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Energy Change Regularities of Crystal Lattice of Lanthanide Borohydrides

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Abstract Thermodynamic characteristics of lanthanides' borohydrides are defined by tensimetric, calorimetric and semiempirical methods. Lanthanides' borohydride crystal energy lattice is defined by compiled Born-Haber cycle and their change regularity within the whole lanthanide's row is determined.

Keywords Thermodynamic Characteristics, Lanthanides, Borne-Haber Cycle, Crustal Lattice Energy, Change Regularities, Tetrad-effect

1. Introduction

Thermodynamic characteristics – substance formation enthalpy ($\Delta_f H^0_{298}$) and/or Gibbs energy ($\Delta_f G^0_{298}$) are used as criteria for thermodynamic stability of crystal compounds [1-5]. These values are summarized constituent of energy characteristics of multiple intermediate process stages for compounds obtaining. Often these intermediate process stages have big energy characteristics values in comparison with final, additive values.

In such cases, it is difficult to identify crystal compounds stability criteria. For example, energy cycle analysis for carbide, silicide and other compounds formation process [3-6]. Small values of carborundum $\Delta_f H^0_{298}$ =-51,9 kJ/mole is due to big energy expenditures and atomization of silicon and carbon crystals but not due to weak binding energy in carborundum (Nat. = -1255,2 kJ/mole).

2. Objectives

In continuation of series of research on thermal and thermodynamic characteristics of complex hydride compounds [7-10], the present work is devoted to enthalpy formation ($\Delta_f H^0_{298}$) and crystal lattice energy (U_k) identification of complex borohydrides – $Ln(BH_4)_3$ (Ln-lanthanides) and their change regularity determination.

3. Material and Methods

Limited literatures are available which cover issues of crystal lattice energy determination of complex hydride compounds. Only works [11, 12] determine crystal lattice energy values for complex boro- and alumohydrides of IA and IIA subgroups elements.

Born-Lande, Born-Mayer, Huggins and other equation use for U_k calculation requires availability of many nondescript values, which limits possibilities for these equations application, especially for complicated complex compounds.

Kapustinskiy equation, difference methods and comparative calculation of thermodynamic substance properties, tensimeter, RPA, Poluektov semiemperical method are applied for U_k determination of lanthanides borohydrides.

Semiempirical equation for approximate U_k calculation (kilojoule/mole) of any famous or hypothetical ionic compounds proposed by A.F. Kapustinskiy [1], which is expressed by:

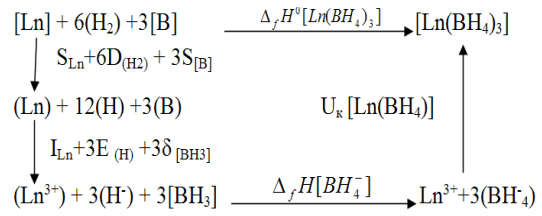
$$U_K = \frac{1200{,}5 \cdot V \cdot Z_k \cdot Z_a}{r_k + r_a}\left[1 - \frac{0{,}345}{r_k + r_a} + 0{,}00435(r_k + r_a)\right] \quad (1)$$

where: V – number of ions in one formula unit; Z – cation or anion charge, and, r – their radius.

While making calculations by equation (1), where V=4 – ion numbers in one formula unit, lanthanide cations Ln^{3+} radius values are used with coordination number 8, specific for studying compounds and determined according to X-ray structure investigation of lanthanide borohydride [13-16].

Unknown value for thermochemical radius of BH_4^- ion in literature is revealed by us according to energy difference of identical crystal lattice of compounds with equal anions, namely alumohydrides and alkali metal borohydrides [1, 2]. It was equal to $r_{BH_4^-}$ = 0,23 nm.

Thermochemical balance of $Ln(BH_4)_3$ formation can be described by the following Born-Haber cycle:



(2)

where: *Ln* – lanthanides; parentheses – gaseous, square brackets – solid state of substance; *S* - sublimation enthalpy, *D* – dissociation enthalpy, δ – formation enthalpy and *E* - sensitivity to component system's electrons.

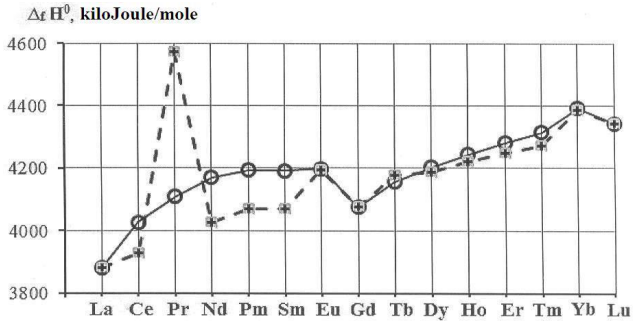
4. Results and Their Discussions

Thermochemical calculations according to Born-Haber cycle are possible in case of data availability for each stage of the cycle. Formation enthalpy value for gaseous borohydride's ion is equal to $\Delta_f H^0_{298(BH_4^-)}$ =-96,2±20 kJoule·-mole^{-1}. Literature data on enthalpy formation value ($\Delta_fH^0_{298,}$ Ln^{3+}) for gaseous lanthanides' ion in oxidation level (+3) [8-10] are fragmentary and considerably different. N.S. Poluektov's semiempirical method and others [21, 22] is applied for identification and/or precise value definition $\Delta_fH^0_{298,}$ Ln^{3+} of gaseous lanthanides' ion. Calculation is carried out according to the following correlation equation:

$$\Delta_fH^0_{298,}\ Ln^{3+} = \Delta_fH^0_{298,}\ La^{3+} + \alpha N_f + \beta S + \gamma' S_{(Ce-Eu)} (\gamma'' L_{(Tb-Yb)} \quad (3)$$

α coefficient – takes into account 4f – electrons influence, β- and γ – spin influence (S) – and orbital (L) – lanthanides' atoms and ion motion moments on unknown quantity. γ' coefficients relates to lanthanides of cerium subgroups, and γ'' – to metals of yttrium subgroup. Equation coefficients values (3), are equal to α =32,36; β =-9,00; γ'=9,83 and γ''=4,04. Calculation results $\Delta_fH^0_{298,}$ Ln^{3+} of lanthanides' ion are presented in table 1.

$\Delta_fH^0_{298,}$ Ln^{3+} lanthanides' ion-nature change diagram is presented in Fig. 1.



(-calculated, - literature data).

Figure 1. Gaseous lanthanides' ion–nature enthalpy formation change diagram

Diagram has complicated character with clear separation by lanthanide's sub-groups. In cerium sub-group, $\Delta_fH^0_{298,}$ Ln^{3+} value increase is observed with maximum in the middle Pr^{3+} ion of the subgroup. In yttrium subgroup, almost linear symbasis increase of $\Delta_fH^0_{298,}$ Ln^{3+} value is observed with lanthanide's atomic number increase. Deviation from considered characteristics for Eu^{3+} and Yb^{3+} ions is conditioned by their distinct structure with partial and full orbital occupancy by f-electrons. Large values of α coefficient specifying dominating role of 4f-electrons on $\Delta_fH^0_{298}$ values of lanthanides' ions.

Table 1. Gaseous lanthanides' ion enthalpy formation

$\Delta_fH^0_{298,}$ Ln^{3+} kJoule ·mole^{-1}	Lanthanides														
	La	**Ce**	**Pr**	**Nd**	**Pm**	**Sm**	**Eu**	**Gd**	**Tb**	**Dy**	**Ho**	**Er**	**Tm**	**Yb**	**Lu**
Calculation	3881	3971	4018	4056	4084	4102	4160	4076	4157	4202	4244	4281	4314	4392	4334
Literature	3881	3928	4571	4025	4071	4071	4193	4076	4176	4188	4221	4247	4273	4385	4334
Difference in %	0,00	1,10	12,00	0,77	0,32	0,76	0,79	0,00	0,45	0,33	0,54	0,80	0,96	0,16	0,00

Experimental values for enthalpy formation ($\Delta_fH^0_{298}$, kJoule/mole) of some lanthanides' borohydrides (*La, Nd, Sm, Gd* and *Lu*) [13-16] allowed to calculate current characteristics by equation (3) for the whole lanthanides' borohydrides series (table 2). Equation coefficient values (3) are equal to: α = -8,26; β =3,20; γ' = -15,3 and γ''=0,30.

Table 2. Standard values for -$\Delta_fH^0_{298}$ (kJoule/mole) of lanthanide's borohydrides

a) cerium subgroup $Ln(BH_4)_3$						
La	*Ce*	*Pr*	*Nd*	*Pm*	*Sm*	*Eu*
505,9±30	566,7	603,9	604,6±40	632,5	641,1±40 623,9	547,7

б) yttrium subgroup							
Gd	*Tb*	*Dy*	*Ho*	*Er*	*Tm*	*Yb*	*Lu*
552,6±30	571,0	578,1	585,1	598,4±40 598,0	606,5	632,9	621,5±40

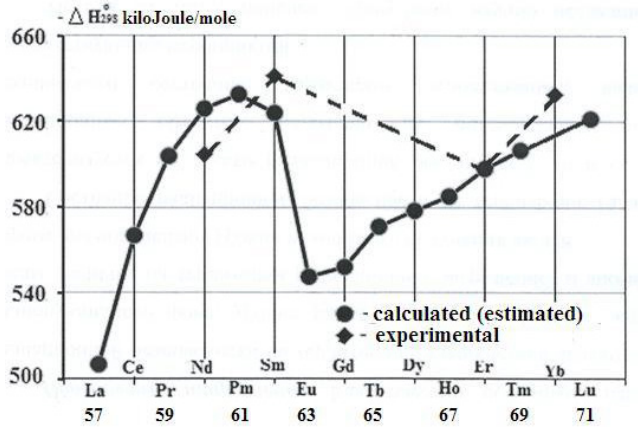


Figure 2. Borohydrides enthalpy formation – lanthonides atomic number diagram.

Lanthanide borohydride enthalpy formation – atomic number diagram curve (Fig.2) is complicated with tetrad-effect development. Sharp borohydrides' enthalpy formation value increase for cerium sub-group elements is observed as far as cainosimmetric 4f orbital are filled by electrons (f^2-f^6). Sharp decrease of enthalpy formation value for europium borohydride is due to partial filling of 4f orbital by one electron and considerable influence of orbital motion moments of lanthanides' ion.

For yttrium subgroup borohydrides, starting from gadolinium, symbasis, almost linear increase of enthalpy formation values for lanthanides' borohydrides is observed with increase of 4f-electrons number.

From Born-Haber cycle, $U_к$ value of lanthanide borohydride is identified by the following equations:

$$U_к[Ln(BH_4)_3] = -\Delta_f H^0[Ln(BH_4)_3] + S[Ln] + 6D(H_2) + 3S[B] +$$
$$+ I(Ln) + 3E(H) - 3\delta[BH_3] = -\Delta_f H^0[Ln(BH_4)_3] + \{S[Ln] + I(Ln)\} +$$
$$+ 6\{\frac{D}{2}(H_2) + E(H)\} + 3S[B] - 3\delta[BH_3] = -\Delta_f H^0[Ln(BH_4)_3] +$$
$$+ \Delta_f H^0(Ln^{3+}) + 3\Delta H(H^-) - 3\delta[BH_3] = -\Delta_f H^0[Ln(BH_4)_3] +$$
$$+ \Delta_f H^0(Ln^{3+}) + 3\Delta_f H^0(BH_4^-)$$

U_K calculation by equation (3) also is carried out, with coefficients which is equal to α=23,91; β=-5,81; γ'=15,7 and γ''=7,04. U_K calculation results by three independent methods are presented in table 3.

Table 3. $\Delta_f H^0_{298}$ (kJoule/mole) values and Uк (kJoule/mole) of lanthanides borohydrides

Lanthanides	r, Å	$\Delta_f H^0_{298}$	U_K			
			(2)	(1)	Δ,%	(3)
La	1,16	506	3664,1	3811,09	7,5	3664,1
Ce	1,14	567	3747,5	3788,56	3,7	3751,6
Pr	1,13	604	3794,4	3840,22	3,1	3814,3
Nd	1,12	615	3843,9	3850,02	1,5	3845,2
Pm	1,09	632	3840,0	3879,75	1,9	3866,5
Sm	1,08	632	3849,6	3889,76	2,0	3871,5
Eu	1,07	548	3905,1	3899,82	0,8	3901,5
Gd	1,05	553	3811,1	3920,10	3,6	3811,1
Tb	1,04	571	3875,0	3930,32	2,3	3883,0
Dy	1,03	578	3913,3	3940,59	1,8	3923,9
Ho	1,02	585	3947,5	3950,92	1,8	3957,7
Er	1,00	598	3971,4	3971,73	1,1	3984,5
Tm	0,99	606	3996,2	3982,22	0,7	4004,3
Yb	0,99	533	4047,8	3982,22	0,4	4057,0
Lu	0,97	622	3998,8	4003,37	0,7	3998,8

Specific features of lanthanides borohydrides thermochemical properties change is visually shown in Figure 3 within the group. It is necessary to notice that almost rectilinear character of this diagram is obtained according to Kapustinskiy equation which assumes purely ion nature of binding and considers only lanthanides' ion cation size change.

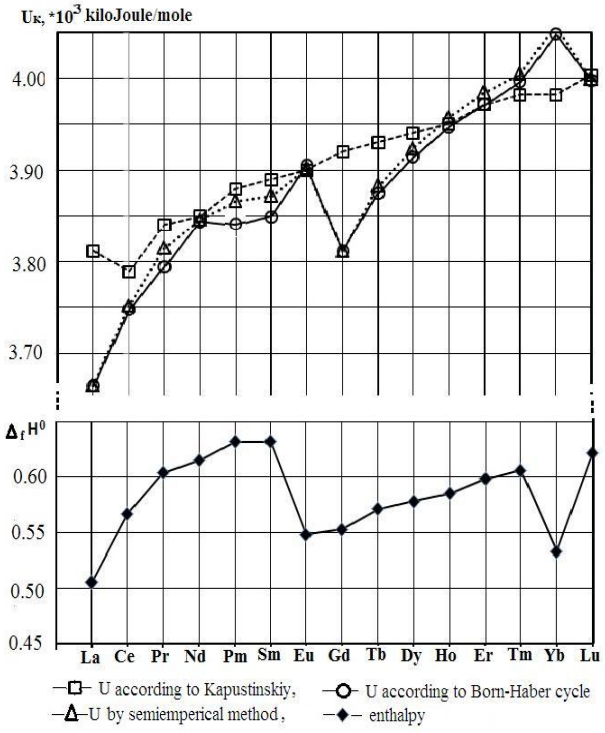


Figure 3. U_K (a) and $\Delta_f H^0$ (b) dependence of borohydride from lanthanide atomic nuvber.

4. Conclusions

Thus, obtained results allowed to reveal the following features in thermochemical characteristics change of borohydrides:

a) with lanthanides atom nucleus increase charge:

- sybasis change and increase of enthalpy formation values and crystal lattice energy of lanthanides borohydrides is observed;
- diagrams of these curves have identical character with tetrad-effect development and with clear separation of lantanides' subgroups;
- characteristics deviation for europium and ytterbium compounds from general regularities due to their partial and full fillings by 4f orbital electrons of these elements atoms, extra stability in crystal field and spin-orbital interaction of 4-f-electrons.

b) U_K values difference calculated by thermochemical cycle and Kapustinskiy formula indicates on certain fraction of covalent nature of chemical binding in borohydrides, by dominating character of ion binding.

c) U_K values coincidence, calculated by different methods for europium and ytterbium borohydrides indicates on purely ion character binding in compounds of these metals.

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