Anomalous properties of chloroborosilicate glasses in the $\text{K}_2\text{O}-\text{BaO}-\text{Al}_2\text{O}_3-\text{B}_2\text{O}_3-\text{SiO}_2-\text{BaCl}_2$ system

NILANJANA SHASMAL^{1,2}, ANAL TARAFDER¹ and BASUDEB KARMAKAR^{1,*}

¹Glass Science and Technology Section, Glass Division, CSIR-Central Glass and Ceramic Research Institute, Kolkata 700 032, India

²Academy of Scientific and Innovative Research, Taramani, Chennai 600 113, India

MS received 31 March 2015; accepted 15 June 2015

Abstract. A series of chloroborosilicate glass having composition (in mol%) $(100-x)(42\text{SiO}_2-30\text{B}_2\text{O}_3-20\text{BaO}-4\text{K}_2\text{O}-4\text{Al}_2\text{O}_3)-x\text{BaCl}_2$ (where $x = 0-30$) has been prepared by the melt quench technique yielding transparent monolithic glasses up to $x = 22.5$. Structural investigation by infrared reflection and UV-vis-NIR absorption revealed the bridging action of Cl atom and decrease in non-bridging oxygens with the increase in BaCl_2 content. Thermal properties (T_g , T_d and T_s) were measured by the dilatometry and softening point measurement. Viscosity was calculated using the Vogel–Fulcher–Tammann equation. Elastic constants were measured by the ultrasonic method. Other mechanical properties like hardness, fracture toughness were also measured. All of the thermal and mechanical properties exhibited a similar trend of anomalous variation as a function of the BaCl_2 content, showing maxima at 10 mol% and a sharp increase at 25 mol% BaCl_2 content. The anomaly has been explained by the structural point of view with the help of the aforementioned spectroscopic data.

Keywords. Chloroborosilicate glass; anomalous property; viscosity; hardness; mechanical property.

1. Introduction

The phenomenon of anomalism is not very common in the structure–property relationship of glasses. Most of the properties usually exhibit monotonous trend of variation with the addition of various modifiers. Anomaly takes place when some structural change is involved, the extent of which depends on the composition. Up to certain composition some of the properties show gradual change followed by a sudden change of trend starting from a definite point of structural inversion. The most well-known anomaly is associated with the addition of alkali oxides, R_2O ($\text{R} = \text{Li}, \text{Na}$ and K) to borate glass which is famous as ‘boron oxide anomaly’ or ‘borate anomaly’. This phenomenon refers to the appearance of extrema in various property vs. composition relations for borate glasses, particularly alkali borate glasses. The best-known example is the minima observed in the curves of coefficient of thermal expansion vs. R_2O concentration.^{1,2} The anomalies have been explained as the competition between the formation of four-coordinated borons (which lowers α -values) and the formation of non-bridging oxygens (NBOs) (which raises α -values). At small concentrations of R_2O , the formation of four-coordinated borons was suggested to dominate and after a certain value, the formation of NBOs begin to dominate.^{3,4} According to Bischoff and Warren,³ for sodium borate glasses, up to 16%, Na_2O does not break linkages in the glass network by forming NBO, but transforms BO_3 units to BO_4 tetrahedral units. The latter participates in building

up the three-dimensional (3D) network thereby strengthening the glass matrix. The occurrence of such borate anomaly in glass is interpreted as $[\text{BO}_3] \rightarrow [\text{BO}_4] \rightarrow [\text{BO}_3]$. A number of structure models for boron oxide glass and molten boron oxide are reviewed by Krogh-moe.⁵ Two main types of models have been proposed, namely the random network model and the molecular model.⁶ The other models assume the glass to be built up from B_4O_6 molecules.⁷ The models are discussed with reference to spectroscopic data, diffraction data and other physical properties for boron oxide. Of the various structural models proposed for boron oxide glass, a random 3D network of BO_3 triangles with a comparatively high fraction of six-membered rings (boroxol rings) seems to give the best explanation for the available data.^{6–10}

Another well-known example is ‘germanate anomaly’ which is very much similar to the previous one. In vitreous germania (v-GeO_2) the coordination number of Ge is 4. Adding alkali oxide R_2O ($\text{R} = \text{Li}, \text{Na}, \text{K}$ and Rb) the density increases and shows a maxima near 15% R_2O .^{11–17} The reason behind this anomaly is assumed to be the change of coordination number of Ge, i.e., the formation of $[\text{GeO}_6]$ octahedra in the range of 0–15 mol% R_2O leading to densification, followed by the formation of $[\text{GeO}_4]$ tetrahedra and NBO above 15 mol% R_2O with the usual consequence of loosening the network.¹¹ This assumption was supported by different experiments such as optical^{12–15} and elastic^{16,17} measurements, EXAFS,^{18,19} Raman spectroscopy,¹⁹ neutron²⁰ and X-ray diffraction.^{21,22} Similar phenomenon is observed in case of ‘aluminium anomaly’ appearing in Al-doped silica glasses. It is found that the cause of the property anomaly is

*Author for correspondence (basudebk@cgcir.res.in)

the variation of Al coordination states. All the Al atoms are in such a position as to form $[\text{AlO}_4]$ units when the property variations are anomalous. The anomalous variation takes place in the range of 0–0.4 mol% Al_2O_3 . At 0.4 mol%, it is supposed that $[\text{AlO}_6]$ units begin to appear.²³ Another remarkable anomaly was found by Schultz in TiO_2 – SiO_2 system.²⁴ In the 0–10 wt% TiO_2 range, the 25–700°C thermal expansion coefficient (α_{25-700}) becomes more and more negative as TiO_2 content increases. When the TiO_2 content had reached 10 wt%, α_{25-700} had decreased to $-2.4 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$. Glasses in the 12–17 wt% TiO_2 range were metastable and showed structural rearrangements on heat treatment. Thermal treatment can produce almost any desired expansion from $\alpha_{-200+700} = -5$ to $10 \times 10^{-7} \text{ }^\circ\text{C}^{-1}$. This happens due to the change of coordination number of Ti, i.e., the phase separation of $[\text{TiO}_6]$ unit at higher TiO_2 content from the previous $[\text{TiO}_4]$ units present at TiO_2 content ≤ 10 wt%. Zero expansion between 0 and 550°C was obtained.²⁴

Nowadays halide glasses have become a centre of an increasing interest, due to the different kind of structure of glasses as compared to the conventional oxide glasses as well as for their potential use for making infra-red optical components and ultra-low-loss optical fibres.^{25–28} The history and present developments of glass chemistry are largely dominated by oxide systems. Halides, being the most electronegative elements, when associated with a metal, they have the tendency to form a purely ionic bond therefore forming a crystalline phase. So the challenge involved in obtaining a glassy state is to suppress the crystallization tendency so that the glass network formation can take place. Only a few metal halides have overcome it giving a 3D framework stabilized by strong covalent bonds. This kind of difficulty is responsible for their late discovery and limited use in everyday materials.^{29–32}

Although glasses based on ZnCl_2 were first observed over 80 years ago, practical application of ZnCl_2 glass is difficult due to its highly hygroscopic nature.^{29,33} CdCl_2 has also been reported as a glass-former material in the systems like CdCl_2 – BaCl_2 – NaCl , CdCl_2 – CdF_2 – BaF_2 , etc. But the system requires very high cooling rate to avoid the fast crystallization, therefore only thin hygroscopic samples have been obtained.³⁴ The glass-forming ability of BiCl_3 and ThCl_4 has been reported in systems like BiCl_3 – KCl and ThCl_4 – NaCl – KCl , etc. But they also exhibit very poor chemical durability in the presence of moisture.³⁵ The most stable composition includes both chlorides and fluorides in ternary or more complex combinations like CdCl_2 – BaCl_2 and CdCl_2 – BaF_2 systems.^{25,29} ZnBr_2 and CdI_2 have been reported as glass formers and they form far-IR transmitting glasses. The addition of PbCl_2 , PbI_2 , TlI and CsI enhances their chemical durability. But as their glass transition temperature is very low, they exhibit very poor stability.^{25,36}

Therefore it is evident that the biggest challenge for halide glasses is their hygroscopic nature as well as their high tendency towards crystallization. This is partially overcome in the oxychloride system Sb_2O_3 – PbCl_2 – ZnCl_2 . For this system the degradation of glass in the presence of moisture is

very small as compared to the halide glasses.³⁷ Oxychloride glasses in the Sb_2O_3 – CdCl_2 – SrCl_2 system is fairly stable having average glass transition around 300°C.³⁸ In recent times it was observed that the lead–antimony–tellurium oxychloride system with composition 70TeO_2 – $10\text{Sb}_2\text{O}_3$ – 20PbCl_2 forms stable glasses in a broad range of compositions as reported by Bošák *et al.*³⁹ Ternary glasses have been synthesized and studied in the Sb_2O_3 – PbCl_2 – MoO_3 system by Goumeidane *et al.*⁴⁰ The glass-forming regions in the PbCl_2 – PbBr_2 – P_2O_5 system were explored by Zhou *et al.*⁴¹ Oxychloride glasses based on the TeO_2 – ZnO – ZnCl_2 system provides a wide and stable glass formation range in which a T_c – T_g gap beyond 140°C.⁴² Bulk oxychloride glasses have been prepared in the TeO_2 – ZnO – ZnCl_2 and TeO_2 – PbO – PbCl_2 systems, they yield stable glass of good optical quality.⁴³ Barium chloride–oxide tellurite glasses in the system BaCl_2 – BaO – TeO_2 are studied by Sokolov *et al.*⁴⁴ where continuous network of barium chloride–oxide tellurite glass has been proved to be formed. However, demonstration of anomalous thermal and mechanical properties on the incorporation of BaCl_2 in borosilicate glass was not reported previously.

Thus it can be observed that chloride and oxychloride glass systems are not extensively investigated as compared to the conventional oxide systems so far. No anomalous structure or property has been reported. A series of chloroborosilicate glasses having composition (in mol%) $(100-x)(42\text{SiO}_2-30\text{B}_2\text{O}_3-20\text{BaO}-4\text{K}_2\text{O}-4\text{Al}_2\text{O}_3)-x\text{BaCl}_2$ (where $x = 0-25$) were prepared and characterized by Shasmal *et al.*⁴⁵ In this paper, further details of these glasses were investigated and found an anomalous trend in properties which can be explained by structural point of view. Anomalies are found in their several thermal and mechanical properties. They have been characterized by infrared reflection spectroscopy, UV–vis–NIR spectroscopy, dilatometry and viscosity, elastic constants, hardness and fracture toughness measurements.

2. Experimental

2.1 Glass preparation

The raw materials were quartz, SiO_2 (GR, Bremthaler, Quarzitwerk, Usinger, Germany), boric acid, H_3BO_3 (GR, 99%, LobaChemie, Mumbai, India), barium carbonate, BaCO_3 (GR, 99%, FlukaChemie GmbH, Buchs, Switzerland), potassium carbonate, K_2CO_3 (GR, 99%, LobaChemie, Mumbai, India), aluminium oxide, Al_2O_3 (GR, Aldrich Chemical Company Inc, Milwaukee 53233, USA) and barium chloride, $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (GR, dihydrated extra pure LobaChemie, Mumbai, India). They were used directly without any further purification. Briefly, 60 g of glasses were prepared by melting the well-mixed batches of calculated composition in a high-purity platinum crucible at 1400°C for 1.5 h with intermittent stirring for 0.5 min in air in a raising hearth electric furnace. All the molten samples were cast into an iron

plate in air and annealed at 550°C for 1 h in order to remove the residual thermal stresses, followed by a slow cooling down to room temperature. The monolithic glasses thus obtained were cut and polished into the desired shapes and sizes required for the different characterizations, as described below.

2.2 Characterization

The infrared reflection spectra (FT-IRRS) in the range of 400–4000 cm^{-1} were recorded with a Fourier transform infrared (FTIR) spectrometer (FTIR 1615, Perkin-Elmer Corporation, Norwalk, CT) and with the help of a specular reflectance attachment accessory at an incident angle of 15° and a resolution of ± 1 cm^{-1} by taking 256 scans. The UV–vis absorption spectra were obtained with a double-beam spectrophotometer (Lambda 950, Perkin-Elmer Corporation, Norwalk, CT). The uncertainty of the band position is ± 0.1 nm. All the measurements were carried out at room temperature.

The glass transition temperature (T_g) and dilatometric deformation temperature (T_d) were measured using a horizontal vitreous silica dilatometer (DIL 402C, Netzsch-Gerätebau GmbH, Bavaria, Germany) with a heating rate of 4 K min^{-1} after calibration with a standard alumina supplied with the instrument by the manufacturer. The T_g and T_d values were reproducible with $\pm 1^\circ C$ for all samples. The softening point (T_s) of each of the bulk samples was measured five times by a glass softening point system (Harrop/Labino, Model SP-3A) and the average values are reported. They are accurate to $\pm 2^\circ C$. The instrument was previously calibrated with a NBS (National Bureau of Standards, USA) standard glass of known softening point. The elastic constants were measured by the ultrasonic method in ultrasonic flaw detector (EPOCH 1000 series, Olympus, Japan) using longitudinal and shear contact transducers of frequency 5 MHz and shear wave couplant. The hardness and indentation fracture toughness properties of the samples were measured by taking micro-indentation on the polished surface of the samples. A microindentation hardness testing system (Clemex CMT, Longueuil, Canada) equipped with a conical Vickers and Knoop indenters was used at load of 25 g. Ten indents were taken for each sample under identical loading conditions and their averages are reported. The diagonals of the Vickers and Knoop indents were measured using an optical microscope attached to the equipment. All the measurements were carried out at room temperature.

3. Results

A series of samples were prepared having composition (mol%) $(100-x)(42SiO_2-30B_2O_3-20BaO-4K_2O-4Al_2O_3)-xBaCl_2$ (where $x = 0, 5, 7.5, 10, 15, 20, 22.5, 25, 27.5$ and 30). Up to $x = 22.5$ transparent monolithic glasses were obtained. All of them have been found to be X-ray amorphous. For $x = 25$ a devitrified glass was obtained which

Table 1. Composition of investigated samples.

Glass ID	Composition (mol%)					
	SiO ₂	B ₂ O ₃	BaO	K ₂ O	Al ₂ O ₃	BaCl ₂
N1	42.00	30.00	20.00	4.0	4.0	0
N2	39.90	28.50	19.00	3.8	3.8	5.0
N3	38.85	27.75	18.50	3.7	3.7	7.5
N4	37.80	27.00	18.00	3.6	3.6	10.0
N5	35.70	25.50	17.00	3.4	3.4	15.0
N6	33.60	24.00	16.00	3.2	3.2	20.0
N7	32.55	23.25	15.50	3.1	3.1	22.5
N8	31.50	22.50	15.00	3.0	3.0	25.0
N9	30.45	21.75	14.50	2.9	2.9	27.5
N10	29.40	21.00	14.00	2.8	2.8	30.0

Figure 1. Fourier transformed infrared reflection spectra (FT-IRRS) of the polished glasses N1–N8 (for composition see table 1).

was transparent but slightly cloudy in appearance. For $x = 27.5$ and 30, crystallized broken pieces were obtained. Their compositions are listed in table 1.

3.1 Fourier transformed infrared spectroscopy

The infra-red reflection spectra were recorded for all the transparent samples (N1–N8), as shown in figure 1. Sharp bands were found in the regions 1360, 1251, 1010–968, 907, 840, 685, 618, 481 and 429 cm^{-1} . The band around 1360 is due to B–O vibration related to $[BO_4]$ groups and 1250 cm^{-1} is due to B–O vibration related to $[BO_3]$ groups.^{45,46} The band having highest intensity is around 1010–968 cm^{-1} , is due to anti-symmetric stretching vibration of Si–O–Si bond of $[SiO_4]$ units,^{30,47} gradually shifting to lower wavenumber region from N1 to N8. The bands around 907 cm^{-1} is due to $-O-Si-O-$ stretching vibration with two NBOs.⁴⁸ These bands are prominent for N8–N10, which are devitrified materials. This is because the crystallization of $BaCl_2$ results in the formation of NBOs. Bands around 840 cm^{-1} are due to

Table 2. IR band position and assignment.

Band position (cm^{-1})	Assignment of band
1360	B–O vibration related to tetraborate $[\text{BO}_4]$ groups
1251	B–O vibration related to triborate $[\text{BO}_3]$ groups
1010–968	Anti-symmetric stretching vibration of Si–O–Si of $[\text{SiO}_4]$ units
907	$^-\text{O}-\text{Si}-\text{O}^-$ stretching vibration with two NBOs
840	Stretching vibrations of B–O of $[\text{BO}_4]$ units
685	B–O bending vibration modes of $[\text{BO}_3]$ units
618	O–Si–O symmetric stretching vibration of $[\text{SiO}_4]$ units
481–429	Si–O–Si bending modes of $[\text{SiO}_4]$ units

stretching vibrations of B–O of $[\text{BO}_4]$ units and B–O bending vibration modes of $[\text{BO}_3]$ units, respectively.^{49–51} The bands around 618 and 481–429 cm^{-1} are due to O–Si–O symmetric stretching vibration and Si–O–Si bending modes of $[\text{SiO}_4]$, respectively.^{47,48} The band assignments are shown in table 2.

3.2 UV-vis-NIR spectroscopy

The ultraviolet-visible-near infrared absorption spectra were measured for bulk samples of 2 mm thickness in the range of 250–3300 nm. The glasses are transparent within the whole visible region. Two absorption bands were observed in the range 250–350 and 2700–3200 nm. Figure 2 represents the absorbance within the whole experimental range. The inset shows the variation of absorbance in the UV region. From this figure it is evident that the position of the cut off wavelength or fundamental absorption edge for a particular value of absorbance shifts to lower wavelength region. For example, at 0.75 absorbance unit UV cutoff wavelength shifts from 292 to 273 nm with the increase in BaCl_2 content from N1 to N7. From N1 to N7 the decrease in UV cutoff wavelength is linear. After that N8 exhibits a sharp increase to 310 nm.

Figure 2. Representative UV-vis-NIR absorption spectra of the polished glasses N1, N2, N3, N4, N6 and N8. Inset shows the absorbance in the UV range in enlarged form showing the variation of UV cutoff wavelength (for composition see table 1).

3.3 Dilatometry

Glass transition temperature (T_g) and dilatometric softening point (T_d) were measured by dilatometric measurement taking a cylindrical sample of approximately 25 mm length and 5 mm diameter and heating it at a rate of 5 K min^{-1} up to the temperature where the glass softens. The value of T_g gradually increases from 621 to 642°C for N1–N4 and then it decreases to 612°C up to N7. For N8, T_g again increases to 632°C. The value of T_d also exhibit the same trend as T_g . T_d values are about 30–40°C higher than T_g values. It gradually increases from 664 to 678°C for N1–N4 and then decreases to 650°C up to N7. For N8 it is much higher. It is about 130°C higher than its T_g . The variation of T_g and T_d as a function of BaCl_2 content is shown in figure 3.

3.4 Softening point measurement

Softening point (T_s) was measured by a glass softening point system taking a glass block of approximately 5 mm length,

Figure 3. Variation of T_g , T_d and T_s as a function of BaCl_2 content (for composition see table 1).

5 mm width, and 3 mm thickness and heating it at a rate of 25 K min^{-1} up to the temperature where the glass softens. The values of T_s are in between 50°C above the T_d values. The T_s values also follow the same pattern as T_g and T_d . T_s gradually increase from 711 to 721°C for N1–N4, then decreases to 703°C for N6. T_s values for the rest of the samples cannot be recorded for instrumental limitation up to 800°C . The variation of T_s as a function of $BaCl_2$ content is shown in figure 3.

3.5 Viscosity

An estimate of viscosity values at high temperatures has been done using an indirect method. The relationship between temperature and viscosity of glasses can be calculated indirectly using the data provided by dilatometry and softening point measurement. The calculation is based on the Vogel–Fulcher–Tammann (VFT) equation

$$\log \eta = A + \frac{B}{T - T_0}. \quad (1)$$

The parameters A , B and T_0 have been determined by introducing three pairs of known viscosity–temperature (η , T) values into this equation. The calculations are based on the assumption that the viscosity of glasses at several characteristic points can be considered constant. At glass transition temperature (T_g), $\eta = 10^{13}$, at dilatometric softening point (T_d), $\eta = 10^{12}$ and at Littleton softening point (T_s), $\eta = 10^{7.6}$ dPa S (1 dPa S = 1 poise).^{30,31}

By solving the system of equations and applying VFT equation, the values of viscosity have been calculated over the entire temperature range in between the glass transition temperature and softening temperature. The calculation has been carried out using the data obtained from dilatometry and softening point measurement. The variation of viscosity as a function of $BaCl_2$ content at different temperatures is shown in figure 4. From the figure it is evident that at lower temperature the values of viscosity do not differ much with composition. But at relatively higher temperature ($\geq 680^\circ\text{C}$) the variation is clearly visible. The viscosity coefficient appears to be a function of $BaCl_2$ content. It also exhibits the same trend of variation as T_g , T_d and T_s , showing a gradual increase followed by a gradual decrease having a maxima for N4, i.e., at 10 mol% $BaCl_2$ content.

3.6 Mechanical properties

3.6a Elastic constants: The elastic constants were calculated using the following equations for calculation of the elastic constants of the glass specimen at room temperature by the ultrasonic method using the measured density (ρ), longitudinal velocity (V_L) and shear velocity (V_s).^{52,53}

3.6b Longitudinal modulus (L): The ratio between longitudinally applied stress and the longitudinal strain is obtained for longitudinal wave propagation as

$$L = \rho V_L^2. \quad (2)$$

Figure 4. Variations of log viscosity as a function of $BaCl_2$ content at different temperatures (for composition see table 1).

The values of L vary in the range 79–128 GPa. The variation of L as a function of $BaCl_2$ content is shown in figure 5a.

3.6c Shear modulus (G): The shear modulus can be found from shear velocity as

$$G = \rho V_s^2. \quad (3)$$

The values of G vary in the range 27–39 GPa. The variation of G as a function of $BaCl_2$ content is shown in figure 5b.

3.6d Bulk modulus (K): The ratio between bulk stress and bulk strain is obtained from the ultrasonic velocities as

$$K = L - (3/4) G. \quad (4)$$

The values of K vary in the range 43–75 GPa. The variation of K as a function of $BaCl_2$ content is shown in figure 5d.

3.6e Young's modulus (E): It is defined as the ratio between unidirectional stress and resultant strain and is given as

$$E = 2G(1 + \sigma), \quad (5)$$

where σ is Poisson's ratio. The values of E vary in the range 67–101 GPa. The variation of E as a function of $BaCl_2$ content is shown in figure 5c.

3.6f Poisson's ratio (σ): It is the ratio between lateral and longitudinal strain produced when tensile force is applied, as given by the relation

$$\sigma = (L - 2G) / 2(L - G). \quad (6)$$

Figure 5. Variation of (a) longitudinal, (b) shear, (c) Young's and (d) bulk moduli of the samples as a function of BaCl₂ content (for composition see table 1).

The values of Poisson's ratio vary between 0.24 and 0.3. Values of σ are listed in table 3.

3.6g Acoustic impedance (Z): The transmission and reflection of sound energy in the glass specimen is determined using the acoustical impedance

$$Z = V_L \rho. \quad (7)$$

The values of acoustic impedance vary between 16,654 and 21,822 kg m⁻² s⁻¹. Values of Z are listed in table 3.

3.6h Mean ultrasonic velocity (V_m): V_m can be calculated using the relation

$$V_m = \left[\frac{1}{3} \left(\frac{1}{V_L^3} + \frac{1}{V_S^3} \right) \right]^{-1/3}. \quad (8)$$

The calculated values of V_m have been listed in table 3.

3.6i Debye temperature (θ_D): The Debye temperature θ_D of the samples is calculated from the relation

$$\theta_D = \frac{h}{K} \left(\frac{9N}{4\pi V} \right)^{1/3} V_m, \quad (9)$$

where h , K , N , V and V_m are Planck's constant, Boltzmann's constant, Avagadro's number, the molar volume and the mean ultrasonic velocity of the sample, respectively. The values of θ_D are listed in table 3.

3.6j Microhardness (H): Microhardness can be calculated from the relation

$$H = (1 - 2\sigma) \frac{E}{6(1 + \sigma)}. \quad (10)$$

The calculated microhardness values are listed in table 3.

Table 3. Some calculated and measured mechanical properties.

Properties	Glass ID/property values							
	N1	N2	N3	N4	N5	N6	N7	N8
<i>Calculated properties</i>								
Poisson's ratio, σ	0.2266	0.2827	0.2831	0.2920	0.3054	0.3081	0.2408	0.2762
Acoustic impedance, Z ($\text{kg m}^{-2} \text{s}^{-1}$)	16,654	18,580	19,001	19,479	19,473	19,038	17,034	21,822
Mean ultrasonic velocity, V_m (m s^{-1})	3468	3424	4172	4146	3982	3819	3688	4468
Debye temperature, θ_D (K)	496	491	462	435	417	502	496	491
Microhardness, H (GPa)	5.6516	4.5491	4.6016	4.4208	3.8655	3.5534	4.6729	5.9109
<i>Measured properties</i>								
Vickers hardness, HV (GPa) ± 0.05 GPa	5.7456	5.9132	5.4593	4.8592	4.6705	5.9534	5.4992	5.6102
Knoop hardness, KHN (GPa) ± 0.05 GPa	5.5593	5.7599	6.2082	5.5917	5.1973	4.6461	4.5621	4.9891

Figure 6. Representative images of Vickers indentation impressions on (a) N1 and (b) N8, and Knoop indentations on (c) N1 and (d) N8.

3.6k Knoop and Vickers hardness: The hardness was calculated using the standard equations for the Vickers and Knoop geometry⁵⁴

$$HV = 1.8544P/d^2, \quad (11)$$

$$KHN = 14.23P/d^2, \quad (12)$$

where HV and KHN are the Vickers and the Knoop hardness number, respectively, in kg mm^{-2} , P is the normal load in kg, and d the average diagonal length of the indentation in mm. The values of hardness are converted in GPa by multiplying the factor 0.009807 and listed in table 3. KHN and HV vary between 4.5–6.2 and 4.6–5.9 GPa. They are accurate to ± 0.05 GPa. They show almost the same trend as the elastic constants giving a maxima region around 5–10 mol% $BaCl_2$ content. Representative images of Vickers and Knoop indentations are shown in figure 6.

It may be mentioned here that the Vickers hardness data do not correlate well with other mechanical properties, for example different moduli and fracture toughness (discussed later) of the glasses investigated here. For this reason, the Knoop hardness (KHN) of the glasses have been evaluated and these data are found to be more correlated with the other mechanical properties of the glasses than that of Vickers hardness. Consequently, the Knoop hardness (KHN) data have also been considered and presented here.

3.6l Fracture toughness (K_{Ic}): Antis *et al*⁵⁵ proposed the following equation for calculation of the fracture toughness (K_{Ic}) from the cracks generated during indentation:

$$K_{Ic} = \alpha \left(\frac{E}{H} \right)^{0.5} \left(\frac{P}{C^{1.5}} \right). \quad (13)$$

Here, P is the applied load and C the mean length of the two radian cracks. E and H Young's modulus and the hardness of the sample, respectively, measured at the same applied load P at which the K_{Ic} for the sample is measured. For Vickers indenters α -value was taken as 0.016. Fracture toughness is in between 0.18 and 0.23 $\text{MPa m}^{0.5}$. The trend of variation of K_{Ic} as a function of $BaCl_2$ content is also as same as all the elastic constants, as shown in figure 7.

4. Discussion

In FT-IRRS it is observed that the band having highest intensity is gradually shifting to lower wavenumber region from N1 to N8. This can be explained by the change of bond connectivity taking place with $BaCl_2$ incorporation. The fundamental vibration frequency, ν (in cm^{-1}) of a linear harmonic oscillator can be expressed by the Szigeiti relation as follows:⁵⁶

$$\nu = (k/4\pi^2c^2\mu)^{0.5}, \quad (14)$$

where k is the force constant, c the speed of light and μ the reduced mass. The μ can be defined as

$$\mu = m_1^{-1} + m_2^{-1}, \quad (15)$$

Figure 7. Variation of fracture toughness of the samples as a function of BaCl₂ content (for composition see table 1).

where m_1 and m_2 are the masses of the two bond forming atoms or ions (e.g., $m_1 = \text{Si}^{4+}$ and $m_2 = \text{O}^{2-}$). Thus the IR absorption edge shifts to lower wavenumber (lower ν) for heavier atomic masses or due to reduced force constant (k) of the bond by the weak Columbic interaction. Therefore the shifting may be attributed to some structural alteration caused by the incorporation of BaCl₂. Possible reactions for structural modifications are

Thus the replacement of O atom in Si–O–Si bond by Cl atom, thus forming Si–Cl–Si bond and therefore increasing the reduced mass which leads to shifting the reflection band to a lower wavenumber region, from 1010 to 968 cm^{−1}. Therefore this shifting indicates the replacement of both bridging and NBO groups with Cl atoms. Such bridging actions of Cl atom have also been observed in systems like CdF₂–PbCl₂³⁴ and BaF₂–ZrF₂Cl₂.⁴⁷ The structural models of these systems clearly show that Cl has the capacity of forming bridging bond between two glass former cations. The band at 907 cm^{−1} which is due to the NBO atoms in [−]O–Si–O[−] unit is more prominent in N8 which is a devitrified glass. This indicates the phase separation of crystallized components, resulting in the formation of more NBOs.^{57,58}

In case of UV–vis–NIR spectroscopy the UV cutoff wavelength shifts towards lower wavelength region up to N7. This is because the decrease in number of NBO atoms. This is the effect of increasing amount of BaCl₂ incorporation. As more and more amount of BaCl₂ is added to the system,

the chloride ion behaves like a bridging element by linking two glass former cations (Si and B). As indicated from FTIR spectra, some of the chloride ions replace some of the bridging oxygen atoms between the glass former cations and some of them form bridging bonds replacing some NBOs therefore reducing the number of NBOs. As result some of the Si–O–Si linkages get transformed into Si–Cl–Si linkage. Also some glass forming cations which were not connected before get connected through some Cl atoms. On the other hand, with increasing amount of BaCl₂ addition, number of Ba²⁺ ions also increases, which are responsible for the increase in NBOs. Each Ba²⁺ ion creates 2 NBOs. So for each BaCl₂ molecule, the system is getting 2 NBOs from the Ba²⁺ part and 4 bridging bonds (2 for each Cl[−]) from the Cl[−] part. Clearly the bridging effect predominates over the effect of the formation of NBOs, resulting in net decrease in number of NBOs, consequently shifting of UV cutoff wavelength to a lower value. For N8, which is a devitrified glass, the cutoff wavelength is shifted to a much higher wavelength. This is due to the Rayleigh and Mie scattering effect manifested by the tiny crystals present within it,^{59,60} as well as the increase in NBOs due to the phase separation of nanocrystalline BaCl₂ from the glass network.

The glass transition temperature (T_g), dilatometric softening point (T_d) and softening point (T_s)—all of them show the same trend of variation, a gradual increase followed by a gradual decrease with the increase in BaCl₂ content, having a maxima at 10 mol% BaCl₂ (figure 3). Not only the thermal properties; viscosity, all the elastic constants, fracture toughness exhibit the same trend of variation. They can be explained by a structural alteration taking place with the increase in the amount of BaCl₂. This has been represented by the schematic diagram (figure 8) showing the effect of chloride ions in the borosilicate glass system.

Figure 8a represents the structure of borosilicate glass before the addition of BaCl₂. Figure 8b shows the change in the structure in the presence of BaCl₂ (≤ 10 mol%). As shown in the figure the chloride ions form a bridging bond between the glass forming cations, therefore increasing the network connectivity of the glass system. The bridging action has been confirmed by the shifting of reflection band in FTIR spectra, as well as, by the decrease in UV cutoff wavelength in UV–vis–NIR spectra, as discussed earlier. This strengthening effect is observed up to 10 mol% BaCl₂ inclusion. At this point the system gets maximum network connectivity therefore achieves maximum strength. This is reflected in all the thermal and mechanical properties. Maximum bridging bonds give maximum compactness in structure which results in requirement of maximum energy to cause thermal or mechanical deformation. This kind of phenomenon was observed by Iezid *et al* in the Sb₂O₃–CdCl₂–SrCl₂ system. In this system an increase in T_g up to a certain amount of CdCl₂ incorporation was observed which was described to be the effect of the intercalation process of ionic species (Cd²⁺, Sr²⁺ and Cl[−]) between (SbO₃)_n layers. The electrostatic interaction between anions and cations increases the overall stability of the material. As a result, the thermal energy

Figure 8. (Colour online) Schematic diagram of the glass network in the SiO_2 – B_2O_3 – BaO – K_2O – Al_2O_3 system (a) before $BaCl_2$ addition, (b) after the addition of $BaCl_2$ up to 10 mol%, (c) after addition of 10–22.5 mol% $BaCl_2$ and (d) after the addition of $BaCl_2$ beyond 22.5 mol% causing devitrification (for composition see table 1).

required to reach glass transition also increases. There was only the possibility of ionic interaction due to the structural geometry of glass forming units, i.e., SbO_3 groups. SbO_3 has pyramidal structure giving no scope to the Cl atoms for any bonding interaction.³⁸ But in borosilicate system the glass forming units, which are SiO_4 , BO_3 and BO_4 groups, do not have such structural hindrance, therefore allowing the bridging possibility of Cl atoms.

Beyond 10 mol%, further addition of $BaCl_2$ exhibits the opposite effect. This is because of the size factor of the incoming species. The ionic radius of Ba^{2+} is 1.49 Å which is huge compared to the rest of the constituents (covalent radii of Si = 1.11 Å, O = 0.73 Å and B = 0.82 Å).^{61,62} Initially up to certain amount of $BaCl_2$ incorporation, the system can accommodate the huge Ba^{2+} ions and the bridging effect of Cl predominates. But beyond that point, the system can no longer make space for the incoming Ba^{2+} ions and gets compelled to expand itself to accommodate the increased number of Ba^{2+} ions. As result the individual molecular chains get separated from each other, as shown in figure 8c. And this kind of structural alteration results in looser network, consequently the T_g , T_d and T_s values gradually go down. Also the viscosity and all the elastic constants gradually decrease.

For N8, i.e., for $x = 25$ mol% the glass gets devitrified. As shown in figure 8d, the bridging Cl groups combine with Ba^{2+} ions forming nanocrystalline phase of $BaCl_2$ and thereby reformation of NBOs take place. Thus the number of NBOs get increased which was also indicated by FTIR and UV–vis spectra. Due to the presence of the crystalline phase the system becomes more strong and rigid. That is why a sharp increase for N8 in all the thermal and mechanical properties was obtained.

5. Conclusions

Chloroborosilicate glasses having composition (in mol%) $(100-x)(42SiO_2-30B_2O_3-20BaO-4K_2O-4Al_2O_3)-xBaCl_2$ (where $x = 0-30$) were prepared by the melt quench technique and characterized. The following conclusions may be drawn from their thermal and mechanical properties and structural investigations:

- Transparent and X-ray amorphous glasses were obtained up to $x = 22.5$. Beyond that, the glass gets devitrified.
- Both FTIR and UV–vis–NIR spectra reveal that the Cl atoms act as bridging element. As the $BaCl_2$ content increases the number of NBOs decreases.

- Glass transition temperature (T_g), dilatometric softening point (T_d) and softening temperature (T_s) show a gradual increase followed by a gradual decrease giving a maxima at 10 mol% BaCl₂ content.
- Calculated viscosity coefficients also exhibit the same anomalous trend of variation as a function of BaCl₂ content. The anomaly is more clearly visible at higher temperatures.
- Longitudinal, shear, bulk and Young's modulus—all the elastic constants show a maxima at 10 mol% BaCl₂ content and a sharp increase for the devitrified glass. Fracture toughness values also exhibit the same kind of variation.
- These anomalies can be explained by a structural alteration taking place with BaCl₂ incorporation. Up to 10 mol% the bridging effect of Cl predominates over the size factor of Ba²⁺, increasing the compactness of the system. Further addition of BaCl₂ causes loosening of structure due to the presence of excess Ba²⁺. At 25 mol%, development of BaCl₂ nanocrystalline phase results in sharp increase in mechanical strength.

Acknowledgements

We are thankful to Mr Kamal Dasgupta, Acting Director of the institute and Dr Ranjan Sen, Head, Glass Division for their encouragement and support. We are also thankful to Dr Kalyandurg Annapurna for recording of FTIR spectra. NS would like to express her sincere gratitude for the financial support of the Academy of Scientific and Innovative Research (AcSIR) and Council of Scientific and Industrial Research (CSIR).

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