Journal of
Ceramic Science
and Technology

J. Ceram. Sci. Tech., 07 [01] 79-86 (2016)
DOI: 10.4416/JCST2015-00035
available online at: http://www.ceramic-science.com

Synthesis, Microstructure and Dielectric Properties of $(Sr,Bi)TiO_3$ Borosilicate Glass-Ceramics

C.R. Gautam*[1, 2], C.W. Manpoong[3], S.S. Gautam[3], A.K. Singh[1], A. Madheshiya[1], M. Tamuk[3]

[1]Advanced Glass and Glass-Ceramic Research Laboratory, Department of Physics, University of Lucknow, Lucknow, India-226007.
[2]Department of Materials Science and Nano Engineering, Rice University, Houston, Texas, USA-7005.
[3]Department of Mechanical Engineering, North Eastern Regional Institute of Science and Technology, Itanagar 791109, India

received July 18, 2015; received in revised form September 12, 2015; accepted October 6, 2015

Abstract

Strontium bismuth titanate glass compositions were prepared with the conventional melt quench method in the glass system $60[(Sr_{1-x}Bi_x)\cdot TiO_3]$-$39[2SiO_2B_2O_3]$-$1[CeO_2]$. X-ray diffraction and transmission electron microscopy analyses of the glass samples confirmed their amorphous nature. Scanning electron microscopy and contact angle measurements were performed to study the surface morphology of the major phase crystallites. The addition of CeO_2 resulted in development of well-interconnected crystallites formed as major phase of perovskite strontium titanate. The dielectric constant (ε_r) and dissipation factor (tan δ) were studied as a function of temperature. The effective value of the dielectric constant, ε_r, was observed for glass-ceramic sample SBTC0.0850S with composition, x = 0.0, which is the order of 90 000 at low frequency, 1 Hz.

Keywords: $(Sr,Bi)\cdot TiO_3$, XRD, molar volume, SEM, TEM, dielectric properties, contact angle

I. Introduction

Ceramics are divided into fully crystalline materials, fully amorphous materials called glass, and partially crystalline materials called glass-ceramics [1]. The unique combination of the properties that can be achieved for glass-ceramics opens up entirely new fields where no alternative material can satisfy the technical requirements. They are truly engineered materials capable of a wide range of microstructure and properties [2]. They combine the ease of fabrication of a glass with the generic properties such as high strength and stiffness, etc. of a ceramic material. Strontium bismuth titanate glass-ceramic has shown great potential with regard to energy storage capacity [3,4] and microwave tunable shifter applications [5]. In these applications, control of the microstructure is necessary to optimize the properties. The microstructure is known to be highly sensitive to preparation conditions and the crystallization process. Glass-ceramics based on $SrTiO_3$ have found application in cryogenic capacitive temperature sensors [6]. These glass-ceramics may also be suitable for the applications where stability of dielectric behavior is desired [7].

The preparation of glass-ceramics involves several stages. First, a glass is melted and formed into the appropriate shape. The glass sample then undergoes heat treatment to nucleate and grow crystals in its volume until a material with the desired amount of crystallite size is produced. The discovery of the role of nucleating agents in initiating glass crystallization from a multitude of centres was the major factor allowing the introduction of glass-ceramics [8]. The presence of these agents in the parent glass is essential to promote the development of a high density of nucleation sites. It is necessary to obtain a fine-grained microstructure for good ceramic materials. To produce an appropriate parent glass for crystallization, the addition of the nucleating agents is often required. The addition of nucleating agents enhances the nucleation and growth during the heat treatment process. The nucleating agent is soluble in the molten glass, but either during controlled cooling or during reheating of the initially quenched glass it takes part in or promotes structural change within the glass [9]. Many studies have been conducted on the glass and glass-ceramic systems $(Pb_xSr_{1-x})\cdot TiO_3$ and $(Pb_xBi_{1-x})\cdot TiO_3$ [10–21]. The nucleating agent may in some cases precipitate out by homogeneous nucleation in a highly dispersed form. The nuclei formed in this way can then promote heterogeneous nucleation of major crystal phases. Certain requirements must be fulfilled in order for the nucleating agents to function in this manner. The rate of homogeneous nucleation must be high, requiring a low free energy of activation for nucleation. In addition there is a possibility that nucleating agents may serve in the process of heterogeneous nucleation and growth. The interfacial energy between two liquids is very small

* Corresponding author: gautam_ceramic@yahoo.com

and may be almost zero whereas that between a crystalline nucleus and glass is appreciable [22]. The change in the structure and mobility of various atomic species that result from glass phase separation may increase the probability of homogeneous nucleation within one or both of the two phases. In this way the nuclei may serve to provide heterogeneous nucleation for other crystal phases. Some factors that influence the properties of the major crystalline phase in a glass-ceramic are the surrounding glass matrix, their crystallization kinetics and nucleation mechanism, particle size and presence of other crystalline phases [23, 24].

Dielectric materials with improved electric energy-storage performance have attracted attention to meet the urgent demand of high power capacitors/multilayer capacitors and compactness as well as miniaturization. Substantial research and development of perovskite glass-ceramics has been devoted to achieving the goal of improved properties. Several modifications have been found with regard to perovskite materials in the form of either solid solutions or dopant additions. The recently reported review on perovskite glass-ceramics concerning crystallization behavior describes that various glass systems are crystallized in the perovskite phase [25]. The crystallization behavior can be enhanced with the addition of certain nucleating agents such as La_2O_3, Nb_2O_3, Fe_2O_3 and Bi_2O_3. These nucleating agents promote crystallization of major perovskite phase and reduce the amount of secondary phase [26]. Dielectric properties of strontium bismuth titanate glass-ceramics depend on crystallization, the composition of the glass-ceramic system and doping elements. More recently, our group reported on the preparation, crystallization, microstructure and dielectric properties of lead bismuth titanate borosilicate glass-ceramics doped with La_2O_3 and found the maximum value of the dielectric constant in the order of 1100 [27]. In this research paper we are reporting our results on the microstructural as well as the dielectric behavior of the strontium bismuth titanate glass-ceramics doped with 1 mole percent of CeO_2.

II. Experimental Procedures

The analytical reagent grade chemicals $SrCO_3$ (Himedia 99 %), Bi_2O_3 (Himedia 99.99 %), TiO_3 (Himedia 99 %), SiO_2 (Himedia 99.5 %), H_3BO_3 (Himedia 99.8 %) and CeO_2 (Himedia 99 %), were used for the preparation of various glass samples. The appropriate amounts of different reagents, as per the composition of glasses, were properly weighed and mixed in an agate mortar using acetone as mixing medium and were then dried. The glass batches weighing 20 g were melted in a high-grade alumina crucible in open-air atmosphere using a programmable electric furnace having silicon carbide heating elements. The melting temperatures for different compositions were in the range of 1000 – 1340 °C. The melt was maintained at the casting temperature 1340 °C in the furnace for 30 min for refining and homogenization. The melt was poured into a steel mould and was pressed by a thick aluminum plate. It was then immediately transferred into a preheated muffle furnace for annealing at 450 °C for 4 h to remove the residual stresses owing to the temperature gradient, which is produced as a result of the rapid cooling of the glass melt. During the casting of the glass melt, a very high cooling rate of ~ 400 K/min was employed. The glasses were cooled to room temperature inside the furnace after annealing. The annealed glass samples were converted into glass-ceramics in accordance with a suitable heat treatment schedule.

X-ray diffraction (XRD) of the glass and glass-ceramic samples was performed on a Rigaku Miniflex-II X-ray diffractometer, (Japan) using Cu-Kα radiation to check the amorphous and crystalline state. The density strongly depends on the composition and structure of glass-ceramic samples. Transmission electron microscopy (TEM) images with diffraction pattern were employed using a JEOL 2100 Field Emission Gun Transmission Electron Microscope, (Japan) to prove the amorphous nature of the prepared glass. For preparation of the TEM sample, a small amount of powder was taken and bath-sonicated in isopropyl alcohol for 3 h. A few drops were then cast onto the holey carbon grid and allowed to dry in vacuum. The TEM sample was then left in vacuum overnight. The glasses were heat-treated by heating them at a rate of 5 K/min at the optimized temperature 850 °C and holding them for 6 h. The samples were then cooled to room temperature at a cooling rate of 10 K/min. The density of the glass-ceramic samples was determined with the liquid displacement method based on the Archimedes principle [28]. Distilled water was used as the liquid medium. The density of the glass-ceramic samples was calculated using the formula.

$$\rho = \frac{(W_2 - W_1)}{(W_4 - W_1) - (W_3 - W_2)} \quad (1)$$

ϱ = Density (g/cm^3)
W_1 = Weight of empty specific gravity bottle (g)
W_2 = Weight of specific gravity bottle with sample (g)
W_3= Weight of specific gravity bottle with sample and distilled water (g)
W_4= Weight of specific gravity bottle with distilled water (g)

The molar volume was calculated using the relation

$$V_M = \frac{\sum X_i M_i}{\rho} \quad (2)$$

where, M_i is the molecular weight of the i^{th} component and X_i is the molar fraction of the i^{th} component [29].

Scanning electron microscopy (SEM) (LEO 430 Cambridge Instruments Ltd. UK) is one of the most versatile instruments available for the examination and analysis of the microstructural characteristics of solid objects. The glass-ceramic samples were ground and polished successively using silicon carbide powders (mesh no. 120, 600, and 800) on a flat glass plate. The final polishing was done on a blazer cloth using diamond paste (1 micron). The polished samples were etched for approximately 1 min with a 30 % HNO_3 + 20 % HF solution to delineate the morphology of crystallites and their distribution. The etched samples were cleaned thoroughly with distilled water. Samples were prepared for SEM examination by sputtering gold films onto the etched surfaces of the glass-ceramics to prevent charge build-up. The samples were then examined using SEM. The glass-ceramic samples

were mounted on the stubs with carbon tape and photographs were recorded at a magnification of 10 KX and size was measured from the micrographs according to the linear intercept method. A systematic comparative study of the microstructure helps in identifying the morphology of different crystalline phases in different glass-ceramic samples [30]. An advanced goniometer (500, Rame-Hart, Inc. USA) was used to measure the contact angle, θ^o. A syringe was used to inject deionized (DI) water slowly onto the well-polished solid surface of the glass-ceramic samples. All the contact angle measurements were performed under equilibrium conditions. All the experiments were performed in similar air-conditioned laboratory environments.

For dielectric measurement of the glass-ceramic samples, both the surfaces of the glass-ceramic samples were ground and polished using SiC powders in order to attain smooth surfaces. The electrodes were made by applying silver paint to both sides of the specimen and curing at 475 °C for 10 min. The dielectric constant measurements were performed in a locally fabricated sample holder using an automated measurement system during heating. The sample was mounted in the sample holder, which was kept in a programmable heating chamber. The leads from the sample holder were connected to a high frequency meter (Wayne Kerr 6500 P, UK) through scanner relay boards, which in turn was connected to a computer and a printer. Measurement operational controls and data recording were done through the computer. The sample was heated in the heating chamber to the required temperature at a rate of 2 K/min. The dielectric constant and dissipation factor of the samples were recorded at 1, 10, 111 Hz, 1.1, 12, 130 KHz and 1.3, 10 MHz at equal intervals of time during heating in the temperature range from room temperature to 350 °C.

(1) Nomenclature of Glass and Glass-Ceramic Samples

This nomenclature is not a standard; however, it is a code used by the author to describe the glass chemical composition and the heat treatment conditions. Five-letter glass codes refer to the composition of the glasses. The first three letters SBT designate the content of strontium bismuth titanate. The fourth letter C indicates that 1 wt% CeO_2 is used as an additive, while the fifth letter, i.e. 0.0, 0.1, 0.2 or 0.4, indicates the fraction of x in the glass system. For the nomenclature of the glass-ceramic sample, the following methodology has been adopted. The first five letters in the codes for the glass-ceramic sample are similar to the codes of their parent glasses and refer to the composition of glasses, and the next three digits indicate the crystallization temperature. The last letter, S, refers to the holding time at crystallization temperature for 6 h. Take the glass-ceramic sample SBTC0.1850S as an example: the first three letters SBT represent the content of strontium bismuth titanate, the fourth letter, C, indicates that 1 wt% CeO_2 is used as an additive, while 0.1 represents the value of composition ($x = 0.1$), 850 is the crystallization temperature and S indicates the 6 h soaking time. The codes for the glass-ceramic samples along with the sample compositions are listed in Table 1.

III. Results and Discussion

(1) Phase Composition

Transparent and thin glasses in the glass system $60[(Sr_{1-x}Bi_x)\cdot TiO_3]$-$39[2SiO_2B_2O_3]$-$1CeO_2$ with composition ($0.0 \le x \le 0.4$) in molar ratio were synthesized with a conventional melt quench technique. The XRD patterns of the glass and glass-ceramic samples SBTC0.0, SBTC0.0850S, SBTC0.1 and SBTC0.1850S are shown in Figs. 1 (a-d) respectively. The XRD patterns of the glass samples SBTC0.0 and SBTC0.1 exhibit a broad diffuse scattering at different angles instead of crystalline peaks, confirming a long-range structural disorder characteristic of an amorphous glassy network. Both the glasses were crystallized at 850 °C for 6 h heat treatment schedule and their XRD pattern shows the major phase formation of perovskite strontium titanate (P) along with secondary crystalline phases of rutile (TiO_2) and strontium borate ($Sr_2B_2O_5$) (Figs. 1b and d). As the concentration of Bi^{3+} content in the Sr^{2+} sites increases, the peaks in the pattern shift towards the left side (decrease in the 2θ position), which shows the shift in 2θ position clearly. This shift is obvious because of the substitution of smaller ionic size Bi^{3+} (1.17Å) in place of larger ionic size Sr^{2+} (1.19 Å).

Table 1: Glass-ceramics code, glass-ceramics compositions, density, molar volume and grain size of the glass-ceramic samples of the system $60[(Sr_{1-x}Bi_x)\cdot TiO_3]$-$39[2SiO_2B_2O_3]$-$1[CeO_2]$.

Glass-ceramic samples code	Glass-ceramics Composition (mole %)						Density (g/cm^3)	Molar volume (cm^3/mole)	Grain size (nm)
	$SrCO_3$	Bi_2O_3	TiO_2	SiO_2	H_3BO_3	CeO_2			
SBTC0.0850S	38.93	0	21.07	19.25	19.75	1	2.69 ± 0.13	37.17 ± 1.8	817
SBTC0.1850S	30.79	10.69	18.52	19.25	19.75	1	2.92 ± 0.14	46.27 ± 2.3	692
SBT0.1850S	30.80	10.70	18.51	19.75	20.25	0	2.93 ± 0.14	45.90 ± 2.2	-
SBTC0.2850S	24.42	19.07	16.51	19.25	19.75	1	3.00 ± 0.15	50.28 ± 2.5	529
SBTC0.4850S	15.06	31.37	13.58	19.25	19.75	1	3.04 ± 0.15	60.70 ± 3.0	-

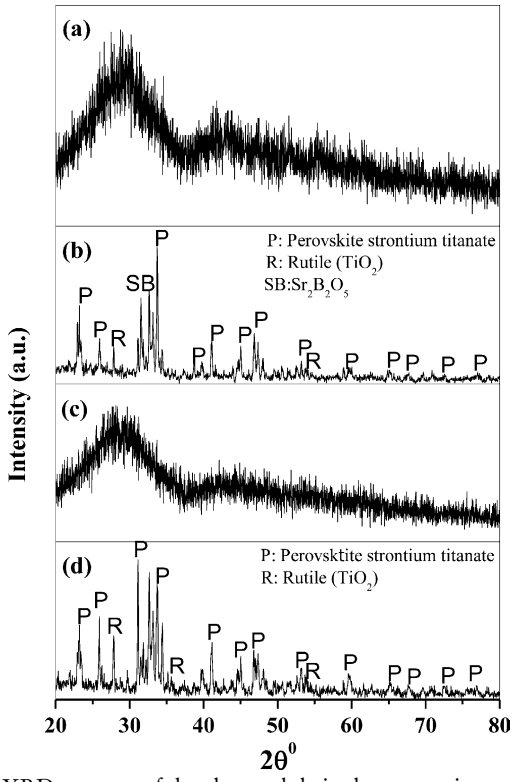

Fig. 1: XRD patterns of the glass and their glass-ceramic samples (a) SBTC0.0 (b) SBTC0.0850S (c) SBTC0.1 and (d) SBTC0.1850S.

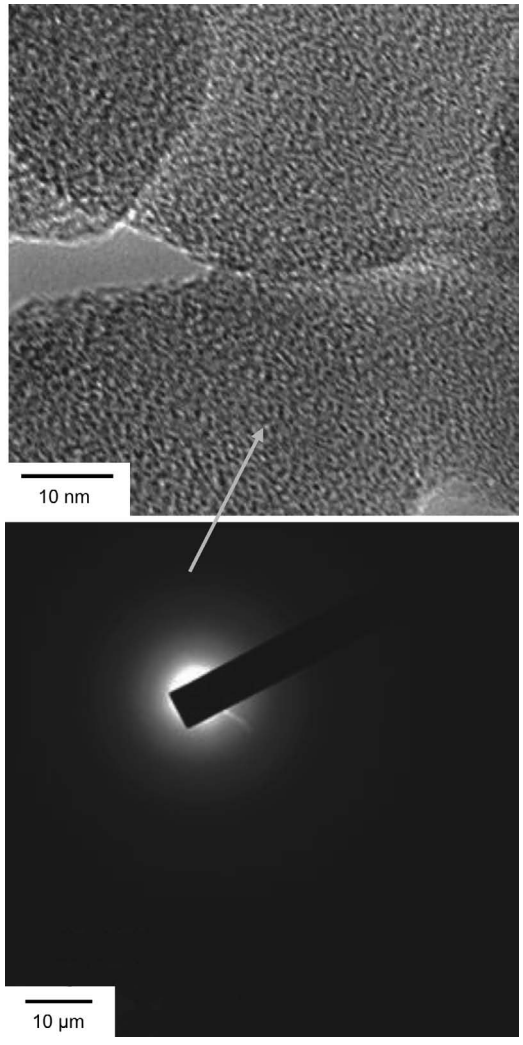

Fig. 2: HRTEM micrograph and electron diffraction pattern of a glass sample SBTC0.1..

(2) Transmission electron microscopic analysis

Fig. 2 shows a high-resolution transmission electron microscopy (HRTEM) and electron diffraction pattern of a thermally quenched glass sample SBTC0.1. The diffraction pattern shows a diffusion halo and indicates the absence of precipitation. Moreover, the absence of any nanocrystalline phase in the diffraction pattern confirms that this glass sample material consists of only a pure glassy structure in amorphous phase. The HRTEM image further shows a highly disordered structure without any sign of nanocrystals or ordered clusters, again confirming the fully glass nature. These results are consistent with the XRD observations (Fig. 1a and c).

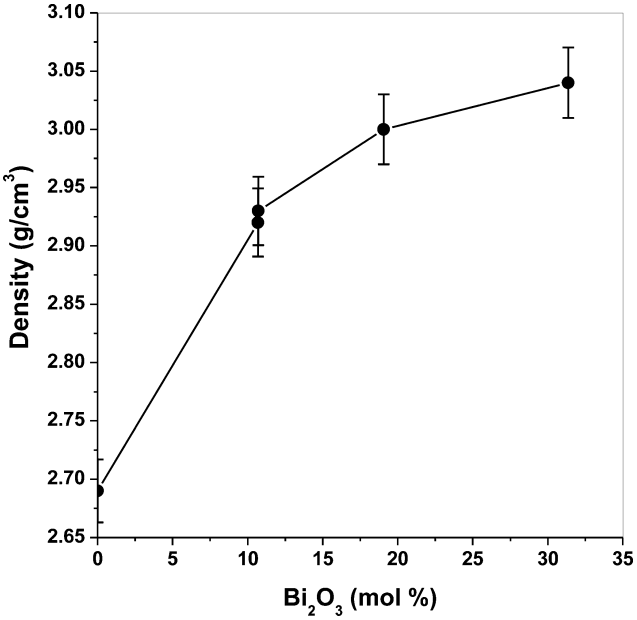

Fig. 3: Variation of density of glass-ceramics vs. Bi_2O_3 content.

(3) Density and molar volume of glass-ceramic samples

The variation in the values of density and molar volume of the glass-ceramic samples is listed in Table 1. It is well known that density is an important tool to explore the structural compactness/softening, the change in geometrical configurations and coordination number [31]. Thus it helps to reveal the degree of change in the structure with change in composition in any glass system. The value of density of strontium bismuth titanate borosilicate glass-ceramic samples was found to be between 2.69 and 3.04 g/cm^3. It increases with an increasing concentration of Bi_2O_3. This may be due to the high density of Bi_2O_3 (8.90 g/cm^3). The variation of density versus bismuth content of the glass-ceramic samples is shown in Fig. 3 and the variation of the molar volume versus bismuth content in glass-ceramic samples is shown in Fig. 4; it is clear that with an increase in Bi_2O_3, the density and molar volume also increased. This is due to the replacement of all SiO_2 and H_3BO_3 (molecular weight is 60.084 and 61.83 g/mol, resp.) with Bi_2O_3 (molecular weight is 465.959 g/mol) [32]. The molar volume which is defined as the volume occupied by the unit mass of glass-ceramic increases from 37.17 to 60.70 (cm^3/mol) as the Bi_2O_3 content increases from 0.0 to 31.37 mol% [33]. From Fig. 3, it

is observed that the density and mol% of Bi_2O_3 of SBT borosilicate glass-ceramic samples almost varied exponentially while the molar volume of the glass-ceramic samples vs Bi_2O_3 content varied almost linearly (Fig. 4).

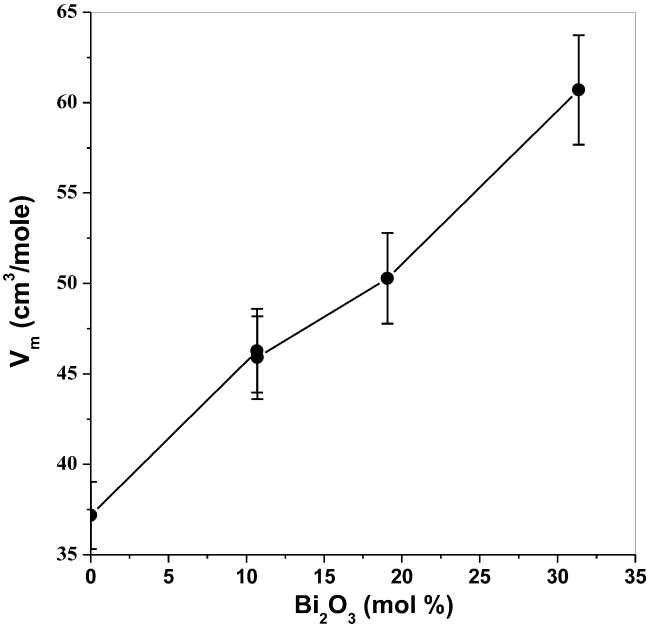

Fig. 4: Variation of molar volume of glass-ceramics vs Bi_2O_3 content.

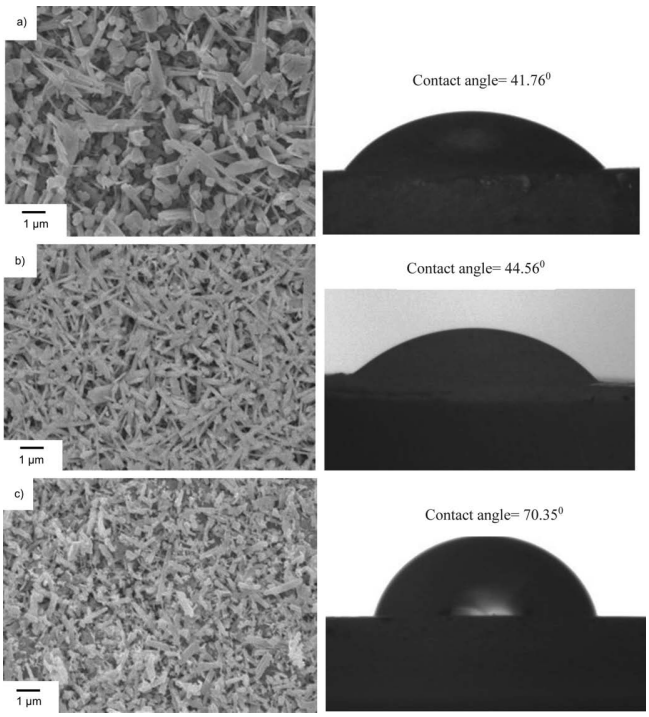

Fig. 5: SEM images and contact angles micrographs of glass-ceramic samples: (a) SBTC0.0850S, (b) SBTC0.1850S and (c) SBTC0.2850S.

(4) Surface morphology and contact angle analysis

Scanning electron micrographs and contact angle images of different glass-ceramic samples SBTC0.0850S, SBTC0.1850S and SBTC0.2850S are shown in Fig. 5(a, b and c) respectively. Fig. 5(a) shows randomly agglomerated crystallites of major phase of perovskite strontium titanate with some residual glassy phase. Fig. 5(b) shows well-interconnected grains of the major phase of strontium bismuth titanate and the secondary phase formations of rutile (TiO_2) and strontium borate ($Sr_2B_2O_5$) whereas in Fig. 5(c) the grains are loosely packed. The coexistence of both coarse as well as fine grains is also observed in these micrographs. The micrographs of all glass-ceramic samples were found to be composed of interconnected fine crystallites of $SrTiO_3$/(SrBi)TiO_3 phase, which are dispersed in the glassy matrix. The minimum and maximum values of grain size of the glass-ceramic samples were found to be 529 nm and 817 nm respectively. The sample codes, compositions and grain size are listed in Table 1. The calculated values of contact angles of the samples are 41.7°, 44.56° and 70.35° respectively. It is observed that the values of the contact angles of these ceramic samples are increasing owing to the increase in the concentration of bismuth oxide, which is also responsible for increase in the density of the samples. The increment in the values of the contact angles reveal that the hydrophobicity increases with the increase in the concentration of Bi_2O_3.

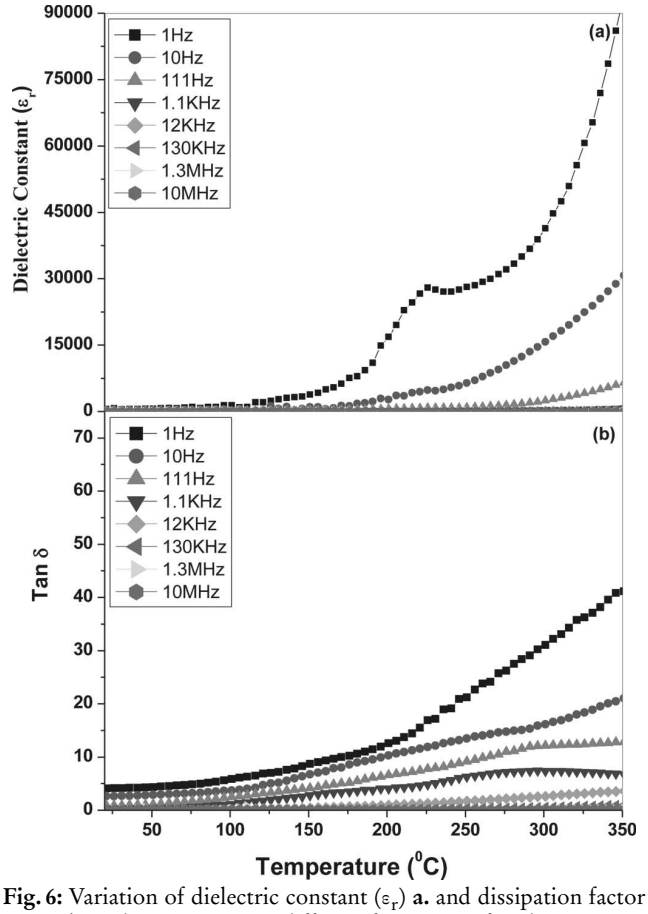

Fig. 6: Variation of dielectric constant (ε_r) **a.** and dissipation factor (tan δ) **b.** with temperature at different frequencies for glass-ceramic sample SBTC0.0850S.

(5) Dielectric properties

The dielectric constant (ε_r) and dissipation factor (tan δ), were measured as a function of temperature within the temperature range of 20 – 350 °C at various selected frequencies from 1 Hz to 10 MHz for tentative glass-ceramic samples SBTC0.0850S, SBTC0.1850S and SBTC0.2850S. Fig. 6 shows the variations of ε_r and tan δ with temper-

ature for glass-ceramic sample SBTC0.0850S. The value of ε_r was found to increase with the increase in temperature at low frequency range from 1 Hz to 111 Hz, while the value of ε_r was found to be constant and revealed the temperature-independent behaviour at the different high frequencies. The interfacial polarization arises at the crystal to glass interface, which explains the high value of the dielectric constant. This causes the effective value of ε_r in the order of 90 000 [34]. The maximum value of the dielectric constant is found to be the order of 90 000 along with dissipation factor value 41.1 at 1 Hz. Fig. 7 shows the plots of the dielectric constant ε_r and tan δ vs temperature for glass-ceramic sample SBTC0.1850S. Both plots show similar trends but has a decrease in the value of ε_r and an increase in the value of tan δ as compared to the results for glass-ceramic sample SBTC0.0850S, which may be due to increase in the electrical conduction with the increase in temperature [35]. The value of ε_r was found to increase with increasing temperature at low frequency range from 1 Hz to 100 Hz, whereas the value of ε_r was found to be constant, indicating the temperature-independent behaviour at high frequencies. The maximum value of the dielectric constant was found to be in the order of 700 along with dissipation factor value 52.3. The difference in the value of dielectric constant as well as dissipation factor strongly depends upon the compositional changes. The content of Bi_2O_3 plays an important role in enhancing the dielectric constant in comparison to the content of $SrCO_3$. It is worthwhile to make high energy charge storage capacitors if the dissipation factor is lowered. Further, efforts are continued to reduce the loss in these materials. Fig. 8 shows the plots of dielectric constant ε_r and dissipation factor tan δ vs temperature for the glass-ceramic sample SBTC0.2850S. It is observed that the value of ε_r gradually increases up to certain temperature and then rapidly increases with increasing temperature at low frequency range from 1 Hz to 111 Hz, while the value of tan δ was found to be temperature-independent up to 200 °C. Thereafter it increased with increasing temperature for 1 Hz and 10 Hz. The maximum value of dielectric constant was found to be in the order of 575 along with dissipation factor value 26.7. This is due to the hopping of conduction of the ions at high temperature, and hence samples SBTC0.0850S, SBTC0.1850S and SBTC0.2850S revealed a high value for tan δ. The highest value of ε_r was observed in the order of 90 000 for glass-ceramic sample SBTC0.0850S with composition, x = 0.0, while the loss was found to be more for glass-ceramic sample SBTC0.1850S with composition, x = 0.1, in the glass system $60[(Sr_{1-x}\ Bi_x)\cdot TiO_3]$-$39[2SiO_2\cdot B_2O_3]$ doped with 1 mol% of CeO_2 crystallized at 850 °C for 6 h. The value of tan δ was observed to be much lower for glass-ceramic sample SBTC0.3850S with composition, x = 0.3, in the system $60[(Sr_{1-x}\ Bi_x)\cdot TiO_3]$-$39[2SiO_2\cdot B_2O_3]$ doped with 1 mol% of CeO_2 crystallized at 850 °C for 6 h.

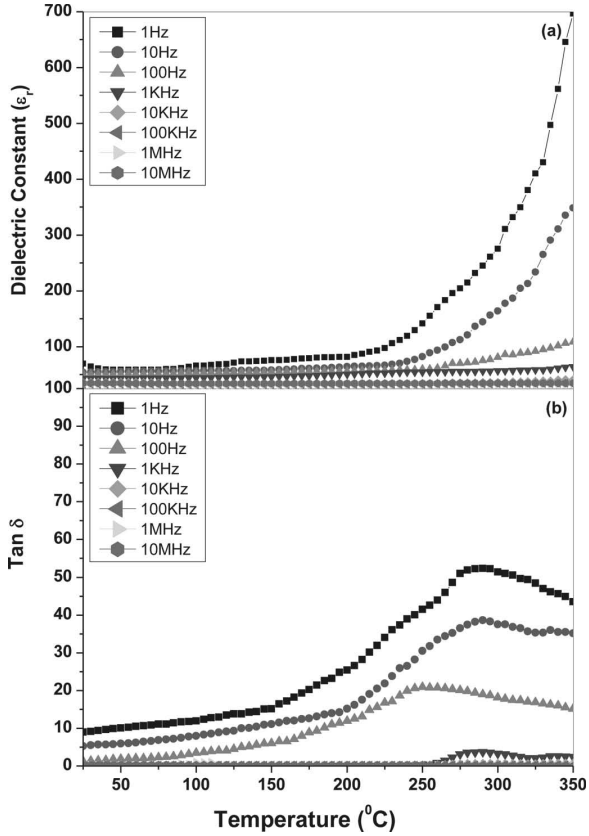

Fig. 7: Variation of dielectric constant (ε_r) **a.** and dissipation factor (tan δ) **b.** with temperature at different frequencies for glass-ceramic sample SBTC0.1850S.

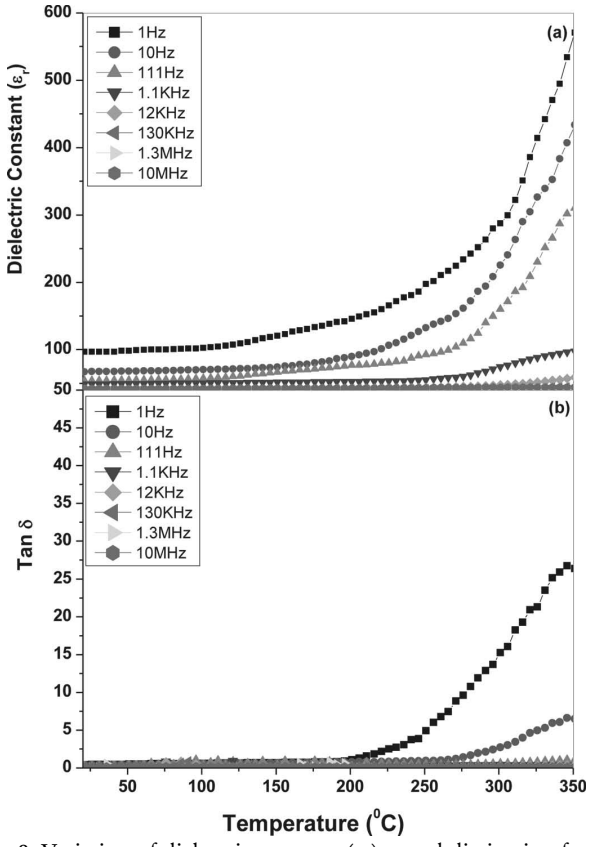

Fig. 8: Variation of dielectric constant (ε_r) **a.** and dissipation factor (tan δ) **b.** with temperature at different frequencies for glass-ceramic sample SBTC0.2850S.

IV. Conclusions

Bulk glasses were prepared with the melt quench technique in the glass system $60[(Sr_{1-x}\ Bi_x)\cdot TiO_3]$-$39[2SiO_2\cdot B_2O_3]$ doped with 1 mol% of CeO_2. The XRD pattern of

the glass samples exhibits broad diffuse scattering at different angles instead of crystalline peaks, confirming a long-range structural disorder characteristic of amorphous glassy phase while the XRD pattern of the glass-ceramic samples shows sharp polycrystalline peaks and confirms the perovskite major phase of strontium titanate. The values for the density and molar volume of SBT borosilicate glass-ceramic samples increased with increasing content of Bi_2O_3. A scanning electron micrograph shows randomly agglomerated crystallites of the major phase of SBT with some residual glassy phase. The minimum and maximum values of the grain size of the glass-ceramic samples were found to be 529 nm and 817 nm respectively. It is also concluded that the values of the contact angles, 41.7°, 44.56° and 70.35° of these ceramic samples increased owing to the increasing concentration of Bi_2O_3. The highest value of dielectric constant ε_r observed for glass-ceramic sample SBTC0.0850S (x = 0.0) is ~90 000. The loss observed was more for glass-ceramic sample SBTC0.1850S (x = 0.1).

Acknowledgements

The authors are grateful to the Uttar Pradesh Council of Science and Technology, Lucknow (India) for financial support under the "Young Scientist Scheme" as major research project No. CSTT/YSS/D-3913. Authors are also thankful to Prof. R. K. Shukla, for his constant support and for extending the dielectric measurement facility at Department of Physics, University of Lucknow, Lucknow-226007, India. C.R. Gautam also acknowledges the financial support from University Grants Commission, New Delhi, Government of India, for the Raman Fellowship.

References

1 Wolfram, H., George, B.: Glass-ceramic technology, American Ceramic Society, Ohio, (2002).

2 Harper, McMillan, P.W.: Glass-ceramics, London, Academic Press 2nd edition, (1974).

3 Gorzkowski, E.P., Pan, M.J., Bender, B.C., Wu, C.M.: Glass-ceramics of barium strontium titanate for high energy density capacitors, *J. Electroceram.*, **18**, 269 – 276, (2007).

4 Chen, J., Zhang, Y., Deng, C., Dai, X.: Improvement in the microstructures and dielectric properties of barium strontium titanate glass-ceramics by AlF_3/MnO, *J. Am. Ceram. Soc.,* **92**, 1863 – 1866, (2009).

5 Kageyama, K., Takahashi, J.: Tunable microwave properties of barium titanate based ferroelectric glass-ceramics, *J. Am. Ceram. Soc.,* **87**, 1602 – 1605, (2004).

6 Lawless, W.N.: Thermometer equations for low-temperature glass-ceramic capacitance thermometers, *Cryogenics*, **42**, 561 – 566, (1972).

7 Swartz, S.L. Lanagan, M.T., Schulze, W.A., Cross, L.E., Lawless, W.N.: Dielectric properties of $SrTiO_3$ glass-ceramics, *Ferroelectrics,* **50**, 313 – 318, (1983).

8 Stookey, S.D.: Method of making ceramics and product thereof, United States Patent 2920971, 829, British Patent, **447**, (1960).

9 Kokubo, T., Tashiro, M.: Dielectric properties of fine-grained $PbTiO_3$ crystals precipitated in a glass, *J. Non-Cryst. Solids*, **13**, 328 – 340, (1974).

10 Gautam, C.R., Singh, A., Madheshiya, A.: Preparation and optical investigations of $[(Sr_{1-x}Bi_x)\cdot TiO_3]$-$[2SiO_2B_2O_3]$-$[CeO_2]$ glasses, *Adv. Optics*, **2014**,1 – 7, (2014).

11 Sahu, A.K., Kumar, D., Parkash, O., Thakur, O.P., Prakash, C.: Dielectric properties of glass-ceramics in the system $[(Pb_{1-x}Sr_x)OTiO_2)]$-$[2SiO_2$-$B_2O_3]$-$[K_2O]$, *Brit. Ceram. Trans.*, **102**, 148 – 152, (2003).

12 Sahu, A.K., Kumar, D., Parkash, O., Prakash, C.: Effect of K_2O/BaO ratio on crystallization, microstructure and dielectric properties of strontium titanate borosilicate glass-ceramics, *Ceram. Int.*, **30**, 477 – 483, (2004).

13 Sahu, A.K., Kumar, D., Parkash, O., Thakur, O.P., Prakash, C.: Lead-strontium titanate glass-ceramics: II – dielectric behavior, *J. Mater. Sci.*, **41**, 2087 – 2096, (2006).

14 Bahrami, A., Nemati, Z.A., Alizadeh, P., Bolandi, M.: Crystallization and electrical properties of $[(Pb_{1-x}Sr_x)TiO_3]$-$[(2SiO_2B_2O_3)]$-$[K_2O]$ glass-ceramics, *J. Mater. Process. Tech.*, **206**, 126 – 131, (2008).

15 Gautam, C.R.: Study of crystallization, microstructure and electrical behaviour of lead strontium titanate borosilicate glass-ceramics with La_2O_3 and Nb_2O_5 as additives, Ph.D. Thesis, Institute of Technology, Banaras Hindu University, India, (2005).

16 Gautam, C.R., Kumar, D., Parkash, O., Thakur, O.P., Prakash, C.: Dielectric behaviour in the glass-ceramic system $[(Pb_{1-x}Sr_x)OTiO_2]$-$[2SiO_2$-$B_2O_3]$-$[3K_2O$-$7BaO]$ with addition of La_2O_3 ($0.0 \le x \le 0.5$), International Symposium of Research Students *on Material Science and Engineering,* Chennai, India, 1 – 11, (2004).

17 Gautam, C.R., Kumar, D., Parkash, O.: Dielectric and impedance spectroscopic studies of $(Sr_{1-x}Pb_x)TiO_3$ glass-ceramics with addition of Nb_2O_5, *Bull. Mater. Sci.,* **34**, 1393 – 1399, (2011).

18 Gautam, C.R., Kumar, D., Singh, P., Parkash, O.: Study of impedance spectroscopy of ferroelectric (Pb,Sr)TiO_3 glass-ceramic system with addition of La_2O_3, *ISRN Spect.*, **2012**, 1 – 11, (2012).

19 Gautam, C.R., Kumar, D., Parkash, O.: Controlled crystallization of (PbSr)TiO_3 borosilicate glass-ceramics doped with Nb_2O_5, *Glas. Phys. Chem.*, **39**, 162 – 173, (2013).

20 Gautam, C.R., Dixit, S., Madheshiya, A.: Synthesis and structural properties of lead strontium titanate borosilicate glasses with addition of chromium trioxide and graphene nanoplatlets, *Spect. Lett.*, **48**, 280 – 285, (2013).

21 Gautam, C.R., Madheshiya, A., Dwivedi, R.K.: Synthesis, crystallization, and dielectric behaviour of lead bismuth titanate borosilicate glasses with addition of 1% La_2O_3, *Ind. J. Mater. Sci.*, **2015**, 1 – 10, (2015).

22 Oda, K., Yoshino, T., Oka, K.O.: Preparation and dielectric properties of (Ba,Sr)TiO_3-Al_2O_3-SiO_2 glass-ceramics, *Memoirs of the School of Engineering Okayama University*, **17**, 97 – 105, (1983).

23 Herczog, A.: Microcrystalline $BaTiO_3$ by crystallization from glass, *J. Am. Ceram. Soc.,* **47**, 107 – 116, (1964).

24 McCauley, D., Newnham, R.E., Randall, C.A.: Intrinsic size effects in a barium titanate glass-ceramic, *J. Am. Ceram. Soc.*, **81**, 979 – 987, (1998).

25 Yadav, A.K., Gautam, C.R.: A review on crystallization behavior of perovskite glass-ceramics, *Adv. Appl. Ceram.,* **113**, 193 – 207, (2014).

26 Yadav, A.K., Gautam, C.R.: Dielectric behavior of perovskite glass-ceramics, *J. Mater. Sci.: Mater. El.,* **25**, 5165 – 5187, (2014).

27 Gautam, C.R., Madheshiya, A., Mazumder, R.: Preparation, crystallization, microstructure and dielectric properties of lead bismuth titanate borosilicate glass-ceramics, *J. Adv. Ceram.*, **3**, 194 – 206, (2014).

28 Gautam, C.R,Yadav, A.K.: Synthesis and optical investigations on (Ba,Sr)TiO_3 borosilicate glasses doped with La_2O_3, *Opt. Photo. J.*, **3**, 1 – 7, (2013).

[29] Thombare, M.D.: Study of physical properties of lithium borophosphate glasses, *Int. J. Res. Pure and Appl. Phys.*, **4**, 9 – 15, (2014).

[30] Venktaraman, A., Hiremath, V.A., Date, S.K., Kulkarni, S.D.: A new combustion route to γ-Fe_2O_3 synthesis, *Bull. Mater. Sci.*, **24**, 617 – 621, (2001).

[31] Rajendran, V., Palanivelu, N., Modak, D.K., Chaudhuri, B.K.: Ultrasonic investigation on ferroelectric $BaTiO_3$ doped $80V_2O_5$-20PbO oxide glasses, *Phys. Stat. Sol. A*, 180, 467 – 477, (2000).

[32] Marzouk, S.Y., Gaafar, M.: Ultrasonic study on some borosilicate glasses doped with different transition metal oxides, *Solid State Commun.*, **144**, 478 – 483, (2007).

[33] Soppe, W., Van der Marel, C., Van Gunsteren, W.F., Den Hartog, H.W.: New insights into the structure of B_2O_3 glass, *J. Non-Cryst. Solids*, **103**, 201 – 209, (1988).

[34] Gautam, C.R., Singh, P., Thakur, O.P.: Synthesis, structure and impedance spectroscopic analysis of $[(Pb_xSr_{1-x}) \cdot OTiO_2]$–$[(2SiO_2 \cdot B_2O_3)]$-7[BaO]-3[$K_2O$] glass-ceramic system doped with La_2O_3, *J. Mater. Sci.*, **47**, 6652 – 6664, (2012).

[35] Kumar, D., Gautam, C.R., Parkash, O.: Preparation and dielectric characterization of ferroelectric $(Pb_xSr_{1-x})TiO_3$ glass-ceramics doped with La_2O_3, *Appl. Phys. Lett.*, **89**, 112908 – 112911, (2006).