

## Vibrational spectra and structure of fluoroindate glasses

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A series of fluoroindate glasses, both binary ( $x\text{InF}_3 \cdot [1-x]\text{MF}_2$ ,  $M = \text{Sr}, \text{Ba}$ ) and multicomponent ( $\text{InF}_3\text{-ZnF}_2\text{-SrF}_2\text{-BaF}_2\text{-CdF}_2$ ), have been prepared and their infrared absorption and reflection spectra were measured. Polarized Raman spectra were also recorded for all the different glass compositions. Starting with the binary compositions, some structural conclusions were derived for these fluoroindate glasses, whose structure is still virtually unknown. The In atoms appear to be always in octahedral coordination, as inferred from both the infrared and Raman spectra, the latter being dominated by a highly polarized high frequency mode at  $\sim 509\text{ cm}^{-1}$ , in a fashion similar to fluorozirconate glasses. Other features in the vibrational spectra provided additional insight into the structural environments of the glass cations, namely, Zn.

### 1. Introduction

Heavy metal fluoride glasses are important infrared transmitting materials [1]. Current applications include bulk optical components and fiber optics for the near and middle infrared (IR). The main problems remaining with fluoride glasses such as those based on  $\text{ZrF}_4$  are related to their poor chemical durability, relatively high tendency for crystallization and limited middle IR transparency. Fluoroindate glasses (based on  $\text{InF}_3$ ) appear to have somewhat better physico-chemical characteristics than fluorozirconates [2], although they are still very incompletely characterized. In particular, their structure is virtually unknown at present.

One of the properties of interest for fluoroindate glasses is their IR transmission, but the fundamental IR spectrum was only recently studied by Almeida et al. [3] for a  $40\text{InF}_3\text{-}20\text{ZnF}_2\text{-}20\text{SrF}_2\text{-}20\text{BaF}_2$  (mol%) glass. In that paper, it was suggested that this glass appeared to be composed mostly of discrete  $\text{InF}_6^{3-}$  anions

bonded together by  $\text{Ba}^{2+}$  cations, without significant bridging. The present work, where fundamental IR spectra of fluoroindate glasses have been recorded in transmission and in reflection, as well as polarized Raman spectra, was undertaken with the purpose of elucidating the dominant structural features of these glasses.

### 2. Experimental

The glasses studied had the compositions given in table 1. The raw materials were  $\text{In}_2\text{O}_3$  (Preusag, 99.99%),  $\text{ZnF}_2$  (Riedel de Haen, technical),  $\text{CdF}_2$  (Fluka, >95%) and  $\text{BaF}_2$  (BDH, 97%).  $\text{In}_2\text{O}_3$  was first fluorinated with  $\text{NH}_4\text{F} \cdot \text{HF}$  and the glass batches were then melted in a dry box. The melts were poured and cooled between preheated brass plates. Fourier transform IR spectra

Table 1  
Nominal batch compositions (mol%) of fluoroindate glasses

Fluoride					Sample designation
$\text{InF}_3$	$\text{ZnF}_2$	$\text{SrF}_2$	$\text{BaF}_2$	$\text{CdF}_2$	
60			40		A
40	20	20	15	5	B
20	40	20	15	5	C

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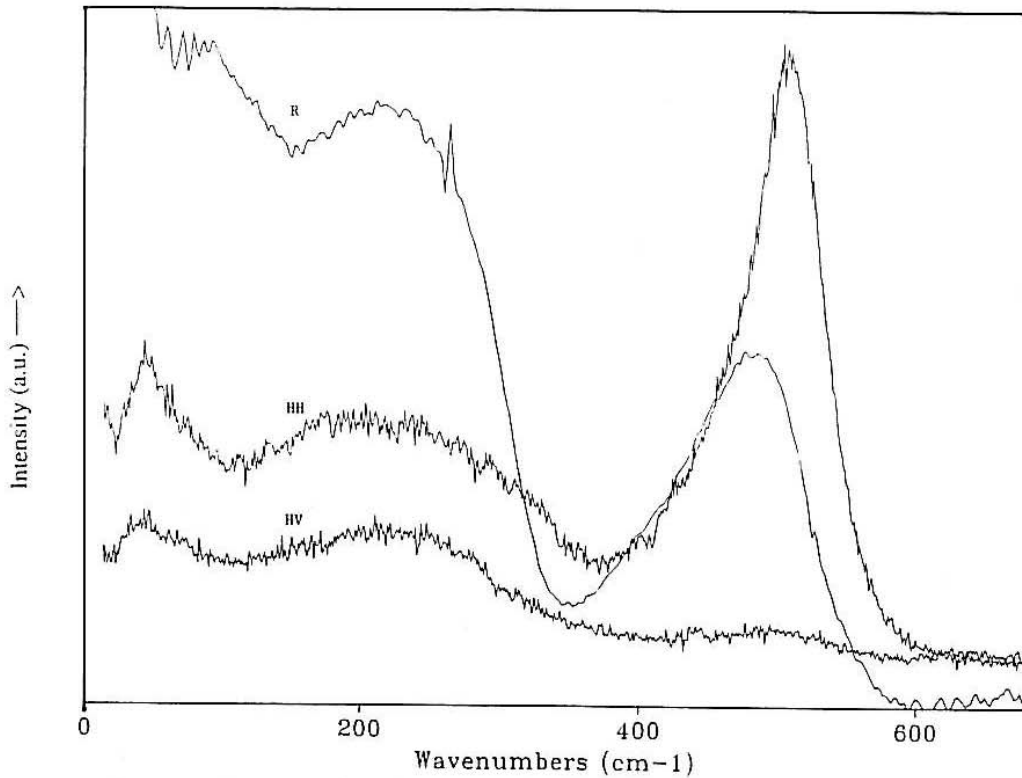


Fig. 1. Reflectance (R) and polarized Raman spectra (HH, HV) of glass A.

were recorded, both in the transmission (polyethylene pellets) and near-normal reflectivity (SPECAC specular reflectance accessory at  $10^\circ$  off-

normal) modes, in a Nicolet 20 F evacuated spectrometer at  $4\text{ cm}^{-1}$  resolution, for an average of 400 scans. Polarized Raman spectra were col-

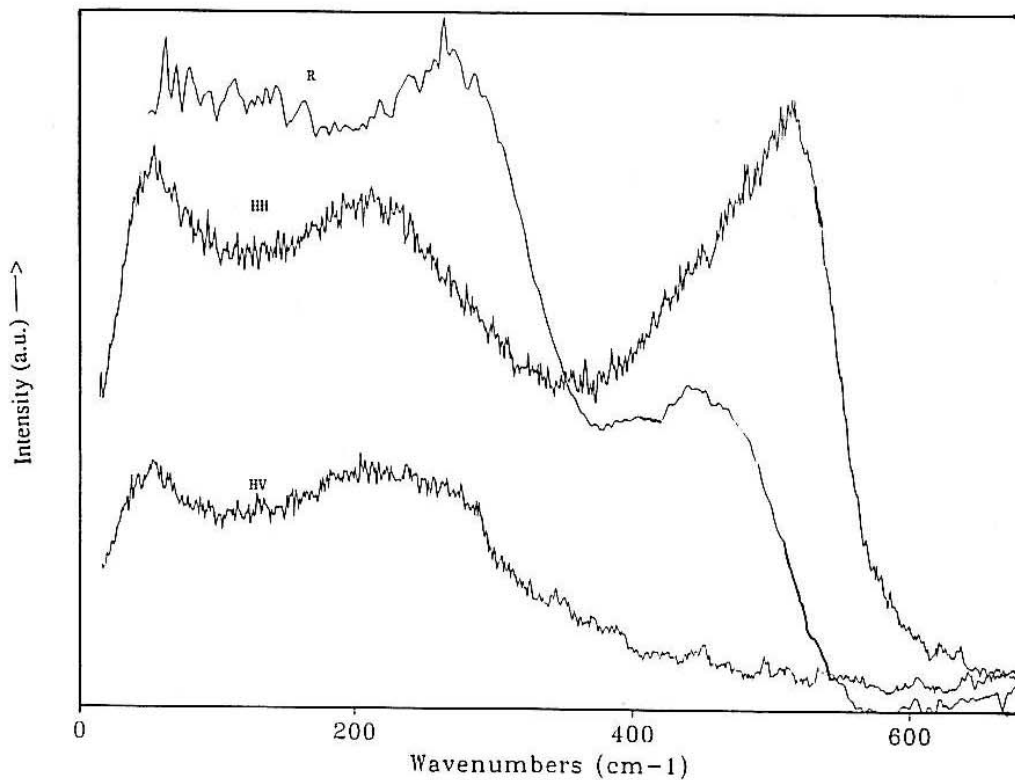


Fig. 2. Reflectance (R) and polarized Raman spectra (HH, HV) of glass C.

lected for all glasses with a system consisting of a Spex 1403 double monochromator, a Spectra Physics 2016 Ar ion laser and a Hamamatsu photomultiplier detector; these spectra were taken at room temperature, with a resolution of  $5\text{ cm}^{-1}$ , in the  $90^\circ$  scattering geometry, for the polarized (HH) and depolarized (HV) configurations [4].

### 3. Results

Figure 1 shows a superposition of the reflection and Raman spectra of binary barium fluoroindate glass A. For the sake of clarity, only the reflection spectra are included in the figures and not the absorption, but the two types of spectral curve were very similar. Figure 2 shows a superposition of the reflection and Raman spectra of glass C and fig. 3 shows a similar spectral superposition for glass B.

### 4. Discussion

The absorption and Raman spectra of glass A were similar to those previously recorded for a quaternary glass with 40%  $\text{InF}_3$  [3] and the reflection spectrum showed the usual blue shifts relative to the absorption curve. The vibrational spectra of fig. 1 may be assigned almost completely in terms of the vibrational modes of the  $\text{InF}_6^{3-}$  octahedral complex ion [3,4], without any vibrations clearly due to the network modifying  $\text{Ba}^{2+}$  cations. In fact, the IR modes at  $\sim 225$  and  $484\text{ cm}^{-1}$  (in reflection) are probably the bending and antisymmetric stretches of the non-bridging fluorine ( $\text{F}_{\text{nb}}$ ) atoms,  $\delta_1(\text{F}_{\text{nb}}-\text{In}-\text{F}_{\text{nb}})$  and  $\text{AS}(\text{F}_{\text{nb}})$ , respectively, whereas the Raman modes at  $\sim 203$  and  $507\text{ cm}^{-1}$  (this one strongly polarized) are bending and symmetric stretches of the non-bridging fluorine atoms,  $\delta_2(\text{F}_{\text{nb}}-\text{In}-\text{F}_{\text{nb}})$  and  $\text{SS}(\text{F}_{\text{nb}})$ , respectively. Given the stoichiometry of this glass ( $3\text{InF}_3-2\text{BaF}_2$ ), with a F/In ratio of  $13/3 =$

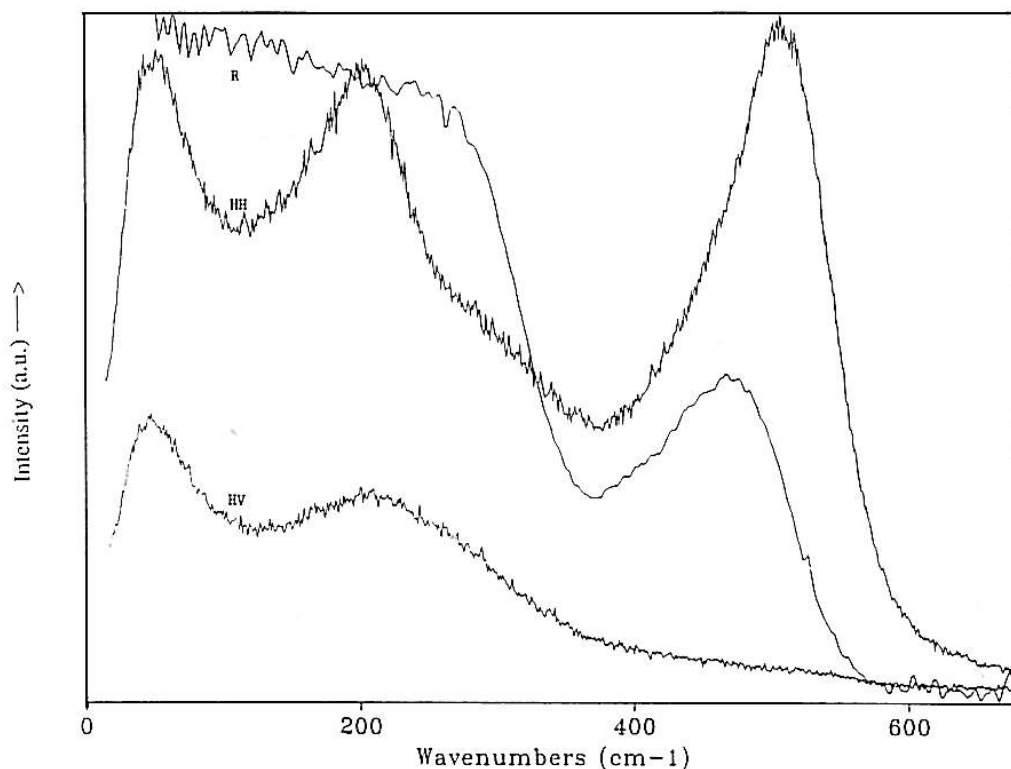


Fig. 3. Reflectance (R) and polarized Raman spectra (HH, HV) of glass B.

4.33, this could imply that each (distorted) octahedron shares  $\sim 3$  of its F atoms, on average, with neighbouring octahedra and, therefore, each octahedron might have about three  $F_b$  and three  $F_{nb}$  species, on average. The possible position of the vibrational modes related to the bridging fluorine ( $F_b$ ) atoms is difficult to estimate at this point. However, the IR absorption spectrum of crystalline  $InF_3$  has its highest frequency mode near  $528\text{ cm}^{-1}$  [3]. This compound has octahedrally coordinated In and 100%  $F_b$  atoms [5], but the In–F–In angles have not yet been established. The  $\gamma\text{-}InF_3$  phase appears to have  $180^\circ$  angles and therefore it is possible that the  $AS(In\text{-}F_b)$  in the glass has a fairly high frequency [1], overlapping in fact with the  $AS(F_{nb})$  mode on the broad IR absorption band found near  $477\text{ cm}^{-1}$ , corresponding to the reflection band at  $483\text{ cm}^{-1}$  in fig. 1. In these highly ionic glasses, however, a distinction between  $F_b$  and  $F_{nb}$  species may be somewhat artificial.

Glass C (fig. 2) contained only 20%  $InF_3$ , compared with 60% for glass A. While the highest frequency IR mode has decreased both in frequency and intensity, major changes also occurred in the Raman spectrum, namely a substantial increase in the  $\sim 204\text{ cm}^{-1}$  band and the appearance of a clear shoulder on the low frequency side of the dominant peak, at about  $420\text{ cm}^{-1}$ ; the frequency of the dominant Raman band remained the same ( $508\text{ cm}^{-1}$ , compared with  $507\text{ cm}^{-1}$  in glass A). The polarized shoulder near  $420\text{ cm}^{-1}$  is probably due to  $SS(F_b)$  in Zn–F–Zn sequences, as observed near  $385\text{ cm}^{-1}$  in ref. [3], and therefore it is likely that the Zn atoms also remain sixfold coordinated in this glass [3]. The fact that the major features remained essentially unchanged may indicate that the vibrational frequencies characteristic of Zn–F bonds in the glasses are not too different from those of In–F bonds. This was observed in the case of crystalline  $InF_3$  and  $ZnF_2$  [3]. The intensity of the high frequency IR mode clearly scaled with the In concentration in the glass, as seen by comparing figs. 1 and 2.

Glass B (fig. 3) contained an intermediate amount of  $InF_3$  (40%), but it had only 20%  $ZnF_2$  and the Raman shoulder near  $420\text{ cm}^{-1}$  was much weaker. The  $202\text{ cm}^{-1}$  Raman mode, on the other hand, became quite strong, which may indicate that most F atoms now became non-bridging. In fact, the similarity between the composition and spectra of this glass and that previously studied in ref. [3] suggests that this one is probably also composed mostly of discrete  $InF_3^{6-}$  complex ions. If this is the case, the effect of a larger degree of bridging in glass A, relatively to glass B, is the increase of the  $AS(F_{nb})$  frequency from  $473$  to  $484\text{ cm}^{-1}$ , as expected [1].

## 5. Conclusions

A series of fluoroindate glasses have been studied by IR and polarized Raman spectroscopy. Their structures appear to vary from a partially bridged glass for the binary composition to an essentially non-bridged structure for the multi-component compositions. The presence of Zn contributes to additional bridges, although a clear distinction between  $F_b$  and  $F_{nb}$  species is not possible in these glasses. Both In and Zn atoms are probably sixfold coordinated in all cases.

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## References

- [1] R.M. Almeida, in: Handbook on the Physics and Chemistry of Rare Earths, ed. K.A. Gschneidner Jr. and L. Eyring, Vol. 15 (Elsevier, Amsterdam, 1991) p. 287.
- [2] J.J. Videau, B. Dubois and J. Portier, C.R. Acad. Sci. 297 (1983) 483.
- [3] R.M. Almeida, J.C. Pereira and R. Alcalá, Phys. Chem. Glasses 33 (1992) 187.
- [4] R.M. Almeida, J. Non-Cryst. Solids 106 (1988) 347.
- [5] L.K. Beck, B.H. Kugler and H.M. Haendler, J. Solid State Chem. 8 (1973) 312.