CRYSTAL STRUCTURE AND OPTICAL PROPERTIES OF SYSTEMS LnF_3-CeF_3 (Ln-Sm, Eu, Yb) AND EuF_3-TbF_3

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The interaction and structure of phases in systems LnF_3-$Ln'F_3$ (Ln-Sm, Eu, Yb Ln'-Ce, Tb) are studied at 700-1100°C. Formation of solid solutions on the basis of binary fluorides of lanthanides is established. Appearance of fluorite-like phases of a structure LnF_{2+x} beginning from 1000°C is observed. The content of the latter notably increases at heat treatment in vacuum. The formation of Ln(II) in systems LnF_3-$Ln'F_3$ is confirmed by appearance of intensive bands of absorption in UV range of a spectrum. They are caused by 4f-5d electronic transitions in ions Ln(II) and charge transfer Ln'(IV) → Ln(III). The intensity of bands of absorption increases with temperature rise and in a series Sm-Yb-Eu and Tb-Ce, that is in agreement with strengthening of interaction in the studied systems.

Samarium, Europium, Ytterbium, Cerium and Terbium fall to elements of a lanthanide series, for which the variable valence Sm(III) and Sm(II), Eu(III) and Eu(II), Yb(III) and Yb(II), Ce(III) and Ce(IV), Tb(III) and Tb(IV) is peculiar. This feature gives a definite originality to interaction between fluorides of the indicated lanthanides. The initial compounds of systems are obtained by a fluorization of oxides of lanthanides by a hydrofluoric acid (H_2F_2) or ammonium hydrofluoride (NH_4HF_2) with the subsequent dehydration and refusing in inert atmosphere [1]. The powders of systems were extruded in tablets and sintered at temperatures 700-1100°C in inert gas (He). A part of last sample was incinerated at 1100°C in vacuum 10^{-1}Pa. One of the tablets was evaporated in the vacuum installation VU1A at residual pressure ~10^{-3}Pa with subsequent deposition of thin-film coating. The optical and operational parameters of coating were determined by a standard technique [1]. The X-ray diffraction and X-ray phase analysis were conducted on the automated vehicle DRON-3 with application of filtrated radiation CuK_α by a specially designed technique [2]. The spectra of a diffuse reflection of powders were measured with the help of the spectrophotometer Lambda 9 in the range 200-2700 nm [3].

The outcomes of the X-ray phase analysis testify that the hyperthermal interaction between fluorides of lanthanides results in formation of solid solutions on the basis of each of components, and, in some cases, the formation of one continuous solid solution (Tab. 1). In the systems SmF_3-CeF_3 and EuF_3-CeF_3 at high temperatures only high-temperature modification (β-LnF_3) takes place. The temperature rise results in stronger change of a phase structure and parameters of lattices of solid phases in comparison with the initial components. At rather high temperatures - 1000°C for a system EuF_3-CeF_3 and 1100°C for a system YbF_3-CeF_3 the appearance of new phases - solid solutions of fluorite-like structure of composition LnF_{2+x} - is observed, the basis of which is formed by ions Ln(II). At hyperthermal processing in vacuum the content of such phases in the indicated systems essentially increases, and also results in appearance of admixture of a similar phase in the system SmF_3-CeF_3. The data of spectroscopy of a diffuse reflection confirm availability of ions Ln(II) in the studied systems.

Table 1. Structure of phases and parameters of their crystal lattices in the systems LnF_3-CeF_3 (Ln - Sm, Eu, Yb) and EuF_3-TbF_3

System, 50 mol. %	Conditions of thermal treating	Structure of phases and their parameters, nm
SmF_3–CeF_3	Annealing in He, 1100°C	CeF_3, hex. (88%), a=0.7020, c=0.7187 β-SmF_3, hex. (12%); a=0.7020, c=0.7187
	Annealing in vacuum, 1100°C	SmF_{2+x}, cub.(<1%), a=0.5680 CeF_3, hex. (>99%), a=0.7036, c=0.7196
EuF_3–CeF_3	Annealing in He, 1100°C	β-EuF_3, hex. (37%); a=0.7039, c=0.7179 EuF_{2+x}, cub. (33%), a=0.5829 CeF_3, hex. (30%); a=0.7167, c=0.7297
	Annealing in vacuum, 1100°C	β-EuF_3, hex. (36%); a=0.7004, c=0.7151 EuF_{2+x}, tetr.(44%), a=0.3968, c=0.7282 CeF_3, hex. (20%); a=0.7107, c=0.7282
YbF_3–CeF_3	Annealing in He, 1100°C	α-YbF_3, rhomb.(52%), a=0.6263, b=0.6820 YbF_{2+x},cub. (8%), a=b=c=0.5471 CeF_3, hex. (40%); a=0.7032, c=0.7185
	Annealing in vacuum, 1100°C	α-YbF_3, rhomb.(21%), a=0.6261, b=0.6830, c=0.4458 YbF_{2+x} cub. (19%), a=b=c=0.5460 CeF_3, hex. (60%); a=0.7012, c=0.7150
EuF_3–TbF_3	Annealing in He, 1100°C	α-EuF_3, rhomb.((Eu, Tb)F_3) (100%), a=0.6579, b=0.6993, c=0.4393

Really, besides weak-intensive peaks of absorption characteristic of ions Ln(III) in visible and near IR range of a spectrum (fig.1), in UV range of a spectrum appearance of broad and high-intensive bands of absorption (fig.2) for annealed samples is observed. Their intensity increases in a series of systems Eu-Tb, Sm-Ce, Yb-Ce, Eu-Ce. The interesting fact is the shift of band maxima in short-wave range at decreasing of a range of symmetry of lattices of the formed phases (Tab.2).

Table 2 - Positions of extrema on the diffuse reflection spectra in the UV interval of powders of the systems LnF_3 - CeF_3 (Ln - Sm, Eu, Yb) and EuF_3 - TbF_3, annealed in He at 1100°C

System	λ_{max}, nm	$F(R)_{max}$	$\Delta H^0_{298,r}$, kJ/mole
SmF_3 - CeF_3	312	1.372	269
EuF_3 - CeF_3	304	3.445	129
YbF_3 - CeF_3	249	2.254	209
EuF_3 - TbF_3	243	1.145	302

These bands are caused by the 4f-5d electronic transitions in ions Ln(II) [4], and also processes of a charge transfer Ln(II)→ Ln(III) and Ln'(III) → Ln'(IV). At rise of heat treatment temperature and effect of vacuum the intensity of bands increases.

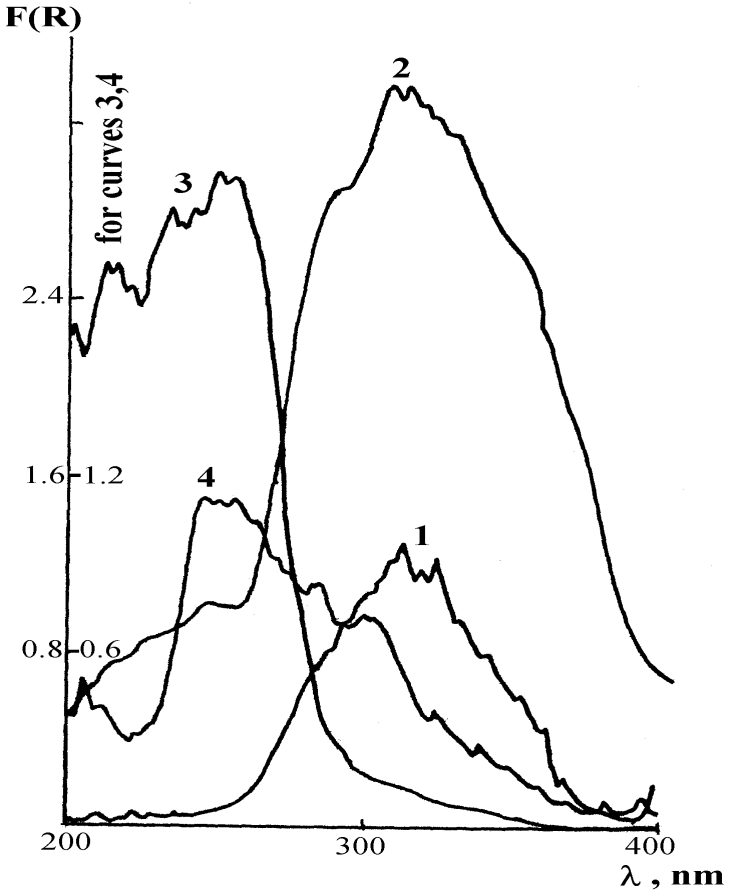

Fig. 1. Diffuse reflection spectra in the UV interval of spectrum for powders of the systems (1100°C, He): 1- SmF_3-CeF_3, 2 - EuF_3-CeF_3, 3 - YbF_3-CeF_3, 4 - EuF_3-TbF_3.

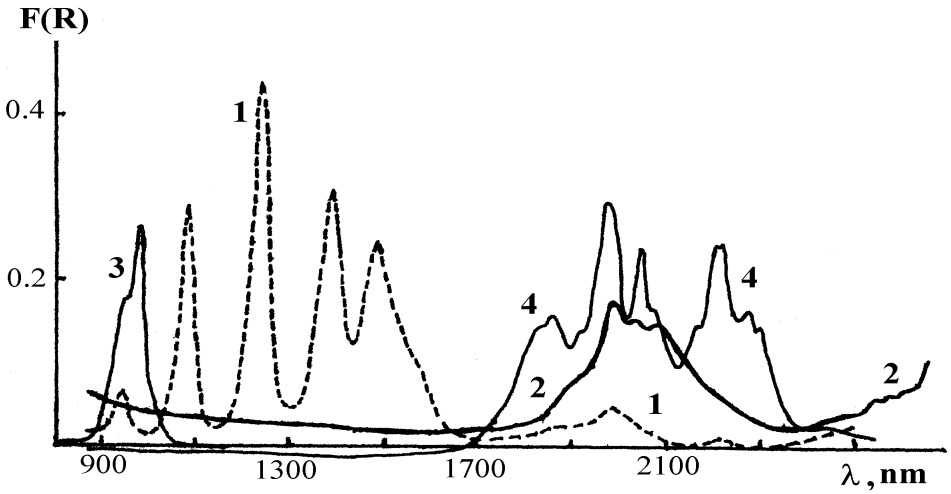

Fig. 2. Diffuse reflection spectra in the near IR interval of spectrum for powders of the systems (1100°C, He): 1- SmF_3-CeF_3, 2 - EuF_3-CeF_3, 3 - YbF_3-CeF_3, 4 - EuF_3-TbF_3.

The possible causes of origin of ions Ln(II) and Ln'(IV) in systems can be redox processes in the indicated systems:

$$LnF_3 + Ln'F_3 \rightarrow LnF_2 + LnF_4$$

As the thermodynamic estimation demonstrates on the basis of the data [5], the probability of such processes is not so high ($\Delta H^0_{298,r} > 0$). However, the temperature rise should essentially move equilibrium of reaction in the side of formation of LnF_2 and $Ln'F_4$. This also is promoted by formation of solid solutions and compounds on the basis of the mentioned fluorides, and also evaporation of Ln'(IV) fluorides, which are rather volatile compounds at high (>1000°C) temperatures [6]. Symptomatic is the availability of inverse relationship of intensity of bands of absorption (as well as content of phases such as LnF_{2+x} from value of $\Delta H^0_{298,r} > 0$) (Tab.2).

Thin-film coatings obtained by vacuum evaporation of samples of systems EuF_3-CeF_3 and YbF_3-CeF_3, have essentially different optical and operational parameters. So, the scattering coefficients have values 0.07-0.1% and 0.4-0.45%, respectively, and their mechanical durability - 17000-19000 and 1000 rotations before wiping of coating, respectively. Apparently the degree of interaction favours improvement of properties of coatings.

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