

IR study of Pb–Sr titanate borosilicate glasses

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MS received 3 January 2009; revised 18 March 2009

Abstract. The infrared spectra (IR) of various glass compositions in the glass system, $[(\text{Pb}_x\text{Sr}_{1-x})\text{O}\cdot\text{TiO}_2]-[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-[\text{BaO}\cdot\text{K}_2\text{O}]-[\text{La}_2\text{O}_3]$, were recorded over a continuous spectral range ($400-4000\text{ cm}^{-1}$) to study their structure systematically. IR spectrum of each glass composition shows a number of absorption bands. These bands are strongly influenced by the increasing substitution of SrO for PbO. Various bands shift with composition. Absorption peaks occur due to the vibrational mode of the borate network in these glasses. The vibrational modes of the borate network are seen to be mainly due to the asymmetric stretching relaxation of the B–O bond of trigonal BO_3 units. More splitting is observed in strontium-rich composition.

Keywords. Lead strontium titanate borosilicate glasses; infrared spectroscopy.

1. Introduction

The infrared spectroscopy has been used since a long time to investigate the structure of different glasses (Kamitsos *et al* 1987). This technique is most readily seen as contributing to the knowledge of structure and chemical bonding in various glasses (Gautam 2005). Alkali borate glasses are an ideal case in comparison to other glass forming systems to demonstrate the effectiveness of the spectroscopic technique in glass science. Borate glasses, in particular, have been the subject of numerous infrared studies due to their structural peculiarities (Wong and Angell 1976; Kamitsos and Karakassides 1989). In borate glasses, B_2O_3 is a basic glass former because of its higher bond strength, lower cation size, and small heat of fusion. In these glasses, B^{3+} ions are triangularly coordinated by oxygen. B_2O_3 units are corner bonded in a random configuration (Yawale *et al* 2000). The structure of borate glasses heavily depend upon the cooling rate of the melt through the range of glass transition temperature (Soppe and Marel 1988). Lead oxide and strontium oxide can enter the glass both as a network former and also as a network modifier. Due to this nature of PbO and SrO, the structure of these glasses are expected to be different from that of alkali borate, phosphate and silicate glasses. In the present investigation, glasses in the system $[(\text{Pb}_x\text{Sr}_{1-x})\text{OTiO}_2]-[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-[\text{K}_2\text{O}]-[\text{BaO}]-[\text{La}_2\text{O}_3]$ with varying lead to strontium ratios ($0 \leq x \leq 1.0$) have been prepared. All the glass samples were found to be completely amorphous in

nature. Various glass ceramic samples were prepared by crystallizing different glasses on the basis of their differential thermal analysis (DTA). XRD patterns of lead-rich glass ceramic samples confirm the formation of tetragonal perovskite crystals similar to lead titanate as major phase. Additional large numbers of peaks were found in the XRD patterns of the lead-rich glass ceramic samples due to the formation of PbTi_3O_7 as a secondary phase. XRD patterns of strontium-rich glass ceramic samples show small number of peaks and structure was found to be cubic unit cell similar to strontium titanate (Kumar *et al* 2006). The difference in the crystallization behaviour of lead-rich and strontium-rich glasses indicates that the structure of glasses changes with changing lead/strontium ratio in the glass.

In this paper, the objective was to explore the structure of lead strontium titanate borosilicate glasses containing varying ratios of PbO/SrO using infrared spectroscopy. This will help in understanding the crystallization behaviour of these glasses.

2. Experimental

2.1 Sample preparation

Glasses in the system, $[(\text{Pb}_x\text{Sr}_{1-x})\text{OTiO}_2]-[2\text{SiO}_2\cdot\text{B}_2\text{O}_3]-[\text{K}_2\text{O}]-[\text{BaO}]-[\text{La}_2\text{O}_3]$, with varying lead to strontium ratios ($0 \leq x \leq 1.0$) have been prepared by melt quench method. Appropriate amounts of highly pure chemicals, PbO (Aldrich, 99%), SrCO_3 (Aldrich, 99.9%), TiO_2 (Aldrich, 99.9%), SiO_2 (CDH, 99%), H_3BO_3 (Glaxo, 99.5%), BaCO_3 (CDH, 99.5%), K_2CO_3 (CDH, 99.9%) and La_2O_3 (Aldrich, 99.99%) were intimately mixed in

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acetone in an agate mortar and pestle until they dried. The dry powders were melted in the temperature range 1120–1290°C in an electrically heated furnace. The melt was poured into an aluminium mould, pressed by a thick aluminium plate and immediately annealed at 300°C for 3 h in another furnace. Infrared absorption spectra of the powdered glass samples mixed with KBr powder and pressed as pellets were recorded using JASCO FT/IR-5300 in the wave number range 400–4000 cm^{-1} at room temperature. IR spectra of various glass samples show the absorption band with different frequencies. In our lead strontium titanate borosilicate glass systems, some of the glass compositions depict the change in the glass structure. The various bands are recorded with respect to different stretching vibrations.

2.2 Nomenclature of glass samples

Five letters glass code refers to the composition of the glass. First two letters PT, 9P etc designate the fraction of lead i.e. x in the glass. PT refers to $x = 1.0$ i.e. 100% lead (Pb) and 0% strontium. 9P, 8P etc refers to $x = 0.9, 0.8$, respectively. The third letter L indicates that La_2O_3 is used as an additive. The last two letters 5B refer to fraction of modifier oxides BaO in the parent glass compositions.

3. Results and discussion

The infrared (IR) spectra for all the glasses are shown in figures 1, 2 and 3, respectively. The IR spectra of these

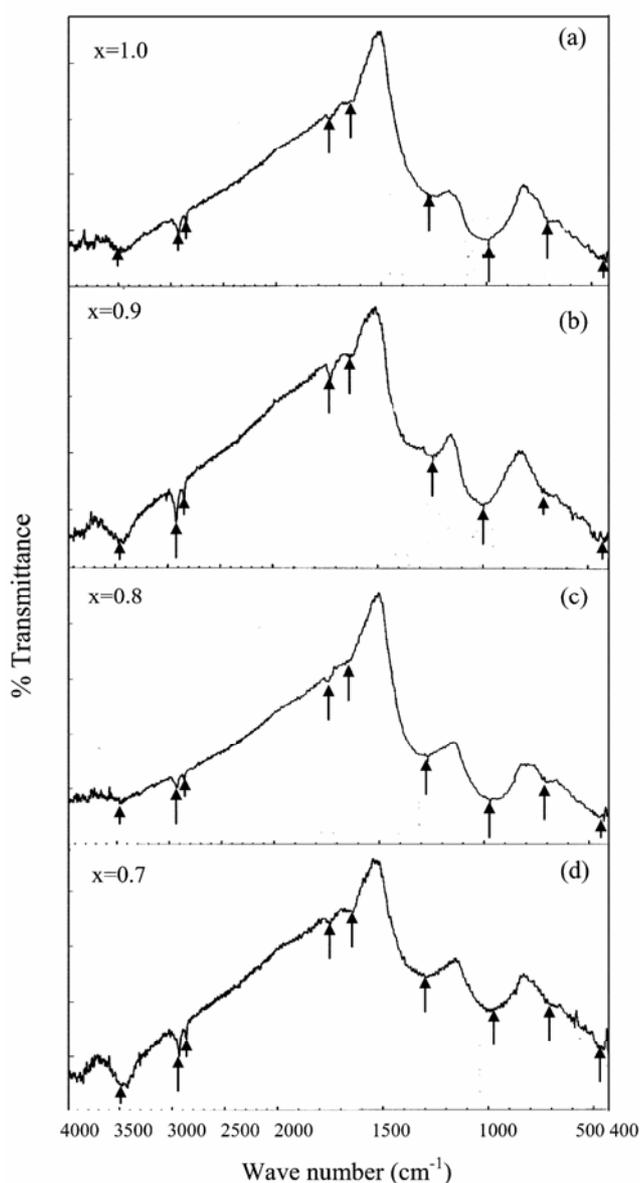


Figure 1. Infrared spectra of glasses (a) PTL5B, $x = 1.0$, (b) 9PL5B, $x = 0.9$, (c) 8PL5B, $x = 0.8$ and (d) 7PL5B, $x = 0.7$.

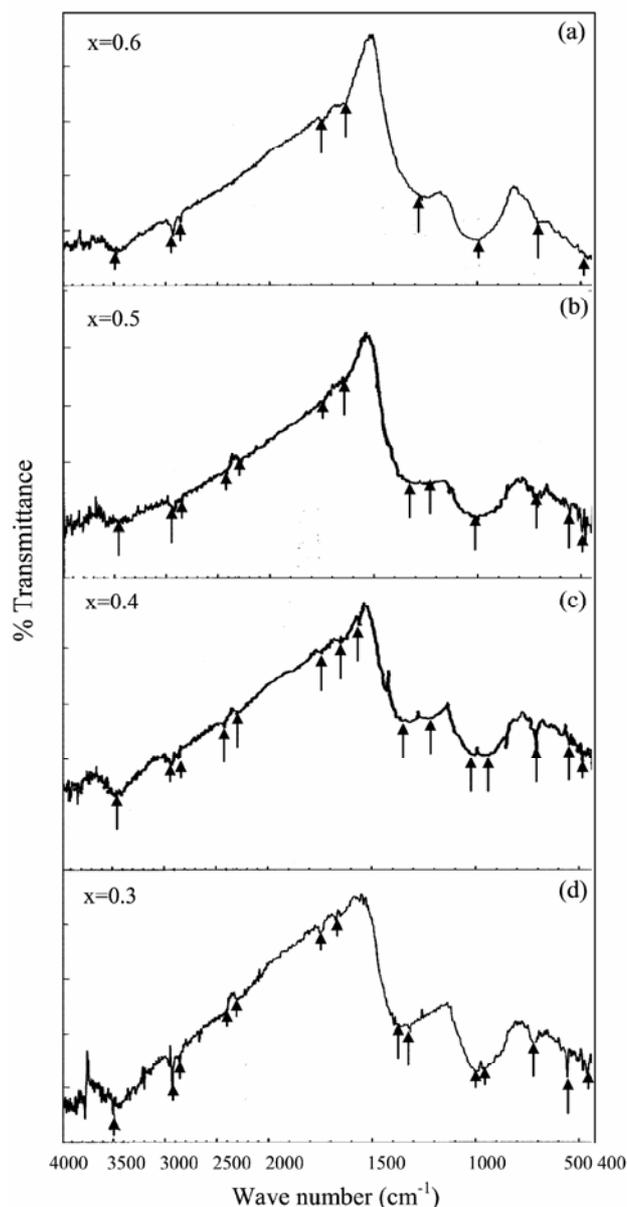
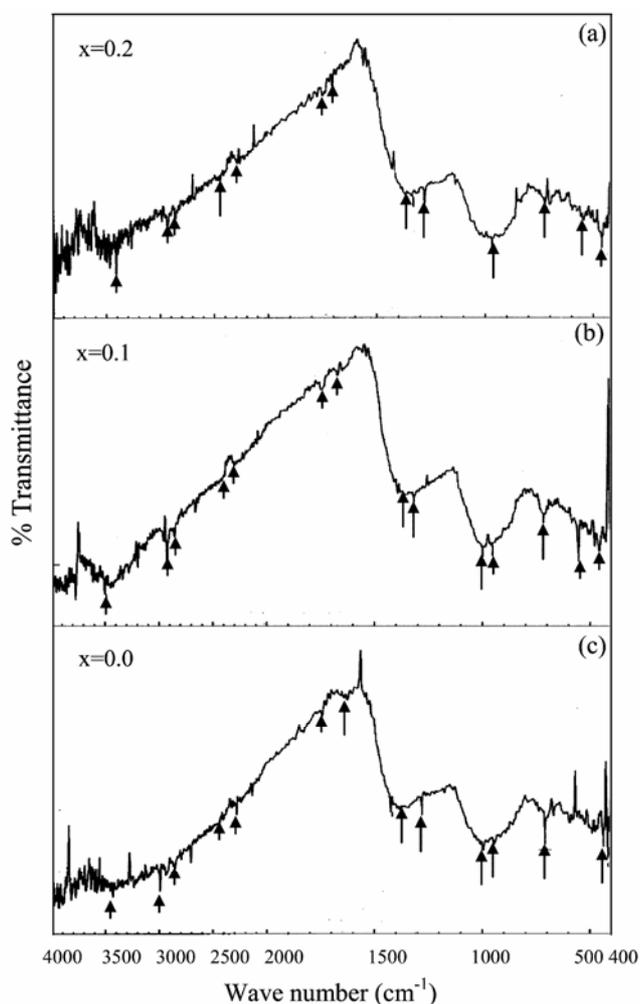


Figure 2. Infrared spectra of glasses (a) 6PL5B, $x = 0.6$, (b) 5PL5B, $x = 0.5$, (c) 4PL5B, $x = 0.4$ and (d) 3PL5B, $x = 0.3$.

Table 1. Wavelengths of different absorption peaks in FTIR spectra of the glasses in the system $[(\text{Pb}_x\text{Sr}_{1-x})\text{O}\cdot\text{TiO}_2]-[\text{2SiO}_2\cdot\text{B}_2\text{O}_3]-[\text{BaO}\cdot\text{K}_2\text{O}]-[\text{La}_2\text{O}_3]$.

Glass codes	x	Wave numbers of different absorption peaks (cm^{-1})														
		1	2		3		4	5	6	7	8		10			
			a	b	a	b					a	b	a	b		
PTL5B	1.0	3483	2915	2890	–	1730	1650	–	1280	995	715	420				
9PL5B	0.9	3472	2991	2860	–	1730	1630	–	1250	1000	725	430				
8PL5B	0.8	3500	2990	2890	–	1730	1630	–	1290	995	730	450				
7PL5B	0.7	3480	2925	2865	–	1750	1645	–	1300	990	705	460				
6PL5B	0.6	3490	2915	2840	–	1740	1638	–	1230	990	701	480				
5PL5B	0.5	3450	2925	2840	2410	2290	1740	1640	–	1310	1210	1000	703	550	480	
4PL5B	0.4	3485	2940	2850	2420	2300	1740	1650	1575	1340	1210	1030	940	703	550	480
3PL5B	0.3	3500	2922	2850	2500	2300	1750	1680	–	1375	1225	1000	960	720	555	440
2PL5B	0.2	3500	2920	2850	2425	2280	1740	1690	–	1360	1285	1005	956	716	540	440
1PL5B	0.1	3501	2920	2850	2395	2305	1740	1680	–	1370	1310	998	955	718	555	456
STL5B	0.0	3425	2992	2850	2425	2290	1740	1620	–	1375	1280	999	955	715	–	438

**Figure 3.** Infrared spectra of glasses (a) 2PL5B, $x = 0.2$, (b) 1PL5B, $x = 0.1$ and (c) STL5B, $x = 0.0$.

glasses consist of broad and sharp bands in different regions ($400\text{--}4000\text{ cm}^{-1}$). These bands are strongly influ-

enced by the increasing substitution of SrO for PbO. The position of these bands shift with composition. Wavelength of different absorption peaks for all the glasses are listed in table 1. The infrared spectra of these glasses show ten absorption peaks. The peaks are sharp, medium and broad in nature. All the absorption peaks have been numbered as 1, 2, ----10 starting from high wave number side. The broad bands are exhibited in the oxide spectra, most probably due to the combination of high degeneracy of vibrational states, thermal broadening of the lattice dispersion band and mechanical scattering from powder samples. The first absorption peak lies in the range $3425\text{--}3501\text{ cm}^{-1}$. This peak is broad in lead-rich glass samples while it is sharp in strontium-rich glass samples. This is due to stretching of O–H⁺ bond inside the glassy network (Bray 1967). The O–H groups form at non-bridging oxygen sites. The peak no. 2 splits into two absorption peaks i.e. 2 (a and b). Both the peaks are very close to each other as shown in table 1. Absorption peak no. 3 is absent in the lead-rich compositions, $x = 1.0\text{--}0.6$, while it is present in the strontium-rich compositions and split into two absorption peaks 3a and 3b.

There are a few absorption peaks in the range $1200\text{--}1750\text{ cm}^{-1}$ (peak nos 4–7) in all the glass samples. There are two absorption peak nos 4 and 5 at 1750 and 1650 cm^{-1} in all glass samples. Peak no. 6 is appearing only for the glass sample 4PL5B ($x = 0.4$) at 1575 cm^{-1} . A single broad absorption peak no. 7 is observed in the glass compositions with $x = 1.0\text{--}0.6$. The same peak splits into two peaks in all the glass compositions, which are rich in strontium. These absorption peaks occur due to the vibrational mode of the borate network. The vibrational modes of the borate network are mainly due to the asymmetric stretching relaxation of the B–O bond of trigonal BO_3 units. These vibrational modes occur at $1200\text{--}1600\text{ cm}^{-1}$ (Kamitsos *et al* 1987; Eldin *et al* 1995; Ghoneun *et al* 1996). The bands at around 1000 cm^{-1} peak (no. 8) are attributed to a stretching vibration of

B–O–Si linkage (Tenny and Wong 1972). A broad absorption peak (no. 9) is observed in all the IR spectra for all the glass samples. This peak lies between 685 and 709 cm^{-1} and is due to the bending of B–O–B linkages in the borate glassy network (Dwoeidari *et al* 1991). Frequency of this peak increases with increasing concentration of the SrO (table 1). The low frequency band (peak no. 10) in the IR spectra of investigated glasses can be attributed to vibration of metal cation such as Pb^{2+} . The same band is also present in $\text{PbO–B}_2\text{O}_3$ glass and is attributed to the vibrations of Pb^{2+} cations (Bray and Keefe 1963).

4. Conclusions

Infrared spectra of glasses in the present system show sharp and diffuse absorption peaks. These peaks occur due to different vibrational modes of the borate network of which asymmetric stretching relaxation of the B–O bond of trigonal BO_3 units contribute only. Low frequency band in the IR spectra of investigated glasses can be attributed to vibration of metal cation such as Pb^{2+} . Strontium-rich IR spectra show more peaks in comparison to lead-rich glass spectra. Lead strontium titanate borosilicate glasses may be used for electronic applications.

Acknowledgements

Authors are highly thankful to DRDO, India, for financial support and Dr Rajesh Singh, Department of Chemistry,

Banaras Hindu University, Varanasi, for extending the IR measurements facility.

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