Research Article

Synthesis, Crystallization, and Dielectric Behaviour of Lead Bismuth Titanate Borosilicate Glasses with Addition of 1% La_2O_3

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Lead bismuth titanate borosilicate glasses were prepared in the glass system $65[(\text{Pb}_x\text{Bi}_{1-x})\cdot\text{TiO}_3]-34[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-1\text{La}_2\text{O}_3$ ($0.0 \leq x \leq 1.0$) doped with one mole percent of La_2O_3 via conventional melt quench method. The amorphous nature of glass samples in this glass system is confirmed by using X-ray diffraction (XRD) study. Differential thermal analysis (DTA) has been employed to determine the glass transition temperature, T_g , as well as crystallization temperature, T_c . DTA measurements were recorded in temperature range from 30 to 1200°C. The prepared glasses were crystallized by regulated controlled heat treatment process on the basis of their DTA results. These samples are carried out for XRD measurements in the 2θ range from 20 to 80° to study the crystallization behaviour and phase formation of the glass ceramic samples. The scanning electron microscopy (SEM) of these glass ceramic samples has been carried out to explore the morphology through nucleation and growth of the crystallites in the glassy matrix. The values of dielectric constant as well as dielectric loss were increased with increasing the temperature within the frequency range from 20 Hz to 100 Hz. The addition of 1 mol% of La_2O_3 to the lead bismuth titanate glasses enhances the crystallization and acts as donor dopant for this glass system.

1. Introduction

Glasses are defined as inorganic product of fusion which has been cooled to a rigid condition without crystallization [1]. The main distinction between glass and crystal is the presence of long range order in the crystal structure. For many years glasses containing transition metal ions have attracted attention because of their potential application in electrochemical, electronic, and electro optics device [2]. Lead bismuth titanate (PBT) borosilicate glasses are analogous to the perovskite lead strontium titanate glass ceramics. The study of various oxide glasses has received considerable attention due to their structural property [3, 4]. These glasses have wide application in the field of electronics, nuclear, and solar energy technologies and acoustic-optics device [5–9]. Glass ceramics are formed by controlled crystallization of glasses. Glass ceramics have become commercially important

materials in the various fields such as consumer products, vacuum tube envelopes, telescope mirror blanks, radomes for the aerospace industry, and protective coating for metals [10]. The properties and hence applications of glass ceramics depend on the complex interrelationship of structural, compositional, and processing variables [11]. Recently, a series of perovskite glass ceramics are investigated [12, 13]. The glass ceramics of these systems were developed with the objective of producing materials for the electronic industry with high dielectric constants or optoelectronic effects. The controlled crystallization of the perovskite type lead titanate, PbTiO_3 , was first reported by Herczog and Stookey in the $\text{SiO}_2\text{-Al}_2\text{O}_3\text{-TiO}_2\text{-PbO}$ system [14]. Glass ceramics containing undoped perovskite titanate such as PbTiO_3 have been extensively investigated [15–22]. Bismuth based glasses are used to produce glass ceramic superconductors (high T_c) with controllable microstructure [23–28]. These glass

ceramics have interesting dielectric properties, resulting from the combination of high-permittivity crystallites and low-permittivity glassy matrix [29, 30]. Various studies have been done on the glasses and their glass ceramic system $(\text{Pb}_x\text{Sr}_{1-x})\cdot\text{TiO}_3$ [31–33]. More recently, optical and electrical properties of $(\text{Pb}_x\text{Bi}_{1-x})\cdot\text{TiO}_3$ borosilicate glass and glass ceramic systems were extensively reported by Gautam et al. [34, 35].

The recent demand to increase the energy storage capability and reliability of capacitors is necessary for future application prospects. In recent years, significant efforts have been made to develop high dielectric constant materials, which are capable of a high energy storage density [36, 37]. Among all glass ceramic materials investigated, lead bismuth titanate (PBT) glass ceramics have been found to be a promising candidate for high energy storage [38]. PBT glass ceramics are currently fabricated mainly in presence of borosilicate and aluminosilicate network forming systems with certain dopant such as La_2O_3 [39]. In the present paper, we report the synthesis, crystallization, and dielectric properties of PBT borosilicate glasses in the glass system $65[(\text{Pb}_x\text{Bi}_{1-x})\cdot\text{TiO}_3]-34[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-\text{La}_2\text{O}_3$.

2. Experimental Procedure

Various amorphous and transparent glasses in the glass system $65[(\text{Pb}_x\text{Bi}_{1-x})\cdot\text{TiO}_3]-34[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-\text{La}_2\text{O}_3$ with $(0.0 \leq x \leq 1.0)$ doped with 1 percent La_2O_3 were synthesized successfully. Analytical reagent grade chemicals PbO (Fisher Scientific, 99%), Bi_2O_3 (Himedia, 99.99%), TiO_2 (Himedia, 99%), SiO_2 (Himedia, 99.5%), H_3BO_3 (Himedia, 99.8%), and La_2O_3 (Himedia, 99.9%) were well mixed for 3 hours in acetone media using mortar and pestle. The dried powders were melted in an alumina crucible at 1100°C and then quenched by pouring onto an aluminium mould and then immediately pressing with a thick aluminium plate. The glass was then annealed at 400°C for 3 hours and then furnace cooled to room temperature. The annealed glasses were cut by diamond cutter to get the desired shape of the samples. DTA was done using NETZSCH (Simultaneous Thermal Analyser 409) to determine the glass transition, T_g , and crystallization temperatures, T_c . Two sets of heat treatment conditions were used to convert glass into glass ceramics for 3 and 6 hours along with $5^\circ\text{C}/\text{min}$ heating rate. XRD patterns were taken using Rigaku Diffractometer employing $\text{Cu K}\alpha$ radiation over a 2θ range of 20° – 80° at a scan rate of $4^\circ 2\theta/\text{minute}$ to study the desired and secondary phases. For microstructure studies the samples were polished and etched using 30% nitric acid and 20% hydrofluoric acid ($30\% \text{HNO}_3 + 20\% \text{HF}$) solution for 30 seconds to 1 minute. After they were etched, the samples were cleaned by distilled water for 2 minutes to remove unwanted debris from the surface prior to gold coating and then dried in electric oven at 100°C to remove the water content from the samples. The SEM images are taken of gold coated glass ceramic samples using a JSM-840 scanning electron microscope (SEM) to study the morphology of different crystalline phases. For dielectric measurement of glass ceramic samples, both the surfaces of the samples were ground and polished using SiC powders for attaining smooth

surfaces. The electrodes were made by applying silver paint on both sides of the specimen and curing at 450°C for 10 min. The capacitance measurements were made 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 HP 4284 A Precision LCR meter through scanner relay boards and GPIB bus, which in turn was connected to a computer and printer. Measurement operational controls and data recording are done through the computer. The sample was heated in the heating chamber to the required temperature at a rate of $2^\circ\text{C}/\text{minute}$. Capacitance, C , and dissipation factor, D , of the samples were recorded at 20, 100 Hz, 1, 10, and 100 kHz, and 1 MHz at equal intervals of time during heating in the temperature range of room temperature to 500°C .

3. Nomenclature of the Samples

The five letter glass codes refer to the composition of the glasses. First three letters PBT are designated to the content of lead bismuth titanate. The fourth letter L indicates that 1 mole percent of La_2O_3 has been used as an additive, while the fifth letter, that is, 0.0, 0.2, 0.4, 0.6, 0.8, or 1.0, indicates the fraction of composition “ x ” in the glass system. For the nomenclature of the glass ceramic samples, the following methodology has been adopted. 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 letters T and S refer to the holding time for the crystallization temperatures for 3 and 6 hours. For example, in glass ceramic sample BTL0.0675T, the first two letters represent the amount of bismuth titanate, and third letter L indicates that 1 mole percent of La_2O_3 has been taken as an additive, while 0.0 represents the value of composition like ($x = 0.0$), and three digit numbers 675 are representing the crystallization temperatures and T indicates the 3-hour soaking time. The glass samples code along with their sample compositions has been listed in Table 1.

4. Result and Discussion

4.1. X-Ray Diffraction Analysis of Glasses. The XRD pattern of the glass samples BTL0.0, PBTL0.2, and PBTL0.4 is shown in Figures 1(a), 1(b), and 1(c), respectively. These figures exhibit a very broad diffuse scattering at different angles along with different peak intensities instead of crystalline peaks, confirming short range structural order characteristics of glassy amorphous phase.

4.2. Differential Thermal Analysis (DTA). The DTA curves of the different glass samples BTL0.0, PBTL0.2, PBTL0.4, PBTL0.6, PBTL0.8, and PBTL1.0 are shown in Figures 2 and 3, respectively. The glass transition temperature, T_g , and crystallization temperatures (T_{c1}, T_{c2}) are listed in Table 1 along with the different composition of the glasses. T_g values for all glass samples are lying from 587 to 637°C . It is evident from Table 1 that the crystallization peak T_{c1} for all the DTA

FIGURE 1: XRD pattern of glass samples: (a) BT1L0.0, (b) PBT1L0.2, and (c) PBT1L0.4.

FIGURE 2: DTA pattern of the glass samples: (a) BT1L0.0, (b) PBT1L0.2, and (c) PBT1L0.4 in the glass system $65[(\text{Pb}_x\text{Bi}_{1-x})\text{TiO}_3]-34[2\text{SiO}_2\text{B}_2\text{O}_3]-1\text{La}_2\text{O}_3$.

TABLE 1: Nomenclature of glass samples, their compositional distribution, glass transition temperature, and DTA peaks of various glass samples in the system $65[(\text{Pb}_x\text{Bi}_{1-x})\cdot\text{TiO}_3]-34[2\text{SiO}_2\text{B}_2\text{O}_3]-1\text{La}_2\text{O}_3$.

Glass sample code	x	Composition (wt %)			DTA peaks ($^{\circ}\text{C}$)		
		$(\text{Pb}_x\text{Bi}_{1-x})\text{TiO}_3$	$(2\text{SiO}_2\text{-B}_2\text{O}_3)$	La_2O_3	T_g	T_{c1}	T_{c2}
BTL0.0	0.0	65	34	1	637	675	916
PBTL0.2	0.2	65	34	1	626	680	941
PBTL0.4	0.4	65	34	1	622	654	875
PBTL0.6	0.6	65	34	1	602	619	630
PBTL0.8	0.8	65	34	1	599	621	777
PBTL1.0	1.0	65	34	1	587	593	810

TABLE 2: Glass ceramic sample code, heating rate, holding time, holding temperature, crystallite size, and crystal structure in the glass system $65[(\text{Pb}_x\text{Bi}_{1-x})\cdot\text{TiO}_3]-34[2\text{SiO}_2\text{B}_2\text{O}_3]-1\text{La}_2\text{O}_3$.

Glass ceramic sample code	Heat treatment schedule			Crystallite size (nm)	Crystal structure
	Heating rate ($^{\circ}\text{C}/\text{min}$)	Holding time (hour)	Holding temperature ($^{\circ}\text{C}$)		
BTL0.0675T	5	3	675	7.28	Orthorhombic
BTL0.0675S	5	6	675	7.37	Orthorhombic
BTL0.0916T	5	3	916	5.80	Orthorhombic
BTL0.0916S	5	6	916	5.89	Orthorhombic

patterns of the glass samples is decreased with increasing the value of “ x ” in the glass system, because viscosity of the lead rich glass melts is less in comparison to the bismuth content glass melts as shown in Table 1. Figure 2(a) depicts the DTA pattern of the glass sample BTL0.0. It is observed from the DTA pattern of this glass sample that there are two exothermic peaks, T_{c1} and T_{c2} , situated at different temperatures, 675 and 916°C . The sharp peak T_{c1} occurs due to the major phase formation of bismuth titanium oxide ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) while peak T_{c2} is due to the secondary phase formation of bismuth oxoborate ($\text{Bi}_4\text{B}_2\text{O}_9$), which is also confirmed from the XRD results. The DTA patterns of the glass samples PBTL0.2 and PBTL0.4 are also shown in Figures 2(b) and 2(c). Both the DTA patterns have similar behaviour and only difference is observed in their peaks positions T_{c1} and T_{c2} . Figure 3(a) depicts the DTA pattern for the glass sample PBTL0.6 and showed a splitting in the exothermic peak at different temperatures, 619°C and 630°C , respectively. Figures 3(b) and 3(c) represent the DTA pattern for the glass samples PBTL0.8 and PBTL1.0. The DTA patterns of these glass samples show the two types of peaks, that is, exothermic as well as endothermic. The peak positions, T_{c1} and T_{c2} , at 621 and 777°C are observed due to major as well as secondary phase formations. The DTA pattern of glass sample PBTL1.0, which is lead-free ($x = 1.0$) (Figure 3(c)), has similar behaviour like DTA pattern of glass sample PBTL0.8, but only a difference has been observed in the peak nature of T_{c1} .

4.3. Crystallization Behaviour of the Glass Ceramics. Glass ceramic sample code, heating rate, holding time, holding temperature, and crystallite size of these glass ceramic samples have been listed in Table 2. A tentative glass sample

BTL0.0 has been taken to crystallize it at two different temperatures, 675 and 916°C , for 3- and 6-hour heat treatment schedule with a heating rate of $5^{\circ}\text{C}/\text{min}$. The XRD of these glass ceramic samples BTL0.0675T, BTL0.0675S, BTL0.0916T, and BTL0.0916S is shown in Figures 4(a), 4(b), 4(c), and 4(d), respectively. The XRD pattern has been indexed with JCPDS file card number 35-0795 and all the peaks were identified corresponding to the higher intensity peak having the value of hkl (171) and marked properly as shown in their plots. Glass ceramic samples BTL0.0675T and BTL0.0675S show similar crystallization behaviour and are consisting of the major as well as pyrochlore phases while the same glass sample crystallized at higher temperature 916°C for 3- and 6-hour heat treatment schedules and the pyrochlore phase completely disappears and only a formation of the major phase of bismuth titanium oxide ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) is there. It is concluded that the observed major crystalline phase for all the glass ceramic samples is of bismuth titanium oxide ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) and the pyrochlore phase of bismuth oxoborate ($\text{Bi}_4\text{B}_2\text{O}_9$). The reported results on XRD of the glass ceramic samples are showing orthorhombic crystal structure having different lattice parameters $a = 5.393 \text{ \AA}$, $b = 32.723 \text{ \AA}$, and $c = 5.483 \text{ \AA}$ (Table 2). The crystallite size from the XRD pattern was calculated by using Scherer formula [40]:

$$\text{Crystallite size } D_p = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where K is the shape factor (0.94), λ is wavelength of $\text{Cu-K}\alpha$ line ($1.54 \text{ \AA}$), and β is full width at half maximum. The minimum and maximum values of crystallite size corresponding to maximum intensity peaks of glass ceramic

FIGURE 3: DTA pattern of the glass samples: (a) PBTL0.6, (b) PBTL0.8, and (c) PBTL1.0 in the glass system $65[(\text{Pb}_x\text{Bi}_{1-x})\text{TiO}_3]-34[2\text{SiO}_2\text{B}_2\text{O}_3]-1\text{La}_2\text{O}_3$.

samples BTL0.0916T and BTL0.0675S have been found 5.80 nm and 7.37 nm, respectively.

4.4. Scanning Electron Microscopic Analysis. The surface morphology of all glass ceramic samples shows fine crystallites of major phases of bismuth titanium oxide ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$). Qualitative inspection of all these SEM micrographs reveals that the relative content of residual glass phase is present in large amount except the SEM micrograph of glass ceramic sample PBTL0.4875S. The coexistence of coarse and fine particles has been also observed in all the glass ceramic sample micrographs similar to the lead titanate based glass ceramics [41, 42]. Figure 5(a) shows that the scanning electron micrograph of glass ceramic sample BTL0.0916T is found to be composed of interconnected fine and uniform crystallites of bismuth titanium oxide ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$). Crystallites are well dispersed in the glassy matrix and separated by developed grain boundaries throughout the micrograph. Figures 5(b) and 5(c) show the scanning electron micrographs of glass ceramic samples PBTL0.2941T and PBTL0.2941S, respectively, and there is a change in the morphology of the crystallites of the major phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. These crystallites are found to have irregular shape and not uniformly distributed in the glassy matrix. The glass ceramic sample PBTL0.4654T (Figure 5(d)) shows the small crystallites which are not properly developed in the glassy matrix and have the crystallite size of the order of 533 nm. Figures 5(e) and 5(f) depict the SEM micrographs of the glass ceramic samples PBTL0.4875T and PBTL0.4875S. The morphology of the crystallites is entirely different and mainly they are differing in terms of the crystal growth and

their distribution. The crystal growths for the glass ceramic sample PBTL0.4875S are well developed in comparison to the glass ceramic sample PBTL0.4875T which is crystallized for 3 hours. It means that the soaking time for the crystallization of these glass ceramic samples strongly influences the nucleation and growth of the crystals. In some of the micrographs, agglomeration of the crystallites has been also observed. Glass ceramic sample codes, heating rate, holding time, holding temperature, and grain size of the synthesized glass ceramic samples in the glass system $65[(\text{Pb}_x\text{Bi}_{1-x})\text{TiO}_3]-34[2\text{SiO}_2\text{B}_2\text{O}_3]-1\text{La}_2\text{O}_3$ have been listed in Table 3. It is also observed that the size of the grains increased with increasing the soaking time from 3 to 6 hours. The minimum and maximum values of the grain size of the glass ceramic samples, PBTL0.4875T and PBTL0.4875S, have been found 330 nm and 750 nm, respectively (Table 3).

4.5. Dielectric Characteristics. The variation of the dielectric constant, ϵ_r , and dissipation factor, D , were measured as a function of temperature within the temperature range from 50 to 500°C at few selected frequencies such as 20, 100 Hz, 1, 10, and 100 kHz, and 1 MHz for the tentative glass ceramic samples PBTL0.2941T and PBTL0.4875T. Figure 6 shows the variations of ϵ_r and D with temperature for glass ceramic sample PBTL0.2941T. The value of ϵ_r has been found to increase with increasing temperature at low frequency range from 20 Hz to 100 Hz, while the value of ϵ_r is found constant, which means that temperature is independent of the higher frequency range. The value of dielectric constant was found to be a maximum at a frequency of 20 Hz. At

FIGURE 4: XRD pattern of glass ceramic samples: (a) BTL0.0675T, (b) BTL0.0675S, (c) BTL0.0916T, and (d) BTL0.0916S.

TABLE 3: Glass ceramic sample code, heating rate, holding time, holding temperature, and average grain size in the glass system $65[(\text{Pb}_x\text{Bi}_{1-x})\cdot\text{TiO}_3]-34[2\text{SiO}_2\text{B}_2\text{O}_3]-1\text{La}_2\text{O}_3$.

Glass ceramic sample code	Heating rate ($^{\circ}\text{C}/\text{min}$)	Heat treatment schedule		Grain size (nm)
		Holding time (hour)	Holding temperature ($^{\circ}\text{C}$)	
BTL0.0916T	5	3	916	375
PBTL0.2941T	5	3	941	420
PBTL0.2941S	5	6	941	600
PBTL0.4654T	5	3	654	533
PBTL0.4875T	5	3	875	330
PBTL0.4875S	5	6	875	750

higher frequencies, the dielectric constant is invariant due to a reduction of the net polarization. This can be explained by the Maxwell-Wagner model of the dielectric constant [43]. The maximum value of dielectric constant ϵ_r is found to be the order of 70,000. The dielectric loss for PBTL0.2941T was also increased with increasing temperature at low frequency range from 20 Hz to 100 Hz. The addition of 1 mol% La_2O_3 to the PBT glasses promotes the crystallization, as discussed earlier in the crystallization kinetics. La^{3+} ions form La_2O_3 which are present in the glassy network and they are diffused into the crystalline phase of PBT at higher temperatures during the heat treatment processes. These ions of La^{3+} make them semiconducting in nature. SEM of the sample PBTL0.2941T showed a change in the morphology of the crystallites of the major phase $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. These crystallites are found to have irregular shape and not uniformly distributed in the glassy matrix. Hence, a large conductivity difference is introduced

between the semiconducting grains and insulating grain-boundary. The conductivity difference is responsible for space charge polarization and hence the effective value of dielectric constant [44]. The order of the dielectric constant, ϵ_r , was higher than that reported earlier for La_2O_3 doped PBT glass ceramics [45]. Figure 7 shows the plots of dielectric constant ϵ_r and dissipation factor D versus temperature for the glass ceramic sample PBTL0.4875T; both plots have similar trends. The pattern shows that the dielectric constant increases gradually at 20 and 100 Hz with increasing temperature and remains invariant at other frequencies. The dielectric loss also increased gradually with increasing temperature. A signature of a broad peak has been observed in the dielectric plot at 20 Hz and 500°C having the very high value of ϵ_r which is the order of 80,000 and maybe it becomes more broadened at higher temperature. The dielectric constant ϵ_r was invariant up to 200°C at lower frequencies and was independent of

FIGURE 5: SEM micrographs of glass ceramic samples: (a) BTL0.0916T, (b) PBTL0.2941T, (c) PBTL0.2941S, (d) PBTL0.4654T, (e) PBTL0.4875T, and (f) PBTL0.4875S.

temperature at higher frequencies. The dielectric constant was strongly dependent on the composition and increased with the addition of PbO in place of Bi₂O₃ in the glassy matrix. The dielectric loss was found to be low in this glass ceramic system. The low dielectric loss was attributed to the addition of La³⁺ ions in the glassy matrix, which have smaller ionic radii than that of Ti⁴⁺ ions. La³⁺ ions act as acceptor ions and are very useful in reducing Ti⁴⁺ ions. La³⁺ ions may even substitute for Ti⁴⁺ sites and prevent the reduction of Ti⁴⁺ to Ti³⁺ by neutralizing the donor action of the oxygen vacancies, causing a decrease in the dielectric loss [46, 47]. If we compare our investigated results with earlier

reported results on crystallization and dielectric behaviors of perovskite (Ba, Sr)TiO₃ borosilicate glass ceramics it is observed that replacement of bismuth oxide in place of strontium oxide with doping of La₂O₃ enhanced the values of dielectric constant as well as dielectric loss [48, 49].

5. Conclusions

DTA pattern of the glass samples BTL0.0, PBTL0.2, and PBTL0.4 shows only two exothermic peaks while the rest of glass ceramic samples show the exothermic as well as endothermic peaks. The values of all exothermic peaks, T_{c1} ,

FIGURE 6: Variation of (a) dielectric constant and (b) dissipation factor with temperature at different frequencies for the glass ceramic sample PBTL0.2941T.

FIGURE 7: Variation of (a) dielectric constant and (b) dissipation factor with temperature at different frequencies for the glass ceramic sample PBTL0.4875T.

for all glass samples shift towards lower temperature side due to the different melting temperature and viscosity of the melts. The glass transition temperature, T_g , decreases as decreasing the amount of Bi_2O_3 . Bi_2O_3 helps in the promotion of the nucleation and growth and acts as nucleating agent. It is concluded that the major phase of bismuth titanium oxide ($\text{Bi}_4\text{Ti}_3\text{O}_{12}$) crystallized along with pyrochlore phase of bismuth oxoborate ($\text{Bi}_4\text{B}_2\text{O}_9$). The pyrochlore phase of bismuth oxoborate ($\text{Bi}_4\text{B}_2\text{O}_9$) disappeared when the same

glass samples crystallized at higher temperature 916°C . XRD patterns of these glass ceramic samples show orthorhombic crystal structure. The effect of heat treatment schedule for 3 and 6 hours changes the surface morphology of the crystallites. Very high value of dielectric constant of the order of 80,000 was found for 3-hour heat treated glass ceramic sample. The high dielectric constant was due to space charge polarization, which was attributed to the conductivity difference between the semiconducting grains and the insulating

grain-boundary in the glass matrix. La_2O_3 plays an important role as a nucleating agent for such type of glass ceramic samples.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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