

Glass formation region and lithium ion conduction in the oxyfluorophosphate glasses

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Oxyfluorophosphate glasses containing about 80 mol % of $[\text{LiF} + \text{Li}_2\text{O}]$ show unusually high lithium ion conductivity at elevated temperatures. A detailed investigation has been carried out on the glasses prepared by both conventional cooling and a rapid quenching technique. Chemical analysis of the glasses reveals fluorine loss during melting and it becomes difficult to make glasses with exact predetermined compositions. Electrical conductivity of the glasses, determined from complex impedance analysis increases with Li_2O content. A glass with nominal composition 70 LiF: 15 Li_2O : 15 $\text{Al}(\text{PO}_3)_3$ shows the highest conductivity ($\sim 1.3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ around 200°C) among all the compositions studied. An interesting feature of the impedance plot is the near perfect semi-circle for bulk relaxation indicating a narrow distribution of relaxation times. This has been explained on the basis of a relatively small proportion of lithium ions which are mobile. The electrical conductivity of the glasses is found to be essentially independent of dissolved water content. The infrared spectra of these glasses (2 to $50 \mu\text{m}$ region) could not produce much useful structural information.

1. Introduction

Solid-state lithium batteries are one of the most promising power sources for various low current electronic devices. This is because of their high energy density, long shelf life and high rechargeability. The search for a suitable solid electrolyte for these batteries is still on. Due to large scale production potential in various sizes and shapes and the relative insensitiveness of the properties to changes of composition, glassy solid electrolytes have been extensively studied in the last few years. It was reported by the present authors [1] and also by others [2, 3] that the glasses in the lithium oxyfluorophosphate system $[\text{LiF}-\text{Li}_2\text{O}-\text{Al}(\text{PO}_3)_3]$ show unusually high conductivity at elevated temperatures. In the present investigation a detailed study on the glass formation was carried out. Electrical conductivity as a function of temperature and lithium ion concentration was measured. The effect of dissolved water on conductivity was also studied. The infrared spectra of the glasses was studied with the hope of obtaining structural information.

2. Experimental details

2.1. Glass preparation

The starting materials, LiF, Li_2CO_3 and $\text{Al}(\text{PO}_3)_3$, were dried at 600°C for 1 h and mixed in appropriate proportions (each batch weighing around 20 g) followed by melting in a platinum crucible at a temperature of 930 to 950°C for 15 to 20 min. The melts were cast in a rectangular brass mould and annealed at 325 to 350°C . Some of the compositions were prepared by a rapid quenching technique. For this purpose, the melts were poured inside a rotating copper drum ($\sim 1500 \text{ rpm}$). The melt spread along the inside wall of the drum forming thin glass ribbons which cooled much faster than if poured into a static mould. The additional advantage of this technique was that it made it possible to incorporate more Li_2O than is possible by conventional cooling. The details of the technique have been reported elsewhere [4].

To study the effect of dissolved water on conductivity a glass of nominal composition 80 LiF: 20 $\text{Al}(\text{PO}_3)_3$ was selected. The specimens with different water contents were obtained by melting

glasses for various durations at a fixed temperature. In some cases inert gas (argon) was bubbled through the melt to reduce the water content of the glass.

2.2. Chemical analysis

The chemical analysis was carried out using a flame photometer (Systronics, MKI-125, India) for lithium, atomic absorption spectrophotometer (Pye Unicam AAS SP 2900) for aluminium and phosphorus and a spectrophotometer (Beckman UV/ VIS/NIR spectrophotometer Model 5270) for the fluorine estimation. A detailed analysis procedure has been reported elsewhere [5].

2.3. Electrical measurements

For conductivity measurements the surfaces of the rectangular glass pieces were ground and polished. The opposite faces of the specimens were painted with silver paint and baked at 120°C in an oven. The samples were sandwiched between two spring loaded platinum foils to provide better electrical contacts. A.C. electrical conductivity of the specimens was measured as a function of temperature in the range 25 to 250°C by a two-probe method with an LF 4192A impedance analyser (Hewlett-Packard). The frequency range extends from 5 Hz to 13 MHz. The temperature was controlled to $\pm 1^\circ\text{C}$ by an Eurotherm temperature controller.

Densities of the glasses have been measured by Archimedes principle with kerosene as an immersion fluid.

2.4. Infrared studies

Infrared spectra of the glasses were studied with powdered glass samples (2 mg) dispersed in caesium iodide (200 mg). The pellet, pressed under vacuum was then mounted in an infrared spectrophotometer (Perkin Elmer 598 Series). The sample was scanned from 4000 to 200 cm^{-1} (2.5 to 50 μm) in 12 min. To study the effect of water content, percentage transmission of the optically polished glass pieces was measured in the same wavelength range. For this purpose, flat rectangular glass pieces (measuring 2.5 cm \times 4.5 cm \times 0.1 cm) were ground on silicon carbide powder and finally optically polished with rouge.

3. Results and discussion

3.1. Glass formation region

Glass formation in the binary system LiF–Al(PO₃)₃ and also in the ternary system LiF–Li₂O–Al(PO₃)₃ were investigated by selecting

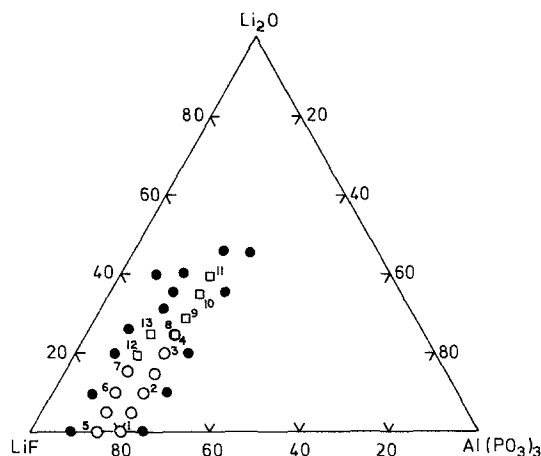


Figure 1 Glass formation region in the LiF–Li₂O–Al(PO₃)₃ system (10 g melt), ○ – conventionally cooled glasses, □ – rapidly quenched glasses, and ● – devitrified.

compositions at 5 mol% interval and using conventional cooling and rapid quenching techniques to prepare the glasses. Under our experimental conditions glasses could be formed only in a limited composition range, as shown in Fig. 1, in which only nominal compositions of the glasses are indicated. Those of the conventionally cooled glasses are marked by open circles, rapidly quenched glasses by open squares and the closed circles represent the compositions which were phase separated. In conventionally cooled glasses only 25 mol% Li₂O could be incorporated whereas rapid quenching extends the boundary of glass formation to 40 mol% Li₂O. The glass formation region along the binary compositions LiF–Al(PO₃)₃, however, does not extend significantly even with the higher rate of quenching.

The limits of the glass formation region obtained in this investigation were slightly different from that reported earlier [2, 3]. The particular glass composition 50 LiF: 30 Li₂O: 20 Al(PO₃)₃ reported by Evastrop'ev *et al.* [2] and also by Jagla and Isard [3] could not be obtained by us in the glassy form, without a higher rate of quenching. This could be due to the differences in starting materials and melting conditions. Evastrop'ev *et al.* melted their glasses in an inert atmosphere at a temperature of 930 to 950°C for 15 to 20 min. However, Jagla and Isard used covered platinum crucibles at a temperature of 900 to 950°C for 30 to 40 min. They reported glass formation in a few binary compositions of LiF–Al(PO₃)₃, with the LiF content varying between 78 and 86 mol%, in addition to the above mentioned ternary com-

TABLE I Physical properties of the conventionally cooled and rapidly quenched glasses

Glass number	Nominal composition (mol %)			Actual composition obtained by chemical analysis (mol %)				Density (g cm ⁻³)	Molar volume (cm ³)	Number of Li ⁺ (x 10 ²² cm ⁻³)	P/Al ratio after melting
	LiF	Li ₂ O	Al(PO ₃) ₃	LiF	Li ₂ O	Al ₂ O ₃	P ₂ O ₅				
1.	80	—	20	50.52	13.46	10.66	23.36	2.5233	34.12	1.60	2.37
2.	70	10	20	46.66	28.65	9.09	25.60	2.4977	31.47	1.92	2.81
3.	60	20	20	40.58	24.15	8.92	26.35	2.5125	31.10	2.08	2.95
4.	55	25	20	40.72	26.01	9.17	24.10	2.5121	30.73	2.13	—
5.	85	—	15	56.14	15.61	8.05	20.20	2.5021	28.07	2.13	2.50
6.	75	10	15	40.34	25.86	8.70	25.10	2.5319	30.06	2.20	2.88
7.	70	15	15	44.07	28.85	7.94	19.14	2.4965	27.94	2.47	—
*8.	55	25	20	40.72	26.01	9.20	24.07	2.5070	31.29	2.11	—
*9.	50	30	20	35.41	31.24	8.96	24.39	2.4570	32.16	2.15	—
*10.	45	35	20	28.49	37.27	8.43	25.81	2.4780	31.80	2.19	—
*11.	40	40	20	24.09	41.63	8.09	26.19	2.4897	31.52	2.31	—

*Represents rapidly quenched glasses.

position. In the present investigation the glasses were melted in air in an open platinum crucible for 15 to 20 min. A large number of other ternary glasses could be prepared with a maximum Li₂O content of 25 mol%. The rapid quenching technique, however, increased the limit to 40 mol% Li₂O. The extension of the glass formation region by the use of certain nonconventional techniques, such as roller quenching, etc., has been earlier demonstrated by several workers [6–8]. The glass formation region in the present system seems to be controlled mainly by Al(PO₃)₃ content, since the rapid quenching failed to extend the limit of Al(PO₃)₃ content in these glasses.

3.2. Chemical analysis

Chemical analysis of the glasses showed fluorine losses which resulted in widely different compositions than was intended to be obtained. The analysed weight percentages of lithium, fluorine, phosphorus and aluminium were converted into LiF, Li₂O, Al₂O₃ and P₂O₅ assuming that these components are present in the glasses. The analysed compositions, P/Al ratio and the nominal compositions are included in Table I.

Isard *et al.* [9] reported fluorine losses from the glass batches, possibly as PF₅, amounting to almost 50% over the batch value and supported by the estimated P/Al ratio varying between 2.7 to 3.0. However, before melting, the value of P/Al should have been 3, as Al(PO₃)₃ was used as the only raw material for aluminium and phosphorus. Fluorine losses were also expected due to the presence of water in the glass batch. Since their glasses were melted for longer durations than in

the present case, and the raw materials were not given any dehydration treatment before melting, fluorine losses due to both HF and PF₅ are possible. Raw materials under the present investigation were pre-dried at 600°C for 1 h and therefore, the fluorine loss was expected only as PF₅. The estimated P/Al ratio between 2.37 to 2.95 (Table I) indicates loss of fluorine only as PF₅. Similar values of P/Al ratio between 2.7 to 3.0 were reported by Isard *et al.* [9] to explain fluorine losses only as PF₅. Fluorine loss as PF₅ has also been reported by Tick [10] in oxyfluoride glasses of zirconium and phosphorus. Loss of fluorine has also been detected in the NaF–Na₂O–B₂O₃ system in which the amount of fluorine retained was found to depend on the temperature and duration of melting [11]. The excess of lithium in the present glasses was presumed to be retained as Li₂O making it difficult to prepare truly binary LiF–Al(PO₃)₃ glasses.

The densities of all the present glasses were around 2.50 g cm⁻³ (Table I) and do not change appreciably with composition. These values together with the analysed compositions were used to calculate molar volume and concentration of the lithium ions in the glasses.

3.3. Electrical conductivity

The bulk conductivities of the glasses were determined from the real axis intercepts of the complex impedance plots. A typical plot for glass no. 1 is shown in Fig. 2 at a few temperatures with blocking silver electrodes. It may be noted that the high frequency data at the lowest temperature (104°C) have been represented by a nearly perfect circular

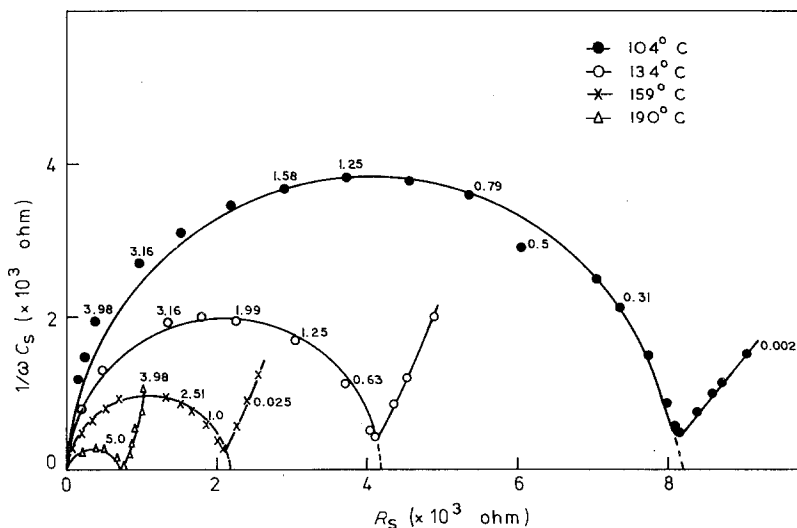


Figure 2 Complex impedance diagram for glass no. 1 (silver electrodes) at various temperature (numbers on the plots indicate frequencies in MHz).

arc which passes through the origin and has its centre slightly below the real axis (making a very small angle of 3° with the real axis). Since the centre is only slightly depressed it may be considered as a perfect semicircle. With the increasing temperature, the high frequency arc, as expected, shifted to higher frequencies and its size also decreased resulting in smaller intercepts on the real axis. At lower frequencies a tail was observed which developed into a straight line at higher temperatures (or lower frequencies).

At lower temperature or higher frequencies the electrical response was dominated by the bulk characteristics and could be simulated by a parallel combination of bulk resistance (R_b) and a geometric capacitance (C_g) originating from the finite dielectric constant of the glasses [5]. As expected, the bulk resistance was strongly temperature dependent. The principal difference between the impedance results obtained in this investigation and those obtained in most of the other glass systems was that the semicircles were not depressed (appreciably). The depressed circular arcs were usually observed for most glassy specimens and were explained in terms of distribution of relaxation times or distributed time constant of the equivalent circuit [12]. Recently, single relaxation time behaviour has been reported for an organic copolymer glass containing iron, where perfect semicircles have been observed [13]. Similar observations have been reported for NaCl [14] and LiGaO₂ [15]. The results were explained on

the basis of a smaller number of charge carriers present in these systems. As explained later in the text, the carrier concentration of the glasses under present investigation ($\sim 10 \times 10^{20} \text{ cm}^{-3}$) is comparable to that of polymeric glasses and is believed to be the origin of the observed semicircles.

The electrical conductivity of the glasses increased with temperature and Li₂O content. The variation has already been reported earlier [1]. Glass no. 7 showed the highest conductivity among all the compositions studied with a value of nearly $1.3 \times 10^{-3} \text{ ohm}^{-1} \text{ cm}^{-1}$ at 230°C . The values compared well with those reported by others [2, 3].

3.3.1. Relation between conductivity and lithium ion concentration

To observe the effect of lithium ion concentration (calculation procedure mentioned earlier) conductivities at three fixed temperatures ($230, 200$ and 150°C) were plotted as a function of concentration of charge carriers (number of Li^+/cm^3) in Fig. 3. Though the concentration did not change appreciably large changes in conductivity were visible and the relationship at each temperature was linear even though with different slopes as expected. It is interesting to note that on extrapolation to zero conductivity each of these lines intersect the concentration axis at a common point corresponding to $C_{\text{Li}^+} = 1.5 \times 10^{22} \text{ cm}^{-3}$.

Ideally, the relationship between the conductivity and charge carrier concentration is linear and

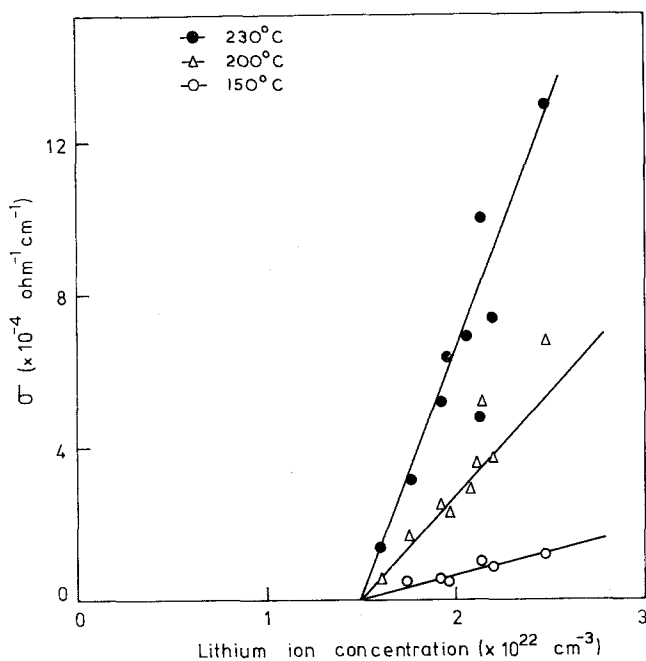


Figure 3 Variation of conductivity with lithium ion concentration in the glasses measured at different temperatures.

the straight line plot should pass through the origin. However, the present results indicate that the glasses should show "zero" conductivity even when they contain a finite concentration of lithium ions (Fig. 3). This leads to the conclusion that not all the lithium ions present in these glasses take part in the conduction process; some of them are comparatively less mobile than the others. Such partial contribution to the conductivity was also reported for a few other ionically conducting glasses containing silver iodide as indicated by thermoelectric power measurements [16–18]. It is probable that the immobile lithium ions were more strongly bound to the glassy backbone than the others. However, the detailed structural information of these glasses is not available at this stage. The large values of electrical conductivity with small fractions of mobile ion indicate their high mobilities. The mobility of lithium ion was calculated from the relation $\sigma = ne\mu$, where μ is the mobility. The calculated value of μ for glass no. 7 at 100°C was nearly $4.8 \times 10^{-9} \text{ cm}^2 \text{ V}^{-1} \text{ sec}^{-1}$ which is about four orders of magnitude higher than the lithium ion mobility reported by Bauck [19] for lithium conducting glass electrodes. Carrier mobilities are thus responsible for the very high conductivities of the glasses.

3.3.2. Effect of water content on conductivity

The infrared spectra of the glasses studied in the

present investigation showed the presence of a hydrogen-bonded hydroxyl group [5]. A particular glass (no. 1) was selected to study the effect of water content on conductivity. For this purpose, the specimens with different water contents were obtained as described earlier. Infrared spectra of the thin optically polished glasses gave absorption bands corresponding to a hydrogen-bonded hydroxyl group. The area under this peak which is proportional to the amount of water present in the glass was used to compare the water contents. The chemical analysis showed that the compositions of the specimens, except water content were almost the same. Bulk conductivities of these specimens were measured as a function of temperature. The values obtained at a fixed temperature of 100°C are included in Table II along with the values of area under the infrared peak. The variation of conductivity against the peak area, as shown in Fig. 4, indicates that the conductivity was not significantly dependent on the water content and the extrapolation of the linear portion to zero water content did not show large deviation in conductivity from that measured for glasses with small amounts of water. Various studies that have been made [20–27] on the effect of dissolved water on ionic transport in glasses show different results. Owen and Douglas [20] showed that the D.C. conductivity of SiO_2 glass was essentially independent of water content. In contrast, an increase in the conductivity of lead silicate glasses with increasing

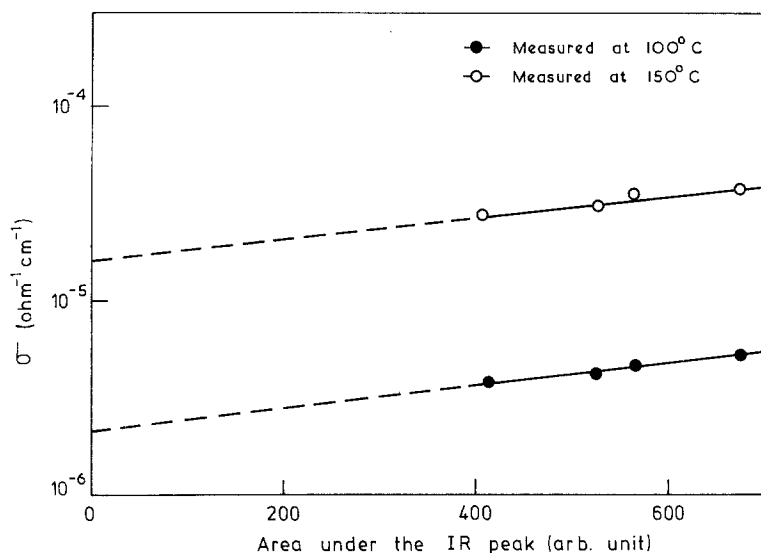


Figure 4 Variation of conductivity as a function of water content.

water content has been reported [23]. "Mixed-alkali" like behaviour of water has been observed in $\text{Na}_2\text{O}-3\text{SiO}_2$ glass [28]. The glasses under the present investigation did not show any significant change of conductivity with water content. However, due to the very low levels of water content in these glasses it was not clear whether the protons did not participate in the conduction process or their contribution was too small to be significant.

3.4. Infrared studies

Infrared spectra of the conventionally cooled and rapidly quenched glasses were studied in the frequency range 4000 to 200 cm^{-1} . Fig. 5 shows infrared spectra of the rapidly quenched glasses of various compositions. The spectrum of conventionally cooled glass no. 4 is also included in the same figure for comparison. It may be noted that the spectra of the glasses prepared by either of the techniques are almost identical. As expected broad

and continuous bands dominate the spectra of these glasses and they do not show any modification with glass composition. The spectra of crystalline $\text{Al}(\text{PO}_3)_3$, LiF and Li_2CO_3 and glass no. 7 are compared in Fig. 6 in the 800 to 200 cm^{-1} region. The $\text{Al}(\text{PO}_3)_3$ spectrum shows a number of bands in the 1350 to 600 cm^{-1} region some of which appear as diffused bands in the glass. It may also be observed that all three materials [LiF , $\text{Al}(\text{PO}_3)_3$ and Li_2CO_3] show absorption bands around 400 cm^{-1} , where the glass also shows a broad absorption band.

Infrared studies of these glasses have also been carried out by Isard *et al.* [9] and they suggested that fluorine-substituted pyrophosphate groups were formed which are hexa-coordinated to Al^{3+} . The infrared spectra of the glasses in the present investigation show that there are absorption bands in 1300 to 600 cm^{-1} , 1200 to 600 cm^{-1} and $< 600\text{ cm}^{-1}$ which are generally assigned to $\text{P}=\text{O}$, $\text{P}-\text{O}$ and the bond bending of $\text{P}-\text{O}-\text{P}$ units, respectively, in the phosphate sublattice [29]. According to Exharos *et al.* [30] the vibrational frequencies of Li^+ generally occur around 400 cm^{-1} . The infrared spectra of the present glasses show a broad band in the region 600 to 200 cm^{-1} with a maximum around 450 cm^{-1} . But the spectra of crystalline LiF , Li_2CO_3 and $\text{Al}(\text{PO}_3)_3$ (Fig. 6) also show absorption bands in this region and it is very difficult to assign these peaks to Li^+ vibration only, without proper resolution. The infrared spectroscopic technique alone is not adequate for this resolution and therefore from these studies it was not possible to elucidate the structure of these glasses. It may be mentioned that the use of the

TABLE II Conductivity of glass no. 1 containing different water contents

Preparation	Area under the curve (mm^2)	$\sigma_{100^\circ\text{C}} \times 10^6$ ($\text{ohm}^{-1}\text{ cm}^{-1}$)
Melted at 950°C , argon bubbled for 15 min	421.47	3.9
Melted at 950°C , argon bubbled for 5 min	524.48	4.7
Melted in air at 900°C for 30 min	563.40	4.8
Melted in air at 950°C for 15 min	666.38	7.0

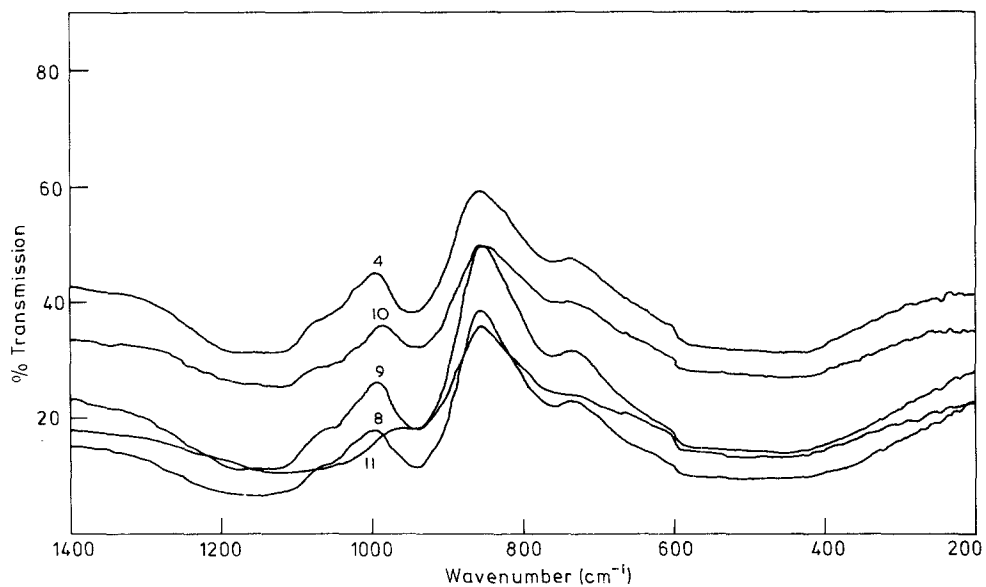


Figure 5 Infrared spectra of $\text{LiF-Li}_2\text{O-Al(PO}_3)_3$ glasses prepared by conventional cooling and rapid quenching.

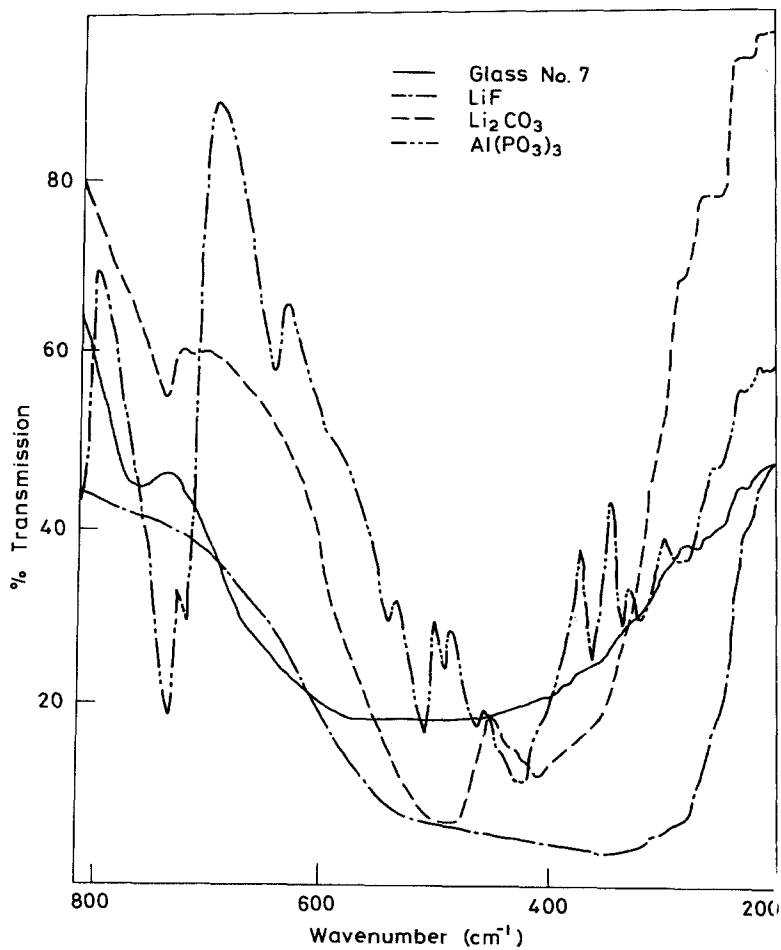


Figure 6 Comparison of infrared spectra for crystalline LiF , Li_2CO_3 and $\text{Al(PO}_3)_3$ with that of glass no. 7.

infrared, NMR and Raman spectroscopic techniques to find out the structure of a glass has been questioned while studying fast ion conduction in chloroborate glasses [31].

The infrared spectra of the present glasses did not show any significant modification of the spectra even under the quenched condition. It seems that the added salts become diluted in the vitreous matrix without any possible interaction with their surroundings. Similar observations have been recorded for the infrared spectra of $B_2O_3-Li_nX$ ($n = 1, X = Cl, Br, I, n = 2, X = SO_4, n = 3, X = PO_4$) and also for chloroborate glasses [32] where no change in the IR spectra was recorded with change of composition.

4. Conclusions

1. Glasses in the lithium oxyfluorophosphate system show a reasonably wide glass formation region. However, due to unavoidable fluorine losses during melting, it is very difficult to obtain glasses with predetermined compositions. The limit of the glass formation region particularly in terms of Li_2O content can be extended by a rapid quenching method.

2. The A.C. response of these glasses, at higher frequencies, is dominated by a parallel combination of bulk resistance and capacitance only. The near perfect semicircles at high frequencies are explained by a small number of charge carriers present in the glasses.

3. The variation of conductivity with lithium ion concentration shows that a part of the total lithium content is not mobile. The high electrical conductivity is, therefore, due to an exceptionally high mobility of the lithium ions in these glasses.

4. The conductivity is essentially independent of water dissolved in these glasses.

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