

High resolution magic angle spinning NMR studies of ^{31}P and ^{11}B in fast ion conducting $\text{AgI-Ag}_2\text{O-P}_2\text{O}_5$ and $\text{AgI-Ag}_2\text{O-B}_2\text{O}_3$ glasses*

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Abstract. Silver iodide-based fast ion conducting glasses containing silver phosphate and silver borate have been studied. An attempt is made to identify the interaction between anions by studying the chemical shifts of ^{31}P and ^{11}B atoms in high resolution (HR) magic angle spinning (MAS) NMR spectra. Variation in the chemical shifts of ^{31}P or ^{11}B has been observed which is attributed to the change in the partial charge on the ^{31}P or ^{11}B . This is indicative of the change in the electronegativity of the anion matrix as a whole. This in turn is interpreted as due to significant interaction among anions. The significance of such interaction to the concept of structural unpinning of silver ions in fast ion conducting glasses is discussed.

Keywords. Fast ion conductor; chemical shift; electronegativity; structural unpinning.

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1. Introduction

Silver iodide-based fast ion conductor (FIC) glasses have been widely investigated (Kunze 1973; Chiodelli *et al* 1974; Minami *et al* 1977a, 1977b, 1980; Lazzari *et al* 1980; Malugani *et al* 1978; Tuller *et al* 1980; Hemalata *et al* 1983). Silver borate and silver phosphate form network glasses and with addition of AgI they have been known to give rise to high ionic conductivity in the glassy state. We have recently investigated the possible origin of fast ion conduction in silver iodide-based glasses (Shastry and Rao 1989) and have suggested that the FIC behaviour can be associated with an index known as structural unpinning number, SUN(S). SUN is determined by the unscreened nuclear charge on the silver ion, z^* , the weighted average electronegativity of the anion matrix, χ_{av} and the specific volume available per silver ion, V_m/N_{Ag} , where V_m is the molar volume and N_{Ag} is the number of Ag atoms per mole of the glass. $S = C \cdot (z^*/\chi_{av})(V_m/N_{Ag})$ where C is a constant that renders S non-dimensional. The postulation of SUN which is basically a chemical approach to FIC, has been found to rationalize a number of observations in different classes of AgI-based FIC glasses. One of the important features of the above postulate is that it is possible to define an average electronegativity of the anion matrix and this implies a chemical interaction among anions. We have argued that such interactions are possible because,

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(a) Ag^+ ions possess a high z^* and hence can strongly polarize the anion matrix causing a reverse flow of electron density from the anion matrix to the valence shells of Ag^+ ions; (b) in turn anions can interact chemically and acquire a non-zero bond order among themselves since reverse electron flow occurs from the antibonding orbitals. We felt that it is necessary to investigate such interanion interaction by studying the chemical shifts of ^{31}P and ^{11}B atoms using HR MAS NMR measurements. We report here our observation on the variation of chemical shifts of ^{31}P which may be attributed to the change in the partial charge on ^{31}P or ^{11}B which in turn is due to the change in the electronegativities of interacting, composition weighted, PO_3^- - I^- pairs in the glasses. However, the evidence in borate glasses is weak. Also ^{11}B NMR is rather complex due to its quadrupole moment and due to the formation of both trigonal and tetrahedral boroxo groups.

2. Experimental

Commercially available AR grade materials were used to prepare the glasses. During the preparation silver salts tended to get reduced to metallic silver. To avoid this reduction we have mixed the charge with ammonium nitrate (mp = 442 K, bp = 473 K) which acts as an *in situ* mild oxidizing agent and prevents reduction very effectively.

Five-to-ten gram batches of the starting materials, AgI , Ag_2O and H_3BO_3 in borate glasses and AgI , Ag_2O and $(\text{NH}_4)_2\text{HPO}_4$ in phosphate glasses were mixed with NH_4NO_3 (up to 5 g) and were gradually heated and melted in quartz crucibles. As the materials melted, NH_4NO_3 gradually decomposed and when the temperature of the melt reached about 673 K the decomposition of ammonium nitrate was complete. The melts were kept at 600–700 K and 800–900 K, respectively, in phosphate and borate glasses for about 15–20 min to ensure homogeneity in the melts and then quenched by pressing drops of the melts between two steel plates cooled in liquid nitrogen. Disc-shaped samples (or pellets in some compositions) so obtained were stored in painted (black) desiccators, as these glasses were photosensitive. Special care had to be taken while preserving borate glasses.

^{31}P and ^{11}B NMR spectra were recorded with a Bruker MSL-300 solid state high resolution spectrometer operating at 121.495 MHz (magnetic field 7.05 T). The relaxation of trigonal boron is significantly faster due to its large quadrupolar interaction as compared to tetrahedral boron (Fyfe 1983). Sufficient time (10 s) was allowed between pulses to ensure relaxation of both the types of borons (the delay between the pulses was 5 s in the case of phosphorus nucleus). A cylindrical rotor spinning at 3 kHz was used in the MAS NMR studies reported here. Side bands were identified by spinning at different frequencies; side bands get shifted by spinning at different frequencies while the positions of proper resonances remain unaltered. Chemical shift values were calculated with respect to ^{31}P resonance in 85% H_3PO_4 and ^{11}B resonance in $\text{BF}_3\cdot\text{O}(\text{Et})_2$ (negative shifts indicate greater deshielding and higher fields of resonance).

3. Results and discussion

3.1 ^{31}P NMR in phosphate glasses

The complete ^{31}P spectrum in a typical AgI - AgPO_3 glass is shown in figure 1a. The

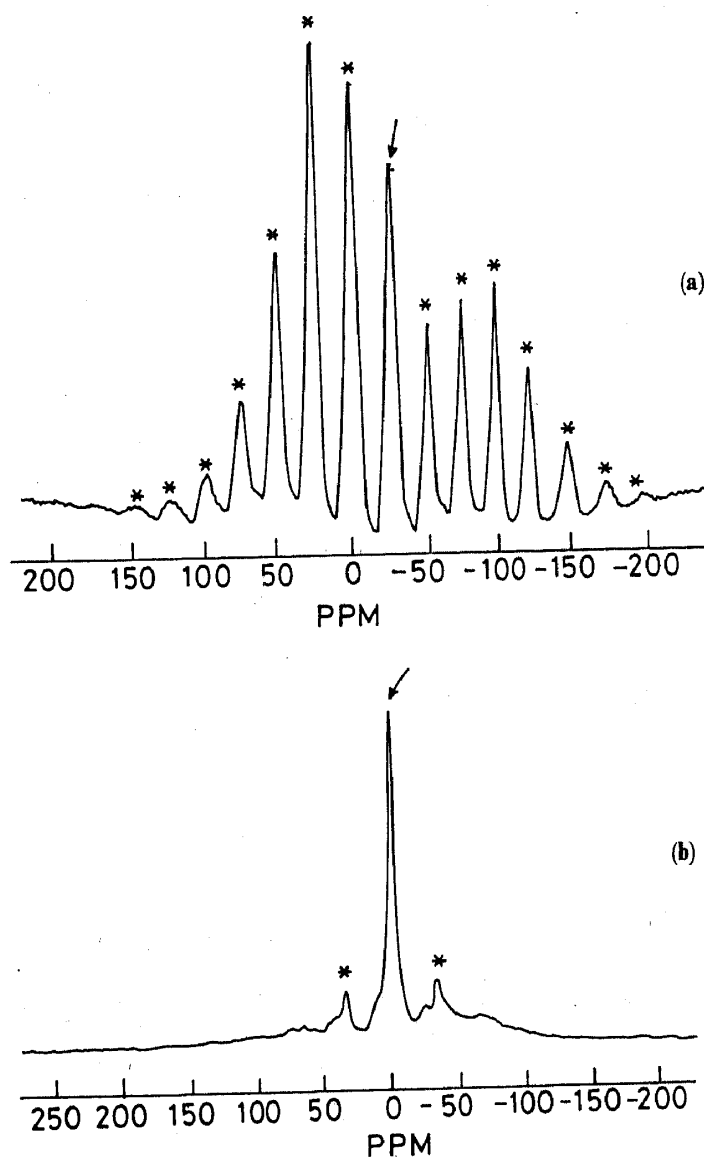


Figure 1. (a) HR MAS NMR spectrum of ^{31}P in a typical AgI-AgPO₃ glass. (b) HR MAS NMR spectrum of ^{11}B in a typical AgI-AgBO₂ glass.

resonance peak is indicated by an arrow. All the other peaks (starred) in the figure 1 are side bands. Chemical shifts of ^{31}P in various glass compositions are listed in table 1. We have shown elsewhere (Prabhakar *et al* 1987) that ^{31}P resonances are related to $(z/r)q$, where z and r are the formal charge and radius of cation, respectively, and q is the partial charge on phosphorus atom in the phosphate group. Since Ag^+ is the only cation present in all the glasses investigated here, it is reasonable to assume that any chemical shift variation is caused by the variation of the partial charge on ^{31}P only. Partial charges are calculated by the method of Sanderson (1983) which is briefly as follows. The anion present in our glasses is PO_3^- , which in the glass structure actually corresponds to a $[\text{POO}_{2/2}\text{O}^-]$ tetrahedral unit, and thus it forms 2-connected chains. Electronegativity of the PO_3 group is calculated as $\chi_{\text{eff}} = [\chi_{\text{P}}(\chi_{\text{O}})^3]^{1/4}$. The partial charge, Δ_{P} , on phosphorus is given by $(\chi_{\text{eff}} - \chi_{\text{P}})/(1.56(\chi_{\text{P}})^{1/2})$. Similarly, Δ_{O} , the partial charge on oxygen is $(\chi_{\text{eff}} - \chi_{\text{O}})/(1.56(\chi_{\text{O}})^{1/2})$. Since the PO_3 group carries

Table 1. Average and mean electronegativities, partial charge and chemical shifts of phosphorus in AgI-Ag₂O-P₂O₅ glasses.

Composition	Partial charge on phosphorus calculated using			Partial charge on oxygen calculated using			Chemical shift ppm	fwhm ppm
	χ_{av}	χ_{mean}	χ_{av}	χ_{av}	χ_{mean}	χ_{mean}		
75 AgI-25 Ag ₂ P ₂ O ₅ *	0.6551	0.3292	-0.7469	-0.8778	-0.9993	-1.1079	-32.67	23.069
75 AgI-25 AgPO ₃ -25 Ag ₂ O ₄	0.7869	0.3483	-0.6940	-0.8702	-0.9554	-1.1015	-32.67	23.069
60 AgI-20 AgPO ₃ -20 Ag ₂ PO ₄ #	0.9617	0.476	-0.6289	-0.8255	-0.8971	-1.0590	-32.67	23.069
60 AgI-40 AgPO ₃	1.1523	0.5212	-0.5473	-0.8007	-0.8971	-1.1059	-27.04	23.069
50 AgI-50 AgPO ₃	1.3959	0.6819	-0.4493	-0.7362	-0.8336	-1.0439	-26.4	9.304
40 AgI-60 AgPO ₃	1.6395	0.8922	-0.3516	-0.6517	-0.7524	-0.9904	-25.6	9.034
30 AgI-70 AgPO ₃	1.8831	1.1672	-0.2538	-0.5413	-0.6075	-0.8287	-24.89	9.034

* , † and # are identical compositions but treated differently for purposes of calculations. In the second composition PO₄³⁻ is ignored.

a formal negative charge of -1 , χ_{eff} is adjusted so as to give $\Delta_P + 3\Delta_O = -1$. The same procedure can be adopted to evaluate the χ_{eff} of the other anionic groups like $\text{P}_2\text{O}_7^{4-}$. Such a procedure, however, yields a single value of the partial charge on phosphorus for all the glass compositions and therefore Δ_P cannot be expected to reflect the variation of chemical shifts of ^{31}P . In order that the calculated Δ_P vary with the chemical shift, $\delta(^{31}\text{P})$ or with the composition, the effect of the other anion in the matrix, namely I^- , should also be considered. This aspect of iodide ion involvement is introduced by defining an average electronegativity. The composition weighted χ_{av} is defined as $\chi_{\text{av}} = x\chi_{\text{I}^-} + (1-x)\chi_{\text{PO}_3^-}$. The electronegativity of I^- is evaluated as $\chi_{\text{I}} - 1.56(\chi_{\text{I}})^{1/2}$; the second term being the correction arising from $\text{I} \rightarrow \text{I}^-$ conversion. We now re-evaluate the partial charges using χ_{av} instead χ_{eff} . The values of the partial charges so calculated are given in table 1. The variation of the chemical shift as a function of the partial charge is shown in figure 2. The variation, although not linear, is satisfactorily monotonic. Therefore the use of χ_{av} and hence involvement of the electronegativity of I^- in the calculation appears reasonable lending credibility to one of the key assumptions of the SUN hypothesis.

It may perhaps be preferable to evaluate the electronegativity of the anion matrix in the limit of strong interaction of the anions as $\chi_{\text{mean}} = (\chi_{\text{I}})^x(\chi_{\text{PO}_3})^{1-x}$. The variation of the chemical shift with the partial charge evaluated using χ_{mean} is also given in table 1 and plotted in figure 2. Since the behaviour is similar we give no preference to either of the procedures at this time.

The resonance peaks in the spectrum shown in figure 3 are all uniformly narrow (the full width at half maximum, fwhm, is given in the table 1) except for the case of pyrophosphate glass. A discussion of this remarkable feature in MAS NMR spectrum is in order. We have shown in earlier publications from this laboratory (Rao 1987; Prabhakar *et al* 1988; Anantharaj *et al* 1988) that pyrophosphate glasses do not

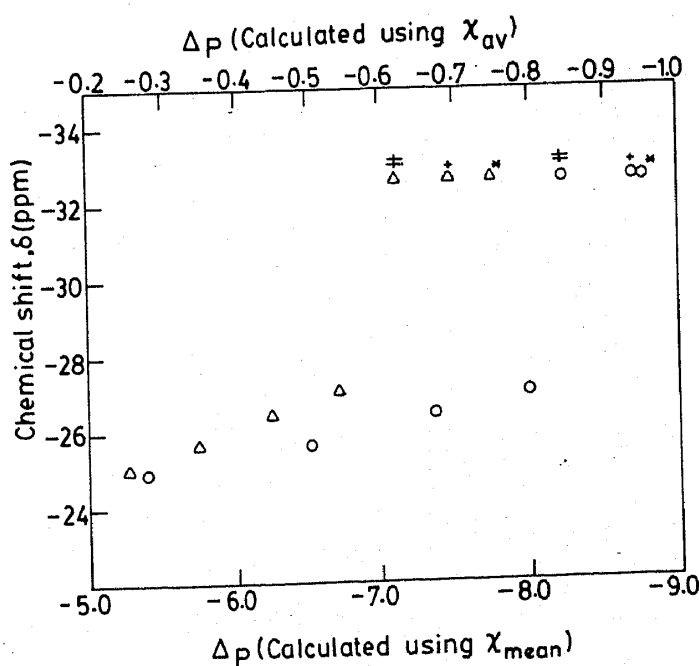


Figure 2. Variation of the chemical shift with partial charge on phosphorus for the glasses in the system $\text{AgI-Ag}_2\text{O-P}_2\text{O}_5$ calculated using χ_{av} (\circ) and χ_{mean} (Δ). *, † and # correspond to the same composition but treated differently (see table 1).

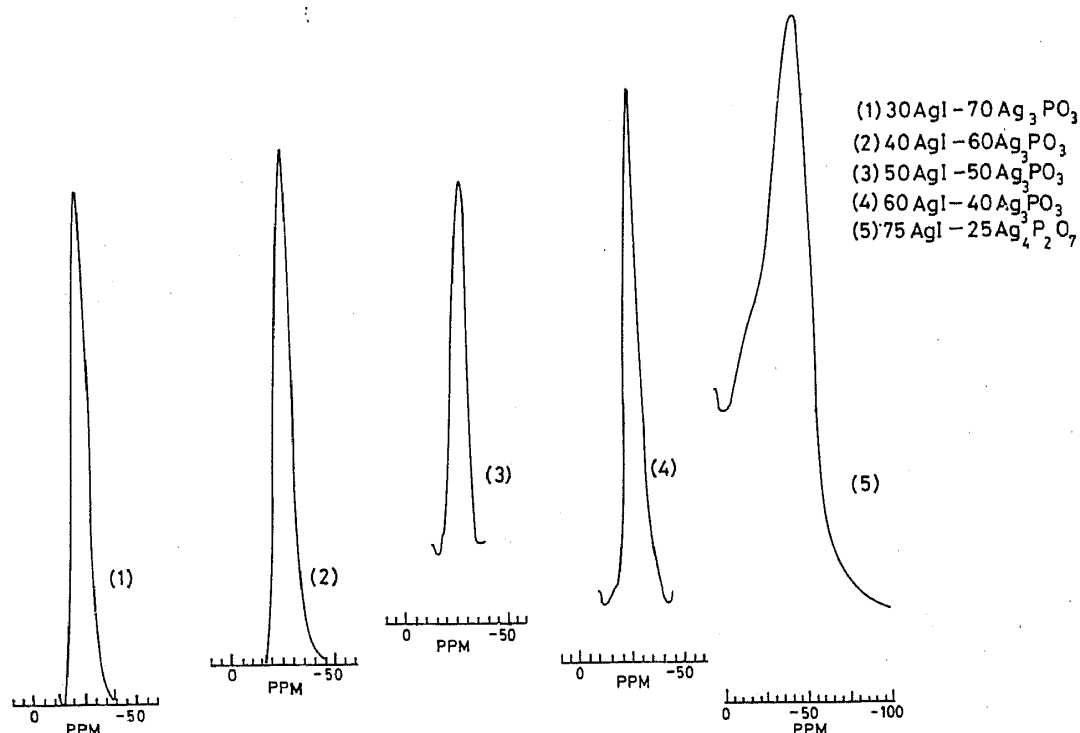


Figure 3. Resonance peaks of ^{31}P for different glass compositions in the system $\text{AgI-Ag}_2\text{O-P}_2\text{O}_5$.

contain discrete pyrophosphate anions but as a result of chemical disproportionation of pyrophosphate units, rings and chains consisting different numbers of metaphosphate units (and thus a variety of anionic species) are present along with PO_4^{3-} . It is the presence of a variety of anionic species which is responsible for the significant spread in the values of partial charges on phosphorus atoms which manifests as a large fwhm in the NMR spectrum. The presence of anionic species in pyrophosphate glasses is thus clearly evidenced in MAS NMR of ^{31}P (figure 3).

3.2 MAS NMR spectra of ^{11}B of silver iodide-silver borate glasses

There are two complicating factors in considering the MAS NMR of silver iodide-silver borate glasses as was pointed out in the introduction. Firstly, ^{11}B is a quadrupolar nucleus with $I=3/2$ and the observed resonance corresponds to $-1/2 \rightarrow 1/2$ transition; the energy of this transition is virtually unchanged by the quadrupolar field. The resonance of trigonal boron has typical quadrupolar split two peak character which only narrows down in the MAS NMR spectrum but is not eliminated. The second complicating factor is that in most borate glasses both trigonal and tetrahedral boron atoms are present. Tetrahedral boron atoms give rise to a single resonance peak since electric field gradient is absent in the tetrahedral geometry. Therefore, the behaviour of the single, fairly sharp, resonance of tetrahedral boron atom can be quite informative.

The complete ^{11}B spectrum of a typical AgI-AgBO_2 glass is shown in figure 1b and the NMR spectra of all the borate glasses are collectively presented in figure 4. It is surprising to note that the MAS NMR spectrum is dominated by the resonance

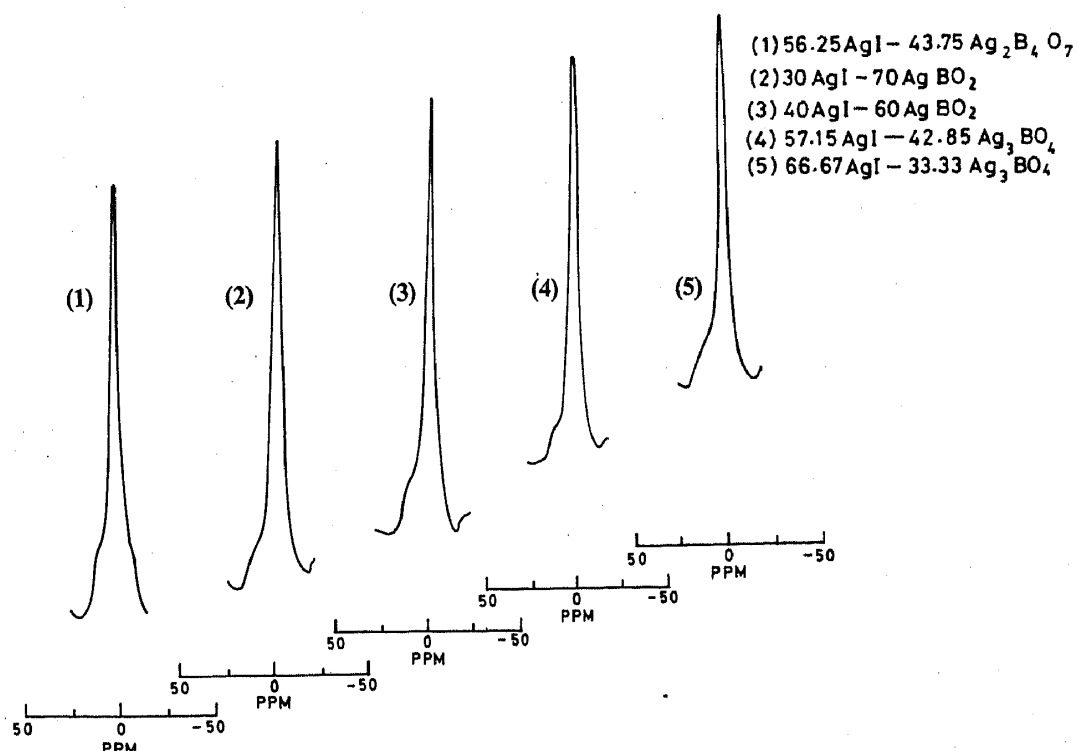


Figure 4. Resonance peaks of ^{11}B for different glass composition in the system AgI-Ag₂O-B₂O₃.

due to tetrahedral boron in all compositions inclusive of the glasses in which the proportion of Ag₂O is quite insufficient to convert all the trigonal boron atoms to tetrahedral boron. Even though it is known that the addition of Ag₂O converts trigonal borons in B₂O₃ to tetrahedral borons without any compositional limit unlike in the case of alkali oxide modification, (Krogh-Moe 1965; Pye *et al* 1978; Prabhakar *et al* (to be published)) the above observation is somewhat surprising. A distinct possibility is that the iodide ion is also involved in the conversion of trigonal to tetrahedral boron. There have been some recent reports with regard to formation of entities like [BO₃I] (Minami *et al* 1983). Unfortunately formation of tetrahedral boron due to addition of the iodide ion alone (in the absence of added Ag₂O) cannot be examined because AgI cannot be dissolved in pure B₂O₃. Our results indicate that all the glass compositions listed in table 2 possess dominantly only tetrahedral borons, unless the resonance signal of trigonal boron is washed out in the presence of silver ions due to as yet unknown relaxational pathways. However, in non MAS averaged (static) spectrum we have seen the evidence for the presence of trigonal boron in some of these glasses (figure 5). Thus MAS appears to have removed significantly the quadrupolar broadening which also appears to contribute to the observed dominance of tetrahedral boron resonance in the spectrum. Even then the origin of such dominance of tetrahedral boron resonance in the spectrum is unclear at this time.

The variation in chemical shift of the boron as a function of glass composition is not high, although it is clearly more than the resolution of the instrument (≈ 0.3 ppm). For comparison we have evaluated the partial charge on boron using the procedure described earlier, and in table 2 (also plotted in figure 6) we give the calculated values of the partial charges on boron assuming both χ_{mean} and χ_{av} . The variation of the

Table 2. Average and mean electronegativities, partial charge and chemical shift of boron in AgI-Ag₂O-B₂O₃ glasses.

Composition	Partial charge on boron calculated using		Partial charge on oxygen calculated using		Chemical shift ppm	fwhm ppm
	χ_{av}	χ_{mean}	χ_{av}	χ_{mean}		
56.25 AgI-43.75 Ag ₂ B ₄ O ₇ *	1.4453	0.6189	-0.3504	-0.6994	0.534	6.7
32.15 AgBO _{3/2} I-50 AgBO ₂ -17.5 BO _{3/2} †	2.3185	2.3052	0.0184	0.0128	0.534	6.7
30 AgI-70 AgBO ₂	1.5938	1.0347	-0.2877	-0.5238	0.892	6.7
40 AgI-60 AgBO ₂	1.3915	0.8046	-0.3731	-0.6029	1.197	6.7
57.15 AgI-42.55 Ag ₃ BO ₄	1.4193	0.4576	-0.3614	-0.7675	1.268	6.7
66.67 AgI-33.33 Ag ₃ BO ₄	1.1434	0.371	-0.4779	-0.8041	1.437	6.7

* and † are identical compositions treated differently for purposes of calculation. The second composition is not plotted in figure 6.

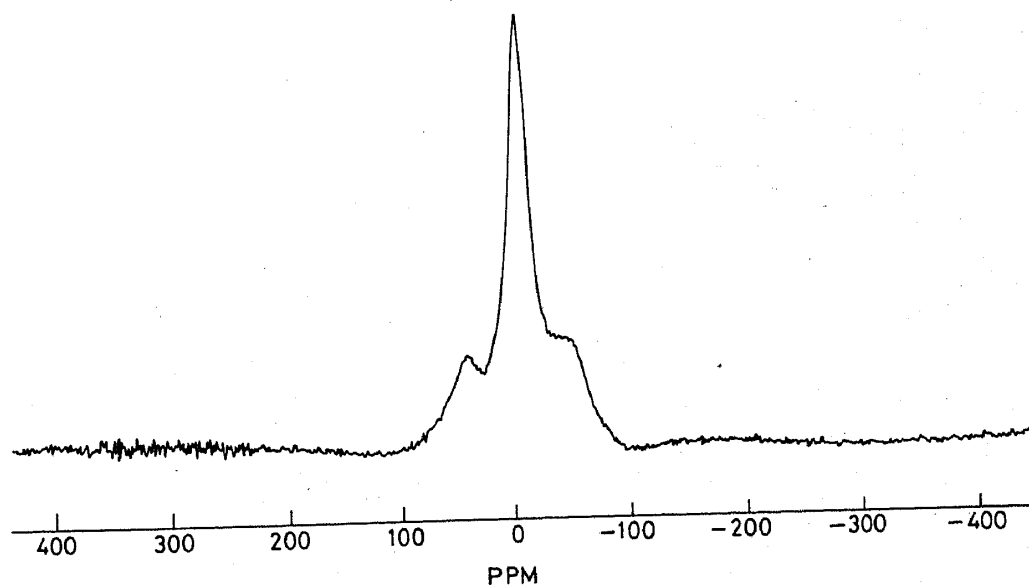


Figure 5. ^{11}B NMR spectrum (powder pattern) of 56.25 AgI-43.75 $\text{Ag}_2\text{B}_4\text{O}_7$ glass.

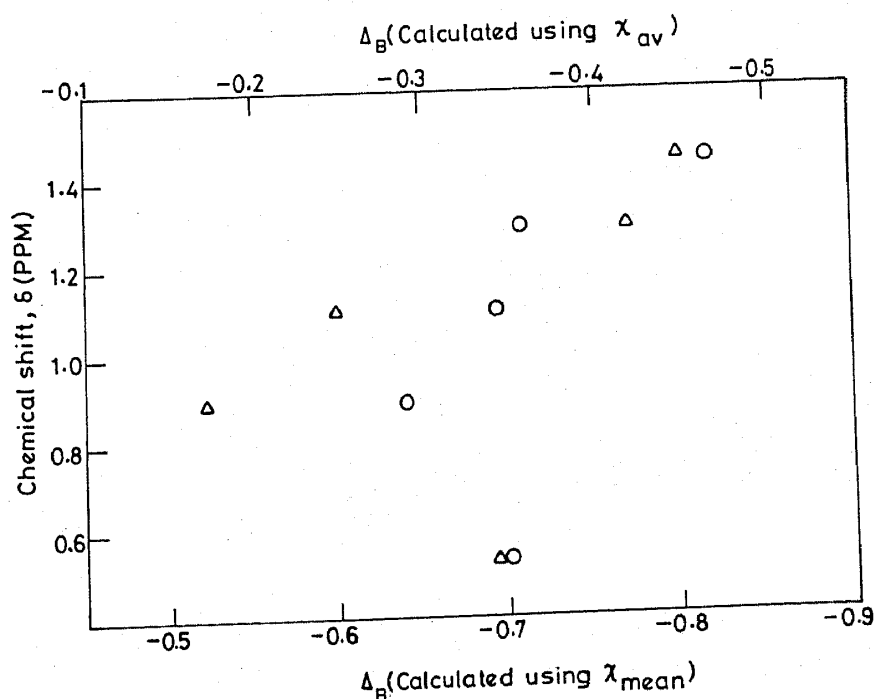


Figure 6. Variation of the chemical shift with partial charge on boron for the glasses in the system AgI- Ag_2O - B_2O_3 calculated using χ_{av} (Δ) and χ_{mean} (\circ). * and † are identical compositions treated differently (see table 2).

chemical shift with the partial charge is essentially monotonic except in borate glass composition in which the proportion of Ag_2O is quite insufficient to convert all the trigonal $[\text{BO}_{3/2}]$ to tetrahedral boron $[\text{BO}_{4/2}]$ units (the starred composition in table 2).

4. Conclusion

This work was intended to examine the possibility of interanion interaction in AgI based fast ion conductors. Examination of HR MAS NMR of ^{31}P and ^{11}B in phosphate and borate glasses appears to be consistent with the notion of an effective electronegativity for the anion matrix defined either as an average or as a mean. This in effect indicates a significant interanion interaction lending support to the model of structural unpinning of silver ion in fast ion conducting AgI based glasses.

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