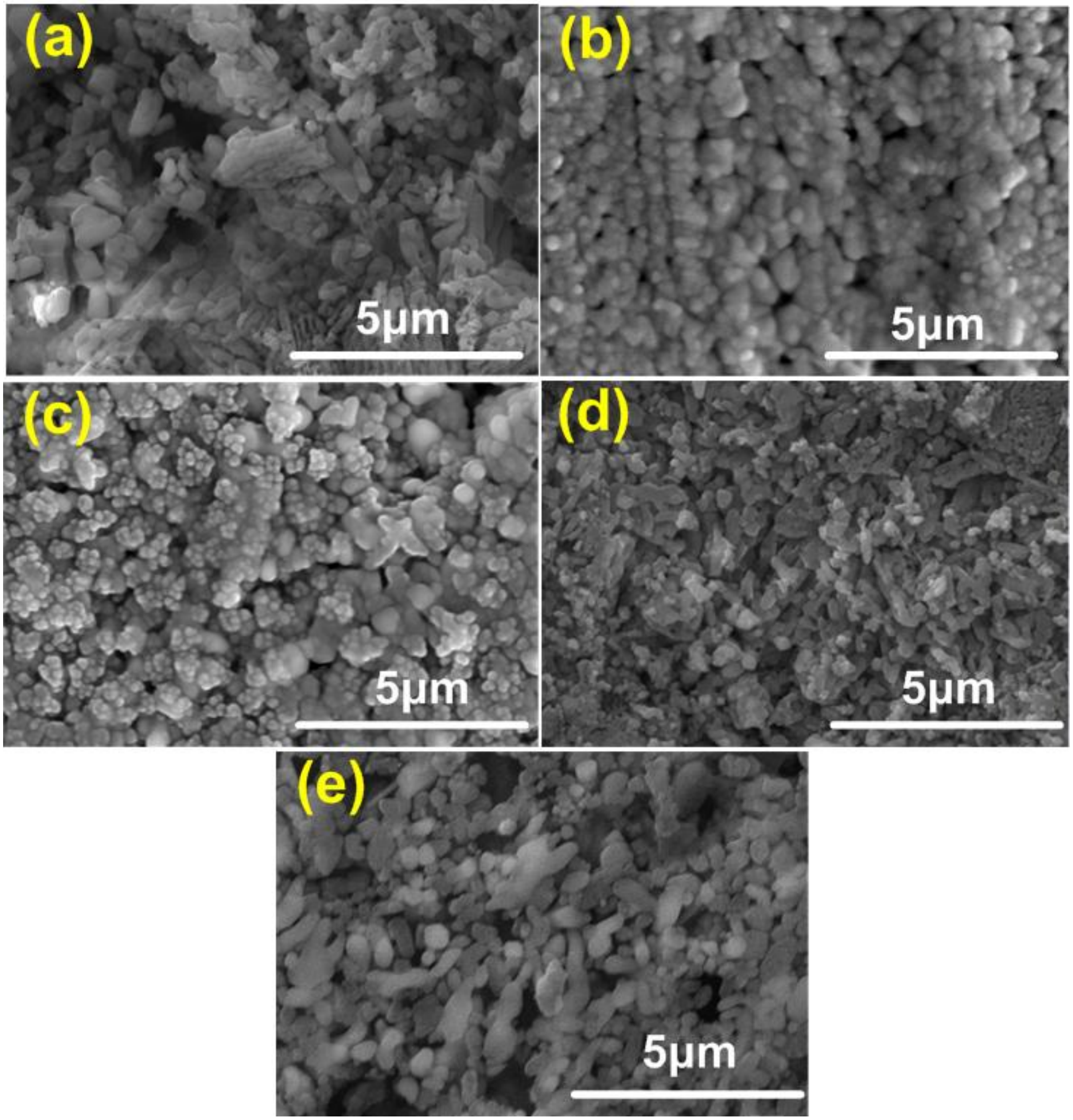


Figure 7.7 SEM Micrographs of MBS glass-ceramic samples at 20K magnification (a) MBS0Ti (b) MBS3Ti (c) MBS7Ti (d) MBS11Ti (e) MBS13Ti.

7.3.4 Microstructure

SEM Micrographs of the MBS glass-ceramic sample shows that TiO_2 enhances the formation of crystalline phases and also influences the microstructure which is quite significant in deciding the thermo-physical properties of glass-ceramics in general [Marques et al. (2010)]. Figure 7.5 shows the formation of agglomerated crystals along with some crystals of size 100 – 250 nm in MBS0Ti. In MBS7Ti, TiO_2 has created a large no. of nucleating sites observed as small spherical grains (Figure 7.6). The MBS glass-ceramics with 11 – 13 wt % TiO_2 have a larger grain size in the range of 290 – 500 nm. SEM images of compositions indicate that average grain size increases with increasing content of TiO_2 (Figure 7.7).

7.3.5 Dilatometry analysis

Fig. 7.8 shows variation of percent thermal expansion of sintered pellets as a function of temperature. The percent thermal expansion was measured from room temperature to 700 ^oC at a heating rate of 10 ^oC per minute. At 300 ^oC, the coefficient of thermal expansion (CTE) lies in range 7.08 – 7.48 ppm/^oC and at 500 ^oC, it was 7.57 – 9.28 ppm/^oC for the MBS glass-ceramic samples. It is suitable for the LTCC module mounted on alumina, since its CTE matches with the CTE of alumina [Tummula et al. (1991)]. The MBS0Ti sample shows linear variation up to 450 ^oC, followed by deviation from the linearity at higher temperature. This is due to softening of B_2O_3. Around 450 ^oC, B_2O_3 melt completely and fill in the interspaces. This causes again a linear expansion above 450 ^oC. While in case of MBS11Ti and MBS13Ti, the thermal expansion curve was found to be linear. This was so because TiO_2 acting as a nucleating agent enhances the crystallization of the glass-ceramics. Figure 7.8 also reflects that as wt. % of TiO_2 increases, thermal expansion decreases indicating better thermal stability. MBS with 13 wt. % of TiO_2 is comparatively more thermally stable.

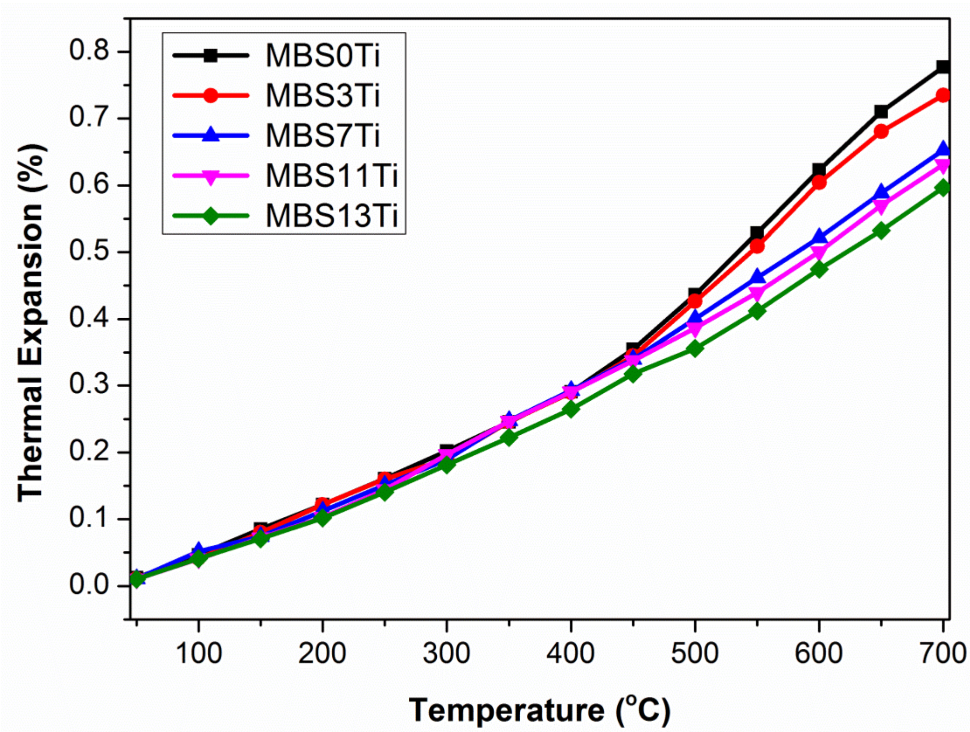


Figure 7.8 The variation of percent thermal expansion of sintered MBS glass-ceramic samples with temperature.

7.3.6 Dielectric Characterization

(a) High temperature dielectric measurement:

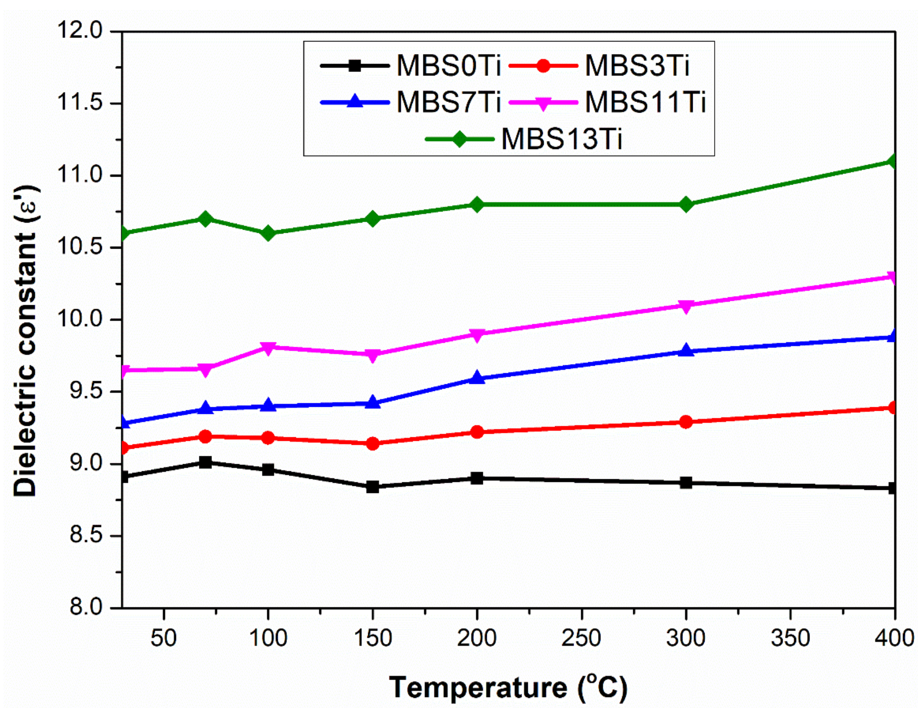
High temperature dielectric measurement of the glass-ceramic pellets was performed in the frequency range 100 KHz – 1 MHz using Alpha-A High Performance Frequency Analyzer (Novo Control Technologies). Figure 7.9(a) shows dielectric constant versus temperature graph of MBS glass-ceramics prepared by adding different amount of TiO_2 at 1 MHz. The average values of the dielectric constant of MBS glass ceramics (MBS0Ti – MBS13Ti) lies in the range 9.1 – 10.7. The variation of dielectric constant within the frequency range 100 KHz – 1 MHz is shown in Figure 7.9(b). The average dielectric constant values of MBS glass-ceramic samples lies in the range 9.42 – 10.7. It is noted from the Figure 7.9(a) and 7.9(b) that addition of TiO_2 in the glass-ceramic samples results in the increase of the dielectric constant values. The dielectric constant values increase with increase in the weight

% of TiO_2 and these are almost constant in the temperature range of 30 – 300 ^oC. It was observed that the dielectric constant values are frequency stable in the range 100 KHz to 1 MHz as well as temperature stable in the temperature range 30 – 300 ^oC.

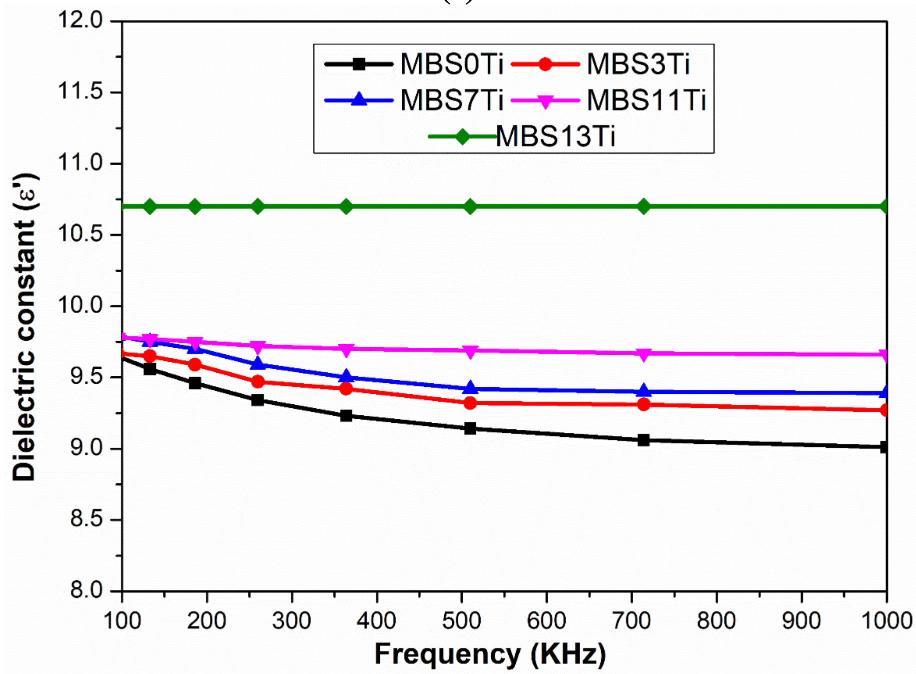
The temperature coefficient of dielectric constant (τ_ε) of MBS glass-ceramic compositions is calculated and analyzed using the following expression [Bhuyan et al. (2014)]

$$\tau_\varepsilon = \frac{(\varepsilon_o - \varepsilon_{oT})}{\varepsilon_o} \frac{10^6}{\Delta T} \quad \text{.................................(1)}$$

where ε_o and ε_{oT} are the dielectric constant values at room temperature and temperature T, respectively. Figure 7.10 shows the variation of τ_ε of MBS glass ceramics compositions. The graph shows that τ_ε is stabilized after increasing the concentration of TiO_2. This is because MBS glass has positive τ_ε (+735) and TiO_2 has negative τ_ε (-800). It was analyzed that MBS13Ti sample is more thermally stable with regard to dielectric constant as compared to other MBS glass-ceramic compositions.



(a)



(b)

Figure 7.9 Dielectric constant of sintered MBS glass-ceramic samples (a) As a function of temperature at 1 MHz (b) As a function of frequency within the range 100 KHz – 1 MHz.

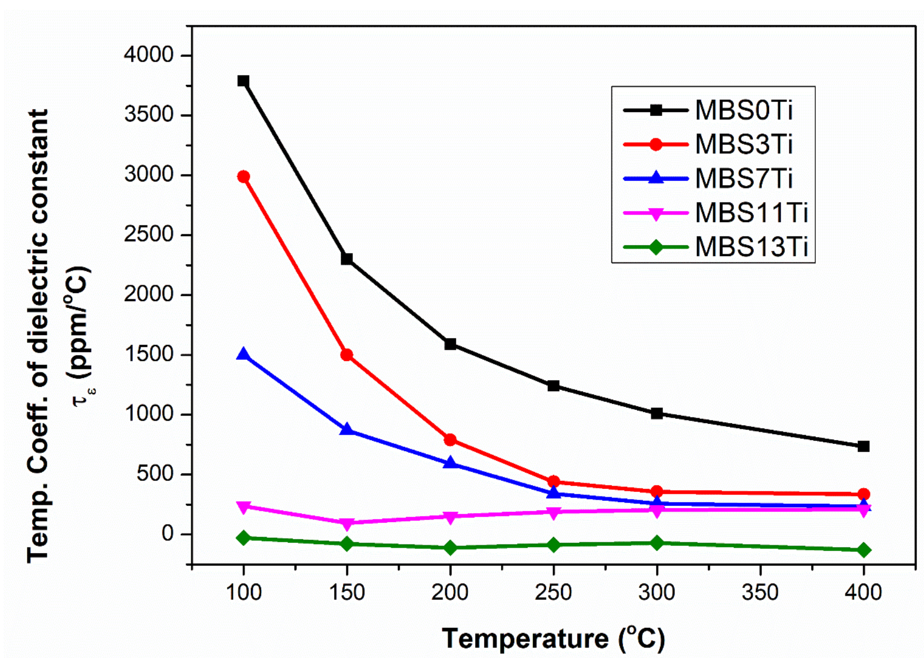


Figure 7.10 Variation of temperature coefficient of dielectric constant with temperature for MBS glass ceramic samples.

(b) Microwave dielectric measurement:

The high frequency dielectric constant (ε_r) measurement was performed by network analyzer. Nicholson–Ross–Weir technique was used to characterize the dielectrics properties of the material from reflection and transmission measurements at microwave frequencies [Tripathi et al. 2015]. The measurement method is described in section 3.2.4 of Chapter 3.

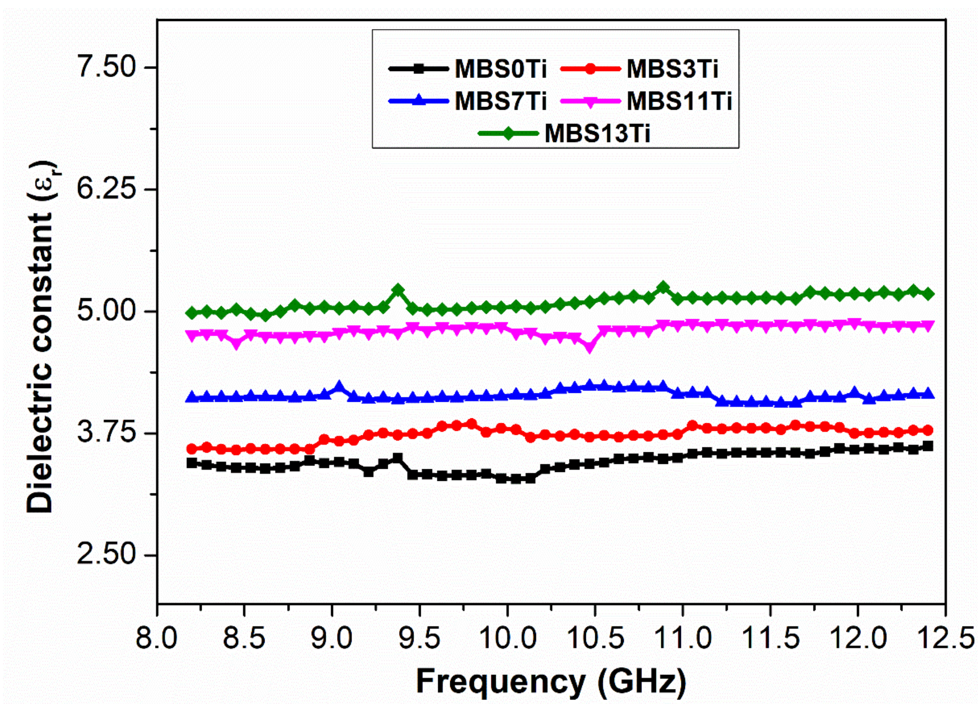


Figure 7.11 Variation of dielectric constant of MBS glass ceramic samples as a function of frequency.

It is noted from Figure 7.11 that the dielectric constant values lie in the range 3 – 5 within the X– Band (8.2 – 12.4 GHz). The dielectric constant value decreases in the GHz frequency range. Due to low dielectric constant values, it can be better used as substrate layer in electronic packaging to increase the speed of signal within the device. The dielectric constant value increases with increase in the content of TiO_2 due to higher dielectric polarizability of

TiO_2 as compared to other constituents in the glass. TiO_2 possesses very high value of dielectric constant i.e. 105 [Yoon et al. (2003)]. The dielectric constant values may also increase with change in crystalline-phase with increase in the content of TiO_2. The average loss tangent values for the glass-ceramic lies in the order of 10^{-3} (0.002 – 0.006). For MBS13Ti, average loss tangent is 0.002, which is lowest of all other samples.

7.4 Summary

The liquid phase sintered $MgO–B_2O_3–SiO_2$ (MBS) glass-ceramics with different amount of TiO_2 were prepared. TiO_2 has enhanced the crystallization process and results in increase in the crystallite/grain size. Thermal expansion coefficients were found to be matching with that of the alumina, so the LTCC can easily be mounted on the alumina. The percent thermal expansion decreases with increase in TiO_2 content in the MBS glass ceramics. All the sintered MBS glass-ceramics exhibit low dielectric constant values of 3 – 5 and loss tangent values 0.002 – 0.006. With the addition of $TiO_{2,}$ increase in dielectric constant was observed. It is worthwhile to mention that MBS13Ti is more thermally stable in terms of thermal expansion and temperature coefficient of dielectric constant (τ_ε). Also addition of TiO_2 enhances the crystallization, which is the reason for low loss tangent value of 0.002 for MBS13Ti. The common benefits observed in all compositions is that their dielectric constant are almost stable with the temperature and frequency variation (Figure 7.9 and 7.11). The present MBS based glass-ceramics can be used with deliberated improved performance in Low temperature co-fired ceramics (LTCC) substrate applications.

In the next Chapter 8, this MBS glass ceramic (MBS13Ti) is used as substrate material for the design of dual segment rectangular dielectric resonator antenna (DS–RDRA) and simulation study has been performed and analyzed.