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INORGANIC SYNTHESIS AND INDUSTRIAL INORGANIC CHEMISTRY

Hydrofluoride Synthesis of Fluorides of Some Rare-Earth Elements

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Abstract—Thermal gravimetric, X-ray phase, IR spectroscopic, and chemical analyses were applied to study the reaction of yttrium and neodymium oxides with NH_4HF_2.

Fluorides of rare-earth elements (REE) are used in electrochemical recovery of these metals by electrolysis of molten salts and in production of glasses for active and passive waveguides; they are of interest for production of laser media based on complex REE fluorides [1–4].

A study of the reaction of REE oxides with ammonium hydrofluoride, including identification of the intermediates, is of interest not only for controlling the process, but also for developing and optimizing the hydrofluoride synthesis of complex fluorides of the composition $M_mLn_nF_{m+3n}$, where M is an alkali metal and Ln is an REE, to be used as stock for growth of single crystals.

A disadvantage of the conventional method for obtaining REE fluorides by precipitation from solution is the relatively high content of oxygen-containing anionic impurities.

Use of ammonium hydrofluoride as a fluorinating agent has a number of advantages, since NH_4HF_2 is close in reactivity to anhydrous hydrogen fluoride, is inexpensive, and can be readily dehydrated and regenerated from gaseous components, and reactions involving this agent can be carried out without complex equipment [5–7].

Despite extensive published data on hydrofluoride synthesis of REE fluorides, there is no common opinion concerning the scheme of the reactions in the literature. Therefore, we performed in this work a detailed study of reactions of yttrium and neodymium oxides with ammonium hydrofluoride and examined the composition and order of thermal decomposition of the intermediates formed. In addition, the methods for obtaining yttrium, neodymium, and gadolinium fluorides by (a) hydrofluoride synthesis and (b) precipitation from solutions were compared with respect to the concentration of oxygen-containing anionic impurities in the final products.

As starting substances we used REE oxides of analytically pure grade and twice recrystallized NH_4HF_2 of the same grade. Thermogravimetric studies were carried out on a Q-1500D derivatograph in platinum crucibles, with weighed portions of 350–400 mg. As reference served calcined Al_2O_3. Measurements were done in dynamic and quasi-isothermal modes at a heating rate of 5 deg min^{-1}. X-ray phase analysis was carried out on a DRON-3 diffractometer with CuK_α radiation. IR absorption spectra were recorded on a UR-20 spectrophotometer. Chemical analysis for fluoride ions was performed by pyrohydrolysis followed by potentiometric determination (with F^--selective electrode). Analysis for metals was done by flame emission spectrometry. The content of ammonia was determined by the Kjeldahl method. The concentrations of oxygen-containing anionic impurities in the final synthesis products was found using linear voltammetry in halide melts [8]. The measurements were done under isothermal conditions in an argon atmosphere. The fluorides synthesized were introduced into a KCl–KF melt of eutectic composition. A glassy carbon (SU-2000) crucible with the melt was placed in a hermetically sealed stainless steel retort. The crucible simultaneously served as a counterelectrode. Molybdenum was used as material of the quasi-reference electrode. Voltammograms were measured on a glassy carbon (SU-2000) electrode using an Autolab computerized electrochemical complex. The residual current densities found from voltammograms of the supporting melt characterized its purity; for oxygen, these current densities were about 5 mA cm^{-2}.

In [9], complex yttrium fluorides were studied thermogravimetrically, and it was demonstrated that the reaction of Y_2O_3 with NH_4HF_2 starts at 60–80°C to give $NH_4Y_2F_7 \cdot NH_4F$, which dissociates into $NH_4Y_2F_7$ and yttrium trifluoride upon heating. In [10], no formation of $NH_4Y_2F_7 \cdot NH_4F$ in the reaction of Y_2O_3 with NH_4F was observed, but yttrium compounds of the composition $(NH_4)_3Y_2F_9$ and $NH_4Y_2F_7$ were synthesized.

A thermogram of a mixture of Ln_2O_3 with NH_4HF_2 in 1 : 6 molar ratio is shown in Fig. 1a. The reaction is accompanied by a series of exo- and endothermic effects. The endothermic effect at 145°C can apparently be attributed to melting of ammonium hydrofluoride, which intensifies the reaction. At 236°C, excess NH_4HF_2 boils, giving an endothermic peak in the DTA curve. Hydrofluorination is complete at a temperature of about 350°C.

To elucidate the scheme of the reaction between Y_2O_3 and NH_4HF_2, we also performed measurements in the quasi-isothermal mode. Figure 2a shows a typical thermogravigram of a mixture of Y_2O_3 and NH_4HF_2 in 1 : 4.5 molar ratio, in which three plateaus can be observed. An analysis of the experimental Δm values corresponding to each of the plateaus revealed the following scheme of the process:

$$Y_2O_3 + 4.5NH_4NF_2 \rightarrow (NH_4)_3Y_2F_9 + 1.5NH_3 + H_2O, \quad (1)$$

$$(NH_4)_3Y_2F_9 \rightarrow NH_4Y_2F_7 + 2NH_3 + 2HF, \quad (2)$$

$$NH_4Y_2F_7 \rightarrow 2YF_3 + NH_3 + HF. \quad (3)$$

The theoretical weight losses corresponding to each stage of synthesis and amounting to, respectively, 16.5, 31.8, and 39.5 wt % are in good agreement with the experimental values (Fig. 2a).

The products formed at 170, 250, and 350°C were analyzed by the methods mentioned above; the results obtained confirmed the reaction scheme represented by Eqs. (1)–(3).

Figure 3 shows X-ray diffraction patterns of $Y_2O_3 : NH_4HF_2$ mixtures with the molar ratio of 1 : 4.5, measured at different temperatures. The results of X-ray phase analysis of the products formed at 170 and 250°C (Figs. 3a, 3b) are in good agreement with [10] and indicate formation of, respectively,

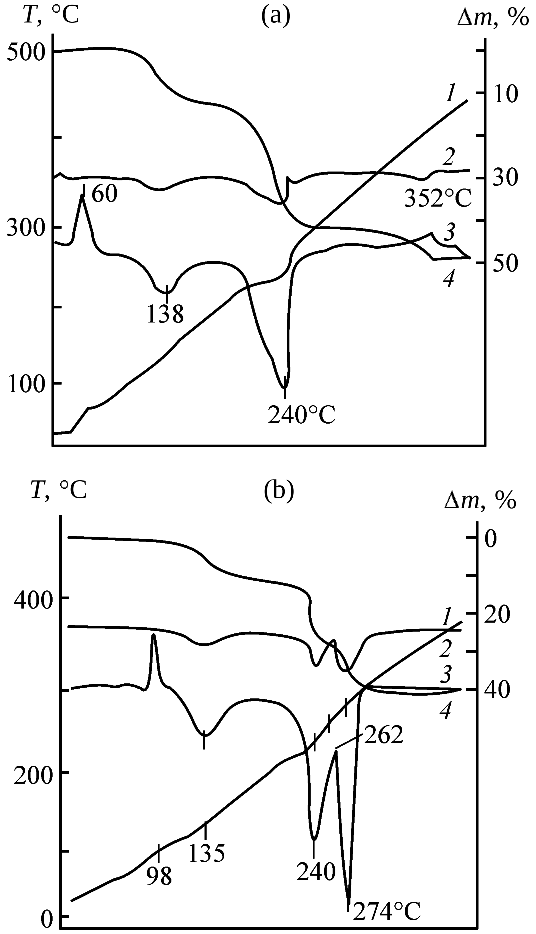

Fig. 1. Thermograms of Ln_2O_3 mixed with NH_4HF_2 in 1 : 6 molar ratio: (*T*) temperature and (Δm) weight loss; the same for Fig. 2. (a) Yttrium oxide and (b) neodymium oxide.

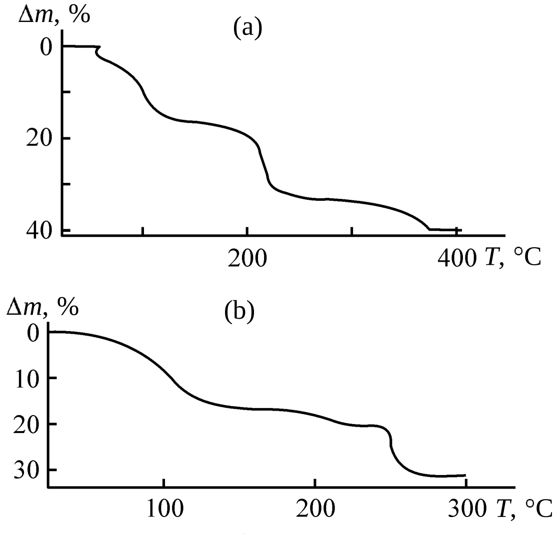

Fig. 2. Thermograms of Ln_2O_3 mixed with NH_4HF_2: (a) yttrium oxide, 1 : 4.5 molar ratio, and (b) neodymium oxide, 1 : 4 molar ratio.

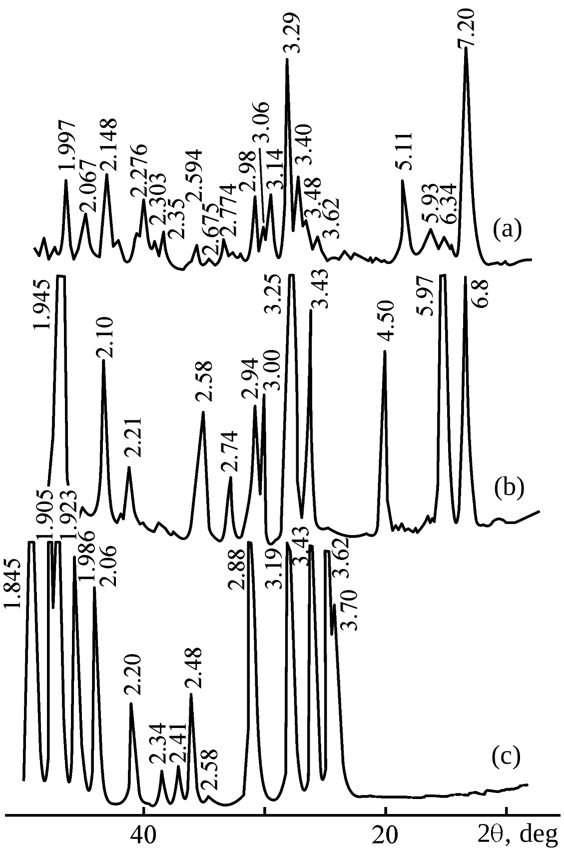

Fig. 3. X-ray diffraction patterns of reaction products formed from a $Y_2O_3 : NH_4HF_2 = 1 : 4.5$ mixture. (2θ) Bragg angle. (a) $(NH_4)_3Y_2F_9$, synthesis temperature 170°C; (b) $NH_4Y_2F_7$, 250°C; and (c) YF_3, 350°C.

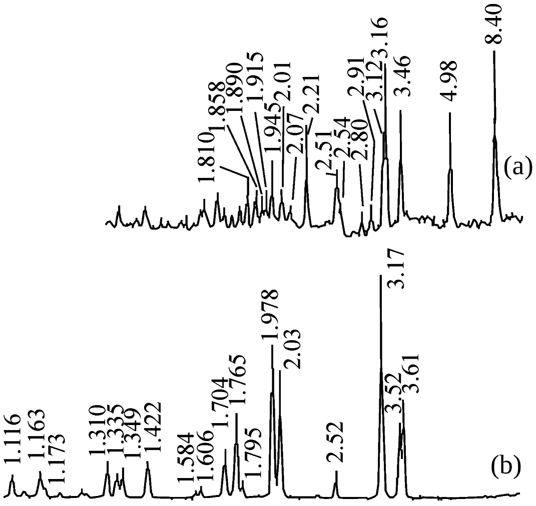

Fig. 4. X-ray diffraction patterns of reaction products formed from an $Nd_2O_3 : NH_4HF_2 = 1 : 4.5$ mixture. (a) NH_4NdF_4, synthesis temperature 150°C, and (b) NdF_3, 250°C.

$(NH_4)_3Y_2F_9$ and $NH_4Y_2F_7$. Figure 3c presents an X-ray diffraction pattern of yttrium trifluoride formed at 350°C.

The results of chemical analysis of intermediate synthesis products also confirm the formation of $(NH_4)_3Y_2F_9$ and $NH_4Y_2F_7$.

Data on the reaction of Nd_2O_3 with ammonium trifluoride were reported in [10], where a compound of the composition NH_4NdF_4 was obtained by keeping a mixture of Nd_2O_3 and NH_4F at 130–150°C for 1–3 days. Rakov presented in his review [6] data obtained by Polish researchers who established that this reaction proceeds in stages to give, in the first stage, the compound $(NH_4)_3NdF_6$, and then, at 350–400°C, NH_4NdF_4, which decomposes at 500°C to yield NdF_3 [6].

A thermogram of a mixture of Nd_2O_3 and NH_4HF_2 in 1 : 6 molar ratio is shown in Fig. 1b. The reaction, accompanied by a series of endo- and exothermic effects, is complete at temperatures higher than 270°C.

The results obtained in studies in the quasi-isothermal mode are presented in Fig. 2b. The thermogravigram of a mixture of Nd_2O_3 and NH_4HF_2 in 1 : 4 molar ratio is characterized by the presence of two plateaus. With account of the experimental values of Δm corresponding to each plateau, the presumed scheme of the process is as follows:

$$Nd_2O_3 + 4NH_4HF_2 \rightarrow 2NH_4NdF_4 + 3H_2O + 2NH_3, \quad (4)$$

$$2NH_4NdF_4 \rightarrow 2NdF_3 + 2NH_3 + 2HF. \quad (5)$$

The theoretical weight losses of 15.6 and 28.7 wt %, corresponding to reactions (4) and (5), are in good agreement with the experimental values (Fig. 2b).

The products of synthesis at temperatures corresponding to the plateaus in the thermogravimetric curve were subjected to X-ray phase analysis. X-ray diffraction patterns of $Nd_2O_3 : NH_4HF_2$ mixtures with the molar ratio of 1 : 4 at 150 and 250°C are shown in Fig. 4. The X-ray diffraction pattern of the product formed at 150°C is in agreement with the results of [10] and indicates the formation of NH_4NdF_4.

As an example of the measurements performed, the table presents the results obtained in determining oxygen in gadolinium fluoride, together with summarized data on the content of oxygen in yttrium and neodymium fluorides prepared by different methods.

With increasing content of gadolinium, neodymium, and yttrium oxides in the melt, the peak corresponding to the oxidation wave of oxygen-containing

Content of oxygen in REE fluorides

Method of LnF_3 synthesis	$(KCl–KF)_{eut}–LnF_3$ melt			Content in LnF_3		
	LnF_3, wt %	j_p^a, mA cm^{-2}	Ln_2O_3, $c \times 10^2$, wt %	Ln_2O_3, wt %	O_2 wt %	O_2 $c \times 10^4$, mol %
Gadolinium fluoride						
Hydrofluoride:						
in air	0.867	2.042	0.851	0.981	0.129	0.964
in air with repeated fluorination	0.331	0.341	0.116	0.350	0.046	0.343
in inert atmosphere	0.579	0.214	0.073	0.126	0.017	0.124
Precipitation from solution with subsequent calcination in a vacuum	0.708	1.203	0.409	0.578	0.076	0.568
LnF_3 of ultrapure grade	3.376	5.728	1.948	0.577	0.076	0.568
Yttrium fluoride						
Hydrofluoride:						
in air	0.487	1.057	2.736	5.623	1.195	13.124
in air with repeated fluorination	0.699	0.528	1.368	1.956	0.416	4.565
in inert atmosphere	0.848	0.264	0.684	0.807	0.172	1.884
Neodymium fluoride						
Hydrofluoride:						
in air	0.878	27.590	38.680	43.959	6.273	52.942
in air with repeated fluorination	1.239	4.109	5.761	4.642	0.663	5.596
in inert atmosphere	1.960	0.839	1.176	0.600	0.0856	0.723

halide complex of a rare-earth metal in voltammograms measured at polarizing voltage sweep rate of 0.1 V s^{-1} becomes more pronounced. Figure 5a shows a typical family of curves for the above process, measured with gadolinium oxide added to the melt. On reaching the limiting solubility of REE oxide (gadolinium oxide in the given case), the anode current at the peak corresponding to oxidation of the oxygen-containing halide complex levels off (Fig. 5a, curves *5*–*7*). The dependences $j_p^a = f([Ln_2O_3])$ show a portion corresponding to constant j_p^a (Fig. 5b). The initial linear portion (before leveling-off of the anode current) is described by the equations

$$j = 294.020c \text{ for gadolinium oxide,} \quad (6)$$

$$j = 38.617c \text{ for yttrium oxide,} \quad (7)$$

$$j = 71.323c \text{ for neodymium oxide,} \quad (8)$$

where j is the anode current density at the peak corresponding to oxidation of the oxygen-containing ion (mA cm^{-2}), and c is the oxide content of the melt (wt %).

Addition of an REE oxide to a melt under study in amounts *a fortiori* exceeding the maximum soluble

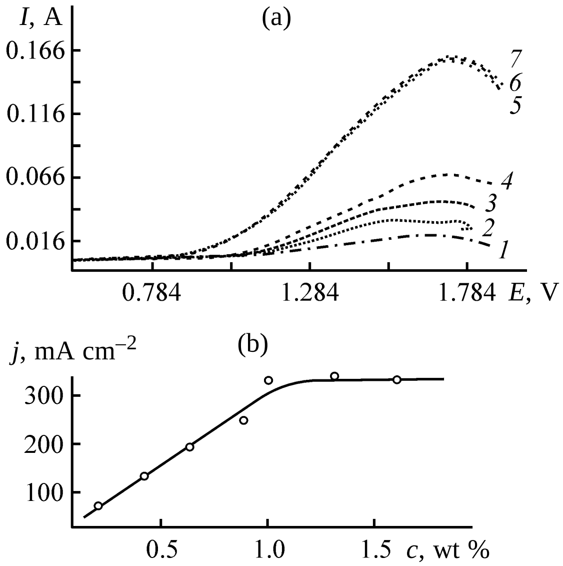

Fig. 5. (a) Voltammograms of oxidation of an oxygen-containing complex of gadolinium in a $KCl–KF–Gd_2O_3$ melt at 735°C on a glassy carbon electrode relative to a molybdenum quasi-reference electrode and (b) oxidation current j of oxygen-containing gadolinium complex vs. Gd_2O_3 content c in a melt of the KCl–KF eutectic at 735°C. (a) Polarization rate 0.1 V s^{-1}. (*I*) Current and (*E*) potential. Electrode area (cm^2): (*1*–*3*) 0.23 and (*4*–*7*) 0.27. Gd_2O_3 content (wt %): (*1*) 0.21, (*2*) 0.425, (*3*) 0.638, (*4*) 0.896, (*5*) 1.012, (*6*) 1.32, and (*7*) 1.617.

amount (about 5 wt % in the case in question) and sampling for determining the content of Ln_2O_3 made it possible to plot the temperature dependences of the limiting solubility of the REE oxides. The functions obtained are described by the equations

$$c_{\lim} = 0.0015T - 0.0794 \text{ for gadolinium oxide,} \quad (9)$$

$$c_{\lim} = 0.0136T - 8.4549 \text{ for yttrium oxide,} \quad (10)$$

$$c_{\lim} = 0.0139T - 0.2602 \text{ for neodymium oxide,} \quad (11)$$

where $c_{\lim}$ is the limiting content of Ln_2O_3 in the melt (wt %), and T is the temperature of the melt (°C).

The use of dependences (6)–(8) and evaluation of the content of oxygen in fluorides of the above-mentioned REEs made it possible to give preference to the hydrofluoride method of LnF_3 preparation in an inert atmosphere [oxygen content of the REE fluoride was $(0.12–1.88) \times 10^{-4}$ mol %].

CONCLUSIONS

(1) Reactions of Y_2O_3 and Nd_2O_3 with ammonium hydrofluoride were studied. Intermediate complex ammonium fluorometallates were isolated and identified.

(2) The content of cationic impurities in the final products, trifluorides of rare-earth elements, was found to be determined by their content in the starting oxides; the content of anionic impurities (oxygen-containing in the first place) can be lowered by creating an inert or fluorinating atmosphere in synthesis. A comparison of various methods for the synthesis of yttrium, gadolinium, and neodymium fluorides as regards the content of oxygen-containing anionic impurities in the final products demonstrated that the best results are obtained with the hydrofluoride method. The content of oxygen was $(0.12–1.88) \times 10^{-4}$ mol %. The use of glassy carbon materials lowered to a minimum the contaminating effect of the apparatus.

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