Full Articles

Thermal properties and thermochemistry of lanthanide chromates

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The behavior of chromates $Ln_2(CrO_4)_3 \cdot 7H_2O$ and $Rb_5Ln(CrO_4)_2$ (Ln = La, Pr, Nd, Sm, and Gd) was studied by derivatography as they were heated in air in a temperature interval of 300—1470 K. The high-temperature enthalpies of $LaCrO_3$ and $YCrO_3$ at 865—1350 K and enthalpies of solution of $La_2(CrO_4)_3 \cdot 7H_2O$ in a solution of nitric acid at 298 K were measured by calorimetric methods. The standard enthalpies of formation were calculated for some compounds of composition $Ln_2(CrO_4)_3 \cdot 2H_2O$ and $LnCrO_3$.

Key words: chromites, chromates, lanthanides, thermochemistry, enthalpy, thermal analysis.

Chromates of rare-earth elements (REE) change their color on heating. Therefore, they can be used as thermal indicators. In addition, they can be introduced as additives into high-temperature ceramic lanthanum-chromite heaters and coatings.

Previously,[1] we measured the enthalpies of reactions of chromates $Ln_2(CrO_4)_3 \cdot 7H_2O$, $Ln_2(CrO_4)_3$ and mixtures $Cr_2O_3 + Ln(NO_3)_3$ with an 0.3 *M* aqueous solution of HNO_3 by solution calorimetry. Based on these data, the standard enthalpies of formation ($\Delta_f H°$) of the corresponding chromates were calculated. The thermodynamic data for chromates of other compositions are lacking, and only few reports on the thermal properties of lanthanide chromate heptahydrates are available.[2] Therefore, in this work we continue the thermochemical study of chromates of different compositions, which are stable products of the thermal dissociation of $Ln_2(CrO_4)_3 \cdot 7H_2O$ (Ln = La, Pr, Nd, Sm, and Gd). The thermal properties of chromates $Ln_2(CrO_4)_3 \cdot 7H_2O$, $Ln_2(CrO_4)_3$ and $Rb_5Ln(CrO_4)_4$ were also studied. In addition, it seemed of interest to calculate the standard enthalpies of formation of these compounds from thermodynamic values for $LnCrO_3$ obtained by the present author and given in literature.

Experimental

Lanthanum, praseodymium, and neodymium chromate heptahydrates were synthesized by precipitation from aqueous solutions of nitrates at certain pH values using a known procedure.[2] To obtain samarium and gadolinium chromates using this procedure, the pH values of precipitation (pH_{pr}) were needed. Accordingly, we used our plot relating the known pH_{pr} values and REE ion radium (Fig. 1). The pH_{pr} values were 4.6 and 4.3 for samarium and gadolinium chromates, respectively. The precipitates corresponded to compositions $Ln_2(CrO_4)_3 \cdot 7H_2O$ with the error <0.8%, estimated by chemical analyses of filtered and acetone-washed products for the content of Ln^{3+} and Cr^{6+}

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 2, pp. 290—295, February, 2005.

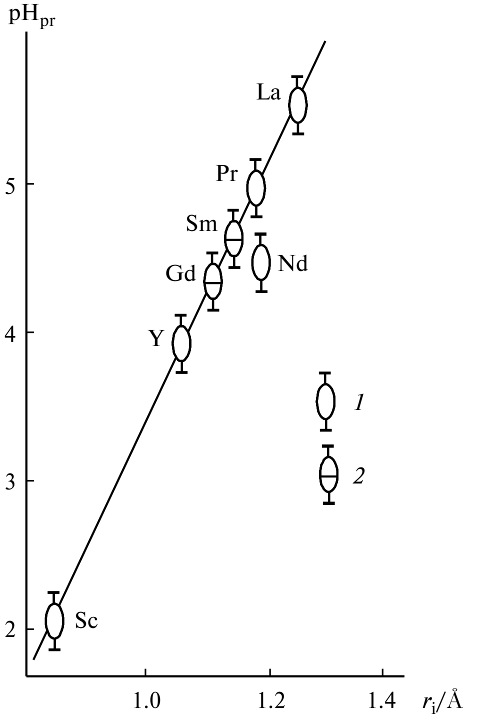

Fig. 1. Plot of the pH of precipitation of REE chromates (pH_{pr}) *vs.* REE ion radius (r_i): experiment (*1*) and calculation (*2*).

(complexonometry and iodometry, respectively). The content of water of crystallization in crystal hydrates was determined by the gravimetric method with the error ≤0.06 mole.

The compounds synthesized were characterized by X-ray diffraction analysis on a Dron-I diffractometer (Cu-Kα radiation, Ni filter). The main interplanar distances in anhydrous finely crystalline chromates of the $Ln_2(CrO_4)_3$ type are presented in Table 1. The corresponding values for the heptahydrates agree with the published data.[2]

Table 1. Temperature of synthesis (T_{syn}), interplanar distances (d), and relative intensities of lines (I) in the X-ray patterns of anhydrous crystalline samples of $Ln_2(CrO_4)_3$

Ln	T_{syn}/K	d/Å	I (%)
La	670	6.492	91
	670	3.567	98
	670	3.069	100
Pr	700	6.559	83
	700	5.438	89
	700	3.069	100
Nd	720	5.372	90
	720	4.917	100
	720	3.058	73
Sm	700	5.375	50
	700	3.624	100
	700	2.688	85
Gd	630	6.63	65
	630	3.65	100
	630	3.04	90

Table 2. Densities (ρ) of crystalline $Ln_2(CrO_4)_3 \cdot 7H_2O$ and $Ln_2(CrO_4)_3$

Ln	$\rho \cdot 10^{-3}$/kg m^{-3}	
	$Ln_2(CrO_4)_3 \cdot 7H_2O$	$Ln_2(CrO_4)_3$
La	2.99±0.02	3.65±0.01
Pr	3.02±0.04	3.63±0.02
Nd	3.04±0.01	3.86±0.02
Sm	3.33±0.03	3.94±0.06
Gd	3.24±0.01	3.80±0.07

Chromate dihydrates $Ln_2(CrO_4)_3 \cdot 2H_2O$ were synthesized by the method of isothermic exposures of the heptahydrates (for 1 h) at temperatures corresponding to the onset of dehydration of the latters.

REE	La	Pr	Nd	Sm	Gd
T/K	380	410	430	410	420

Anhydrous crystalline chromates of the $Ln_2(CrO_4)_3$ type were synthesized at the temperatures corresponding to the crystallization points of the amorphous chromates (see Table 1). The temperatures of synthesis of these salts were determined from the results of thermal analysis of the heptahydrates. The amount of water in the dihydrates was 2.00±0.02 moles, as indicated by the gravimetric data obtained derivatographically.

The picnometric density was measured at 298.0±0.5 K for the heptahydrates and anhydrous crystalline chromates using toluene (Table 2).

Binary chromates $Rb_5Ln(CrO_4)_4$ were obtained from simple chromates by the solid-state synthesis with stepwise heating for 100 h in an interval of 620—870 K.[3] Lanthanum and yttrium chromites $LnCrO_3$ were produced by the activation solid-state synthesis at 1270 K using a known procedure.[4] Thermal analyses of chromates $Ln_2(CrO_4)_3 \cdot 7H_2O$ and $Rb_5Ln(CrO_4)_4$ were carried out on an OD-102 derivatograph in temperature ranges of 300—1470 and 300—1170 K, respectively, with a heating rate of 10 deg min^{-1}. Weighed samples of substances (100—200 mg) were placed in corundum or platinum plate crucibles to increase the dissociation surface. A reference was an alumina powder prepared from a single crystal. For $Rb_5Ln(CrO_4)_4$, derivatograms were also recorded in a regime of natural cooling. The typical derivatograms of chromates $Ln_2(CrO_4)_3 \cdot 7H_2O$ are presented in Fig. 2, and those for $Rb_5Ln(CrO_4)_4$ are shown in

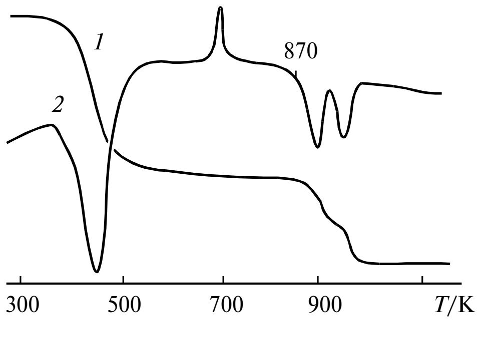

Fig. 2. TGA (*1*) and DTA (*2*) curves obtained on a derivatograph for $La_2(CrO_4)_3 \cdot 7H_2O$.

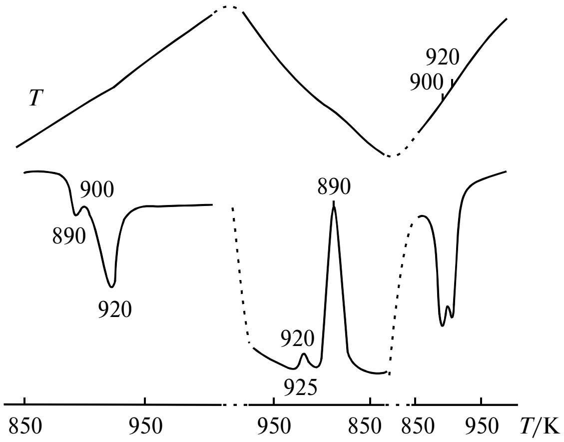

Fig. 3. DTA curve obtained on a derivatograph for $Rb_5Sm(CrO_4)_4$ in the thermal cycling regime.

Table 3. Temperature intervals of transformations of $Ln_2(CrO_4)_3 \cdot 7H_2O$ determined by derivatography

Ln	ΔT/K			
	dehydration	crystallization	dissociation	
			by reaction (3)	by reaction (4)
La	350—430	680—730	900—940	970—1010
Pr	340—510	720—750	880—940	—
Pr*	—	—	910—960	980—1010
Nd	360—460, 490—540	680—730	880—930	970—990
Sm	360—450, 490—570	720—760	850—870	970—1000
Sm**	—	—	860—920	940—980
Gd	380—470, 470—520	630—770	850—930	970—1030

* The sample was stored in a dry atmosphere for 3 years.

** Experiment in a plate platinum crucible.

Fig. 3. The temperature intervals of transformations obtained by analysis of the derivatograms of samarium and gadolinium salts (Tables 3 and 4) served to investigate the composition of the solid-state products of $Ln_2(CrO_4)_3 \cdot 7H_2O$ dissociation. The method is based on different solubilities of chromates with variable oxidation states of chromium. Since the chromates containing Cr^{5+} or Cr^{6+} are soluble,[2] whereas $LnCr^{3+}O_3$ and Cr_2O_3 are insoluble in dilute hydrochloric acid, the samples calcined at temperatures of dissociation onset were treated with a 7% solution of hydrochloric acid. The fraction of the acid-insoluble substance was determined by the weight of a residue non-dissolved after filtration and drying. The residue was also examined by X-ray diffraction and thermal analyses.

Table 4. Temperatures of phase transitions of $Rb_5Ln(CrO_4)_4$ obtained by derivatography

Ln	T_{pt}	T_m	T_{solid}
	K		
La	—	980—1005	1005—980
Pr	—	935—945	945—935
Nd	—	935—945	925—915
Sm	880—890	900—920	900—890
Eu	830—850	880—920	880—870
Gd	770—790	875—915	860—855

Note. T_{pt}, T_m, and T_{solid} are the temperatures of polymorphous transition, melting, and solidification, respectively.

To determine the standard enthalpies of formation of $Ln_2(CrO_4)_3 \cdot 2H_2O$, we used solution calorimetry used earlier[1] to find the enthalpies of formation of $Ln_2(CrO_4)_3 \cdot 7H_2O$. According to this procedure, the following thermochemical cycle was proposed:

$$Ln_2(CrO_4)_3 \cdot 2H_2O(cr) + 6\,HNO_3(s) = 2\,Ln(NO_3)_3(s) + 3\,H_2CrO_4(s) + 2\,H_2O(s), \quad (1)$$

$$2\,Ln(NO_3)_3 \cdot 7H_2O(cr) + 3\,CrO_3(cr) + HNO_3(s) = 2\,Ln(NO_3)_3(s) + 3\,H_2CrO_4(s) + 11\,H_2O(s), \quad (2)$$

where components in the crystalline state and in solution are marked by indices "cr" and "s," respectively.

According to this cycle, we measured the enthalpies of interaction of La, Pr, Nd, Sm, and Gd chromate dihydrates with an 0.3 *M* aqueous solution of HNO_3 at 298.15 K. The chemical reaction that occurs in a calorimeter cell is described by Eq. (1). Six to seven entries were carried out for each compound studied, and the results of their statistical processing are presented in Table 5. The measurement error of enthalpies of reactions (ΔH°_{298}) and enthalpies of formation was estimated as a root-mean-square deviation from the weighed average value.

The standard enthalpy of formation of $LaCrO_3$ was determined by the DSC method. For this purpose, the enthalpies of thermal dissociation of $Ln_2(CrO_4)_3 \cdot 7H_2O$ under helium were measured on a DSC-111 (Setaram) differential scanning calorimeter. The calorimeter was calibrated by the Joule effect and checked by the enthalpy of melting of the reference substance (In, purity 99.9%). The enthalpies of complete dehydration of the heptahydrate, crystallization of the amorphous anhydrous chromate, and complete dissociation of the crystalline anhydrous chromate at the temperature of the effect (ΔH_T) along with the corresponding values recalculated to 298 K (ΔH°_{298}) are presented in Table 6.

The high-temperature enthalpies of $LaCrO_3$ and $YCrO_3$ were measured by the mixing method on an HT-1500 (Setaram) high-temperature heat-conducting calorimeter[5] in a range of

Table 5. Enthalpies of reaction (1) ($\Delta H^\circ_{298}(1)$) and standard enthalpies of formation of lanthanide chromate dihydrates ($\Delta_f H^\circ_{298}$)

Ln	Number of entries	$-\Delta H^\circ_{298}(1)$	$-\Delta_f H^\circ_{298}$
		kJ mol^{-1}	
La	6	82.3±0.8	4556.4±12.6
Pr	6	87.4±0.8	4557.8±12.6
Nd	6	125.5±0.8	4488.9±12.6
Sm	7	108.1±0.5	4450.0±12.6
Gd	7	103.9±0.8	4495.4±12.6

Table 6. Enthalpies of dehydration of $La_2(CrO_4)_3 \cdot 7H_2O$ and enthalpies of crystallization and dissociation of $La_2(CrO_4)_3$ at the average temperature (T_{av}) of the effect ($\Delta H_{T_{av}}$/kJ mol^{-1}) and the corresponding values recalculated to 298 K (ΔH°_{298}/kJ mol^{-1})

Reaction or phase transition	T_{av} /K	Method		
		DSC		solution calorimetry
		$\Delta H_{T_{av}}$	ΔH°_{298}	ΔH°_{298}
Complete dehydration	500	109.2±4.2	95.4±5.9	93.3±1.3
Crystallization	755	−31.4±2.1	−30.5±2.5	−32.6±1.3
Dissociation by reaction (5)	890—1030	231.0	191.7±8.0	—

Table 7. High-temperature enthalpies ($H_T - H_{298}$) of $LaCrO_3$ and $YCrO_3$

Compound	($H_T - H_{298}$)/kJ mol^{-1}		
	865 K	1090 K	1350 K
$LaCrO_3$	—	94.4±3.5	139.2±3.5
$YCrO_3$	65.8±1.9	100.6±4.0	129.8±3.5

865—1350 K under argon (99.98%; <0.0007 wt.% O_2). The calorimeter was calibrated by the enthalpies of α-Al_2O_3 (SOTS-1). The deviation $H_T - H_{298}$ for α-Al_2O_3 (purity 99.999%) was <1.5%. Samples of lanthanum and yttrium chromites as individual fine crystals were thrown in a calorimeter cell with temperature maintained at a specified level. A chromite sample and α-Al_2O_3 crystal sample charged in a cell were alternated during experiment. Three—five measurements were carried out for each substance at a specified temperature. The results of statistical processing of the experimental data are presented in Table 7.

Results and Discussion

The derivatograms of $Ln_2(CrO_4)_3 \cdot 7H_2O$ show several endotherms with the loss in weight, and one exotherm without the loss in weight (see Fig. 2). As found from analyses of the DTA and TGA curves and calculations of the change in the sample weight, the first low-temperature endotherm in the derivatograms is caused by two-step dehydration to form intermediate $Ln_2(CrO_4)_3 \cdot 2H_2O$. The complete dehydration of crystal hydrates is achieved by calcination at temperatures ≥550 K (see Table 3). According to the X-ray diffraction data, anhydrous chromates formed are amorphous to X-rays and they crystallize on heating to 630—720 K (see Table 3). The crystallization is detected in the derivatograms by an exotherm without a change in the sample weight (see Fig. 2). Further heating of crystalline $Ln_2(CrO_4)_3$ produces two endotherms at 850—1030 K accompanied by the loss in weight. According to the chemical (content of Ln^{3+}) and gravimetric analyses, as well as by the X-ray diffraction data and repeated thermal analyses of the dissociation products of samarium and gadolinium chromates, such a two-step dissociation of anhydrous crystalline chromates proceeds through the formation of an intermediate mixture $LnCr^{5+}O_4 + 0.5\ Cr_2O_3$ in the condensed phase, and the final product has the composition $LnCr^{3+}O_3 + 0.5\ Cr_2O_3$. The weight loss is caused by oxygen release according to the following redox reactions:

$$Ln_2(Cr^{6+}O_4)_3 \xrightarrow{850-960\text{ K}} 2\ LnCr^{5+}O_4 + 1.25\ O_2, \tag{3}$$

$$2\ LnCr^{5+}O_4 \xrightarrow{940-1030\text{ K}} 2\ LnCr^{3+}O_3 + O_2. \tag{4}$$

Unlike other salts, crystalline $Pr_2(CrO_4)_3$ formed from the freshly synthesized crystal hydrate decomposes in one step, while the behavior of an aged sample (stored in a desiccator) is completely similar to that of other chromates studied. Thus, the thermal dissociation of $Ln_2(CrO_4)_3 \cdot 7H_2O$, which at the step of anhydrous salt decomposition corresponds to an intramolecular redox process with oxygen release, can be expressed by the following scheme (only dissociation products in the condensed state are presented):

$$\begin{gathered} Ln_2(CrO_4)_3 \cdot 7H_2O \longrightarrow Ln_2(CrO_4)_3 \cdot 2H_2O \longrightarrow \\ \longrightarrow Ln_2(CrO_4)_3(\text{amorph}) \longrightarrow Ln_2(CrO_4)_3(\text{cr}) \longrightarrow \\ 2\ LnCrO_4 + 0.5\ Cr_2O_3 \longrightarrow 2\ LnCrO_3 + 0.5\ Cr_2O_3. \end{gathered}$$

The final dissociation product ($LnCrO_3$) has a high thermal stability (T_m > 2270 K).[2] The scheme of dissociation established in this work is typical of neutral REE chromates of the indicated composition. The evident exception should be $Ce_2(CrO_4)_3$, which was not synthesized in the pure state so far, most likely, because it is difficult to obtain from solution a compound containing both the reducing agent Ce^{3+} and oxidant Cr^{6+}.

The derivatograms of binary chromates $Rb_5Ln(CrO_4)_4$ show that no loss in weight occurs in the whole studied temperature range, and only some effects are detected: endotherms on heating and exotherms on cooling. All chromates melt in a range of 875—1005 K (see Table 4). Binary La, Pr, and Nd chromates melt congruently, while Sm, Eu, and Gd chromates exhibit incongruent melting, because the exotherm of solidification is not reproduced

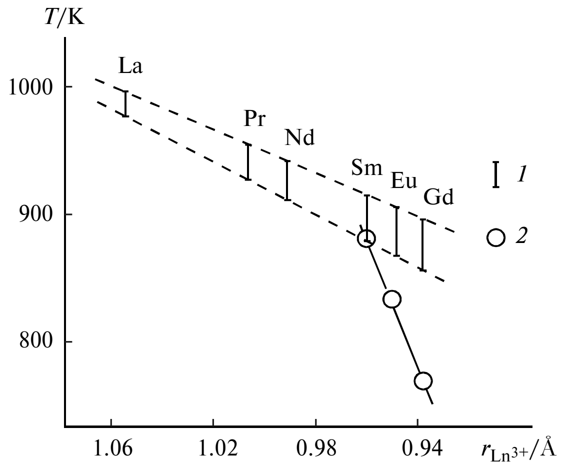

Fig. 4. Plots of the melting points (*1*) and phase transition temperatures (*2*) of $Rb_5Ln(CrO_4)_4$ *vs.* REE ion radius ($r_{Ln^{3+}}$).

when recording the cooling process of an incongruently melting sample.

Binary samarium, europium, and gadolinium chromates undergo a reversible phase transition, whose temperature for each chromate is somewhat lower than the melting point (see Table 4). The temperature of polymorphous transition decreases from Sm to Gd with a decrease in the REE ion radius. It follows from the plot of the melting points and phase transition temperatures of $Rb_5Ln(CrO_4)_4$ *vs.* REE ion radius (Fig. 4) that lanthanum, praseodymium, and neodymium chromates have no polymorphous transition, because the probable temperature region of their polymorphous transformations is higher than the melting points of the compounds. However, REE molybdates and tungstates (Mo and W refer to the Cr Subgroup in the Periodical System) manifest polymorphism in the whole REE series.

Binary chromates are characterized by a higher thermal stability, retaining their composition up to the melting temperatures, in contrast to the chromates $Ln_2(CrO_4)_3 \cdot 7H_2O$ and $Ln_2(CrO_4)_3$ considered above (see Table 5).

In the series of chromates $La_2(CrO_4)_3$ (T_{decomp} = 900 K), $RbLa(CrO_4)_2$ (T_{decomp} = 990 K), $Rb_5Ln(CrO_4)_4$ (T_m = 980—1010 K, T_{decomp} > 1170 K), and Rb_2CrO_4 (T_m = 1267±2 K), the thermal stability of the compounds increases with an increase in the molar fraction of an alkali metal, which is probably related to an enhancement of the ionic character of the bond. Therefore, melting effects and phase transitions characteristic of similar and more stable compounds of other elements of the Chromium Subgroup (molybdates and tungstates) occur consecutively in this series.

Both our[2] and reference data[6] were used for the calculation of the standard enthalpies of formation of $Ln_2(CrO_4)_3 \cdot 2H_2O$ by the above-presented thermochemical cycle. The calculated standard enthalpies of formation of lanthanide chromate dihydrates are presented in Table 5.

The DSC method used for studying the enthalpies of thermal dissociation of $La_2(CrO_4)_3 \cdot 7H_2O(cr)$ made it possible to determine the enthalpy of its complete dehydration and enthalpies of crystallization and complete dissociation of anhydrous crystalline lanthanum chromate (see Table 6). The former two values were recalculated to the standard temperature (298 K) with the help of high-temperature enthalpies and agree, in this form, with the values determined by solution calorimetry within an experimental error (see Table 6). To compute the unknown standard enthalpy of formation of $LaCrO_3$, the enthalpy of complete thermal dissociation of $La_2(CrO_4)_3$(cr) was determined using the DSC method by the reaction

$$La_2(CrO_4)_3 = 2\ LaCrO_3 + 0.5\ Cr_2O_3 + 2.25\ O_2. \quad (5)$$

Using the reference data[6] for $\Delta_f H°_{298}(Cr_2O_3)$ and $\Delta_f H°_{298}(La_2(CrO_4)_3)$ by application of Hess's law and based on $\Delta H°_{298}$ for reaction (5), we calculated the standard enthalpy of formation of $LaCrO_3$ from simple compounds: $\Delta_f H°_{298}(LaCrO_3)$, which is equal to -1591 ± 10 kJ mol^{-1}.

The thermodynamic properties of Y, La, Dy, and Ho chromites have previously[7—10] been studied at 850—1400 K by the electromotive force method with a solid electrolyte CaF_2 + ZrO_2 + MgO. Based on the thermodynamic properties of the substances involved in the potential-forming reactions, the authors determined the temperature dependences of the Gibbs energy (ΔG) for the reaction

$$0.5\ Ln_2O_3 + 0.5\ Cr_2O_3 = LnCrO_3, \quad (6)$$

Ln = La, Ce, Dy, Ho, Y.

Using these dependences, we calculated $\Delta H°_T$ for reaction (6), and the resulting values were referred to the average temperature ($\Delta H°_{T_{av}}(6)$) for the studied temperature range (Table 8). The $\Delta H°_{298}(6)$ values necessary for the computation of the standard enthalpies of formation of $LnCrO_3$ were determined from $\Delta H°_T(6)$ using the $H_T - H_{298}$ values for the chromites (see Table 7 and Refs 11 and 12) and oxides (see Ref. 13). They are also presented in Table 8.

The vapor pressure above $LaCrO_3$ at 1887—2333 K has previously[14] been measured by mass spectrometry, and $\Delta H°_{298}(6)$ was calculated (see Table 8). The standard enthalpies of chemical reactions (6) computed by us for $LnCrO_3$ made it possible to estimate the earlier unknown standard enthalpies of formation of the chromites from simple substances (see Table 8). The data in Table 8 show a considerable scatter of the enthalpy values of formation of $LnCrO_3$ obtained by different methods.

Thus, in this work we reliably determined the standard enthalpies of formation of $Ln_2(CrO_4)_3 \cdot 2H_2O$. The $\Delta_f H°_{298}$

Table 8. Enthalpies of reaction (6) referred to the average temperature ($\Delta H^\circ_{T_{av}}(6)$) for the studied temperature interval (ΔT) and to 298 K ($\Delta H^\circ_{298}(6)$) and standard enthalpies of formation of $LnCrO_3$ ($\Delta_f H^\circ_{298}(LnCrO_3)$)

Ln	ΔT (T_{av}) /K	Method of study	$-\Delta H^\circ_{T_{av}}(6)$	$-\Delta H^\circ_{298}(6)$	$\Delta_f H^\circ_{298}(LnCrO_3)$	Refs
			kJ mol^{-1}			
La	964	DSC	—	—	1591±10	—*
	855—1073	EMF**	44.45	44.3	1511	10
	1887—2333	Mass spectrometry	—	76.8±5.2	1546±6	14
Ce	—	Tensimetry	62.1	36.6	1532±20	7
Dy	1150—1300 (1226)	EMF	43.8±10.5	39.3±11	1541.1±11	11
Ho	1150—1300 (1218)	EMF	33.7±7.5	29.3±8	1540.2±8	11
Y	1200—1400 (1300)	EMF	43.7±11	39.4±11	1562.7±11	8
	1182—1386 (1284)	EMF	81.94	77.6	1600.8	9

* Data of the present work.

** Electromotive force method.

values for $LnCrO_3$ calculated for the first time need further refinement.

The author thanks E. V. Proskuryakova for kindly presented chromate samples $Rb_5Ln(CrO_4)_4$.

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Received August 30, 2001;
in revised form December 2, 2003