The peculiarities of fluoride glass structure. Spectroscopic study

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Abstract

Glass systems based on ZrF 4, InF 3, GaF 3 with added BiF 3, SnF 2, BaF 2, SrF 2, PbF 2 were obtained to analyze changes of the structure and properties of these glasses with the addition of various components. The glass structures were investigated by means of vibration spectroscopy. IFS EQUINOX 55S, T64000 and DFS-24 spectrometers were used for measurements of infrared and Raman spectra. It was shown that BiF 3 and SnF 2 are the second glassformers as ZrF 4, InF 3 and GaF 3. The structures of glassforming polyhedra were determined for each glass type. The structural peculiarities and the length scale of the medium range order were discussed and estimated by the frequency of the ‘boson’ peak in all low frequency Raman spectra of the glasses under study. The medium range order in InF 3-BiF 3-BaF 2 glasses built from InF 6 polyhedra that are not bound directly to BiF 3 polyhedra and Ba-modifier essentially determines the size of the medium range order of the glasses. Nanometer scale separation of mono-component fractions was not observed in glasses of the GaF 3-SnF 2 system.

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1. Introduction

Heavy metal fluoride glasses can have promising potential applications as IR optics materials [1–3]. These glasses are a good matrix for doping by rare earth elements. Variation of compositions in the multicomponent vitreous systems allows to attain the properties which are necessary for practical applications. It was suggested [4–6] that an addition of SnF 2 to the fluoride system may improve the glass properties. In some ZrF 4-based glasses the partial or complete replacement of BaF 2 by SnF 2 results in a decrease of glass transition temperature (T g) by more than 100 °C [4]. Glasses with SnF 2 have high refractive index and high mobility of fluorine ions in their structures [7]. The introduction of BiF 3 in fluorozirconate glasses also results in a significant increase of refractive index [8], which is important for the fabrication of optical fibers with high numerical aperture. It was suggested that an addition of BiF 3 to the glass system should facilitate glass formation due to a decrease of melt temperature. It is evident that the choice of glass composition determines the structure and properties of the glass. In the present paper the glass structures in the ZrF 4-SnF 2–BaF 2, ZrF 4-SnF 2–GaF 3, SnF 2–GaF 3, and InF 3–BiF 3–BaF 2 systems are presented. Primary attention was given to revealing the structural role of glass components.

2. Experimental

The glasses were made from pure anhydrous metal fluorides. All procedures were carried out in the box filled with
dried nitrogen. The appropriate mixtures of fluorides were melted at 700–800 °C for about 15–40 min in a closed vitreous carbon crucible in the electrically heated furnace. The use of higher temperature results in evaporation of components. The glasses were obtained either by quenching between metal plates or by casting into a brass mould. The syntheses of glasses were described in detail elsewhere [9–11]. Raman spectra of glass plates were recorded by T64000 and DFS-24 spectrometers in the range 20–1500 cm−1 (with error ± 1 cm−1). The excitation of spectra was made by radiation of argon laser (Spectra Physics) at 4880 and 5145 Å lines. Polarized (VV) and depolarized (HV) scattering geometries were used. IR spectra of pounded samples were recorded with using the IFS EQUI-NOX 55S spectrometer in the 4000–80 cm−1 range (with error ± 1 cm−1) and analyzed in the spectral range of 800–80 cm−1. The absence of crystalline phases in the glasses was confirmed by X-ray data on D8 ADVANCE diffractometer.

3. Results

The bands at 500–400 cm−1 and 320–200 cm−1 were observed in IR spectra of the researched glass system of ZrF4–SnF2–BaF2 (Fig. 1). The IR spectrum of 60ZrF4–10SnF2–30BaF2 was very similar to the spectrum of 60ZrF4–40BaF2 glass presented in [12]. In the systems with higher SnF2 contents we found that the positions and forms of the bands depended on the ZrF4/SnF2 ratio (Fig. 1).

The obtained IR spectra of glasses of (60–x)InF3–xBiF3–40BaF2 are shown in Fig. 2. The IR spectra of glasses of (60–x)InF3–xBiF3–40BaF2 were compared with IR spectra of 60InF3–40BaF2 glass, the typical glass with one glassformer and network formed by InF6 octahedra bound together by tops in zigzag chains. In general, the IR spectra of all the discussed glasses are similar to 60InF3–40BaF2 spectrum. The assignments of the bands in the IR and Raman spectra are listed in Table 1. In the Raman spectra the bands of v(In–F) observed at 497–466 cm−1 were also sensitive to BiF3 content.

In high-frequency Raman spectra of the glasses in the SnF2–GaF3 system, one should mention two bands at about 560 and 350 cm−1 (Fig. 3). The form and position of the first band depends on the content of GaF3 in the glass. Fig. 4 shows the IR spectra of the glasses in the SnF2–GaF3 system. One can see that complex bands represent the IR spectra of these glasses. The intensities and shapes of bands depend on the GaF3/SnF2 ratio.

In low frequency Raman spectra of all studied glasses we observed a ‘boson’ peak (lower 50 cm−1). The frequency of ‘boson’ peak is related to the structure correlation length (R) of the middle range order (MRO), causing the phonon localization. The middle range length R can be estimated as [13]

\[ R = \frac{s \omega}{v c}, \]

where \( \omega \) – the frequency of ‘boson’ peak in cm−1, \( c \) – the speed of light, \( s \) – factor (0.8 for sphere), \( v \) – the speed of

<table>
<thead>
<tr>
<th>Glass composition</th>
<th>( \omega_{\text{R}} ) (±1) cm(^{-1}) (Raman)</th>
<th>v(In–F), (±1) cm(^{-1})</th>
</tr>
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<tbody>
<tr>
<td>25InF3–35BiF3–40BaF2</td>
<td>46</td>
<td>445</td>
</tr>
<tr>
<td>30InF3–30BiF3–30BaF2</td>
<td>46</td>
<td>450</td>
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<tr>
<td>35InF3–25BiF3–40BaF2</td>
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<tr>
<td>45InF3–15BiF3–40BaF2</td>
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<td>460</td>
</tr>
<tr>
<td>50InF3–10BiF3–40BaF2</td>
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<td>465</td>
</tr>
<tr>
<td>60ZrF4–30BaF2–5LaF3–5AlF3</td>
<td>45</td>
<td>498</td>
</tr>
<tr>
<td>60ZrF4–30SnF2–5LaF3–AlF3</td>
<td>54</td>
<td>510</td>
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<tr>
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<td>50</td>
<td>465</td>
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<tr>
<td>60InF3–40SrF2</td>
<td>60</td>
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Fig. 1. IR spectra of glasses: 1 – 33.3ZrF4–56.7SnF2–10BaF2, 2 – 50ZrF4–30SnF2–20BaF2, 3 – 60ZrF4–10SnF2–30BaF2, 4 – crystal SnF2.

Fig. 2. IR spectra of glasses: 1 – 25InF3–35BiF3–40BaF2, 2 – 50InF3–10BiF3–40BaF2, 3 – 60InF3–40BaF2 and 4 – crystal BiF3.

Fig. 3. IR spectra of glasses in the SnF2–GaF3 system. One can see that complex bands represent the IR spectra of these glasses. The intensities and shapes of bands depend on the GaF3/SnF2 ratio.

Fig. 4. IR spectra of glasses in the SnF2–GaF3 system. One can see that complex bands represent the IR spectra of these glasses. The intensities and shapes of bands depend on the GaF3/SnF2 ratio.
sound in glass (we used 2.1 km/s [14] for heavy metal fluoride glasses).

4. Discussion

4.1. Fluorozirconate glasses

The comparison of IR spectra of crystalline fluorozirconates and various fluorozirconate glasses showed that these glasses were formed from ZrF7 and ZrF8 polyhedra [12]. The bands in IR spectra of our glasses were in the same range and indicate the presence of the fluorozirconate polyhedra. We assume that the changes in IR spectra were caused by a superposition of the bands from ZrFn and SnFn polyhedra. The evidence of this fact is the presence of bands in the range of 400–300 cm\(^{-1}\) in the spectrum of crystalline SnF2 (Fig. 1). Therefore, two glassformers – ZrF4 and SnF2 – were present in the glasses of the ZrF4–SnF2–BaF2 system. Similar conclusion was made for \(x\)ZrF4–(95 – \(x\))SnF2–5GaF3 glasses [15]. The broadening and low frequency displacement of the bands, corresponding to stretching vibrations of fluorozirconate polyhedra, were observed in IR spectra of these glasses in comparison with the spectrum of the ZrF4–BaF2 glass. These effects increase with the increase of SnF2 content. Therefore, the wide band at 500–450 cm\(^{-1}\) is a superposition of bands, corresponding to vibrations of fluorozirconate and fluorostannate polyhedra. In all the Raman spectra of \(x\)ZrF4–(95 – \(x\))SnF2–5GaF3 glasses the bands were observed about 570 cm\(^{-1}\) and 380 cm\(^{-1}\) [15]. Along with increase of the ZrF4/SnF2 ratio, the intensity of the band at 570 cm\(^{-1}\) grows linearly, and the intensity of the band at 380 cm\(^{-1}\) decreases. The band at 570 cm\(^{-1}\) was assigned to Zr–F stretching vibrations of ZrF\(_n\) polyhedra. The band at 380 cm\(^{-1}\) was attributed to vibrations of fluorostannate groups. Such a band is observed in the Raman spectrum of the SnF2 crystal [15].

4.2. Glasses in InF3–BiF3–BaF2 system

A series of fluoroindate glasses were studied earlier [3,10,14,16]. The results of these studies showed that networks of the glasses based on InF3 were formed with groups of InF6. The analysis of IR spectra obtained for (60/\(x\))InF3–\(x\)BiF3–40BaF2 glasses showed that glass networks were too built from InF6 polyhedra. A partial replacement of InF3 by BiF3 results in a spectral shift and a change of spectral shape of the 500–450 cm\(^{-1}\) band and a significant intensity increase of the 260–200 cm\(^{-1}\) band. From comparison with IR spectra of BiF3 crystal (Fig. 2), we assumed that the bands of polyhedra present in the spectra of the discussed glasses. So the glasses of (60 – \(x\))InF3–\(x\)BiF3–40BaF2 have two glass-formers – InF3 and BiF3.

In the Raman spectra the bands characterizing stretching vibrations of InF6 (450–500 cm\(^{-1}\)) and BiF\(_n\) polyhedra (312 cm\(^{-1}\)) are in different spectral ranges, and it is impossible to explain the observed changes of frequencies of its superposition. The bands characterizing vibrations of terminal bonds are usually the most intensive in Raman spectra, and the bands of bridging bonds are weak or are not shown at all [17]. Therefore, the bands at 500–450 cm\(^{-1}\) were assigned to stretching vibrations of terminal fluorines in InF6 polyhedra. The direct correlation between the degree of polyhedra binding and the position of stretching vibration bands of terminal fluorine atoms in the polyhedra was discussed earlier [18]. Our results indicate that incorporation of BiF3 into the InF3–BaF2 system changes the degree of binding of fluoroindate polyhedra in the glass structure. The BiF\(_n\) polyhedra are built between InF6 poly-

![Fig. 3. High-frequency Raman spectra of the glasses in SnF2–GaF3 systems. A, a.u. – intensity.](image-url)

![Fig. 4. IR spectra of glasses: 1 – 65SnF2–35GaF3, 2 – 75SnF2–25GaF3, 3 – 85SnF2–15GaF3, 4 – 55GaF3–35PbF2–10BaF3 and 5 – crystal α-SnF2.](image-url)
hedral in the chains of network, the quantity of In–F–In-bridges decreases, and weaker bridges such as In–F–Bi–F– are formed. A distortion of InF₆ octahedra is decreased and the band at 500–450 cm⁻¹ becomes more symmetric. Finally, it results in extension of the IR transparency range of these glasses.

4.3. Glasses in SnF₂–GaF₃ system

The conclusion was made on the basis of Raman spectra of crystal and glass fluorogallates and other investigations of fluorogallates [18,19] that the glasses in the SnF₂–GaF₃ system were formed from GaF₆ octahedra bound by fluorine bridges. The first band characterizes the stretching vibrations of Ga–F. Comparing these data with the IR spectrum of 55GaF₃–35PbF₂–10BaF₂ in which network only GaF₆ serves as a glassformer, we concluded that the observed bands in the IR spectra of the SnF₂–GaF₃ glass system at about 520 and 250 cm⁻¹ were stretching and bending vibrations of GaF₆ polyhedra, however, the bands characterizing other groups were also observed in the spectra. The intensities of the bands at 450 and 200 cm⁻¹ increase with SnF₂ content while in the spectrum of 55GaG₃–35PbF₂–10BaF₂ the bands in that ranges are absent. However, the bands in that ranges of IR spectrum were present for crystal SnF₂.

The intensity of the band at 350 cm⁻¹ in the Raman spectrum (Fig. 3) increases with the increase of SnF₂ content. We assigned the band at 350 cm⁻¹ in the Raman spectrum and 450 cm⁻¹ in the IR spectrum to stretching vibrations of Sn–F in fluorostannate polyhedra.

Thus, the glasses in the SnF₂–GaF₃ system are formed by two types of groups: GaF₆ and SnF₆. Therefore, there are two glassformers in this system. An additive character of the dependence of Raman spectra on the glass composition allows concluding that mixed networks from GaF₆ and SnF₆ polyhedra are responsible for the formation of glass structure.

4.4. Low frequency Raman spectra

The Raman spectra of our glasses showed the ‘boson’ peak at 46 ± 5 cm⁻¹ in InF₃–BiF₃–BaF₂ system and at 50 ± 5 cm⁻¹ in 60In₃F–40BaF₂ glass [14]. It is virtually the same value. Moreover, the frequency of the ‘boson’ peak does not depend on the InF₃/BiF₃ ratio (Table 1). This result demonstrates that the size of MRO is independent of the concentration of BiF₃ in these glasses and the MRO in these glasses consists from InF₆ polyhedra not bound directly with BiF₆ polyhedra. MRO also includes a modifier (Ba) and essentially determines the size of MRO for given glasses. This suggestion can be also confirmed by the differences of ω in the Raman spectra of 60In₃F–40BaF₂ and 60InF₃–40SrF₂ (Table 1) glasses. The replacement of Ba by Sr results in, according to Eq. (1), a decrease of the MRO correlation length, which correlates with the radius of modifier cation. The same tendency is observed for the frequency of ‘boson’ peak in Raman spectra of fluorozirconate glasses (Table 1).

In the low frequency Raman spectra of glasses of the GaF₃–SnF₂ system, the ‘boson’ peak is observed at 29 cm⁻¹ and it is not displaced to a significant extent by the GaF₃/SnF₂ ratio change. The MRO size is about 19 Å. For the sake of comparison, the Raman spectrum of SiO₂ glass is shown in Fig. 5. One can see that the forms of ‘boson’ peaks of mono- and two-component glasses are almost identical. This fact indicates to the absence of a nanometric scale separation on mono-component fractions in the glasses of the GaF₃–SnF₂ system. One should mention the tendency of increasing the intensity of fast relaxation with reducing the GaF₃ content that can be an indicator of more defective structure between nano-clusters that form the glass structure. It is possible that this is related to the reduction of glass forming ability at low GaF₃ content.

5. Conclusions

Glass systems based on ZrF₄, InF₃, GaF₃ with added BiF₃, SnF₂, BaF₂, SrF₂, PbF₂ were synthesized and investigated by IR and Raman spectroscopy methods. BiF₃ and
SnF₂ are the second glassformers in addition to ZrF₄, InF₃ and GaF₃.

There are peculiarities in the MRO structure in the different glasses. The MRO in glasses with cation-modifier includes the modifier ion, and, therefore, the size of this region correlates with the cation-modifier size. The size of the MRO in the ZrF₄–SnF₂–GaF₃ system is determined by the distance between chains formed by fluorozirconate polyhedra. This distance depends on SnF₂ concentration in the glass. The MRO in glasses of the InF₃–BiF₃–BaF₂ system is not directly related to fluorobismuth polyhedra. The separation of components on a nanoscale is absent in the SnF₂–GaF₃ glass system.

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References