Vibrational spectra and structure of fluoroindate glasses

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A series of fluoroindate glasses, both binary (xInF₃·(1-x)MF₂, M = Sr, Ba) and multicomponent (InF₃-ZnF₂-SrF₂-BaF₂-CdF₂), have been prepared and their infrared absorption and reflection spectra were measured. Polarized Raman spectra were also recorded for all 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 ~ 509 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 ZrF₄ are related to their poor chemical durability, relatively high tendency for crystallization and limited middle IR transparency. Fluoroindate glasses (based on InF₃) appear to have somewhat better physicochemical 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 40InF₃-20ZnF₂-20SrF₂-20BaF₂ (mol%) glass. In that paper, it was suggested that this glass appeared to be composed mostly of discrete InF₆⁻ anions bonded together by Ba²⁺ 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 In₂O₃ (Preussag, 99.99%), ZnF₂ (Riedel de Haen, technical), CdF₂ (Fluka, > 95%) and BaF₂ (BDH, 97%). In₂O₃ was first fluorinated with NH₄F·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>
<thead>
<tr>
<th>Fluoride</th>
<th>Sample designation</th>
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<tr>
<td>InF₃</td>
<td>ZnF₂</td>
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<tr>
<td>60</td>
<td>40</td>
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<td>40</td>
<td>20</td>
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Table 1
Nominal batch compositions (mol%) of fluoroindate glasses
were recorded, both in the transmission (polyethylene pellets) and near-normal reflectivity (SPECAC specular reflectance accessory at 10° off-normal) modes, in a Nicolet 20 F evacuated spectrometer at 4 cm⁻¹ resolution, for an average of 400 scans. Polarized Raman spectra were col-

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

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 cm\(^{-1}\), in the 90° 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% 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 InF\(_6\) octahedral complex ion [3,4], without any vibrations clearly due to the network modifying Ba\(^{2+}\) cations. In fact, the IR modes at \(\sim\) 225 and 484 cm\(^{-1}\) (in reflection) are probably the bending and antisymmetric stretches of the non-bridging fluoride (F\(_{nb}\)) atoms, \(\delta(F_{nb}-In-F_{nb})\) and AS(F\(_{nb}\)), respectively, whereas the Raman modes at \(\sim\) 203 and 507 cm\(^{-1}\) (this one strongly polarized) are bending and symmetric stretches of the non-bridging fluoride atoms, \(\delta(F_{nb}-In-F_{nb})\) and SS (F\(_{nb}\)), respectively. Given the stoichiometry of this glass (3InF\(_3\)-2BaF\(_2\)), with a F/In ratio of 13/3 =

![Fig. 3. Reflectance (R) and polarized Raman spectra (HH, HV) of glass B.](image-url)
4.33, this could imply that each (distorted) octahedron shares ~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 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 $\gamma$-InF$_3$ phase appears to have 180° angles and therefore it is possible that the AS(In–$F_b$) 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 cm$^{-1}$, corresponding to the reflection band at 483 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 ~204 cm$^{-1}$ band and the appearance of a clear shoulder on the low frequency side of the dominant peak, at about 420 cm$^{-1}$; the frequency of the dominant Raman band remained the same (508 cm$^{-1}$, compared with 507 cm$^{-1}$ in glass A). The polarized shoulder near 420 cm$^{-1}$ is probably due to $SS(F_b)$ in Zn–F–Zn sequences, as observed near 385 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 cm$^{-1}$ was much weaker. The 202 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$_3^-$ 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 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