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Raman study of glasses in the $NbO_2F–BaF_2–InF_3–ErF_3$ and $CdNbOF_5–BaF_2–InF_3$ systems

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Glasses in the $NbO_2F–BaF_2–InF_3$ and $CdNbOF_5–BaF_2–InF_3$ systems have been obtained and investigated by means of IR- and Raman spectroscopy. The analysis of the inelastic light scattering spectra was used to identify the contribution of the photoluminescence in the glasses studied. The contribution of the indium photoluminescence into the inelastic light scattering spectrum of the glasses in the $NbO_2F–BaF_2–InF_3$ and $CdNbOF_5–BaF_2–InF_3$ systems has been established by scattering excitation with a laser at a wavelength of 532 nm.

Keywords: oxyfluoride glasses, structure, inelastic light scattering spectrum, Raman spectrum, photoluminescence.

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1. Introduction

The authors with great joy dedicate this article for the anniversary of P. P. Fedorov to our friend and colleague and wish him further creative success. Professor P. P. Fedorov is widely known for his outstanding research on the synthesis, structure, and optical properties of fluoride and oxyfluoride glasses, glass ceramics, and crystalline materials, in which he has been engaged for more than half a century.

Glasses based on NbO_2F were synthesized several years ago, but, among the representatives of optically active materials the systems based on niobium oxyfluoride, they still occupy a prominent place [1, 2]. The structure of the glasses based on niobium oxyfluoride was investigated by us both in an earlier study [3] and a later one [4]. The research conducted in this field resulted in the fabrication of glasses in the systems based on $MnNbOF_5$. The idea of introducing functional components, such as BiF_3, InF_3 and fluorides of rare earth elements to various type of glasses, was implemented in [4–7]. A series of the objects fabricated according to this concept exhibited rather interesting transport and crystallization properties. In particular, the study of the crystallization process in these systems revealed the possibility of obtaining transparent glass-ceramic nanocomposites. In the study of $NbO_2F–BaF_2–InF_3–ErF_3$ glass system, the contribution of erbium photoluminescence to the spectra of inelastic light scattering was recorded [4]. The researchers repeatedly [8, 9] turned to the glasses that contain CdF_2, considering it as a functional component promising for the formation of glass objects. Taking into account the demonstrated in [5] specific features of the glasses crystallization in the $MnNbOF_5–BaF_2–InF_3$ system, it was interesting to investigate the option of synthesizing similar systems with cadmium difluoride. The system of this type ($CdNbOF_5–BaF_2–InF_3$) was synthesized in [10]. During the course of its study [11], the possibility of fabricating transparent glass-crystalline composites containing crystalline phases of CdF_2 and $Ba_3In_2F_{12}$ was established via thermal treatment of glasses.

One of the important features of oxyfluoride glasses consists in the possibility of their doping by rare earth elements [12, 13]. Such glasses, including the glasses in the aforementioned systems [14, 15], often have luminescent properties, which allows them to be considered as candidates for the production of infrared fiber lasers and advanced glass ceramics. Recently, photoluminescence properties have been discovered in glasses containing elements other than only rare earth elements (REEs). Photoluminescence of Bi in glasses based on zirconium tetrafluoride was detected in [16, 17]. Herewith, in [15, 17], a non-trivial approach proposed in [4, 6, 14] for detecting photoluminescence was used. The essence of the approach is to analyze inelastic light scattering spectra in which the contributions of Raman scattering and photoluminescence are separated by using lasers with different wavelengths to excite scattering. This approach allows one to obtain the results which cannot always be achieved using traditional analyses of luminescence spectra.

When studying glasses in the $NbO_2F–BaF_2–InF_3$ system [4], which does not contain REEs, the contribution of photoluminescence, presumably attributed to indium photoluminescence, was recorded in the inelastic light scattering spectra. In the present study, the glasses in the $NbO_2F–BaF_2–InF_3$ system we studied more thoroughly and the above approach for detecting photoluminescence was applied to another system containing indium trifluoride. These are newly obtained glasses in the $CdNbOF_5–BaF_2–InF_3$ system [11].

2. Material and methods

The synthesis methodology of fabrication of the glasses in the NbO_2F–BaF_2–InF_3–ErF_3 and $CdNbOF_5$–BaF_2–InF_3 systems was detailed in our works [4, 11]. Glasses were transparent and resistant to aerobic conditions.

The absence or presence of crystalline phases in the samples was determined using a Bruker D8 ADVANCE diffractometer (CuK_α radiation).

Measurements of the Raman light scattering spectra were performed using a WiTec alpha500 confocal Raman microscope (laser wavelength of $\lambda_0 = 532$ nm, signal build-up time 1, averaging over 100 spectra) and a BRUKER RFS/100 Raman spectrometer (Nd:YAG laser, laser wavelength of $\lambda_0 = 1064$ nm).

IR absorption spectra were recorded on an IFS VERTEX 70 spectrometer (region of 4000 – 350 cm^{-1}, wave number accuracy of 0.5 cm^{-1}). The studied samples were ground to a finely dispersed state in an agate mortar and pressed into tablets with KBr or, in the form of a suspension in liquid paraffin, were applied onto KBr substrates.

The luminescence measuring device was assembled on the basis of the Solar TII MS3504 monochromator, optical lenses and detectors were selected for different ranges. To amplify weak signals, we used a lock-in amplifier (Lock-in) SR-810 (Stanford research) together with an optical modulator. The measurements were carried out according to the method: monochromatic radiation (from the laser) was applied to the sample, the reflected signal was fed into the monochromator.

3. Results and discussion

The structures of oxyfluoroniobate glasses including the discussed in this paper systems were earlier investigated in [5, 11, 14]. The typical structural units in NbO_2F-based glasses are the NbO_3F_3 and NbO_2F_4 polyhedra, connected by oxygen bridges in the glass network. This is indicated by the presence in IR spectra of bands in the ranges of 900 – 800, 700 – 800, and 550 – 420 cm^{-1}, which were assigned to the vibrations of bonds of Nb=O, –Nb–O–Nb– and Nb–F, respectively. Glasses in the $MnNbOF_5$–BaF_2–InF_3–ErF_3, and $CdNbOF_5$–BaF_2–InF_3 systems belong to the structural type of NbO_2F–BaF_2; for this reason, their IR spectra practically do not differ from each other, regardless of which of the components ($MnNbOF_5$, $CdNbOF_5$ or only NbO_2F) forms the glass (Fig. 1).

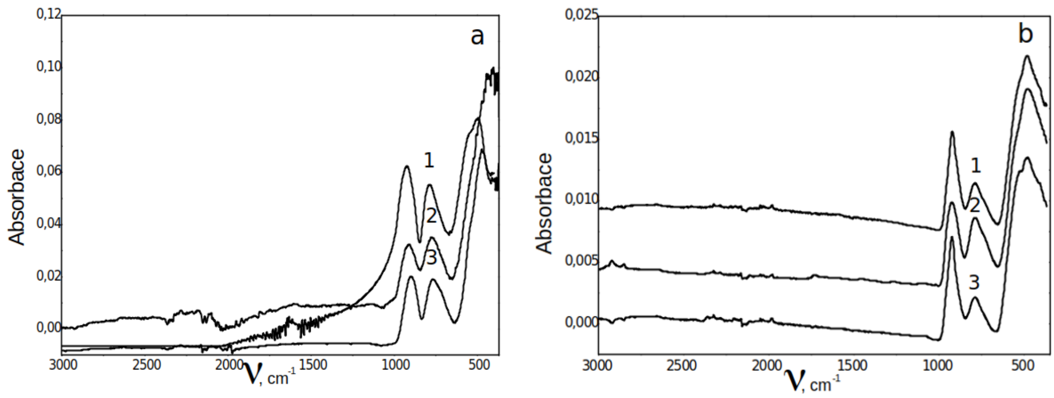

FIG. 1. IR spectra of the glasses in the systems of $MnNbOF_5$–BaF_2–InF_3–ErF_3 and $CdNbOF_5$–BaF_2–InF_3: (a) [11]: 1 – 39$CdNbOF_5$–60BaF_2–1ErF_3; 2 – 30$CdNbOF_5$–40BaF_2–30InF_3; 3 – 40$CdNbOF_5$–60BaF_2; (b) [5]: 1 – 30$MnNbOF_5$–50BaF_2–20InF_3; 2 – 39$MnNbOF_5$–40BaF_2–20InF_3–1ErF_3; 3 – 38$MnNbOF_5$–40BaF_2–20InF_3–2ErF_3

The IR-spectra of the glasses in the system of $MnNbOF_5$–BaF_2–InF_3–ErF_3 doped by rare earth elements do not differ from those of the glasses not containing of ErF_3 due the absence of substantial changes in the structure of glasses. This result is quite expected considering the amount of REE trifluoride in the glasses. The same situation was observed in the IR spectra of glasses in the NbO_2F–BaF_2–InF_3–ErF_3 system studied in [4].

A completely different situation was observed in the Raman spectra of oxyfluorobiobate glasses. For example, the Raman spectrum of the glass of 55NbO_2F–45BaF_2 [4] is represented by two intensive bands at 920 and 410 cm^{-1}, which correspond to stretching vibrations of the Nb=O and Nb–F bonds, respectively.

As soon as the erbium trifluoride, even 0.5 mol %, is introduced into the system, the Raman spectrum was radically altered. The changes were so great that even the most intensive band at 920 cm^{-1} was not observable on the background of two intensive bands, which appeared at 656 and 420 cm^{-1}. The investigations performed in [4] allow one to conclude that the changes observed in the spectra were related to the contribution of erbium photoluminescence into the inelastic light scattering spectrum, and this contribution was so significant that it was impossible to observe even the most intensive Raman bands on its background. Note that the conclusion made was confirmed by direct measurements of photoluminescence. The same pattern was observed in the Raman spectra of the glasses in the $MnNbOF_5$–BaF_2–InF_3–ErF_3 system [5].

When indium trifluoride is introduced to the oxyfluoroniobate system, InF_6 polyhedra are formed in the glass networks [17]. Since $NbO_2F_4^{3-}$ and InF_6^{3-} ions have the same charge, InF_6 polyhedra are situated between oxyfluoroniobate ions, thus forming mixed glass networks or their own layers or regions in the case of high content of indium trifluoride in the glass. However, since there are no radical changes in the structure of glass, noticeable changes in the IR spectra are also absent. All the bands corresponding to oxyfluoroniobate polyhedra remain. The bands corresponding to the In–F vibrations appear in the spectra, but these bands are located in the range of 500 – 400 cm^{-1} and are not always recognized as individual bands: they mask themselves under the band characterizing the Nb–F vibtations, although this leads to its broadening and shifting to the low-frequency region of the spectrum.

In the Raman spectrum of the $55NbO_2F$–$45BaF_2$ glass, the most intensive band at 906 cm^{-1} characterizes the vibrations of ν(Nb=O), below are the bands characterizing the vibrations of Nb–F, which are also clearly visible (Fig. 2).

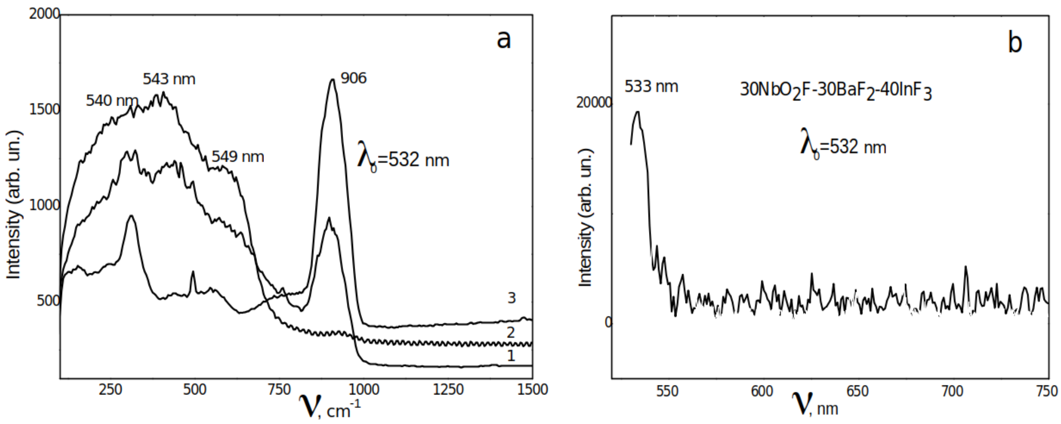

FIG. 2. Inelastic light scattering spectra of glasses (a): 1 – $55NbO_2F$–$45BaF_2$; 2 – $40NbO_2F$–$50BaF_2$–$10InF_3$; 3 – $30NbO_2F$–$30BaF_2$–$40InF_3$, and spectrum of luminescence (b) of $30NbO_2F$–$30BaF_2$–$40InF_3$ glass

However, as soon as indium trifluoride is introduced into the system, the spectrum changes dramatically (Fig. 2a). In the spectrum of the $40NbO_2F$–$50BaF_2$–$10InF_3$ glass, we still see a band characterizing the vibrations ν(Nb=O), but in the spectrum of glass with 40 mol. % indium trifluoride content, even that band is not identified against the background of wide intense bands in the region of 600 – 300 cm^{-1}. We believe that the changes in the spectra are also related to the contribution of photoluminescence in the inelastic light scattering spectrum. A confirmation of this is that in the spectrum obtained using a laser with a different wavelength (1064 nm), all bands are observed that characterize the vibrations of oxyfluorobiobate and fluorindatepolyhedra. This convincing evidence confirms the presence of an intense band at 533 nm in the spectrum of direct measurement of luminescence in $30NbO_2F$–$30BaF_2$–$40InF_3$ glass. These two facts suggest that in the inelastic scattering spectra of the glasses in the NbO_2F–BaF_2–InF_3 system, when using a laser with a wavelength of 532 nm, we observe the contribution of photoluminescence corresponding to emission levels in 500 nm region. The intense bands attributed to photoluminescence observed in the region of 500 – 300 cm^{-1} are amplified with increasing indium trifluoride content in the system. Based on this, is logical to assume that this contribution is due to the presence of indium trifluoride in the glass composition.

Recently the glasses in the $CdNbOF_5$–BaF_2–InF_3 system were fabricated and investigated [10, 11]. As was noted above, analysis of the IR absorption spectra of the glasses in the $CdNbOF_5$–BaF_2–InF_3 system demonstrated the similarity to the IR-spectra of the earlier investigated oxyfluoroniobates in the systems of $MnNbOF_5$–BaF_2–BiF_3, $MnNbOF_5$–BaF_2–InF_3, and NbO_2F–BaF_2–InF_3, which indicates the structural similarity of glass networks of all these oxyfluoroniobate systems. In all cases, including the $CdNbOF_5$–BaF_2–InF_3 system, the IR-spectra demonstrated well-observed bands in the rangesof 920 – 960, 800, and 500 – 400 cm^{-1} [11]. According to the assignments, in the case of the $CdNbOF_5$–BaF_2–InF_3 system, these bands also characterize the vibrations of Nb=O, –Nb–O–Nb–, Nb–F, and In–F bonds, respectively. The structural similarities of the $CdNbOF_5$–BaF_2–InF_3, $MnNbOF_5$–BaF_2–InF_3, and $NbOF_5$–BaF_2–InF_3 glasses suggest there should be similarities in not only their IR-spectra, but of the Raman spectra as well. This was indeed observed in the case of the spectrum of the glass of $40CdNbOF_5$–$60BaF_2$ (Fig. 3). The most intensive band at 912 cm^{-1} characterizes the Nb=O vibrations, at 773 cm^{-1} – those of –Nb–O–Nb–, and at 559 cm^{-1} – those of Nb–F.

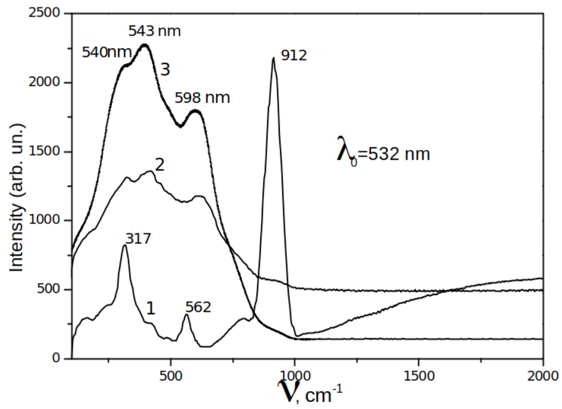

FIG. 3. Inelastic light scattering spectra in the system of $CdNbOF_5$–BaF_2–InF_3: 1 – $40CdNbOF_5$–$60BaF_2$; 2 – $30CdNbOF_5$–$40BaF_2$–$30InF_3$; 3 – $20CdNbOF_5$–$40BaF_2$–$40InF_3$

However, the Raman spectra of the $30CdNbOF_5$–$40BaF_2$–$30InF_3$ and $20CdNbOF_5$–$40BaF_2$–$40InF_3$ glasses displayed a different pattern (Fig. 3). The Raman spectrum was not observed on the background of two intensive bands at 598 and 397 cm^{-1}. A similar pattern was observed in the spectrum of the glass of $30NbO_2F$–$30BaF_2$–$40InF_3$ (Fig. 2). The appearance of these bands was explained by the appearance of the contribution of photoluminescence in the spectrum of inelastic light scattering, wherein, it was shown, this photoluminescence is caused by the presence of indium ions in the glass. Apparently, the same phenomenon takes place in the spectrum of glasses in the $CdNbOF_5$–BaF_2–InF_3 system.

The same of NbO_2F–BaF_2–InF_3 system this suggestion is corroborated by two facts. All the bands corresponding to the Raman spectra of the glasses containing or not containing indium trifluoride are clearly observed in the Raman spectra of the investigated glasses at scattering excitation by the laser with the wavelength of 1064 nm (Fig. 4). The intensities of the bands attributed to photoluminescence (the wide bands in region of 600 – 300 cm^{-1}) grow with increasing indium trifluoride content in the system (Fig. 3). Therefore, we can conclude that for the scattering excitation by the laser with the wavelength of 532 nm, we observed a contribution of indium photoluminescence in the inelastic scattering spectra of glasses in the $CdNbOF_5$–BaF_2–InF_3 system. The revealed photoluminescence corresponds to the emission levels of 549, 543 and 539 nm. The indium photoluminescence in the glasses is not well-known fact; however, there are some examples of photoluminescence properties in the compounds containing indium [18].

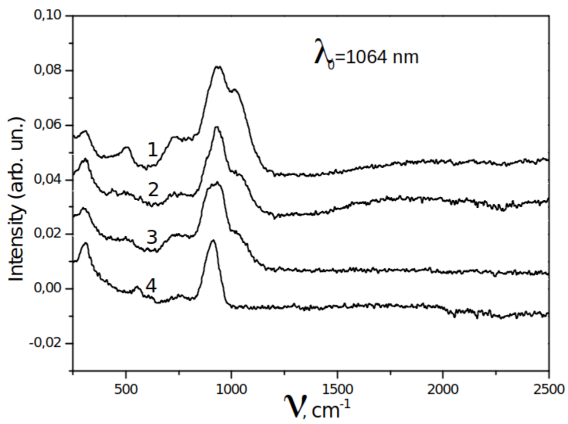

FIG. 4. Inelastic light scattering spectra in the system of $CdNbOF_5$–BaF_2–InF_3: 1 – $20CdNbOF_5$–$40BaF_2$–$40InF_3$; 2 – $30CdNbOF_5$–$40BaF_2$–$30InF_3$; 3 – $40CdNbOF_5$–$30BaF_2$–$30InF_3$; 4 – $40CdNbOF_5$–$60BaF_2$

4. Conclusion

The inelastic light scattering spectra of glasses in the NbO_2F–BaF_2–InF_3 and $CdNbOF_5$–BaF_2–InF_3 systems are studied. In the analysis of the spectra, the contributions of Raman scattering and photoluminescence were separated by using lasers of different wavelengths to excite scattering.

The contribution of indium photoluminescence to the inelastic light scattering spectrum of glasses in the NbO_2F–BaF_2–InF_3 system was established when scattering was excited by a laser with a wavelength of 532 nm. This contribution corresponds to emission levels of 540, 543, 549 nm.

With scattering excitation by the 532 nm laser, we observed a contribution of indium photoluminescence in the inelastic scattering spectra of glasses in the $CdNbOF_5$–BaF_2–InF_3 system. The revealed photoluminescence corresponds to the emission levels of 540, 543 and 549 nm.

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