Optical Analysis of Metal Oxide Borosilicate ($xCaO(1-x-z)\ SiO_2\ zB_2O_3$) glasses with varying concentrations of boric oxide (B_2O_3)

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***Abstract*—Glass sample compositions of $xCaO(1-x-z)\text{-}SiO_2\ zB_2O_3$ with constant nominal CaO of x=33.33 mol% and varying concentrations of B_2O_3 as z=50,60 and 66.67 mol% are prepared by conventional melt quench technique. Fourier transform infrared (FTIR) spectra of $xCaO(1-x-z)\text{-}SiO_2\ zB_2O_3$ glass system has been measured in the spectral range 400–4000 cm^{-1} low-frequency region 1700cm^{-1} to 400cm^{-1} and high-frequency region 4000cm^{-1} to 1700cm^{-1}) at room temperature to understand the characteristic frequencies of the chemical bonds, bonding mechanisms and structure of electron shell of atoms, for the purpose to determine the molecular structure of the composition. It is found that the melting temperature of the glasses decreases with the increase of B_2O_3 concentration and the melting temperature in the range of 950°C-1100°C for the samples which consist of 50, 60, and 66.67 mol% of B_2O_3. In the low-frequency region (1700cm^{-1} to 400cm^{-1}) the spectra of high B_2O_3 containing glass showed an increased number of distinct peaks and several broad Gaussian in the thigh-frequency region (1700cm^{-1} to 400cm^{-1}). All the spectra are based on line corrected and deconvoluted to the appropriate number of Gaussians. Fourier transform infrared (FTIR) deconvoluted spectra were analyzed to determine the exact position and relative amounts of the IR bands responsible for the different silicate borates units. The distinct peaks and peak position of the deconvoluted Gaussians are assigned to Si-O-Si, B-O-B, Si-O-Ca, Si-O etc. bonds based on the previous scientific investigations. The presence of B_2O_3 in the materials suggests that B^{3+} occupies the network position and for the linkage Si-O-B in the glasses. The amorphous nature, the surface topography and composition of the prepared glasses was checked by X-ray diffraction (XRD) and scanning electron microscopy (SEM) techniques respectively on optical inspection, did not show any evidence of phase separation, and all glasses are homogeneous.**

Keywords: Borosilicate glass, Fourier transform infrared (FTIR) spectra, X-ray diffraction, surface topography.

I. INTRODUCTION

Borosilicates are among the most commonly used oxide glasses, finding widespread application in heat and chemical-resistant containers, and in a variety of optical components. In many high-tech glass materials boric oxide (B_2O_3) is widely used as a network forming constituent owing to its contribution to glass-forming ability and low melting temperature and for its optimum impact on thermal, mechanical, and optical properties. The interesting feature of such glass is in alkali borosilicates BO_3 groups converted to BO_4 groups without the formation of significant numbers of non-bridging oxygens (NBOs) [1] but at high alkali or alkaline-earth contents, the excess oxygens act as non-bridging oxygens and result in a de-polymerization of the network and the conversion from BO_4 to BO_3. For the homogeneous speciation reaction $BO_4 \rightleftarrows BO_3 + O_{NBO}$. Temperature and pressure also affect the boron coordination and hence cause changes e.g. in density, thermal expansion and mechanical properties of the glass [2-6]. Borosilicate glass contains glass-forming constituent silica and boron oxide which includes at least five percent boric oxide (B_2O_3) [7]. The boric oxide (B_2O_3) makes the glass resistant to extreme temperature and also improves its resistance to chemical corrosion. Glass formation in the binary system CaO-SiO2 goes up to about 33.33 mol % CaO; however, in a large part of this area liquid-liquid phase separation prevents single-phase glasses [8]. In all crystalline silicates the silicon ions are coordinated by four oxygen ions. The simplest silicate glass is vitreous silica. In vitreous silica all silicon ions are also coordinated by four oxygen ions [9]. There is a certain distribution in the bond angles, evidenced by X-ray analysis, which makes the structure of vitreous silica quite uniform at a short-range, but there is no order beyond several units of SiO_4 tetrahedral [10]. Various other properties of vitreous silica are also in agreement with the random network model, for instance, infrared absorption, XRD. Here SiO_2 and B_2O_3 are the principle modifier. For the quantitative analysis of IR spectra of glasses, the author used the most significant deconvolution method [11,12]. Deconvolution of IR spectra can be considered a useful tool to extract information about glass structure rather than the traditional analysis of IR spectra [13]. An infrared spectrum is commonly obtained by passing infrared radiation through a sample and determining what fraction of the incident radiation is absorbed in particular energy. The energy at which any peak in an absorption spectrum appears corresponds to the frequency of vibration of a part of a sample molecule. The vibrations of molecules will be looked at here, as these are crucial to the interpretation of infrared spectra [14]. The infrared spectrum which contains a large number of absorption bands in a molecule causes to stretch and bend with respect to one another i.e. set into vibration. If the vibration involves a change in the dipole moment of the molecule due to the interaction with infrared radiation, then the transition of vibrational energy levels takes place with the observable spectrum [15,16]. In this work we have collected infrared spectra of $xCaO(1-x)\text{-}SiO_2$ glass with varying amounts of B_2O_3 and qualitative and quantitative analyses of these spectra were performed to understand the bonding

mechanisms, characteristic frequencies of the vibrational chemical bonds, which are liable to the structural and spectral changes. XRD pattern and SEM images of heat-treated samples are also used to study the amorphous nature and the surface topography and compositions of the prepared glasses. It is obvious from the XRD pattern there is no evidence of phase separation.

II. EXPERIMENTAL

For the preparation of the $xCaO(1-x-z)-SiO_2$ zB_2O_3 glasses commercially available raw materials silica (SiO_2), Calcium Carbonate ($CaCO_3$) and Boric Acid (H_3BO_3) were selected as initial materials expressed in mol%. The powder raw materials of appropriate amounts, usually 20 gm batch, were first finished dust by mortar and pestle then homogenized by rolling and shaking on a ball-milled machine for 4-6 hours and then melted in an alumina crucible in an electric furnace. The temperature of the furnace was raised to the required level within 3 hours keeping the sample in a crucible in the furnace and the required temperature was maintained for half an hour. These procedures were used to melt the composition of 50, 60 and 66.67 mol% of B_2O_3. The glass was melted then poured onto a milled steel block coated with graphite and was quenched by pressing with another block of the same materials. The composition, melting temperature, optical quality and XRD information along with their nomenclature are shown in table 1.

To obtain IR absorption spectra of glass samples, the KBr pellet technique is employed. In this work glass samples were grounded in a clean mortar to a fine powder and weighed quantity (~0.003gm) of the powder was mixed intimately with desiccated highly purified (99.99%) KBr powder (0.02gm). The mixture was then pressed with a pressure of 5 tons per square inch to yield a transparent pellet of the approximate thickness of 0.01mm suitable for mounting in the spectrometer. All infrared spectra of the glasses were collected on a Perkin Elmer Spectrophotometer over the range of wave numbers 400 cm^{-1} to 4000 cm^{-1}. The resolution of the instrument was 4 cm^{-1}. The X-ray diffraction spectra were collected to ascertain the non-crystal of glass samples using a BRUKER D8 ADVANCE powder diffractometer utilizing Cu Ka (λ=1.5405). The 2 theta scans were recorded 10^0 to 70^0 with 0.02^0 step width. XRD patterns of heat-treated samples were also collected to determine the phases that crystallize upon heat treatment.

TABLE I. STYLES

Glass Samples	*Nominal composition mol%*			*Melting temperature ^0C*	*Optical quality*	*XRD*	*SEM*
	CaO	SiO_2	B_2O_3				
CaSB50	33.33	16.67	50	1100	Clear	Amorphous	Dense and compact
CaSB60			6.67	60	1050	Clear	Amorphous	Dense and compact
CaSB66.67			0	66.67	950	Clear	Amorphous	Compact and Elongated grain surface

Nominal composition, melting temperature, optical quality and XRD information of glasses of various compositions.

III. RESULT

The infrared spectra recorded for $xCaO(1-x-z)-SiO_2$ zB_2O_3 base glasses are shown in fig.1. The infrared spectra of $xCaO(1-x-z)-SiO_2$ zB_2O_3 have been studied in the frequency range 400 cm^{-1} to 4000 cm^{-1} and interpreted in terms of chemical bonding. For CaSB50 base glass, there are distinct peaks at 480 cm^{-1}, 614 cm^{-1}, 680 cm^{-1}, 754 cm^{-1}, 1144 cm^{-1}, 1291 cm^{-1}, 1679 cm^{-1} in low frequency region. On the other hand, 2378 cm^{-1}, and 3435 cm^{-1} peaks are found in the high-frequency region. Comparably for CaSB60 base glass, there are distinct peak at 472 cm^{-1}, 555 cm^{-1}, 637 cm^{-1}, 780 cm^{-1}, 1181 cm^{-1}, 1307 cm^{-1} 1476 cm^{-1} and 1606 cm^{-1} in the low frequency region and 2018 cm^{-1}, 2378 cm^{-1} and 3437 cm^{-1} in the high frequency region. For the increase of B_2O_3 composition peak positions are slightly shifted. The low-frequency band has a relatively higher intensity than the high-frequency band peaks. From the figure very strong peaks are found at 1291 cm^{-1} for CaSB50, 780 cm^{-1} for CaSB60, 1166 cm^{-1} for CaSB66.67. In the high-frequency, region peaks are broad composition. Shoulders are increased for the increase of composition. Whereas there is no shoulder for composition CaSB50 but by increasing becomes three different shoulders for composition CaSB66.67.

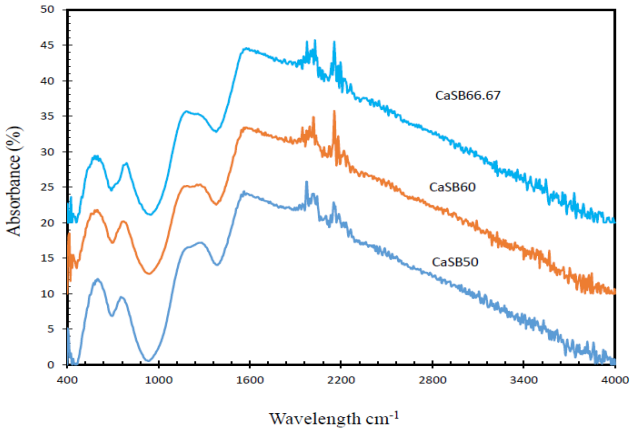
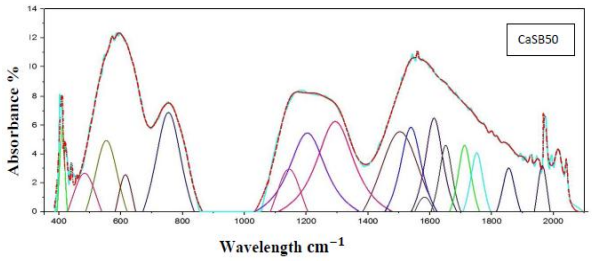


Fig. 1. Base Line corrected Infrared Spectra of $xCaO(1-x-z)-SiO_2$ zB_2O_3 Base Glasses (where z = 50, 60, 66.67 mol%).

The IR spectra in Fig.1 consist of broad absorption bands and it is difficult to identify the exact position of the absorption band. For this reason, deconvolution of these bands can be considered a useful tool to obtain the exact position of the absorption bands. All the spectra of sample glasses are baseline corrected using a baseline computer program (origin pro8). All the spectra are deconvoluted to several Gaussians according to their spectral shape and are considered to be true representations of the spectra. The

position of the bands can be obtained from the deconvolution of the IR spectrum. The deconvoluted parameters described for each band position are summarized in Table-2 for base sample. The process makes it possible to calculate the relative area of each component band. Each component band is related to some type of vibration in a specific structural group.



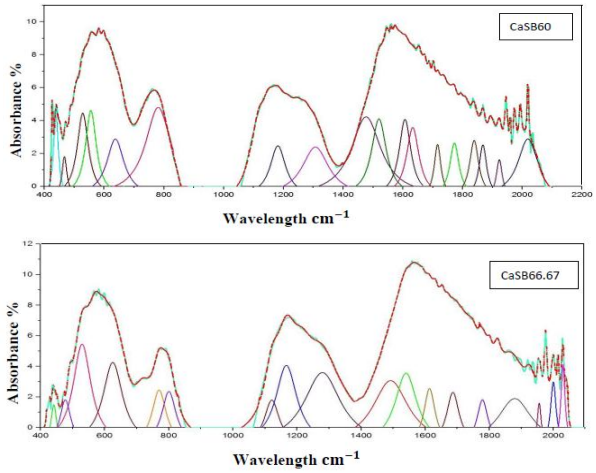


Fig. 2. Deconvoluted spectra of $xCaO(1-x-z)\text{-}SiO_2\,zB_2O_3$ (where z= 50,60 and 66.67mol%).

TABLE II. STYLES

Description of modes	Assigned Chemical bonds	Band Position cm^{-1}			Absorption bands(cm^{-1}) of other glasses	Corresponding Reference
		CaSB50	*CaSB60*	*CaSB66.67*		
Bending vibration	Si-O-Si	480	472	478	~450 ~460 450-480 **472-480**	[17] [18] [19] Present work
Bending vibration	Si-O-B	614	637	625	~680 **614-637**	[20] Present work
Bending vibration	Si-O-H	1202	1476	1279 1491	- **1202-1491**	- Present work
Bending Vibration	B-O-B	410	438	441	423-450 **410-441**	[21,22] Present work
Bending vibration	B-O	614 754	637 780	625 769	400-780 **614-780**	[23] Present work
Bending Vibration	H-O-H	1617 1648	1632 1715	1613 1686	1600-1660 1610-1650 1615-1649 1620-1640 1629 1640 1674 **1613-1715**	[24] [25] [26] [27] [28,29] [30,31] [32] Present work
Bending vibration	O-H	1501 1542	1476 1519	1491 1539	1590-1700 1450-2090 ~1640 1620-1640 1610-1650 1600-1660 **1476-1542**	[33,34] [35] [36] [37] [38] [24] Present work
Asymmetric bending vibration	Si-O-Ca	553 1614	555 637	529 625	570 600-660 **529-637**	[39] [40] Present work
Symmetric stretching vibration	O-Si-O	-	780	800	800 **780-800**	[41] Present work
Stretching vibration	Si-O	1144 1203	1181	1121 1166	~1140 1100-1210 **1121-1203**	[42] [43] Present work
Asymmetric stretching vibration	Si-O-Si	1144	-	1121	~1020 1020-1100 **1121-1144**	[44] [45] Present work
Asymmetric stretching vibration	O-Ca-O	1292	1307	1279	- **1279-1307**	- Present work
Asymmetric stretching vibration	B-O	1144	780 1181 1307	800 1121 1166	780-1145 ~1400 800-1200 1200-1600 **780-1307**	[46,47] [48,49] [50] [51] Present work

Deconvoluted band position, assigned chemical bonds and comparison of the main IR absorption bands observed in the $xCaO(1-x-z)\text{-}SiO_2\,zB_2O_3$ base glasses with other glasses.

IV. DISCUSSION

A. Low and high borate (50-66.67mol% B_2O_3) glasses

Between constituents of SiO_2:B_2O_3 glass, SiO_2 is one of the most common glass-formers and participates in the network with tetrahedral $[SiO_{4/2}]0$ units and all the fourbvoxygens in SiO_4 tetrahedra are shared. In addition to modifiers like boron ions, the Si-O-Si bond is broken and forms Si-O- termination. Thus, the structure is modified. The modification results in the formation of meta, pyro and ortho-silicates in the order: $[SiO_{4/2}]0$, $[SiO_{3/2}O]^-$, $[SiO_{2/2}O_2]_3^-$, $[SiO_4]_4^-$ which are designated as Q^4, Q^3 , Q^2 , Q^1 and , Q^0 respectively [2]. The band is observed band for vitreous SiO_2 in IR spectra at 450 cm^{-1} for Si-O-Si bending vibration [3]. The three bands position is observed for silica in IR at 470, 708, and 1043 cm^{-1} for Si-O-Si, O-Si-O and Si-O-Si respectively [4]. J.I Kohli observed the rare earth aluminosilicate glasses containing 10-20 mol% Samaria within the 451-480 cm^{-1} range [5]. The intensity of these bands is weak, as it is associated with bridging oxygen of tetrahedral. Based on the above observation the band at 451-480 cm^{-1} can be attributed to Si-O-Si bending vibration. In the high B_2O_3 containing glasses, the systematic change in the absorption spectra and development of a new peak in the low-frequency region (Fig.1) gives more information about the structural change. For the increase of B_2O_3 composition peak positions are slightly shifted. The low-frequency band peaks are relatively higher in intensity than the high-frequency band peaks. From the Fig.1 very strong peaks are found at 1291 cm^{-1} for CaSB50, 780 cm^{-1} for CaSB60, 1166 cm^{-1} for CaSB66.67. In the high-frequency region peaks are broad for all compositions. Shoulders are increased for the increase of B_2O_3 composition.

E. N. Plotnikov and V. L. Stolyarova [24] observed a bond at 1020-1100 cm^{-1} for asymmetric stretching vibration of Si-O-Si. In CaO(1-x-z)-SiO2zB2O3 (where z= 50, 60 and 66.67 mol%) glass a very strong band was observed at 1121-1144 cm^{-1} and the relative area of this band almost remain unchanged with an increase of B_2O_3. So the band observed around 1121-1144 cm^{-1} in all the glasses can be assigned to Si-O-Si asymmetric stretching vibration. J. Wong, et al. [27] observed a band at 1140 cm^{-1} for Si-O stretching vibration. The bands at 1121 cm^{-1}, 1144 cm^{-1}, 1166 cm^{-1}, 1181 cm^{-1} and 1203 cm^{-1} may be assigned to Si-O stretching vibration. The frequency of the Si-O band is observed [28] within the range 1100-1210 cm^{-1}.

The band is observed [9] at 570 cm^{-1} for asymmetric bending vibration Si-O-Ca. The band is observed [14] at 600-660 cm^{-1} for Si-O-Ca. The band observed the base samples 529 cm^{-1}, 552 cm^{-1}, 555 cm^{-1}, 614 cm^{-1}, 625 cm^{-1} and 637 cm^{-1} in all glasses can be assigned to Si-O-Ca asymmetric bending vibration. The band observed in the spectra of glass at ~680 cm^{-1} can there be considered a common vibrational mode due to Si-O-B bending vibration [21]. The band position of our results at 614 cm^{-1}, 637 cm^{-1} and 625 cm^{-1}.

The band position of 423-450 cm^{-1} is attributed to the bending vibration of B-O-B bonds [6,7]. The absorption bands for the base samples 410 cm^{-1},438 cm^{-1} and 441 cm^{-1} are assigned to the bending vibration of B-O-B. The described bands emphasize the vitreous network-forming role of B_2O_3 and SiO_2.

The spectra also include the absorption bands 3400 cm^{-1} and 1640 cm^{-1}, which are generally correlated to the stretching and deformation modes for OH groups and molecular water [33]. In this work, the vibrational band for O-H bending modes lies between 1613-1715cm^{-1}. This vibration indicates that the water seems to be nearly free or loosely held by the glass network. The infrared spectra of the $xCaO(1-x-z)-SiO_2$ zB_2O_3 glass system is collected by the KBR pellet procedure which is influenced by the atmospheric condition. The atmospheric moisture absorbed by the sample or by the pellet causes the information of the infrared bands belonging to H_2O molecules, although the samples initially do not contain H_2O as a unit in the glass network. Also B_2O_3 can absorb moisture from the atmosphere. So $xCaO(1-x-z)-SiO_2$ zB_2O_3 glass system can be formed as $xCaO(1-x-z)-SiO_2$ zB_2O_3 .H_2O compositions. The comparison of the deconvoluted and observed chemical bonds with related glasses and crystal phases is arranged in table 2.

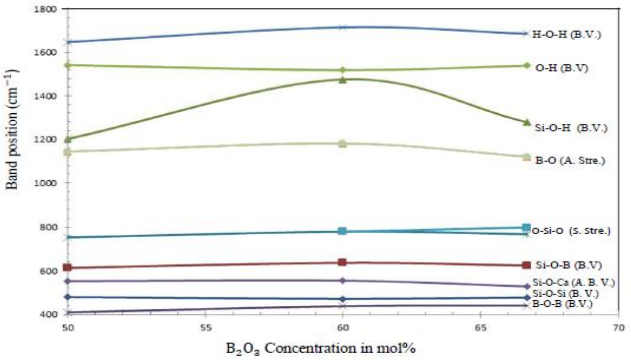


Fig. 3. The composition dependence of B_2O_3 the band position with concentration for base glass system

Where,
BV= Bending Vibration
SV= Stretching Vibration
AS= Asymmetric Stretching Vibration
ABV= Asymmetric Bending Vibration

B. Vibration of band position and relative area

In general, molecular groups Si-O-B, B-O, Si-O-H bending, Si-O-Ca, and B-O asymmetric stretching are identified as a characteristic of borosilicate glassy materials. The frequency of absorption of each of these bands depends on the composition of bonding to other groups. The band position and relative area with 50-66.67 mol% B_2O_3 in the present work are in table 4.4. The dependency of band position and a relative area with the composition of 50-66.67 mol% B_2O_3 is shown in figure 4. This vibration can be explained as the silica network being depolymerized by calcium and boron acting as a network former with the increase of B_2O_3.

TABLE III. STYLES

Structural Groups	Relative area of various chemical bonds in %		
	CaSB50	CaSB60	CaSB66.67
BV(Si-O-B)	6.58	6.4	2.63
BV(Si-O-H)	4.7	3.56	3.9
AS(Si-O-Ca)	6.58	6.89	2.56
SV(Si-O)	4.7	15.9	15.4
AS(Si-O-Si)	4.5	-	15.4
BV(H-O-H)	-	24.71	13.17
BV(O-H)	1.1	3.56	5.5
BV(B-O)	2.57	2.83	5.4
AS(B-O)	4.5	20.45	15.4

Table-3: Relative area of the various chemical bonds of the xCaO(1-x-z)-SiO_2 zB_2O_3 base glasses.

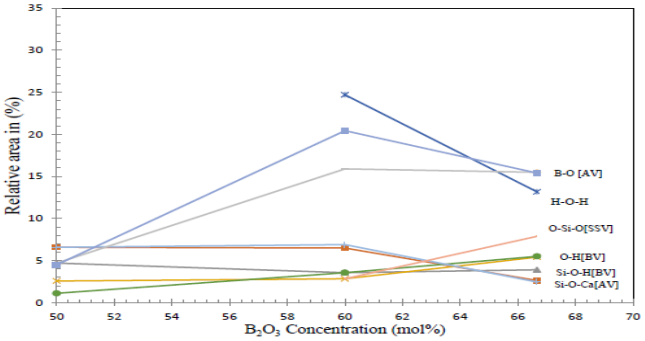


Fig. 4. Variation of relative areas of the various chemical bonds with B2O3 concentration for base sample.

Where,
BV=Bending Vibration,
SV= Symmetric Vibration,
SSV= Symmetric Stretching Vibration,
AV= Asymmetric Stretching Vibration.
AS= Asymmetric Bending Vibration

C. XRD and SEM of heat-treated sample

XRD powder patterns of base glass samples are shown in figure 5. For all the glass samples, the diffuse diffraction patterns seen are typical of amorphous materials. This result ensures that the prepared sample is homogeneous glass and also there is no separation of phase separation.

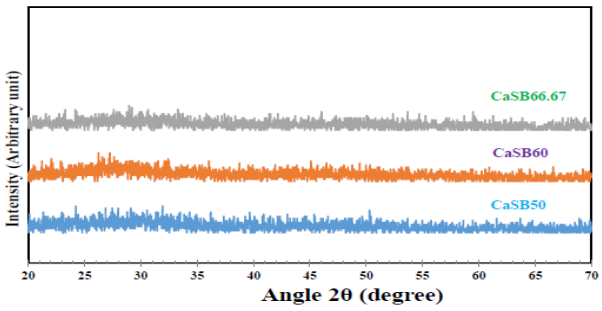
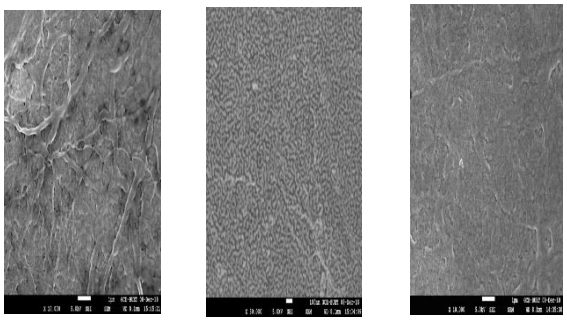


Fig. 5. XRD Patterns of the heat-treated sample.

A scanning electron microscope (SEM) scans a focused electron beam over a surface to create an image. The electrons in the beam interact with the sample, producing various signals that can be used to obtain information about the surface topography and composition.



(i) CaSB50 (ii) CaSB60 (iii) CaSB66.67

Fig. 6. The SEM pictures of the surface of (i) CaSB50 (ii) CaSB60 (iii) CaSB66.67 glass samples.

Fig.6. shows the SEM results of the prepared glass surface topography and composition. It can be seen that with boric acid (B_2O_3) added the glass composition becomes denser and compact as well elongated grains are obvious in the sample (iii)CaSB66.67.

V. CONCLUSION

The glass system xCaO(1-x-z)-SiO_2 zB_2O_3 (z= 50, 60 and 66.67 mol%) were prepared by melt quenching method. It was found that the melting temperature of the glass samples depends on the amount of B_2O_3. The melting temperature of B_2O_3 50 mol% samples was very high and used an electric furnace for their melting. The melting temperature was decreased with the increase of B_2O_3 concentration and the melting temperature was in the range of 950-1100^o C for the samples which contained 50, 60, and 66.67 mol% of B_2O_3. The infrared spectra of the xCaO(1-x-z)SiO_2 zB_2O_3 glass system were interpreted in terms of chemical bonds.

The IR band positions in the glasses have a general tendency to shift towards the high-frequency region with an increase in B_2O_3 concentration. The IR spectral studies indicate that the glass-ceramic samples contain various structural units with the linkages of the types Si-O-Si, B-O-B, B-O, O-Si-O, Si-O-B and O-H. The frequency of these groups depends on their bonding to other groups in the glass network. A general trend of shifting of the band position towards high-frequency also caused by the local field of the Si-O-Ca bonding due to B^{+3} ion. The formation of O-H and H-O-H bands around 1476, 1491, 1501, 1591, 1539 and 1542cm^{-1} express the hygroscopic nature of the glass. The variation in the band position and relative intensities with B_2O_3 concentration suggests the glass system undergoes gradual structural changes. The effect of B_2O_3 is obvious for certain bonding mechanisms where B^{+3} plays a significant role.

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