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Research Article

Regularities of Change in Thermodynamic Characteristics of the Intermetallic Composition Ln_5Pb_3 (Ln–Lanthanides)

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Abstract

Data on the melting temperature and enthalpy, formation enthalpy and heat capacity of intermetallics of the composition Ln_5Pb_3 were obtained by a semi-empirical method. A system analysis was carried out and patterns of change in the specified properties of Ln_5Pb_3 were established depending on the nature of the entire series of lanthanides. The patterns are complex in nature with the manifestation of the "tetrad effect". A deviation from the general pattern is observed for the intermetallics of europium and ytterbium, due to their electron structure.

Introduction

Intensive research is being conducted to develop thermionic converters, in which energy conversion is carried out with high efficiency compared to the technological indicators of other processes used in practice [1,2]. High-temperature thermionic converters include binary Intermetallic (IM) compounds of the La_5Pb_3, Ce_2Pb, Sm_5Pb_3 type and complex compounds of the Zintl phase of the $A_{14}M_nSb_{11}$ type, where A=Yb, Eu [3-7]. Microprocessors used in solar batteries use only the high-frequency region of radiation, and low-frequency heat is lost. Thermionic converters can convert low-frequency thermal energy into electrical energy. Thermionic generators are widely used in space research, as well as for the disposal of waste heat in cars and in other technological processes [3-8]. Fundamental research into the physicochemical properties of compounds exhibiting thermionic properties in groups or periods of the Table of Chemical Elements allows the establishment of patterns of change in various applied characteristics depending on the nature of the system components. It becomes possible to select components and compositions of substances with predetermined, "programmed" operational characteristics under technologically optimal conditions.

The information on the phase diagrams of binary metallic systems is summarized in a fundamental reference book [9] showing that numerous intermetallics are formed in Pb-Ln systems (where Ln are lanthanides), which have high melting points. The most complete information on the melting temperature and enthalpy for some IM Pb-Ln systems, obtained by other researchers [10,11], allowing the establishment of patterns of change within the entire series of lanthanides. It was found that the melting point of the alloys increases in the ranges of 1673–2273 K corresponding with an increase in the lead content in the alloys. Among the IM systems Ln-Pb, the highest melting point is that of the IM of the composition Ln_5Pb_3 [8]. Information on the heat capacity and enthalpy of formation of the IM of the composition Ln_5Pb_3 is given in several publications [8,12,13], which are fragmentary and differ greatly from each other.

Materials and Experimental Procedure

This research determined and/or refined several thermodynamic characteristics - the temperature and enthalpy of melting, the enthalpy of formation and heat capacity of IM-s of the composition Ln_5Pb_3 for the entire series of lanthanides. A system analysis of the properties of IM-s was carried out using a semi-empirical method (calculation 1) [14]. The calculation was made using the correlation equation

$$A_{Pb(x)Ln(y)} = A_{Pb(x)La(y)} + \alpha N_f + \beta S + \gamma' S_{(Ce-Eu)} (\gamma'' L_{(Tb-Yb)}) \quad (1)$$

where the coefficients of the equation take into account the influence: - α – 4f – electrons, β- and γ – spin (S) – and orbital (L) – moments of motion of atoms and ions of lanthanides by the determined value (A) – temperature (T pl.) and the enthalpy of melting (ΔH pl), enthalpy of formation ($\Delta_f H$) and heat capacity (C^o_p) IM. The coefficients γ refer to: γ' - cerium, and γ'' – yttrium subgroups of lanthanides. The values of these coefficients can be calculated from the equations:

$$\alpha = \frac{A_{Lu} - A_{La}}{14}; \beta = \frac{A_{Gd} - A_{La} - \alpha \cdot 7}{3,5}; \gamma = \left[\sum_{l=1}^{n} \frac{A_{Lnl} - A_{La} - (\alpha N_{fl} + \beta S_l)}{L_l}\right]/n,$$

where n is the number of Ln for which the parameter was measured, except for La, Gd and Lu.

The values of the coefficients of the correlation equation (1) are given in Table 1. In the calculations, the values of the enthalpy of formation and heat capacity of IM obtained [8] using the high-temperature calorimetry method were taken as reference values. Values of the coefficients indicate the share of participation of the components of equation (1) in the determined characteristic of the IMs. The determination of the enthalpy of melting of the IMs of the composition Ln_5Pb_3 (calculation 2) was carried out according to equation 2 [15].

$$\Delta H^{0}_{пл.,} Pb_xLn_y = T_{пл.}^{им}(n\Delta H_{пл.}^{Ln}/T_{пл.}^{Ln} + m\Delta H_{пл.}^{Pb}/ T_{пл.}^{Pb})/n+ \quad (2)$$

Table 1: Values of the coefficients of the correlation equation (1).

THEM	Characteristic	α	β	γ'	γ"
Ln_5Pb_3	Тпл., К	3,57	0,00	-24,68	2,89
	C_p	-0,21	-0,96	1.29	0.8
	$\Delta_f H_T$	0,20	1,02	0,43	0,52
	ΔH pl	0,09	0,14	-0,59	0,02

Results and Discussion

The most complete information on the melting point of lanthanides and IM of the composition Ln_5Pb_3 obtained in this way is given in Table 2. The data in Table 2 shows good agreement between the calculated and reference values of the melting point of lanthanides (except for Sm, Ho and Tm), which indicates the validity of the used semi-empirical method [14] and the reliability of the obtained data.

Table 2: Generalized values of the melting point of lanthanides (Ln) and IM of Ln_5Pb_3.

Ln			La	Ce	Pr	Nd	Pm	Sm	Eu
T pl., K	[16,17]		1193	1068	1208	1297	1300	1345	1095
			1191	1077	1204	1291	1441	1347	1100
	Calculation 1		1193	1098	1208	1245	1301	1385	1099
	Ln	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	[16,17]	1585	1629	1679	1734	1770	1818	1097	1925
		1586	1633	1685	1747	1802		1092	1936
	Calculation 1	1585	1629	1683	1722	1770	1830	1094	1928
Ln_5Pb_3			La	Ce	Pr	Nd	Pm	Sm	Eu
T pl., K	[9]		-	-	1768	-	-	1853	1418
	Calculation 1		1918	1851	1805	1784	1788	1816	1760
	Ln_5Pb_3	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	[9]	1943	-	1968	-	-	-	-	1968
	Calculation 1	1943	1959	1968	1975	1978	1979	1820	1968

The obtained values of the melting point of IM of the Ln_5Pb_3 composition made it possible to establish a pattern of its change depending on the nature of the entire series of lanthanides (N) (Figure 1). Figure 1 clearly shows that the graph of the pattern is divided into subgroups of lanthanides - cerium and yttrium, with the manifestation of the so-called "tetrad effect". For IM of the Ln_5Pb_3 composition of the cerium subgroup, with an increase in the atomic number of Ln, a decrease in the melting point is observed in the first half of the subgroup with a minimum at Nd_5Pb_3 and an increase in the second half. For the yttrium subgroup, with an increase in the atomic number of Ln, an almost linear increase in the melting point of IM is observed. The deviation from the general pattern for the IM Eu_5Pb_3 and Yb_5Pb_3 is due to the partial (f7) for Eu and complete (f14) for Yb filling of the f-orbitals with electrons.

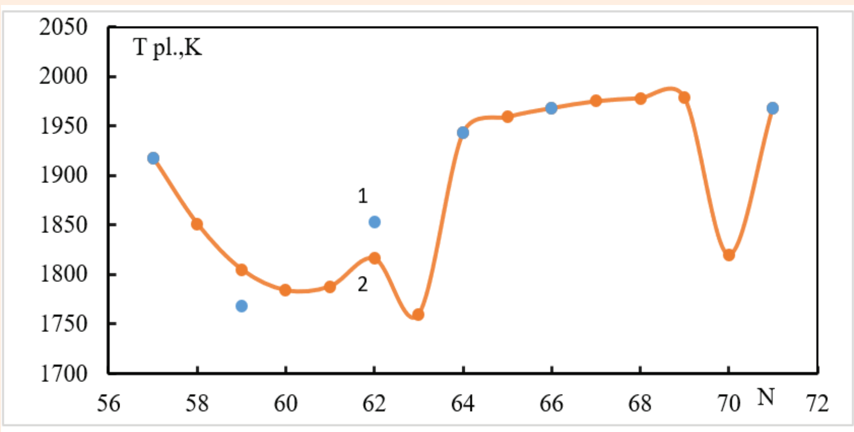

Figure 1: Graph of the regularity of change in the melting temperature of IM Ln_5Pb_3 depending on the nature (N) of lanthanides: 1-literature; 2-calculated. tube (20X).

The data on the thermodynamic functions – heat capacity and enthalpy of formation of IM of the Ln_5Pb_3 composition are presented in Table 2, which are fragmentary. There is a good agreement between the values of the enthalpy of formation of IM of the Ln_5Pb_3 composition obtained from the results of calorimetry [8] (at T = 1373 K) and those calculated by the authors on their basis by a semi-empirical method using equation (1) (calculation 1). The calculated values of the enthalpy of formation, using the Miedema method, exceed the experimental ones [8]. The underestimated values compared to the calorimetry data [8] are possibly due to the temperature dependence of the enthalpy of formation.

The literature values of the heat capacity (Cp) of IM Ln_5Pb_3 [8] determined by the calorimetry method and the Neumann – Kopp model differ significantly. This is possibly due to the temperature dependence of Cp in a wide temperature range. For Sm_5Pb_3, good agreement was noted between the experimental value of Cp (at T=1273 K) and that calculated by the Neumann–Kopp method. The patterns of change in the enthalpy of formation of IM of the composition Ln_5Pb_3 from the nature of lanthanides (Figure 2), in general, have a linear character within the entire group with division into subgroups of lanthanides.

Table 2: Generalized values of high-temperature enthalpy of formation (T= 1373 K) and heat capacity of IM of the composition Ln_5Pb_3.

, kJ/mol-atom	Ln5Pb3		La		Ce	Pr	Nd	Pm	Sm	Eu
	Source	[8]	72.0±2		75.6±4	77.2±3	75.0±4	-	76.5±3	-
		[8]*	83.8		105.9	102.9	104.0	-	102.9	-
		[8]**	54.0		41.0	52.0	52.0	-	52.0	-
		[8]**	54.0		30.0	45.0	49.0	-	-	-
	Calculation 1		72.0		74.2	75.78	76.92	77.64	77.92	64,0
	Ln_5Pb_3		Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	Source	[8]	77.0±4	71.2±3	76.1±3	71.9±4	75.2±3	76.6±3	55.5±2	74.8±2
		[8]*	102.8	101.3	101.4	100.5	100.1	99.7	99.6	99.2
		[8]**	53.0	13.0	52.0	51.0	50.0	48.0	55.0	45.0
		[8]**	-	54.0	53.0	52.0	50.0	48.0	-	45.0
	Calculation 1		77,0	75.29	73.92	73.08	72.76	72.98	55.5	74.8
Cop, kJ/mol-atom		Ln_5Pb_3		La	Ce	Pr	Nd	Pm	Sm	Eu
		[8]		-	32.4±3.4	32.3±2.8	30.4±2	-	39.4±2$_{(т)}$	-
		[8]≠		-	41.6	43.8	45.1	-	39.9	-
		Calculation 1		30,5	34,98	36,87	37,48	36,79	34,82	24
		Calculation 1*		36,3	42,26	43,17	43,19	42,30	40,52	29
		Ln	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
		[8]	27.2±1	31.0±2.5	29.9±2.3	30.0±2.6	34.6±2.7	32.6±2	-	29.1±1.0
		[8]≠	34.8	36.3	34,6	34,5	34,5	33,7	-	33,4
		P-1	27,2	29,67	31,55	32,63	32,9	32,37	28	29,1
		P-1*	34,8	34,83	35,15	35,21	35,01	34,55	30	33,4

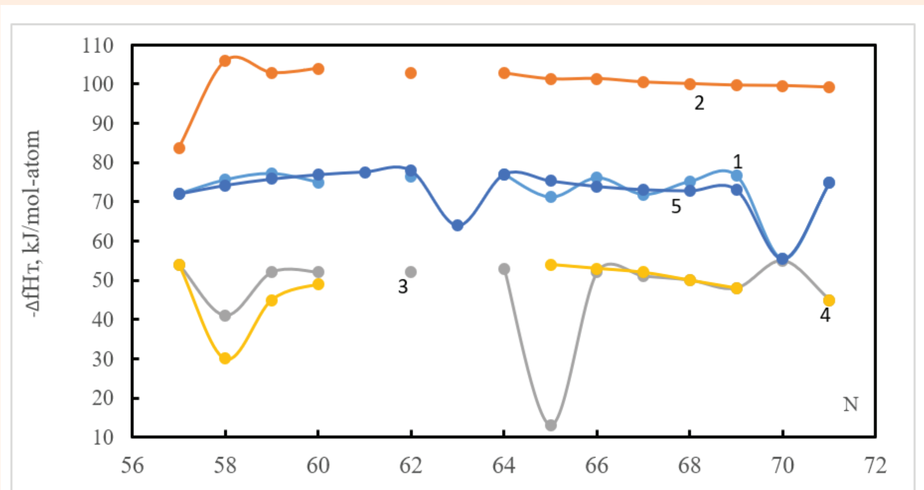

Figure 2: Graph of the regularity of the change in the enthalpy of formation of IM of the composition Ln_5Pb_3 from the nature of lanthanides (N): 1-high-temperature calorimetry method [8] (T = 1373 K); 2 - according to the Meidim model, 3,4 - according to the ab initio model; 5-semi-empirical method (calculation 1).

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Figure 3 shows that with the growth of the ordinal number of lanthanides (N), a gradual decrease in the heat capacity of IM Ln_5Pb_3 with the manifestation of the "tetrad effect" is observed. An increase in temperature leads to a significant increase in the heat capacity of IM of the cerium subgroup and to a change in the nature of the temperature dependence of the heat capacity for IM of the cerium subgroup of lanthanides.

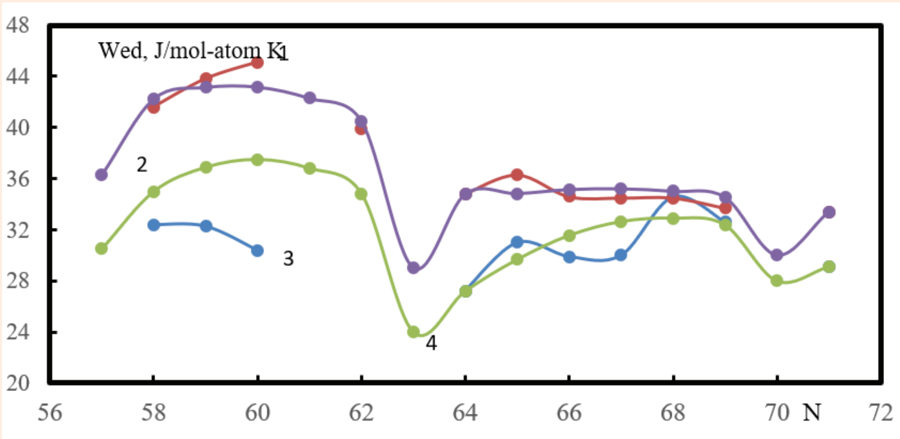

Figure 3: Graph of the dependence of the change in the heat capacity of the IM of the composition Ln_5Pb_3 on the nature of lanthanides (N): 1-calorimetry method [8] (T = 1373 K); 2 - semi-empirical method (P1*); 3 - Neumann - Kopp; 4-semi-empirical method (P1).

To determine the enthalpy of melting of the IM of the composition Ln_5Pb_3 using equation (2) (calculation 2), reference [16,17] was used and refined values of the temperature and enthalpy of melting of lanthanides. The calculated results are given in Table 3. Based on the data obtained on the enthalpy of melting of IM (calculation 2) and for the purpose of comparing the results, a similar calculation was carried out using the semi-empirical method using equation (1) (calculation 1).

Table 3: Generalized values of the enthalpy of melting of the IM composition Ln_5Pb_3.

ΔHpl., kJ/mol-atom	Ln_5Pb_3		La	Ce	Pr	Nd	Pm	Sm	Eu
	Calculation 1		21,45	19,87	18,79	18,30	18,39	19,08	17,96
	Calculation 2		21,45	19,51	19,78	18,26	18,43	19,18	17,96
	Ln_5Pb_3	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu
	P - 1	22,12	22,35	22,48	22,58	22,66	22,72	19,19	22,69
	P - 2	22,12	22,65	22,63	22,76	22,84	21,79	19,19	22,69

The data obtained (Table 2) allowed us to establish the patterns of change in the enthalpy of melting of IM of the composition Ln_5Pb_3 depending on the nature of the lanthanides (Figure 4). The graphs of the pattern are identical in nature to the pattern of change in the enthalpy of formation of IM (Figure 1).

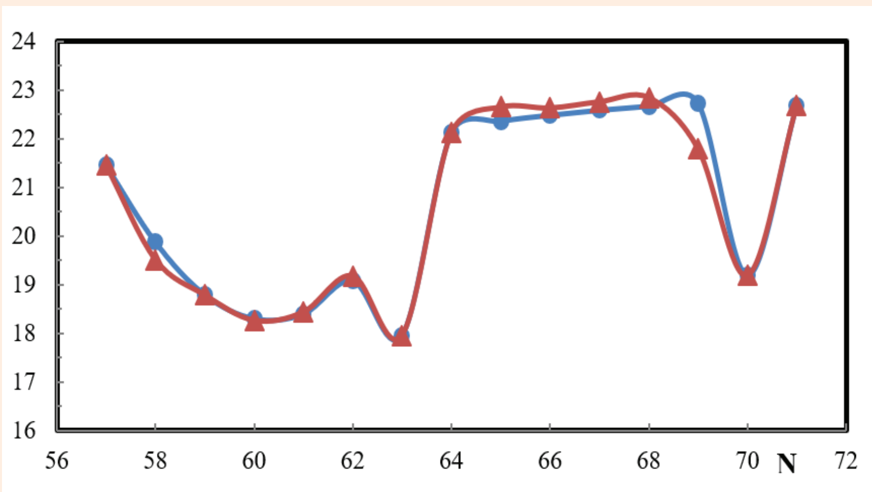

Figure 4: Dependence of the change in the enthalpy of melting of the IM composition Ln_5Pb_3 on the ordinal number of Ln: ● – Calculation 1; Δ – Calculation 2.

The most complete data obtained on the thermal characteristics of the IM of the Ln_5Pb_3 composition allowed mathematical modeling of the regularity of change depending on the nature of the lanthanides. Modeling was carried out using the standard MICROSOFT EXCEL program. Based on the different nature of the regularities in the changes in properties, data processing was carried out separately for the cerium and yttrium subgroup of lanthanides. The calculations did not consider the values of the characteristics for europium and ytterbium alloys, since they fall outside the general regularities. The difference is due to the features of the electronic structure of the atoms of these metals. Equations (Table 3) were obtained by mathematical modeling, which express the established regularities for the lanthanide subgroups with high reliability.

Table 3: Equations for the dependence of changes in the thermal characteristics of the IM composition Ln_5Pb_3 on the nature of lanthanides (by subgroups). Note: (a) - cerium and (b) yttrium subgroup of lanthanides; TT - trend type; P - polynomial; R2 - degree of reliability.

IM	Property		Type of Equations	TT	R^{2*}
Ln_5Pb_3	Tpl.	(a)	$y = 12,125x^2 - 1397x + 41398$	П	0,87
		(б)	$y = 0,5792x^2 - 29,067x + 1072,9$	П	0,99
	C_p^o	(a)	$y = -0,4008x^2 + 47,632x - 1371,9$	П	0,99
		(б)	$y = -0,1162x^2 + 15,575x - 486,61$	П	0,97
	ΔH^0pl	(a)	$y = 0,233x^2 - 28,192x + 871,15$	П	0,86
		(б)	$y = -0,0296x^2 + 4,0497x - 115,85$	П	0,82
	$\Delta_f H^0T$	(a)	$y = -0,2329x^2 + 28,883x - 817,75$	П	0,99
		(б)	$y = 0,2477x^2 - 33,766x + 1223,3$	П	0,99

Conclusion

a. Based on fragmentary literature data [8-13], the most complete information on thermal characteristics - heat capacity, enthalpy of formation, temperature and enthalpy of melting of IM of the Ln_5Pb_3 composition of the entire series of lanthanides were obtained by semi-empirical and calculation methods.

b. The obtained information made it possible to establish patterns of change in the noted thermal characteristics of IM of the Ln_5Pb_3 composition from the nature of lanthanides, which occur with the manifestation of the so-called “tetrad effect”. It was established that the graphs of the patterns are of different nature in the subgroups of lanthanides.

c. Thermal properties of IM of the Eu_5Pb_3 and Yb_5Pb_3 systems deviate from the general pattern, due to their electronic structure.

d. The compiled mathematical models allow us to predict the composition of IM and its thermal characteristics with high reliability, based on the requirements of applied problems.

e. The information obtained is fundamental and will add new data to the bank of thermodynamic characteristics of metallic systems.

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