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Phase transformations in LnF_3–(Ln, Zr)–ZrF_4 systems, where Ln = Sm, Eu, Tm, Yb

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ABSTRACT

Phase transformations in LnF_3–(Ln, Zr)–ZrF_4 systems (where Ln = Sm, Eu, Tm, Yb) in the temperature range 700–900 °C have been investigated by chemical and X-ray phase analyses, UV and IR spectroscopy. Synthesis conditions of nonstoichiometric samarium, europium, ytterbium and thulium fluorides, which are products of interaction between LnF_3 and Ln and original substances for the preparation of compounds such as $LnZrF_6$ are given. The crystal lattice of the fluorozirconates obtained is similar to the $Yb_{27}F_{64}$ superstructure. Thulium fluorozirconate ($TmZrF_6$), whose structure is indexed as the $Tm_{13}F_{32-\delta}$ superstructure of hexagonal system, is an exception. For all compounds obtained, the lattice parameters have been calculated and the absorption bands of IR spectra have been interpreted.

1. Introduction

The unique optical properties of zirconium, rare-earth and alkaline-earth fluorides enable them to be used for the creation of materials for fiber optics, medium IR range optical waveguides with low optical loss (10^{-2} to 10^{-5} db/km). Glass containing rare earth and transition-metal fluorides is used as active medium for lasers and for magnetooptical devices. Fluoride glass is characterized by a high transparency in the IR region of optical spectrum in the range of 2–4 μm [1].

Among all fluoride glasses, fluorozirconate glass is best studied, for which the system ZrF_4–BaF_2 which a glass-forming range of 50–80 mol% became a basis; according to other data, the glass-forming range is much narrower: 52–74, 60–70, 60–75 [2]. However, a disadvantage of two-component glass is that it readily crystallizes in a narrow temperature range of transition to the crystalline state ($t_{cryst} - t_{vitr} = 60^\circ$). To stabilize glass and to control its viscosity and refractive index, zirconium and barium fluorides are partially replaced by rare-earth fluorides. The main glass compounds in the systems ZrF_4–BaF_2 and LaF_3–ZrF_4–BaF_2 are $BaZrF_6$, $BaZr_2F_{10}$, and $LaZr_2F_{11}$ [2]. Besides trifluorides, glass is doped with fluorides of rare earths (REs) in lower oxidation states [3].

According to literature data, the fluorides of rare earths in lower oxidation states, LnF_{2+x}, where Ln = samarium, europium, thulium and ytterbium, are similar to alkaline-earth fluorides (fluorite structure) in radiographic characteristics [4]. Therefore, in glass-forming ZrF_4–BaF_2 systems, formation of $Ln^{II}ZrF_6$ type is possible in the presence of nonstoichiometric RE fluorides. We have found no information about the investigation of $Ln^{II}F_2$–ZrF_4 systems (Ln = Sm, Eu, Tm, Yb). There is information about the synthesis of $M^{II}ZrF_6$ compounds (where M^{II} = Mg, Ca, Ni, Fe, Co, Mn, Zn) [5–7], which have a cubic crystal system, and $BaZrF_6$, which has a rhombic crystal system (structural type $PbZrF_6$) [7]. In view of this, obtaining analogous substances with rare-earth difluorides and studying their properties are of scientific interest for the identification of phases during glass synthesis.

It is known that the synthesis of nonstoichiometric samarium, europium, thulium, and ytterbium fluorides by the reduction of trifluorides with appropriate rare-earth element or hydrogen takes place at rather high temperatures (1000–1600 °C) (expert ytterbium, 800 °C) under vacuum and requires special equipment [4,8–13]. This paper presents results of the synthesis of nonstoichiometric LnF_{2+x} compounds under milder condition (at 700–900 °C under vacuum) and their interaction with zirconium tetrafluoride.

2. Experimental

Compounds of the composition LnF_{2+x} (where Ln = Sm, Eu, Tm, Yb) were synthesized be the reaction:

$$(2+x)LnF_3 + (1-x)Ln = 3LnF_{2+x} \quad (1)$$

using chemically pure RE trifluorides and comminuted metals (appropriate M-1 lanthanides) in evacuated sealed quartz ampoules, which were held at 700–900 °C for 2–7 h.

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Table 1
Preparation conditions, phase composition and lattice parameters of nonstoichiometric RE fluorides.

Molar ratio LnF_3:E (where E = Ln (Sm, Tm, Yb), Si)	Phase composition	Powder color	Structural type and lattice parameters (Å)	Synthesis conditions	
				t (°C)	Time (h)
2	SmF_{2+x}	Dark blue	Not determined (literature a = 5.866 [9])	750	2
2	$SmF_{2,01}$	Red	Cubic a = 5.777	750	2
2.5	$SmF_{2,35}$	Dark red	Tetragonal a = 4.109 c = 5.856	800	3
4[a]	$EuF_{2,09}$	Light beige	Cubic a = 5.8252	950	5
2	$TmF_{2,38}$	Dark brown	Hexagonal a = 3.9546 c = 9.4827	820	3
2	$TmF_{2,42}$	Brown	Hexagonal a = 3.9449 c = 9.7129	750	3
2	$YbF_{1,91}$	Dark green	Cubic a = 5.6078	750	7
2	$YbF_{2,07}$	Light green	Cubic a = 5.5949	890	1
2.5	$YbF_{2,03}$	Green	Cubic a = 5.5978	750	7.5
	Superstructure $YbF_{2,37}=Yb_{27}F_{64}$	Beige	Cubic a = 16.7304		
3.26	$YbF_{2,37}$	Dark ochreous	Cubic a = 5.5827	750	7.5
	Superstructure $YbF_{2,37}=Yb_{27}F_{64}$	Beige	Cubic a = 16.7367		

[a] E = Si.

After the synthesis was complete, formation of a metal deposit (which is most typical of mixtures with ytterbium and thulium) on the interior walls of the ampoule was observed; this deposit performed a protective function and prevented interaction between fluoride and the quartz ampoule. Depending on synthesis condition, compounds obtained has different colors: SmF_{2+x}, dark blue, which changed quickly into red; YbF_{2+x}, from light green to dark ochreous; TmF_{2+x}, from light to dark brown.

The solid-phase synthesis of EuF2 + x was curried out in glassy carbon crucibles, using silicon as a reluctant, at 950 °C and the molar ratio EuF_3:Si = 4:1 by the reaction [14]:

$$4EuF_3 + Si \rightarrow 4EuF_2 + SiF_4\uparrow \tag{2}$$

The europium fluoride obtained had a nonstoichiometric composition and was light beige.

Fluorozirconates of the composition $LnZrF_6$ (where Ln = Sm, Eu, Tm, Yb) were prepared by the following reactions:

$$LnF_{2+x} + ZrF_4 = LnZrF_6; \tag{3}$$

$$LnF_3 + 3/4ZF_4 + 1/4Zr = LnZrF_6 \tag{4}$$

using the following original substances: chemically pure zirconium tetrafluoride, monocrystalline zirconium with a particle size of ≤0.1 mm and nonstoichiometric RE fluorides obtained by the reactions (1) and (2) [5].

The mixtures were pounded in an agate mortar, placed in quartz ampoules, which evacuated and sealed. The ampoules with substances were places in a shaft furnace. The samples were held at 700–800 °C for 3–4 h.

The phases obtained were investigated by chemical and X-ray phase analyses and by IR and electron spectroscopy.

Using chemical analysis, the percentage of constituents in the compounds obtained was determined: RE and zirconium as oxides after fusing a weighed sample with potassium persulfate and fluorine with the aid of an ion-selective electrode (a weighed sample was fused with sodium peroxide or carbonate in the presence of silicon oxide).

The X-ray phase analysis was performed on a DRON-3 M diffractometer (Cu Kα radiation) by the powder method. The X-ray diagrams were interpreted by means of an Ident computer program.

The IR spectroscopy was performed on a Specord M-80 spectrophotometer in a range of 4000–200 cm^{-1} on palletized samples with potassium bromide.

Diffuse reflection spectra were studied on a Lambda 9 spectrophotometer (Perkin-Elmer) in a range of 200–2500 nm.

3. Result and discussion

3.1. System LnF_3–Ln, where Ln = Sm, Tm, Yb

At the molar ratio SmF_3:Sm = 2.0, a dark blue unstable samarium fluoride phase has been obtained, which had been synthesized and described by Catalano et al. [8,9] and changes quickly into a red phase. A chemical and an X-ray phase analysis of the red SmF_{2+x} phase showed it to correspond to the $SmF_{2.01}$ compound and to have a cubic lattice with the parameter a = 5.777 Å (Table 1). At the molar ratio SmF_3:Sm = 2.5, a dark red phase has been obtained, which correspond to the $SmF_{2.35}$ compound, described in literature, of pseudotetragonal system with the parameters: a = 4.109 Å, c = 5.856 Å (literature data: a = 4.106 Å, c = 5.825 Å) [9].

In the system TmF_3–Tm, compounds $TmF_{2.38}$ and $TmF_{2.42}$ have been obtained at the ratio of 2:1 and synthesis temperatures of 750–800 °C. We, as the authors of [12], failed to synthesize stoichiometric thulium difluoride under these conditions. An X-ray phase analysis showed the compounds $TmF_{2.38}$ and $TmF_{2.42}$ to have a hexagonal crystal system with the lattice parameters: a = 3.9546 Å, c = 9.7129 Å (literature data: a = 3.9609 Å, c = 9.7129 Å) and a = 3.9449 Å, c = 9.7129 Å (literature data: a = 3.9500 Å, c = 9.7076 Å), respectively (Table 1). Diffractograms also showed metallic thulium and thulium trifluoride impurities even after long heating of mixtures at 800 °C. This fact indicates that the equilibrium:

$$TmF_3 + Tm \leftrightarrow TmF_{2+x}$$

is set up synthesis.

Nonstoichiometric fluorides with the general formula YbF_{2+x}, where x fakes on values of 1.91–2.37, have been obtained by the interaction of ytterbium trifluoride with metallic ytterbium at different molar ratios. Fig. 1 shows diffractograms of these compounds. An X-ray phase analysis of ytterbium compounds which are closely related to the stoichoimetric compound showed that the samples have a cubic crystal system with lattice parameters (Table 1) which almost coincide with those given in Ref. [4]. On interaction between the original substances with molar ratios of 2.5 and 3.26, two phases are formed: of green (or dark ochreous) and beige color. According to the result of the X-ray phase analysis, the main phase has a cubic crystal system and is a basic structure for the other phase, whose lattice parameter a is

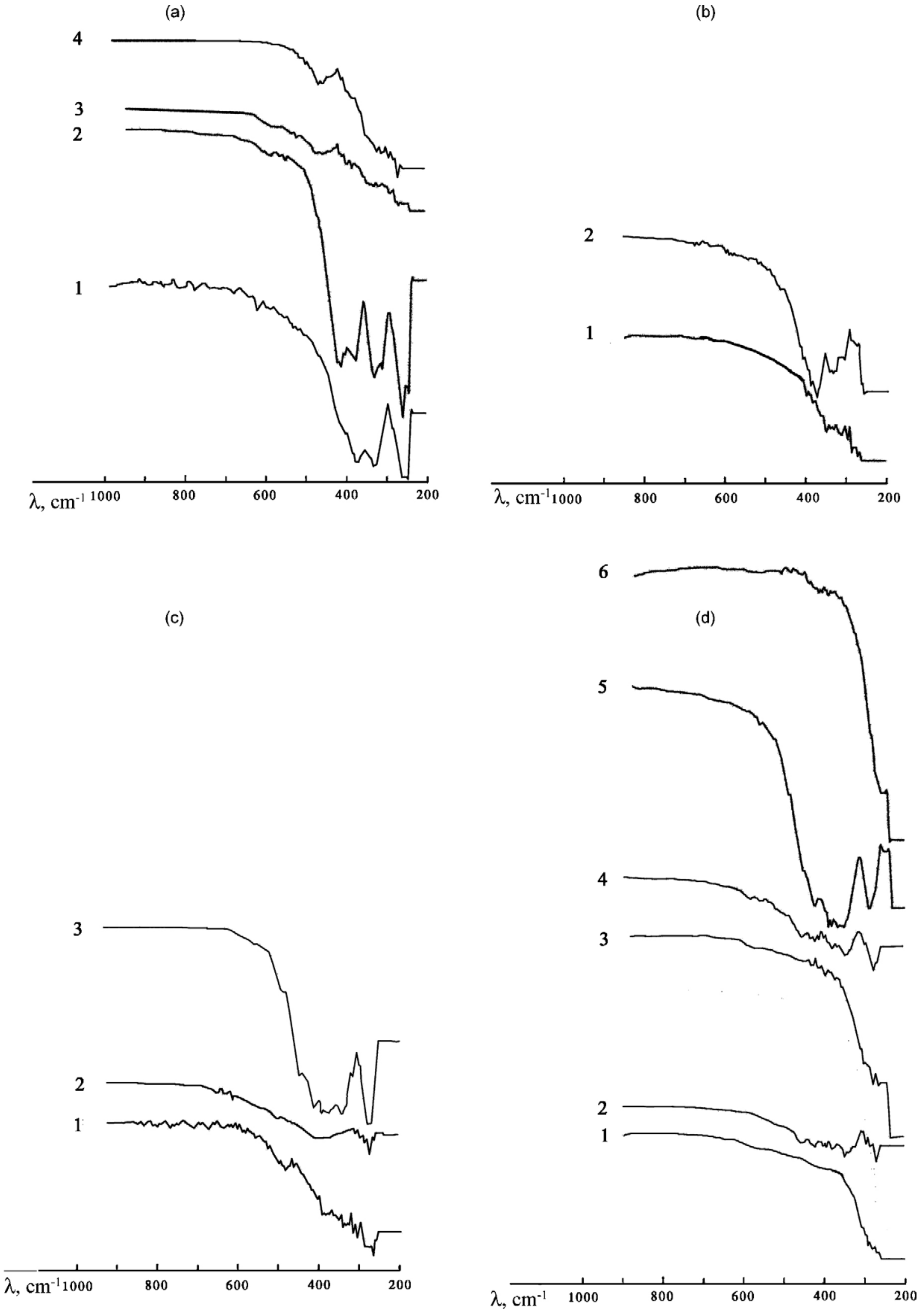

Fig. 1. IR spectra of fluoride compounds of: (a) samarium: (1) SmF_3; (2) dark blue SmF_{2+x} phase, (3) cubic $SmF_{2,01}$, (4) pseudotetragonal $SmF_{2,35}$ phase, (b) ytterbium: (1, 3) cubic $YbF_{2,03}$ and $YbF_{2,37}$ phase, respectively, (2, 4) phases with $Yb_{27}F_{64}$ superstructure, (5) YbF_3, (6) BaF_2; (c) thulium: (1) $TmF_{2,38}$, (2) $TmF_{2,42}$, (3) TmF_3; (d) europium: (1) $EuF_{2,09}$; (2) EuF_3.

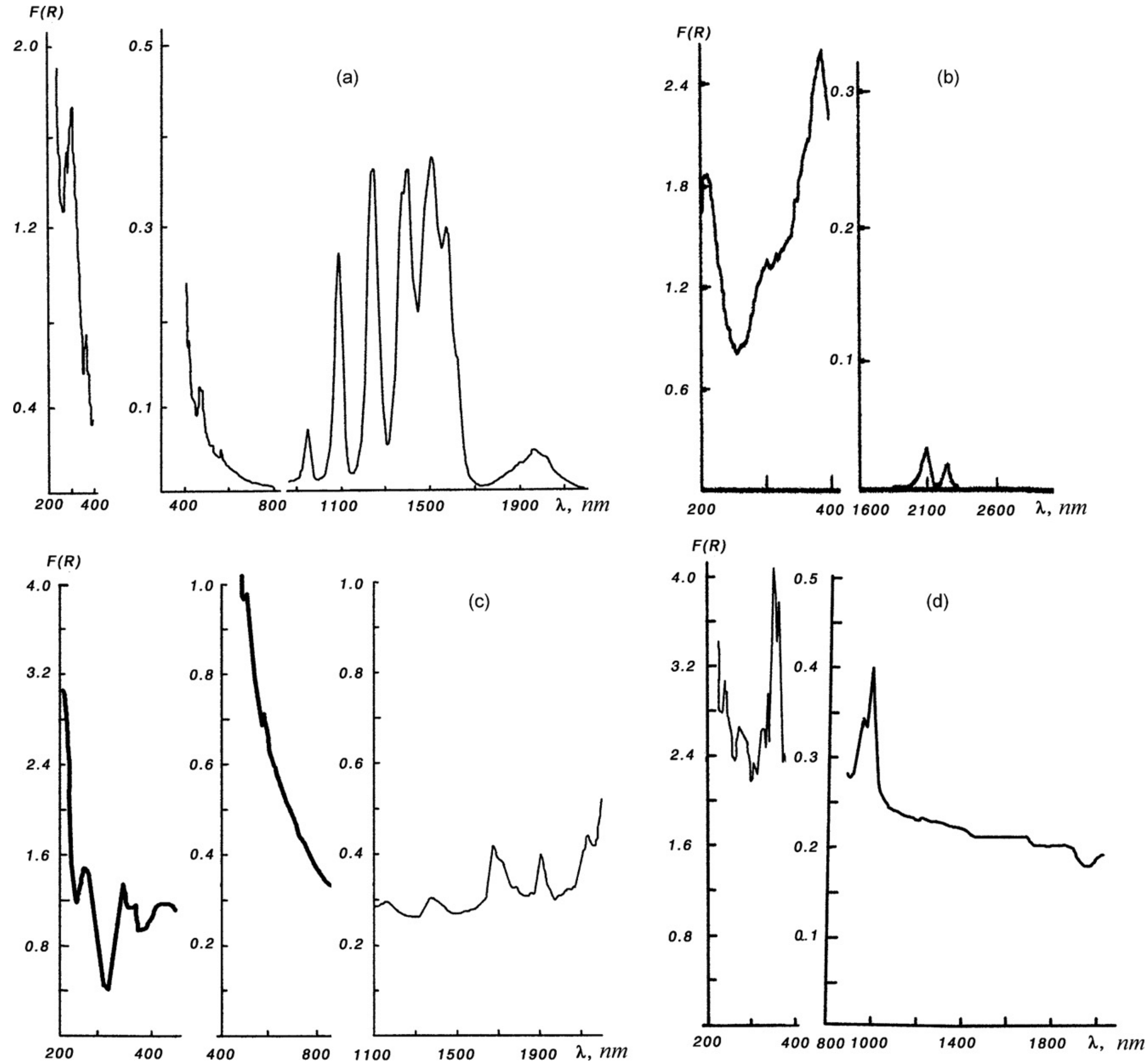

Fig. 2. Electronic spectra of LnF_{2+x}, where Ln is: (a) Sm, (b) Tm, (c) Yb, and (d) Eu.

triple $[a(Yb_{27}F_{64})(\text{superstructure})] = [3a(YbF_{2,37})(\text{basis structure})]$ [4]. The phases obtained are fairly easily separated when being removed from the reactor.

The IR absorption spectra of samarium and ytterbium trifluorides agree with those presented in publications [15]. No IR spectra of thulium trifluoride and nonstoichiometric RE fluorides have been found in literature. There is information on fundamental vibration frequencies calculated theoretically for ytterbium difluoride [16]. The absorption frequencies of nonstoichiometric RE compounds (Fig. 1) are approximately in the same range as those of trifluorides but with lower definition of maxima, greater smearing and some shift of bands to the long-wavelength region. According to literature data [17], the absorption bands in the range 400–500 cm^{-1} relate to antisymetric stretching vibrations and in the range 200–400 cm^{-1} to deformation vibrations of Ln–F bond. It should be noted that the spectra of the nonstoichiometric ytterbium fluorides (which have a cubic crystal system) described above are similar to the IR spectrum of BaF_2 [18]. For the compounds of the nonstoichiometric composition $Yb_{27}F_{64}$, which crystallize as superstructure, the spectrum approaches to a greater degree the spectrum of ytterbium trifluoride with decreasing intensity of the main absorption bands and their shift to the long-wavelength region.

Electronic diffuse reflection spectra of nonstoichiometric fluorides are shown in Fig. 2. Two regions can be discerned in the spectra obtained: 200–400 and 800–2200 nm. In the region 200–400 nm, absorption bands due to 4f–5d electron transitions in Ln^{2+} ions are observed [19]. In the region 800–2200 nm, absorption bands show which are connected with 4f–4f electron transitions, which are typical of Ln^{3+} ions. The intensity of these bands is low (lower by a factor of 10–20 that for LnF_3).

3.2. System LnF_{2+x}–ZrF_4 (LnF_3–ZrF_4–Zr), where Ln = Sm, Eu, Tm, Yb

The investigation of samples obtained by heating LnF_{2+x} (Ln = Sm, Eu, Tm, Yb)-ZrF_4 mixtures allowed us to find that an interaction between the constituents takes place, as a result of which phases of different colors: from black to white are formed (Table 2). According to the data of an X-ray phase analysis, the binary fluorozirconate compounds with Ln(II), where Ln = Sm, Eu,

Table 2
Synthesis conditions for and lattice parameters of RE (Sm, Eu, Tm, Yb) fluorozirconates.

Compounds obtained	Structural type and lattice parameters	Color of compounds	Synthesis conditions	
			t (°C)	Time (h)
$SmZrF_{6+x}$	$a = 16.7170$ Å cβ	White	700	3
$EuZrF_{6+x}$	$a = 16.7364$ Å cβ	Brown	730	3
$EuZrF_{6+x}$[a]	$a = 16.7132$ Å cβ	Black	700	3
$TmZrF_{6+x}$	$a = 14.2680$ Å $c = 9.7004$ Å hex.[b]	Grey	700	3
$TmZrF_{6+x}$[a]	$a = 14.3027$ Å $c = 9.6539$ Å hex.[b]	Grey	700	3
$YbZrF_{6+x}$[c]	$a = 16.7036$ Å cβ $a = 10.3668$ Å $c = 19.4769$ Å rhα[d]	Black	720	3
$YbZrF_{6+x}$	$a = 16.7248$ Å cβ	Black	800	3
$YbZrF_{6+x}$	$a = 16.7104$ Å cβ	Black	700–750	1
$YbZrF_{6+x}$[e]	$a = 16.7028$ Å cβ	Black	600	1

$x \approx 0.1$–0.2. The parameters have been calculated on the basis of superstructure [10,13]: $Yb_{27}F_{64}$ ($a = 16.712$ Å).

[a] The synthesis was carried out according to the reaction: $LnF_3 + 3/4ZrF_4 + 1/4Zr = LnZrF_6$.

[b] $Tm_{13}F_{32-\delta}$ (hex. $a = 14.2648$ Å; $c = 9.7067$ Å).

[c] The synthesis was carried out according to the reaction: $YbF_{2+x} + ZrF_4 = YbZrF_{6+x}$, evacuated ampoule.

[d] $Yb_{13}F_{33}$ ($R\bar{3}$ hex.: $a = 10.3671$ Å; $c = 19.4894$ Å).

[e] The synthesis was carried out according to the reaction: $2Yb + 3ZrF_4 = 2YbZrF_6 + Zr$.

Yb, crystallize as cubic ($Yb_{27}F_{64}$) superstructure and with thulium as hexagonal ($Tm_{13}F_{32-\delta}$) superstructure [9,12].

On the basis of data for cubic and hexagonal superstructures (of ytterbium and thulium, respectively) [9,12], the lattice parameters of the compounds obtained have been calculated (Table 2).

It has been found that the lattice parameters of the compounds obtained depend on synthesis temperature and holding time. Besides, they decrease from $a = 16.736$ Å (europium) to 16.7104 Å (ytterbium) under the same synthesis conditions. This series does not include samarium, for whose compound the lattice parameter $a = 16.7170$ Å. This anomaly can be attributed to the fact that samarium fluorozirconate is formed at higher temperatures (>600 °C) than $LnZrF_{6+x}$, where Ln = europium, thulium and ytterbium. It should be noted that the lattice parameters for thulium and ytterbium compounds persist independent of the procedure for their synthesis be the reaction (3) or (4). According to the results of an X-ray phase analysis, when europium interacts with zirconium and zirconium tetrafluoride according to the reaction (4), formation of a texture is observed, the main reflections of which agree with the X-ray diagram of the

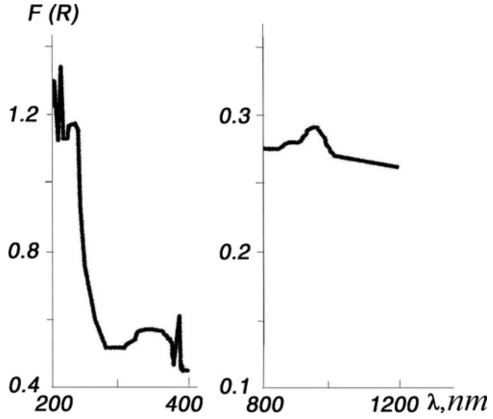

Fig. 3. Diffuse reflection spectrum of ytterbium fluorozirconate $YbZrF_{6+x}$.

Table 3
Absorption frequencies of IR spectra of fluorozirconate compounds of samarium, europium, thulium and ytterbium (II), as well as starting compounds.

No.	Compounds compositions	Frequencies (ν cm^{-1}) and intensity of absorption bands			
1	ZrF_4	270–290 (h)	380, 400 (m)	450 (m), 515 (h)	680 (l)
2	ZrF_{2-x}	285 (m)	325 (l)	440 (s), 500 (h)	
3	$SmF_{2,25}$	250–400 (h)	450 (m)		
4	$SmZrF_{6+x}$	280 (h)	360 (h)	420, 495 (h)	570, 620 (l)
5	SmF_3	270 (h)	335, 385(h)	430 (s)	
6	$SmZrF_7$[a]	250 (h)	330, 375 (h), 400 (s)	450–680	
7	$EuF_{2,1}$	270, 285(l)	300, 315, 350 (l), 400 (s)		
8	$EuZrF_{6+x}$	265, 285 (l)	350 (m), 370 (l)	420 (h)	
9	EuF_3	270–285 (h)	360 (h)	420 (s)	
12	$EuZrF_{6+x}$[b]	280, 305 (m)	330–340 (m)	450 (h)	
13	$TmF_{2,38-2,42}$	275 (h)	In the range 375–600, total absorption with maximum at 400		
14	$TmZrF_{6+x}$	290 (h)	350 (m)	420, 450, 500 (h)	575 (l)
15	TmF_3	290 (h)	340 (s), 360, 387 (h)	465, 510 (s)	
16	$TmZrF_{6+x}$[b]	275–290 (m)	325 (l), 350 (m), 395 (l)	450 (l), 515 (h)	
17	$YbF_{2,1}$	270, 280 (l)			
18	$YbZrF_{6+x}$[c]	270 (m), 290(l)	355 (h)	425, 500 (h)	575 (l)
19	$YbZrF_{6+x}$[d]	280 (l)		520 (h)	

$x \approx 0.1$–0.2; h, high; m, medium; l, low; s, shoulder.

[a] The synthesis was carried out according to the reaction: $SmF_3 + 3/4ZrF_4 + 1/4Zr = SmZrF_6$.

[b] Synthesis by the reaction: $LnF_3 + 3/4ZrF_4 + 1/4Zr = LnZrF_6$.

[c] Synthesis by the reaction: $YbF_{2+x} + ZrF_4 = YbZrF_{6+x}$, evacuated ampoule.

[d] Synthesis by the reaction: $YbF_{2,4} + ZrF_4 = YbZrF_{6,4}$.

compounds obtained by the reaction (3). In the case of samarium, compound of the $SmZrF_{6+x}$ type is not identified under the above synthesis condition. $SmZrF_7$ with SmF_2, SmF_3 and ZrF_4 impurities has been found in the reaction products.

The results given in Table 2 allow one to conclude that thulium compounds crystallize as superstructure of the same type as the $Yb_{13}F_{32-\delta}$ compounds, which has the same structure as $Na_7Zr_6F_{31}$. The cubic superstructure (cβ) of ytterbium may be regarded as a combination of the $Yb_{14}F_{33}$ (rhα) and $Yb_{13}F_{32-\delta}$ (rhβ) structures. Similar $LnZrF_{6+x}$ compounds (where Ln = Sm, Eu) are of the same type as $Yb_{27}F_{64}$.

Data on the IR spectra of the compounds synthesized are given in Table 3. The absorption bands in the range 250–290 cm^{-1} may be assigned to asymmetric deformation vibrations of Ln–F bond and to deformation vibrations of fluorozirconate groupings. In the range 300–400 cm^{-1}, asymmetric Ln–F bond stretches are observed. The absorption bands in the ranges 420–520 cm^{-1} and 570–620 cm^{-1} relate to Zr–F bridge and nonbridge bond stretches, which allows one to assume the presence of fluorozirconate polyhedral in structure of the compound [20].

Fig. 3 shows a diffuse reflection spectrum of ytterbium fluorozirconate. The bands in the range 200–400 nm with maxima at 220, 275 and 350 nm corroborate the presence of Yb(II) in the compound and the maximum at 980 nm the presence of a small amount of Yb(III).

4. Conclusions

On contact interaction between samarium, thulium and ytterbium fluorides and Sm, Tm and Yb lanthanides in a temperature range of 700–900 °C under a vacuum of 1.33–1.33×10^{-1} Pa, nonstoichiometric compounds of lanthanides in lower oxidation states, LnF_{2+x}, are formed, where x takes on values of 2.01–2.35 for samarium, 2.38–2.42 for thulium, 1.91–2.37 for ytterbium.

The composition of the phases formed depends on the mixture ratio. When the molar ratio LnF_3:E (E = Sm, Tm, Yb, Si) is increased, the fluorine content of the compounds of the LnF_{2+x} type obtained increases. In the case of ytterbium, the formation of a phase with superstructure at molar ratios YbF_3:Yb = 2.5–3.26 and in the case of holding the mixture at 750 °C for 7.5 h has been established.

Electronic diffuse reflection spectra (intense absorption bands in the UV region) corroborate the presence of lanthanide compounds in lower oxidation states in the samples synthesized.

IR spectra of nonstoichiometric fluorides of the LnF_{2+x} type (Ln = Sm, Eu, Tm, Yb) have been presented for the first time. For ytterbium fluoride with basis cubic structure, no absorption bands have been found in the range 400–4000 cm^{-1}.

A number of compounds with the general formula $LnZrF_{6+x}$, where Ln = Sm, Eu, Tm, Yb, have been obtained for the first time. X-ray phase studies showed that all of them, except thulium, crystallize as cubic (cβ) $Yb_{27}F_{64}$ superstructure. The cubic superstructure (cβ) of ytterbium may be regarded as a combination of $Yb_{14}F_{33}$ (rhα) and $Yb_{13}F_{32-\delta}$ (rhβ) structures. Thulium compounds crystallize as $Tm_{13}F_{32-\delta}$ superstructure of rhombohedral system ($R\bar{3}$) with hexagonal distortion. The thulium fluorozirconates obtained are of the same type as the rhombohedral compound $Yb_{13}F_{32-\delta}$, which has the same structure as $Na_7Zr_6F_{31}$. The lattice parameters for europium, thulium and ytterbium compounds decrease, which is accounted for by lanthanide compression. Samarium compound, for which the lattice parameter is larger, is an exception. This phenomenon can be attributed to the fact that samarium fluorozirconate is formed at higher temperatures (>600 °C) than $LnZrF_{6+x}$, where Ln = Eu, Tm, Yb.

Analysis of the IR spectra of the binary compounds synthesized allows one to conclude that they are made up of fluorozirconate frameworks, which consist of ZrFn polyhedral joined by bridge bonds.

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