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Substitution of Lanthanum and Barium Fluorides in ZNBL Glass-Forming Systems by Fluorides of Samarium, Europium and Ytterbium in Lower Oxidation States

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ABSTRACT : *Glass formation in fluorozirconate glass of the compositions ZrF_4(53.5) – NaF(20) – BaF_2(20) – LaF_3(6.5-x) – LnF_2(x) (1 ≤ x ≤ 6.5 mol %) and ZrF_4(53.5) – NaF(20) – BaF_2(20-x) – LaF_3(6.5) – LnF_2(x) (1 ≤ x ≤ 20 mol %), where Ln=Sm, Eu, Yb, has been studied by differential thermal and X-ray phase analysis, IR and electron spectroscopy. It has been found that when lanthanum fluoride is substituted by samarium and europium difluorides (1-6.5 mol %), a colorless transparent glass is formed. In the case of substitution by ytterbium difluoride, a green transparent glass is formed. The degree of substitution of barium fluoride increases with the atomic number of the REE. Whereas only up to 5.0 mol % of BaF_2 can be substituted by samarium difluoride, up to 7.0 mol % of BaF_2 can be substituted by europium difluoride and up to 10.0 mol % of BaF_2 by ytterbium difluoride. At a larger percentage of REE(II) fluorides, glass-crystalline phases are formed. According to the Hruby criterion, the glass samples in which 2.0 mol% of lanthanum trifluoride is substituted by $EuF_{2.11}$ (K=0.86), or 5.0 mol % of barium difluoride is substituted by $SmF_{2.07}$ (K=0.78), have the best crystallization stability.*
The results of IR spectroscopy suggest that the synthesized glass samples consist of fluorozirconate frameworks, which are composed of ZnF_n polyhedra linked by bridge bonds. The electronic diffuse reflectance spectra and luminescence spectra indicate the presence of REE cations in different oxidation states in the synthesized glass samples.
KEYWORDS: *fluorozirconate glass, REE fluorides, IR spectroscopy, Hruby criterion, electronic spectroscopy, luminescence.*

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I. INTRODUCTION

Thanks to transparency in a wide spectral range (0.2-6 μm) [1-3], a low optical loss, which is 1-3 orders of magnitude lower than that of glass based on oxygen compounds [4], a high mechanical stability and moisture resistance, fluorozirconate systems show promise in different fields of modern science and technology. REE fluorides as dopants made a good show in the manufacture of optical materials based on fluorozirconate glass, which is transparent in the infrared spectral range, light guides, solar energy concentrators, phosphors, materials for memory devices, low-temperature fiber lasers and pulsed lasers [5-10]. In spite of the large body of experimental information available to date, which concerns glass formation in fluorozirconate systems of different composition, the information on the effect of fluorides of REEs in different oxidation states on this process and on the spectral characteristics of glass that is formed in this case is very limited.

I view of the fact that fluorozirconate glass has already won a strong position in the modern market of optical materials and has good prospects for wider use, research aimed at search for new glass-forming compositions based on compounds of zirconium and REEs is undoubtedly topical and is not only of scientific, but also of practical interest.

Among the known glassy fluorozirconate materials, the systems ZBNLA {ZrF_4(53.0) – NaF(20.0) – BaF_2(20.0) – LaF_3(4.0) – AlF_3(3.0 mol%)} and ZBNL {ZrF_4(53.5) – BaF_2(20.0) – NaF(20.0) – LaF_3(6.5 mol %)} are considered to have the most promise in practical applications [1-3, 11-14].

This paper presents the results of a study of the effect of partial substitution of lanthanum and barium fluorides by fluorides of REEs in lower oxidation states (SmF_{2+x}, EuF_{2+x}, YbF_{2+x}) on the glass-forming ability of the fluorozirconate system ZBNL. The limiting percentage of substituents has been determined, the stability of the glass that is formed has been assessed, its spectral characteristics have been investigated.

II. EXPERIMENTAL

The fluorozirconate glass samples in the systems $ZrF_4(53.5) – NaF(20) – BaF_2(20) – LaF_3(6.5\text{-}x) – LnF_2(x)$ ($1 \le x \le 6.5$ mol %) and $ZrF_4(53.5) – NaF(20) – BaF_2(20\text{-}x) – LaF_3(6.5) – LnF_2(x)$ ($1 \le x \le 20$ mol %), where Ln=Sm, Eu, Yb, were obtained from chemically pure zirconium, sodium, barium, lanthanum fluorides and samarium(II), europium (II), ytterbium (II) fluorides, synthesized by the procedure described in [15].

The synthesis was carried out in evacuated (1.33×10^{-1} – 1.33 Pa) quartz ampoules in a temperature range of 700-900 °C for 7-80 h by reducing REE trifluorides with their REEs. Under the above synthesis conditions and at the stoichiometric ratio of the starting substances LnF_3:Ln =2.0, LnF_{2+x} fluorides ($x \le 0.11$) are generally formed, which have a cubic lattice.

To obtain glass, mixtures of the substances were heated in a platinum crucible to 659-800 °C under argon and held in the molten state for 0.5-1.0 h. After that, the melt was poured onto a platinum or glassy carbon plate (cooling rate ~ 15-20 deg/s). The substitution of lanthanum trifluoride by a REE(II) fluoride was performed in a concentration range of $1.0 \le x \le 6.5$ 5 mol % and that of barium fluoride in a concentration range of $1.0 \le x \le 20.0$ mol %.

The obtained glassy phases were investigated by differential thermal analysis (DTA) and X-ray phase analysis (XPA), IR and electron spectroscopy, and the luminescence method.

The DTA was made on a Q1500 (Paulik-Paulik-Erdey) derivatograph in platinum crucibles under argon. The heating temperature range was 20-800 °C, the heating rate was 10 deg/min. The XPA was made on a DRON-3M diffractometer with CuK_α radiation by the powder method. The phases were identified with the aid of the ASTM file [16]. The IR spectroscopy was performed on a Specord M-80 spectrophotometer in a range of 4000-200 cm^{-1} on pelleted samples with potassium bromide. The diffuse reflectance spectra were examined on a Lambda 9 spectrophotometer (Perkin-Elmer) in a range of 200-2500 nm. The luminescence studies were carried out by means of an SDL-1 automated diffraction spectrometer with FEU-79 photomultiplier in a range of 400-670 nm. Luminescence was excited with a DRSh-250 mercury lamp, the ultraviolet was separated with a UFS-2 light filter. The necessary bands were isolated from the source emission spectrum by means of an MSD-1 monochromator, a FEU-106 photomultiplier served as a detector.

III. DISCUSSION OF RESULTS

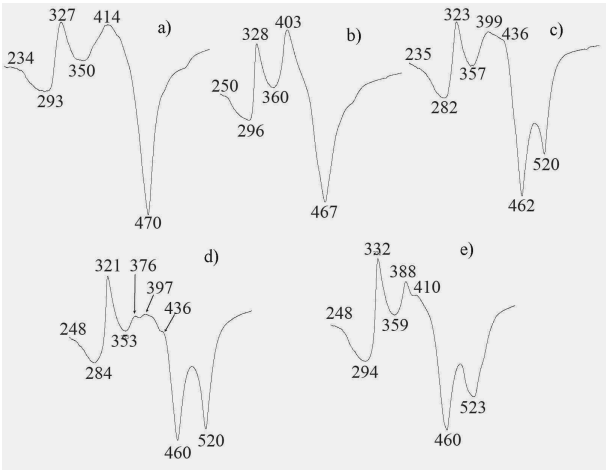
3.1. Glass formation in the fluorozirconate system ZBNL-samarium difluoride

Samarium fluoride of the composition $SmF_{2.07}$ was used for research. An analysis of the obtained results showed that the glass formation in the case of substitution of lanthanum and barium fluorides and the percentage of fluoride of samarium in lower oxidation states in the synthesized samples are greatly affected by temperature. In the temperature range of 650-750 °C, we succeeded in synthesizing colorless glass samples, which contained not over 3.0 mol % of $SmF_{2.07}$, in the case of substitution of both lanthanum trifluoride and barium difluoride. When the synthesis temperature was raised to 850 °C, colorless glass samples were formed on the complete (6.5 mol %) substitution of lanthanum trifluoride. The maximum amount of $SmF_{2.07}$ by which BaF_2 could be substituted was not over 5.0 mol %.

The DTA curves for $ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0) – LaF_3(6.5\text{-}x) – SmF_{2.07}(x)$ samples, where $1.0 \le x \le 6.5$ mol % (Fig 1), exhibit several thermal effects: an endo-effect of glass transition, t_g, at 234-250 °C, two crystallization exo-effects: t_{x1} at 321-332 °C and t_{x2} at 376-414 °C and a melting endo-effect t_{melt} at 460-470 °C. The thermograms for the glass samples containing over 3.0 mol % of $SmF_{2.07}$ exhibit an endo-effect at about 520 °C.

DTA curves for the samples in which barium fluoride is partially substituted by $SmF_{2.07}$ are shown in Fig 1. The glass transition temperature (t_g) of all investigated samples with a $SmF_{2.07}$ content of not over 10.0 mol % is almost the same and is 242-245 °C. The thermograms exhibit two crystallization effects: t_{x1} at 337-350 °C and t_{x2} at 392-408 °C, and a melting endo-effect t_{melt} at 464-469 °C.

As in the previous case of substitution of lanthanum trifluoride, endo-effects are also observed after the melting of samples at 484-550 °C. These endo-effects can be accounted for in both cases by the nonequilibrium state caused by the formation of complex fluorozirconates: α – (β) – $BaZrF_6$, $NaZrF_5$, $Na_7Zr_6F_{31}$, $SmZrF_7$, $SmZrF_6$ and phase transitions.



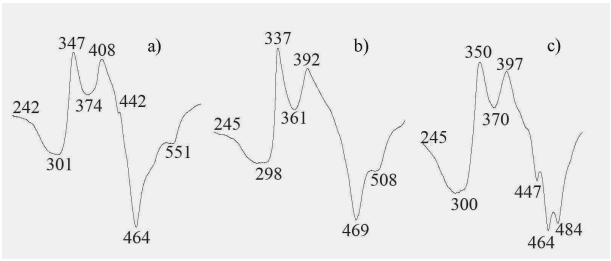


Fig 1. DTA (heating) curves for samples of the system

I

ZrF_4(53.5) – NaF(20.0) – BaF_2 (20.0) – LaF_2 (6.5-x) – $SmF_{2.07}$(x) at x: (a) 1.0, (b) 2.0, (c) 3.0, (d) 4.0, (e) 6.5 mol %

II

ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0-x) – LaF_3(6.5) – $SmF_{2.07}$(x) at x: (a) 1.0, (b) 3.0, (c) 5.0 mol %

According to the results of an XPA, the obtained glass samples are X-ray amorphous in the case of complete substitution of lanthanum trifluoride or partial substitution of barium fluoride by up to 5.0 mol % of samarium (II) fluoride (Fig 2).

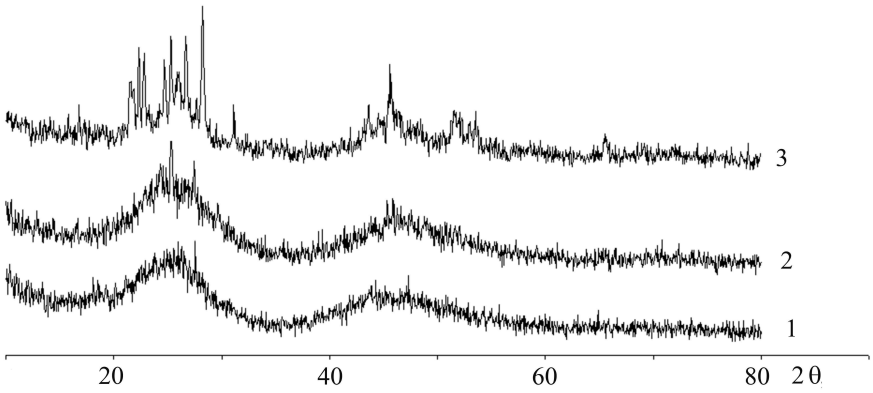


Fig 2. X-ray patterns of glass samples of the compositions (mol %):

1. **ZrF_4(53,5)-BaF_2(20,0)-NaF(20,0)-LaF_3(5,5)-$SmF_{2,07}$(1,0);**
2. **ZrF_4(53,5)-BaF_2(17,0)-NaF(20,0)-LaF_3(6,5)-$SmF_{2,07}$(3,0);**
3. **ZrF_4(53,5)-BaF_2(10,0)-NaF(20,0)-LaF_3(6,5)-$SmF_{2,07}$(10,0).**

When barium fluoride is substituted by a larger amount of $SmF_{2.07}$, glass-crystalline samples are formed. The diffractograms exhibit reflections, which are typical of the compounds α-$BaZrF_6$ and ZrF_4.

3.2. Glass formation in the fluorozirconate system ZBNL – europium difluoride

An analysis of the obtained results showed that transparent, colorless, X-ray amorphous glass samples are formed on the complete (6.5 mol %) substitution of lanthanum trifluoride and partial (not over 7.0 mol %) substitution by europium (II) difluoride of the composition $EuF_{2.11}$. When over 7.0 mol % of barium fluoride is substituted, glass-crystalline phases are formed (Fig 3). The reflections that are identified in the X-ray patterns of samples with a $EuF_{2.11}$ content of over 10.0 mol % are related to ZrF_4 and $BaZrF_6$.

The DTA (heating) curves for the glassy samples formed on the substitution of lanthanum trifluoride exhibit depending on $FuF_{2.11}$ content (Fig 4): an endo-effect of glass transition (t_g) in the range of 220-245 °C, two or three crystallization effects (t_{x1} at 320-345 °C, t_{x2} at 385-420 °C, t_{x3} at 440 °C), a melting endo-effect (t_{melt} at 470-500 °C). At a $EuF_{2.11}$content of the synthesized glass samples of over 3.0 mol %, the DTA curves exhibit in the range of 520-600 °C additional endo-effects, which are caused by their nonequilibrium state.

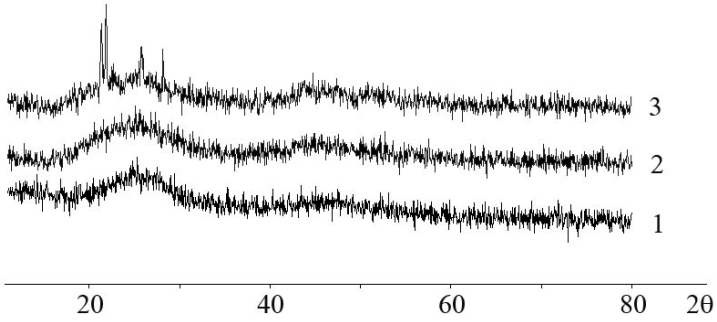


Fig 3. X-ray patterns of glass samples of the compositions (mol %):

1. **ZrF_4(53,5)-BaF_2(19,0)-NaF(20,0)-LaF_3(6,5)-$EuF_{2,11}$(1,0);**
2. **ZrF_4(53,5)-BaF_2(17,0)-NaF(20,0)-LaF_3(6,5)-$EuF_{2,11}$(3,0);**
3. **ZrF_4(53,5)-BaF_2(10,0)-NaF(20,0)-LaF_3(6,5)-$EuF_{2,11}$(10,0).**

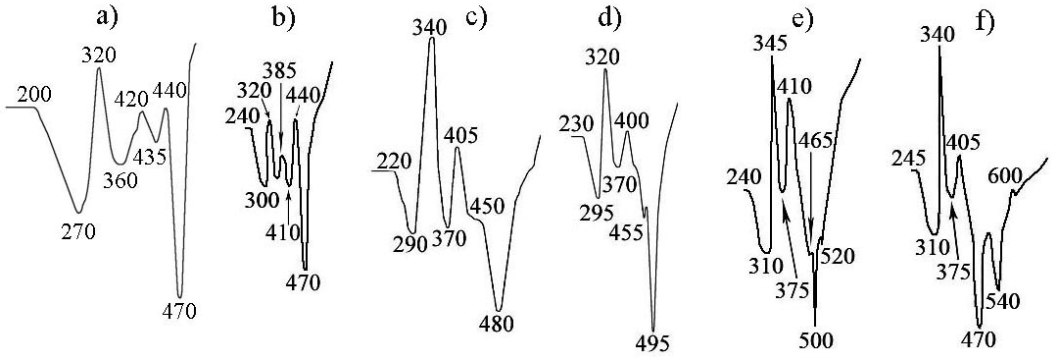


Fig 4. DTA (heating) curves for samples of the system ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0) – LaF_3(6.5-x) – $EuF_{2.11}$(x) at x: (a) 0,0, (b) 1.0, (c) 2.0, (d) 3.0, (e) 4.0, (f) 6.5 mol % of $EuF_{2.11}$

In the case of substitution of barium difluoride in the system ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0-x) – LaF_3(6.5) – $EuF_{2.11}$(x) (mol %), where $1.0 \leq x \leq 20.0$ mol %, as in the case of substitution of lanthanum trifluoride, the heating curves for the synthesized samples also exhibit a number of thermal effects: an endo-effect of glass transition (t_g) is in the range of 237-265 °C; two or three crystallization effects are in the ranges: t_{x1} at 290-330 °C, t_{x2} at 355-380 °C, t_{x3} at 390-420 °C depending on the $EuF_{2.11}$ content of glass; and a melting endo-effect is in the range of 450 – 485 °C (Fig 5). When the $EuF_{2.11}$ concentration in glass samples is increased (above 10.0 mol %), the DTA curves exhibit in the temperature range of 530 – 570 °C additional endo-effects, which can be accounted for by their nonequilibrium state. When barium fluoride is substituted by over 10.0 mol % of europium(II) fluoride, glass-crystalline phases are formed (Fig 3, curve 3).

3.3. Glass formation in the fluorozirconate system ZBNL-ytterbium difluoride

To synthesize the samples to be investigated, ytterbium difluoride of the composition $Ybf_{2.07}$ was used. By contrast to the previous systems, transparent green glass samples were formed in this system. The color intensity increased on increasing the ytterbium difluoride content of samples.

The evidence of the fact that just glassy (amorphous) phases were formed during the synthesis was the absence from the X-ray patterns (XPA) of reflections typical of starting fluorides, from which samples of particular glass-forming compositions were made (Fig 6).

An analysis of the results of differential thermal studies of the synthesized samples (Fig 7) showed that the DTA (heating) curves for the samples of the system ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0) – LaF_3(6.5-x) – $YbF_{2.07}$(x), where x takes on values of 1.0-6.5 mol %, exhibit several thermal effects: an endo-effect of glass transition (t_g) in the range of 200-250 °C and crystallization exo-effects (t_{x1} at 305-340 °C, t_{x2} at 375-405 °C, t_{x3} at 400-440 °C). The substitution of lanthanum trifluoride by ytterbium (II) fluoride does not practically affect the melting temperature of the samples (460-490 °C). When the $YbF_{2.07}$ content of the glass samples is increased ($\leq$ 3.0 mol %), the thermograms exhibit endo-effects in the range of 545-610 °C, which can be attributed to the formation of a eutectic mixture with ytterbium fluorozirconate.

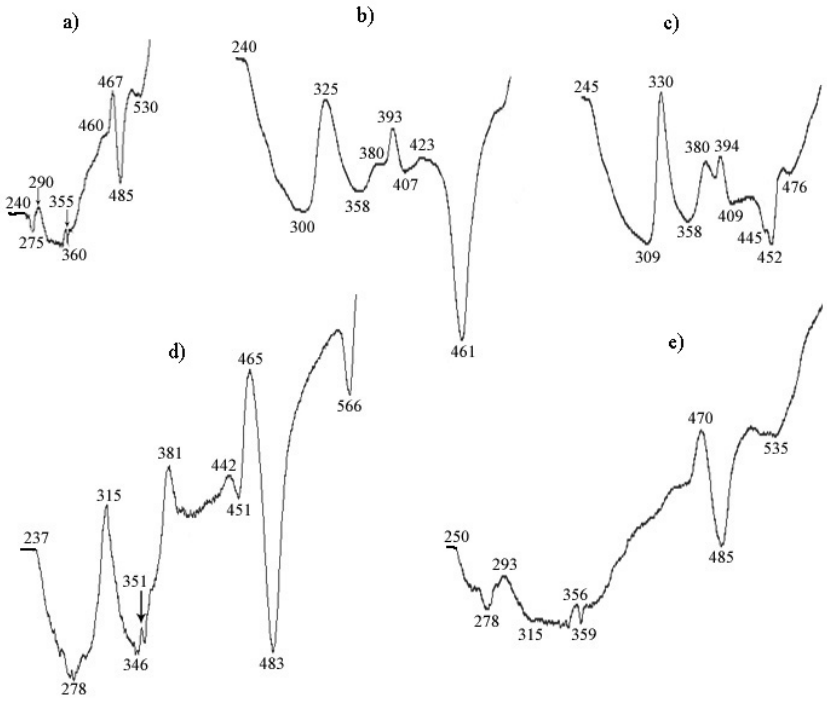


Fig 5. DTA (heating) curves for samples of the system ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0-x) – LaF_3(6.5) – $EuF_{2.11}$(x) at x: (a) 1.0, (b) 3.0, (c) 5.0, (d) 10.0, (e)15.0 mol % of $EuF_{2.11}$

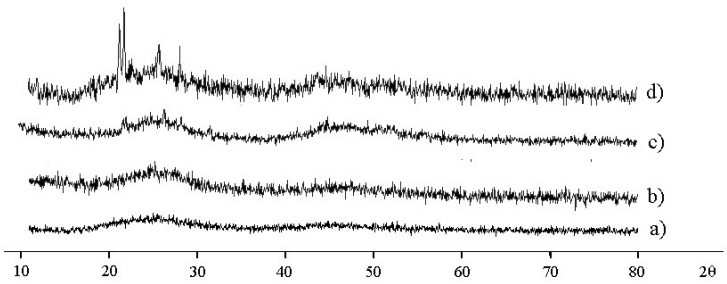


Fig 6. X-ray patterns of synthesized samples of the compositions (mol %):

a) ZrF_4(53,5)-BaF_2(20)-NaF(20)-LaF_3(3,5)-YbF_2(3),
ZrF_4(53,5)-BaF_2(17)-NaF(20)-LaF_3(6,5)-YbF_2(3);
b) ZrF_4(53,5)-BaF_2(20)-NaF(20)-YbF_2(6,5);
c) ZrF_4(53,5)-BaF_2(12)-NaF(20)-LaF_3(6,5)-YbF_2(8);
d) ZrF_4(53,5)-BaF_2(10)-NaF(20)-LaF_3(6,5)-YbF_2(10).

The results of a DTA of glassy samples of the system ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0-x) – LaF_3(6.5) – $YbF_{2.07}$(x), where x takes on values of 1.0 – 20.0 mol%, are presented in Fig 8. The glass transition temperature (t_g) of the samples formed on the substitution of up to 15.0 mol % of barium fluoride has approximately the same values, which are in the range of 230-240 °C. On the complete substitution of BaF_2 by $YbF_{2.07}$, the glass transition temperature rises to 305 °C. The thermograms exhibit two or three crystallization effects: t_{x1} at 320-340 °C, t_{x2} at 380-460 °C, t_{x3} at 415-490 °C. For the samples with an $YbF_{2.07}$ content of ≤ 3.0 mol %, one thermal effect of melting at t_{melt} = 460-490 °C is observed. The thermal effects of crystallization in the case of substitution of BaF_2 by $YbF_{2.07}$ (≤ 15 mol %) can be attributed to the formation of compounds analogous with those described above in the case of substitution of lanthanum fluoride by ytterbium difluoride. In the glass samples with an ytterbium difluoride content of 5.0 – 20.0 mol %, we noted an increase in melting temperature and the appearance of new endo-effects, which are caused by the melting of ytterbium (II) fluorozirconates. The sample in which barium difluoride is fully substituted (20.0 mol %) by fluoride of ytterbium in lower oxidation states has the highest melting temperature (570 °C)of ytterbium in lower oxidation states (Fig 8 (f)).

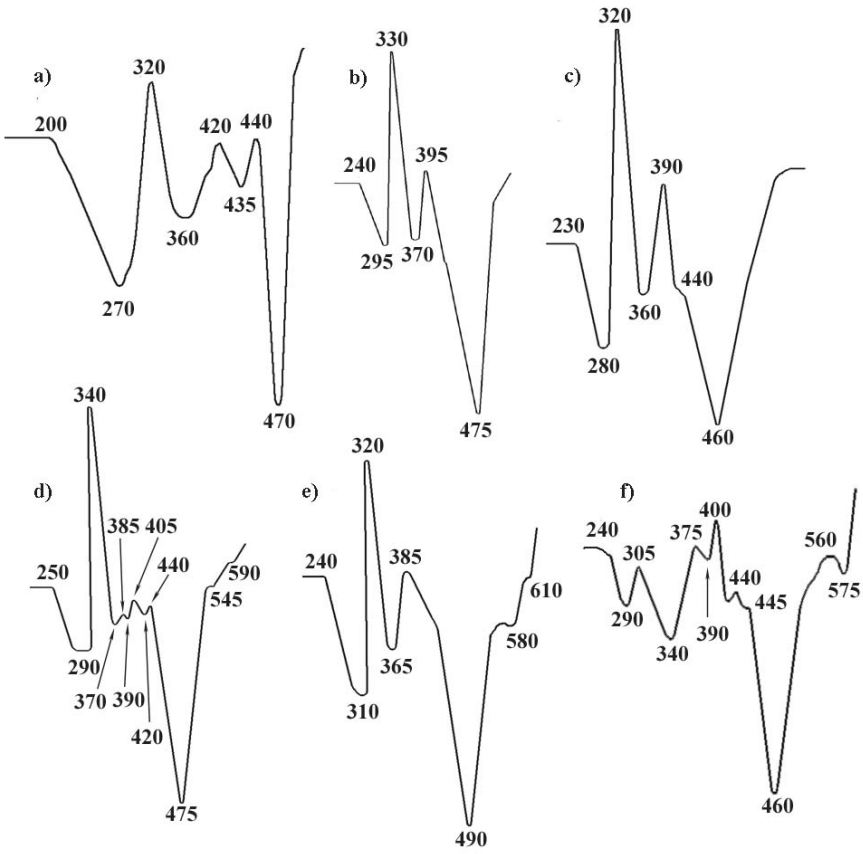


Fig 7. DTA (heating) curves for samples of the system ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0) – LaF_3 (6.5-x) – $YbF_{2.07}$(x) at x: (a) 0, (b) 1.0, (c) 2.0, (d) 3.0, (e) 4.0, (f) 6.5 mol % of $YbF_{2.07}$

To account for the crystallization effects, the synthesized glass samples were held under isothermal conditions at the temperature of each exothermic effect. The obtained phases were identified by XPA. The first crystallization effect can be accounted for by the formation of the phases β-$BaZrF_6$, β-$BaZr_2F_{10}$, $NaZrF_5$. The second effect can be accounted for by the formation of the phases $Na_7Zr_6F_{31}$ and α-$BaZr_2F_{10}$, of which the following phase transformations are characteristic:

β-$BaZr_2F_{10}$ → α-$BaZr_2F_{10}$
$NaZrF_5$ → $Na_3Zr_4F_{19}$ + $Na_7Zr_6F_{31}$.

The third crystallization effect is attributed to the formation of the phases $NaBaZr_2F_{11}$ and $LaZr_2F_{11}$. At the temperatures corresponding to the third crystallization effect, REE fluorides and (or) fluorozirconates, e.g. $SmZrF_7$ and $SmZrF_6$, EuF_2 and $EuZrF_6$, $YbZrF_6$, are formed depending on the system being investigated.
For all synthesized samples, an evaluation of the Hruby criterion K:

$$K = \frac{t_x - t_g}{t_{melt} - t_x} = \frac{\Delta t}{t_{melt} - t_x}$$

has been performed, which is a general measure of glass stability [17]. The closer it is to unity, the higher the crystallization stability of glass. The obtained results are listed in Table 1.

It is evident from the table that the glass samples in which 2.0 mol % of lanthanum trifluoride is substituted by $EuF_{2.11}$ (K=0.86), and 5.0 mol % of barium difluoride is substituted by $SmF_{2.07}$ (K=0.78) have the best Hruby criterion values. An analysis of the results of IR spectroscopic studies showed that the IR spectra of all synthesized samples (Figs 9-10) exhibit in the region of 400-600 cm^{-1} a diffuse band with the absorption maximum at 500 cm^{-1}, which characterizes stretching vibrations of Zr-F bridge and non-bridge bonds. When barium fluoride is substituted by samarium (II) fluoride and europium (II) fluoride (≤ 10.0 mol %), the IR spectra exhibit bands in the regions of 270-420 cm^{-1} (Fig 9(b)) and 400-420 cm^{-1} (Fig 10, I (2)) respectively, which characterize Sm(Eu)-F bond vibrations. In the samples containing over 15.0 mol % of ytterbium (II) fluoride, several bands appear in the region of 250-320 cm^{-1} (Fig 10, II, curves 4, 5), which can be assigned to Yb-F bond vibrations.

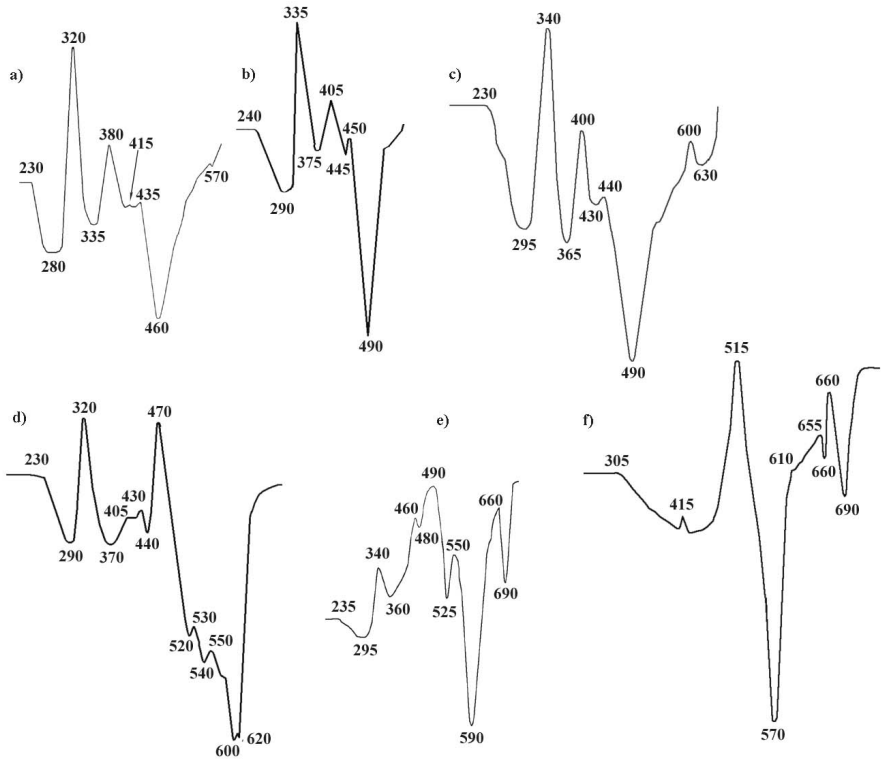


Fig 8. DTA (heating) curves for samples of the system ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0-x) – LaF_3(6.5) – $YbF_{2.07}$(x) at x: (a) 1.0, (b) 3.0, (c) 5.0, (d) 10.0, (e) 15.0, (f) 20.0 mol % of $YbF_{2.07}$

Table 1. Hruby criterion of synthesized ZBNL fluorozirconate glass samples with different percentage of REE difluorides

Percentage of LnF_2 (x) (mol %)	Δt	$t_{melt} - t_x$	**К**	Percentage of LnF_2 (y) (mol %)	Δt	$t_{melt} - t_x$	**К**
ZrF_4(53,5)-NaF(20,0)-BaF_2(20,0-y)-LaF_3(6,5-x)-$SmF_{2,07}$ (x, y)							
0,0	120	150	0,80	0,0	120	150	0,80
1,0	93	143	0,65	1,0	105	204	0,51
2,0	78	138	0,56	3,0	92	171	0,54
3,0	88	197	0,45	5,0	105	134	0,78
4,0	73	199	0,37				
6,5	84	191	0,44				
ZrF_4(53,5)-NaF(20,0)-BaF_2(20,0-y)-LaF_3(6,5-x)-$EuF_{2,11}$ (x, y)							
0	120	150	0,80	0	120	150	0,80
1,0	80	150	0,53	1,0	50	240	0,21
2,0	120	140	0,86	3,0	85	136	0,63
3,0	90	140	0,64	5,0	85	146	0,58
4,0	105	175	0,60	10,0	78	251	0,31
6,5	95	200	0,48	15,0	43	242	0,18
ZrF_4(53,5)-NaF(20,0)-BaF_2(20,0-y)-LaF_3(6,5-x)-$YbF_{2,07}$ (x, y)							
0	120	150	0,80	0	120	150	0,80
1,0	90	145	0,62	1,0	90	140	0,64
2,0	90	140	0,64	3,0	95	155	0,61
3,0	90	135	0,67	5,0	110	290	0,38
4,0	80	260	0,31	10,0	80	280	0,29
6,5	65	270	0,24	15,0	105	350	0,30

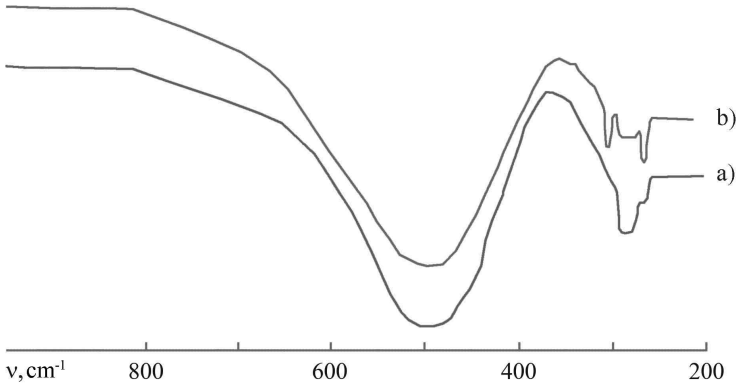


Fig 9. IR spectra of samples of the compositions (mol %):
a) ZrF_4(53,5)–BaF_2(20)–NaF(20)–LaF_3(5,5)–SmF_2(1);
b) ZrF_4(53,5)–BaF_2(10)–NaF(20)–LaF_3(6,5)–SmF_2(10).

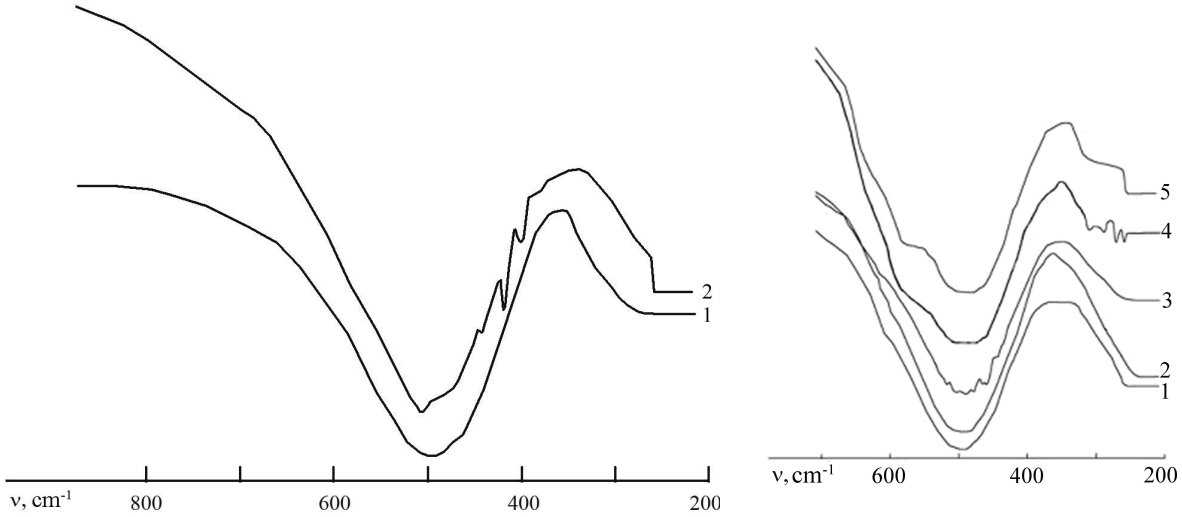


Fig 10. IR spectra of glass samples of the compositions (mol %):

I

1. **ZrF_4(53,5)-BaF_2(20,0)-NaF(20,0)-LaF_3(5,5)-EuF_2(1,0);**
2. **ZrF_4(53,5)-BaF_2(10,0)-NaF(20,0)-LaF_3(6,5)-EuF_2(10,0).**

II

1. **ZrF_4(53,5)–BaF_2(20,0)–NaF(20,0)–LaF_3(6,5);**
2. **ZrF_4(53,5)–BaF_2(20,0)–NaF(20,0)–LaF_3(4,5)–$YbF_{2,07}$(2,0);**
3. **ZrF_4(53,5)–NaF(20,0)–LaF_3(6,5)–BaF_2(15,0)–$YbF_{2,07}$(5,0);**
4. **ZrF_4(53,5)–NaF(20,0)–LaF_3(6,5)–BaF_2(5,0)–$YbF_{2,07}$(15,0);**
5. **ZrF_4(53,5)–NaF(20,0)–LaF_3(6,5)–$YbF_{2,07}$(20,0).**

The results of IR spectroscopy suggest that the glass in the investigated compositions consists of fluorozirconate frameworks, which are composed of ZrF_n polyhedra (n=6-8) linked by bridge bonds. The absence of the absorption bands characterizing the Ba-F and Ln-F bonds indicates that the Ba^{2+} and Ln^{2+} cations are in the voids of the fluorozirconate framework and form ionic bonds to fluorine anions. The simultaneous change in the ratios Zr/Ba and Zr/Ln gives rise to absorption bands typical of Ln-F bonds. When barium fluoride is substituted by fluorides: $SmF_{2.07}$, $EuF_{2.11} \leq 10.0$ mol % or $YbF_{2.07} \leq 15.0$ mol %, glass-crystalline phases are formed, and additional absorption bands appear, which points to the fact that the barium and lanthanide cations are in different voids of the fluorozirconate framework.

The fact that the synthesized glass samples contain REEs in the oxidation state 2+ is indicated by the results of diffuse reflectance spectroscopy (Figs 11-13). The band in the region of 200-400 nm characterizes the 4f-5d electron transitions in Ln^{2+} ions [18-27]. The spectra of the samples containing samarium(II) fluoride exhibit low-intensity bands in the region of 900-1600 nm, the spectra of glass samples with europium (II) fluoride in the region of 2000-2200 nm, and in the case of samples with ytterbium (II) fluoride, at ~980 nm. These bands are associated with 4f-4f transitions in Ln^{3+} ions [18, 23-26]. At a low ytterbium (II) fluoride content of the sample (~ 1 mol %), the bands typical of Yb^{3+} ion are not observed. When the ytterbium difluoride content of the sample is increased from 2.0 to 6.5 mol %, the intensity of the reflectance band of Yb^{3+} does not practically change.

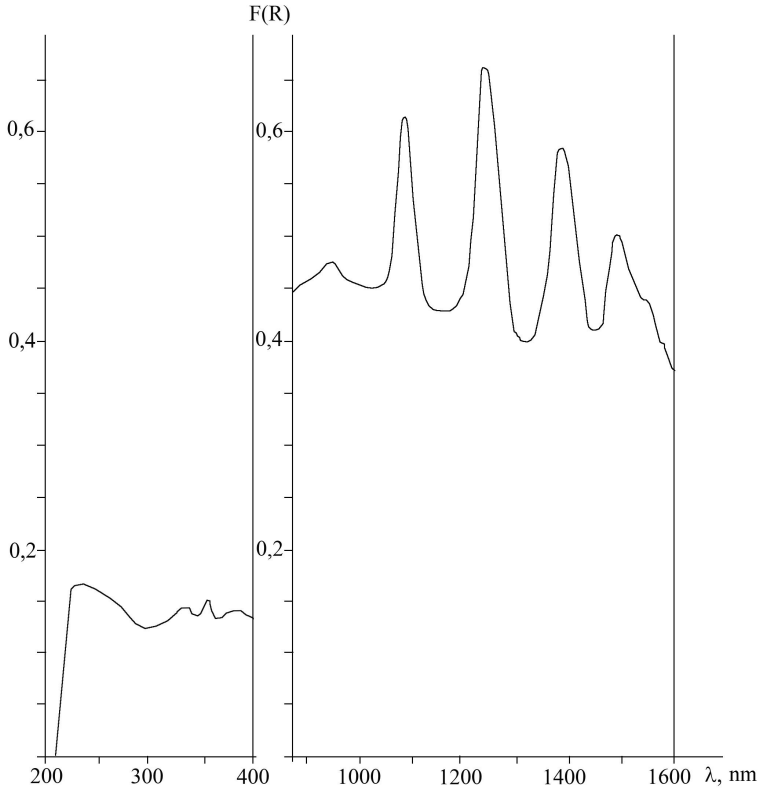


Fig 11. Diffuse reflectance spectrum of a sample of the compositions (mol %): ZrF_4(53.5) – BaF_2(20.0) – NaF(20.0) – LaF_3(3.5) – $SmF_{2.07}$(3.0)

An additional information on the spectral characteristics of the synthesized glass samples has been obtained when examining luminescence spectra (Fig 14). The luminescence spectra of the glass samples with samarium difluoride (Fig 16 (a)) exhibit bands typical of electron transitions both in Sm^{3+} ions: 560 nm ($^4G_{5/2} \rightarrow {}^6H_{5/2}$), 590 nm ($^4G_{5/2} \rightarrow {}^6H_{7/2}$), 640 nm ($^4G_{5/2} \rightarrow {}^6H_{9/2}$) and in Sm^{2+} ions: 400-500 nm ($^5D_0 \rightarrow {}^7F_0$), 720 nm ($^5D_0 \rightarrow {}^7F_2$) [18, 28-30]. The spectra of the samples containing europium difluoride also exhibit bands typical both of trivalent ions: 510-555 nm ($^5D_1 \rightarrow {}^7F_0, {}^7F_2$), 590 nm ($^5D_0 \rightarrow {}^7F_1$), 615 nm ($^5D_0 \rightarrow {}^7F_2$), 680nm ($^5D_0 \rightarrow {}^7F_3$) and of bivalent ions: 420-490 nm ($^4F_{3/2} \rightarrow {}^4I_{1/2}$) [18, 28, 31, 32](Fig 16(b)). The bands in the region of 400-580 nm, which are observed in the luminescence spectra of the samples containing ytterbium difluoride, are typical of Yb^{2+} ions ($^2F_{7/2} \rightarrow {}^1S_0$) (Fig 16 (c)), and the bands at 980 nm ($^2F_{7/2} \rightarrow {}^2F_{5/2}$) are typical of Yb^{3+} ions [18, 28, 33].

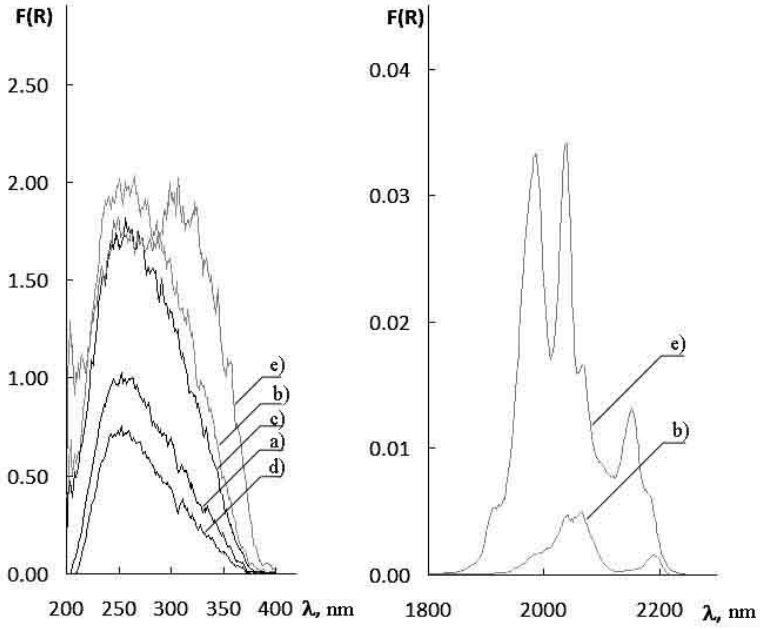


Fig 12. Electronic diffuse reflectance spectra of synthesized glass samples of the systems ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0) – LaF_3 (6.5-x) – $EuF_{2.11}$(x) at x: (a) 1.0, (b) 6.5 and ZrF_4 (53.5) – NaF(20.0) – BaF_2(20.0-x) – LaF_3(6.5) – $EuF_{2.11}$(x) at x: (c) 1.0, (d) 5.0, (e) 15.0 mol % of $EuF_{2.11}$

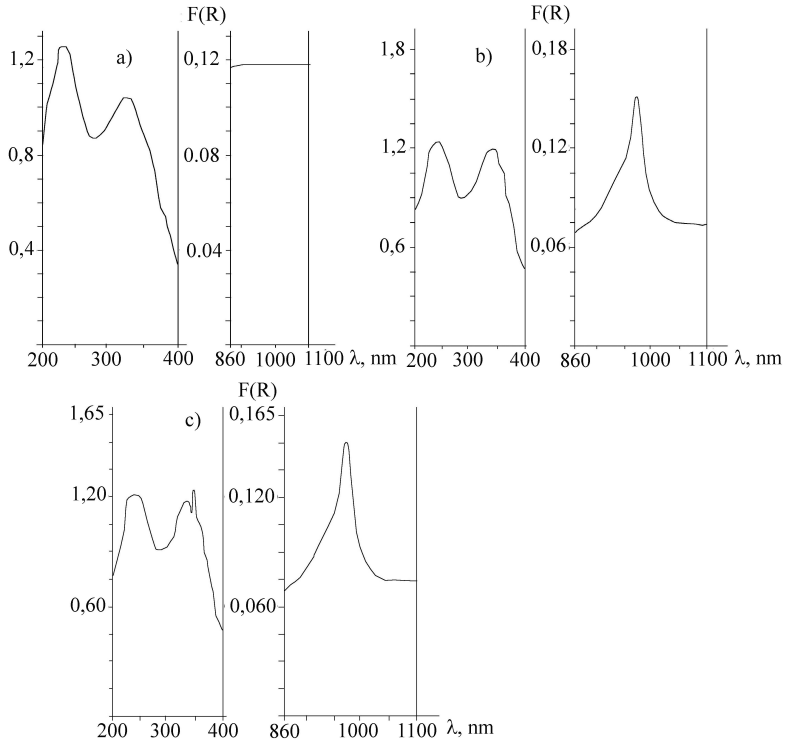


Fig 13. Electronic diffuse reflectance spectra of samples of the system ZrF_4(53.5) – NaF(20.0) – BaF_2(20.0) – LaF_3(6.5-x) – $YbF_{2.07}$(x) at x: (a)1.0, (b) 2.0 , (c) 6.5 mol %

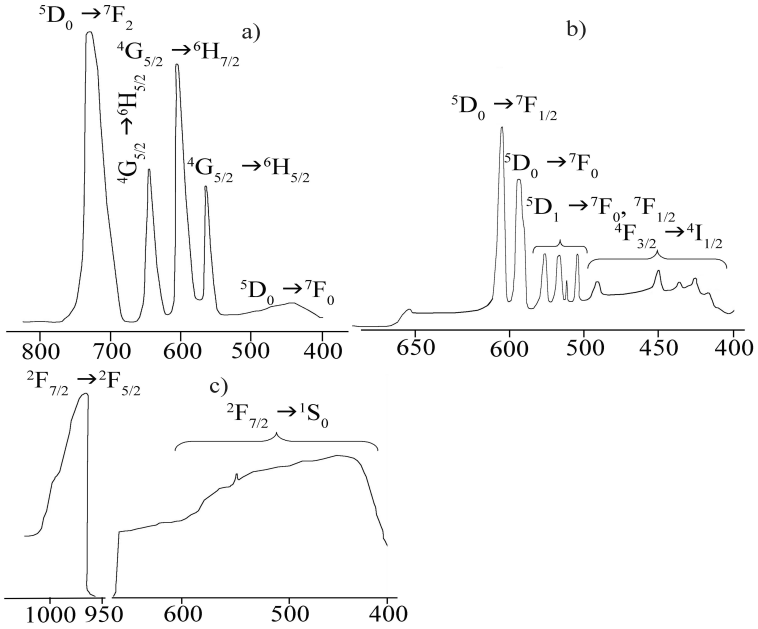


Fig 14. Luminescence spectra of glass samples of the system (mol %): ZrF_4(53.5) – BaF_2(20.0) – NaF(20.0) – LaF_3(6.5-x) – M(x), where M is (mol %): (a) $SmF_{2.07}$(3.0), (b) $FuF_{2.11}$(2), (c) $YbF_{2.07}$(1)

The obtained results also point to the fact that the synthesized glass samples contain ions of REEs in different oxidation states.

IV. CONCLUSIONS

It has been found that in the system ZrF_4(53.5) – NaF(20) – BaF_2(20) – LaF_3(6.5-x) – LnF_2(x) ($1.0 \leq x \leq 6.5$ mol %), where Ln = Sm, Eu, Yb, lanthanum fluoride can be completely (6.5 mol %) substituted by samarium, europium and ytterbium difluorides. Barium fluoride in the system ZrF_4(53.5) – NaF(20) – BaF_2(20-x) – LaF_3(6.5) – LnF_2(x) ($1.0 \leq x \leq 20.0$ mol %), where Ln = Sm, Eu, Yb, can be only partially substituted by fluorides of REEs in lower oxidation states. The oxidation state of barium fluoride increases with the atomic number of REE. Whereas only up to 5.0 mol % of BaF_2 can be substituted by samarium difluoride, up to 7.0 mol % of BaF_2 can be substituted by europium difluoride and up to 10.0 mol % of BaF_2 by ytterbium difluoride. At a larger percentage of REE(II) fluorides, glass-crystalline phases are formed.

The samples of ZBNL fluorozirconate glass obtained by substitution by fluorides of samarium and europium in lower oxidation states are colorless and transparent. The glass samples containing $YbF_{2.07}$ are transparent and have a green color, whose intensity increases with ytterbium difluoride concentration.

The results of IR spectroscopy suggest that the synthesized glass samples consist of fluorozirconate frameworks, which are composed of ZrF_n polyhedra linked by bridge bonds. The absence of the absorption bands typical of Ba-F and Ln-F bonds indicates that the barium and lanthanide cations are in the voids of the fluorozirconate framework. On the significant substitution of barium cations by REE(II) cations, glass-crystalline samples are formed, in whose IR spectra additional absorption bands appear, which indicate that these cations are located in different voids of the fluorozirconate framework depending on the oxidation state.

The electronic diffuse reflectance spectra and luminescence spectra confirm the presence of REE cations in different oxidation states in the synthesized glass samples. Thanks to the presence of REE cations, glassy materials can be used as phosphors.

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