

Standard Entropy of Lanthanide-Iron Double Oxides of Garnet Structure

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The data of thermodynamic parameters at standard temperature are the most important values for the preliminary analysis of high-temperature industrial processes at complex oxide formation. In this study, we present the main thermodynamic quantities, such as standard entropy, enthalpy, and Gibbs energy, for the isostructural series of rare earth-iron double oxides with garnet structure $R_3Fe_5O_{12}$ (where R varies from Sm to Lu) as these compounds generated sustained interest as basic composition to work out the new multicomponent materials with advanced magnetic, electric, and other physical properties. To identify the thermodynamic properties at standard temperature the data of low-temperature heat capacity $C_p(T)$ was used. The experimental study on the temperature dependence of heat capacity was carried out by a low-temperature adiabatic calorimeter with an accuracy of 0.25% in the temperature range 20-300K. The heat capacity, entropy, enthalpy, and Gibbs energy are presented in the paper. The obtained results are discussed in connection with the specific crystal and magnetic structure of three-sublattice garnets. © 2024 Bull. Georg. Natl. Acad. Sci.

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Thermodynamic parameters of compounds (such as entropy, heat capacity, enthalpy, and Gibbs energy) are very important quantities for the energetic evaluation of chemical reactions and for choosing the optimal conditions of the relevant industrial processes.

The thermodynamic analysis of chemical reactions at high temperatures is based on a well-known equation:

$$\Delta G = \Delta H_{298.15} - \Delta S_{298.15}T + \int_{298.15}^T \Delta C_p dT - T \int_{298.15}^T \Delta C_p d \ln T, \quad (1)$$

where ΔG , $\Delta H_{298.15}$, $\Delta S_{298.15}$, and ΔC_p are respectively the changes in Gibbs energy, enthalpy, entropy, and heat capacity as the result of a chemical reaction.

For obtaining accurate results using equation (1), reliable data of thermodynamic parameters for reagents and products of reaction are to be employed. For this purpose, numerous data banks are currently available, and also many scientific works are publishing [1-8].

Standard entropy and enthalpy of chemical compounds are the most required quantities for the thermodynamic evaluation of chemical processes. The reliable data of standard entropy and enthalpy (as well as their temperature functions) are usually obtained as the result of calorimetric heat capacity measurements for the wide temperature range. Namely, the low temperature ($T < 298.15\text{K}$) heat capacity data are used for the determination of the value of entropy at standard temperature – $S_{298.15}$, and high-temperature heat capacity – for calculation of the temperature functions of entropy and other related thermodynamic parameters (enthalpy, Gibbs energy) according to the following expressions:

$$S_T = \int_0^T C_p dT + \sum (\Delta H_i / T_{tr}) \text{ and } H_T - E_0 = \int_0^T C_p dT + \sum (\Delta H_i), \quad (2)$$

where ΔH_i and T_{tr} are the enthalpy and temperature of phase transitions.

In recent years, special interest has been directed to the complex inorganic oxide systems because many of them manifested properties, valuable from the viewpoint both of fundamental and applied sciences. The high-temperature solid-state reaction of starting oxides is one the most applied methods to produce multi-component oxides. Therefore, the preliminary thermodynamic analysis of corresponding chemical reactions is a very important task and for this purpose, the reliable thermodynamic data (including standard entropy) of involved compounds are to be employed.

Among various complex oxide systems, the rare earth-iron double oxides with garnet structure $R_3\text{Fe}_5\text{O}_{12}$ (where R varies from Sm to Lu) have generated sustained interest, because they are used as basic composition to work out the new multicomponent materials with advanced magnetic, electric, and other physical properties. Currently, many works with structural, magnetic, electric, elastic, and other physical characteristics of garnet-type compounds are published [5,8]. The thermodynamic properties

are also the object of increasing interest [1-4, 6, 7]. Nevertheless, the investigation of thermodynamic parameters of rare-earth garnets is still an actual problem, especially the heat capacity in the low temperature ($T < 298.15\text{K}$) region, which gives the possibility to calculate related functions – entropy, enthalpy, and Gibbs energy at standard temperature. All these parameters are the initial information for up-to-date thermodynamic evaluations of chemical processes involving rare-earth iron garnets. Thus, the main purpose of this study is to present the values of the standard entropy and other thermal parameters of double iron-lanthanide oxides as data used for the thermodynamic calculations.

In the present work, the standard entropy of investigated garnets is obtained by the calorimetric study of low-temperature heat capacity in the temperature interval 20(50)-320K. Using a combination of literature data for the temperature range 0.4-20K [2,3], we have obtained the reference data for entropy, enthalpy, and Gibbs energy for standard temperature.

Materials and Methods

Sample characteristics. The garnet samples were synthesized by high-temperature solid-state reaction. The starting materials were high-purity (99.9%) Fe_2O_3 and R_2O_3 oxides. Thoroughly mixed oxide powders underwent two stages of intermediate grinding and calcination at 1300 K. The final syntheses of pressed tablets were performed at 1650 K for about 50 hours in the air.

The products were identified by chemical, X-ray diffraction, and magnetic characteristics (magnetic moments, Curie temperatures), which agree well with the literature data [1-5]. All samples have garnet-type crystal structures, exhibit ferromagnetic properties, and have Curie temperatures that decrease in the direction of reducing the radius of lanthanide ions.

Low-temperature heat capacity measurements. The standard entropy of RGI was obtained based on

a calorimetric investigation of the temperature dependence of heat capacity using the low-temperature adiabatic vacuum micro-calorimeter [5-7]. The calorimeter is provided with a standard platinum-resistance thermometer which forms an assembly with the gold-plated copper container ($\sim 5\text{cm}^3$) filled with helium. Two automatically regulated shields are employed to control the adiabatic regime of the calorimetric system. The measurement of the heat capacity of benzoic acid as a reference compound shows the accuracy of the obtained data to be about 0.25%. For every sample, over the temperature range 20(50)-310 K 80-100, the experiments were carried out by the periodical stepwise heating.

The evaluation of derived integral thermodynamic properties – entropy, enthalpy, Gibbs energy – requires smoothing the row experimental heat capacity data, and extrapolating the heat capacity function below the temperature of the lowest experimental determination to 0, K. The first procedure was carried out using the spline-fitting method. The entropy and enthalpy values for the lowest experimental temperature were determined based on the data on the heat capacity of lanthanide-iron garnets for the temperature range of 0.4-20 K, given in publications [2, 3]. In some cases, certain expressions with a combination of Debye and Einstein functions were applied.

Results

The smoothed heat capacity, corresponding entropy, and enthalpy data are given in Tables 1 and 2. Experimental investigation of heat capacity of $\text{Sm}_3\text{Fe}_5\text{O}_{12}$, $\text{Gd}_3\text{Fe}_5\text{O}_{12}$, $\text{Tb}_3\text{Fe}_5\text{O}_{12}$, $\text{Dy}_3\text{Fe}_5\text{O}_{12}$, $\text{Er}_3\text{Fe}_5\text{O}_{12}$ and $\text{Lu}_3\text{Fe}_5\text{O}_{12}$ were fulfilled in the temperature range 20(15) – 320K, while for $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ and $\text{Tm}_3\text{Fe}_5\text{O}_{12}$ the experimental temperature domain was 50-320K. Therefore, the methods of extrapolation to 0, K are different for these two groups of garnets.

The entropy at standard temperature can be calculated as the sum of the entropy change for the investigated temperature range and entropy for the domain below our experimental determinations. Therefore, the following cases are considered: a) For the first group of garnets, the heat capacity data for the 0.4-20 K are presented in [2,3]. In the overlapping temperature domain, the disagreement between our data and the data given in [3] is ~ 1.5 -2.0%. This makes it possible to compute the standard entropy values as $S_{298.15} = S_{20} + (S_{298.15} - S_{20})$, where the S_{20} values are determined by the graphical integration of the C_p/T function below 20K using the [2, 3] data, and $(S_{298.15} - S_{20})$ are derived from our heat capacity measurement by Equation 2. b) The second group contains garnets the heat capacity of which has not been studied below 20 K experimentally yet. Only very low-temperature domain 0.4-4.5 K is reported for $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ [2]. The correspondent entropy, determined by numerical integration, is $S_4 = 0.418 \text{ J/K mole}$. For the interval 4-50K, the equation containing the Debye and Einstein functions, and the excess ferromagnetic term, was selected. Using the results for every temperature domain the standard entropy of $\text{Eu}_3\text{Fe}_5\text{O}_{12}$ is calculated as: $S_{298} = S_4 + (S_{50} - S_4) + (S_{298.15} - S_{50})$. The same procedure was carried out in the case of $\text{Tm}_3\text{Fe}_5\text{O}_{12}$.

The results are listed in Tables 1 and 2. Comparing our data with the publications [1], we can observe some disagreements, especially in the case of low-temperature entropy. The cause of the difference between our data and the data in [1] can be the narrow and fragmentary temperature intervals of experimental investigation of heat capacity, based on which the entropy values have been determined in [1].

Neel's theory explains the specific magnetic properties of garnet-type ferrites based on their three-sublattice crystal structure. The antiferromagnetic interactions between paramagnetic ions distributed over sublattices of three types (octahedral $2\text{Fe}^{+3}-a$, tetrahedral $3\text{Fe}^{+3}-d$, and dodecahedron $3\text{R}^{+3}-c$) result in the magnetic moments as

Table 1. Low-temperature heat capacity of rare-earth iron garnets (RIG)

Heat Capacity Cp (J/K.mole)								
Temperature (T.K)	SmIG	EuIG	GdIG	TbIG	DyIG	ErIG	TmIG	LuIG
20	13.05	10.12	21.91	15.21	17.68	24.82	12.84	5.394
40	49.20	40.00	54.87	63.02	60.15	59.11	58.16	36.56
60	94.10	75.31	94.43	101.17	102.32	97.50	102.4	77.03
80	137.40	123.55	134.5	140.75	142.86	138.30	145.3	119.3
100	180.30	175.80	175.0	183.0	182.6	178.7	184.2	160.8
120	221.30	223.90	213.8	223.8	221.2	220.2	223.6	201.4
140	258.40	267.10	250.1	261.1	258.3	257.2	259.3	239.8
160	291.95	304.70	283.5	295.0	292.1	292.3	293.1	272.6
180	322.10	337.20	314.9	324.8	322.5	321.3	324.2	303.8
200	349.10	365.20	340.5	351.3	349.7	348.9	350.7	331.8
220	375.50	387.85	363.3	374.8	373.6	372.3	374.8	355.0
240	395.50	410.50	384.0	395.4	394.7	393.2	395.0	476.8
260	414.50	428.35	404.9	414.0	413.5	413.2	412.3	395.3
280	432.50	446.20	419.8	430.8	429.8	430.4	429.6	413.1
298.15	447.00	459.00	433.1	444.4	442.7	443.5	442.8	424.8

$M=3Mc-[3Md-2Ma]$ [5]. When heated, the disordering process of the cation magnetic interactions of a and d iron sublattices occurs, which affects energetic parameters and creates excess cooperative ferromagnetic contribution to the heat capacity – C_f . The other cooperative magnetic heat capacity component (C_R) is expected to appear in some garnets at low temperatures because of destroying magnetic exchange ($a-c$, $b-c$) interactions with the participation of lanthanide ions. Because of the special electronic structure of lanthanides, besides these two anomalies of a cooperative nature, we should expect the non-cooperative heat capacity Schottky-type anomaly (C_{sh}) due to the redistribution of lanthanide f -electrons on exited Stark levels. So, the morphology of heat capacity functions of RIG, taking into account all expected excess components, can be presented as:

$$C_p(RIG) = C_{reg} + C_f + C_R + C_{sh}. \quad (3)$$

Lanthanide-iron garnets form a series of structural analogs. Crystal parameters, volumetric properties, and Debye temperatures of these compounds differ slightly [1-5]. Therefore, we can say that the regular (crystal-phonon) part of heat capacity $C_{p(reg)}$ in the isomorphous group also changes

negligibly. At the same time, the diversity of magnetic structures of compounds of the series, especially below 298.15K, should affect the energetic state of garnets and cause the additional components of heat capacity and entropy of different magnetic origins. Meanwhile, separating the components of the total heat capacity from each other is still the most problematic task, especially for compounds with complex crystalline and magnetic structures, such as garnets, since the temperature regions of the anomalies overlap and there are no reliable input data for their evaluation and correct separation.

Table 2. Thermodynamic parameters at standard temperature (298.15K) of lanthanide-iron

RIG	Heat capacity Cp(298.15) J/K mole	Entropy S _{298.25} J/K mole	Enthalpy H _{298.15} - H ₀	Gibbs energy G(298.15) J/K mole
Sm	447.0	462.2	74295	212.9
Eu	459.0	449.4	75135	197.4
Gd	433.1	465.0	72540	221.7
Tb	444.4	476.7	75095	224.9
Dy	442.7	476.2	74669	225.8
Er	443.5	485.9	75200	233.7
Tm	442.8	473.1	74800	222.1
Lu	424.8	415.7	70065	183.5

The results in Table 2 show that LuIG with diamagnetic Lu(III) ions has the lowest heat

capacity and of other thermochemical parameters in the garnet group since this compound is characterized neither by the "low-temperature heat capacity anomaly" nor the Schottky effect. At the same time, other representatives of the series with paramagnetic lanthanide cations have such types of the above-mentioned anomalies that cause additional excessive increments of heat capacity and, consequently, other thermodynamic properties.

Conclusion

The reference data of thermodynamic parameters at standard temperature are the most required values for the preliminary energetic analysis of high-temperature industrial processes at the synthesis of complex oxides. In the present work, the main thermodynamic properties, such as standard entropy, enthalpy, and Gibbs energy, for the

isostructural series of rare earth-iron double oxides with garnet structure $R_3Fe_5O_{12}$ (where R varies from Sm to Lu) were studied. To identify the thermodynamic properties at standard temperature (298.15 K), the data of low-temperature heat capacity $C_p(T)$ was applied. The experimental study of heat capacity was carried out by a low-temperature adiabatic calorimeter with an accuracy of 0.25% in the temperature range 20(15)–300 K. The related thermodynamic parameters for standard temperature such as entropy, enthalpy, and Gibbs energy were determined and presented in the form of reference tables. The low-temperature heat capacity and related thermodynamic functions revealed the significant effects of excess components of cooperative and noncooperative magnetic nature. The results are discussed in connection with the crystal and magnetic structure of garnets.

ფიზიკური ქიმია

ლანთანოიდ-რკინის ორმაგი ოქსიდების სტანდარტული ენთროპია

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გრანატის ტიპის კრისტალური სტრუქტურის მქონე ლანთანოიდ-რკინის ორმაგი ოქსიდები – $R_3Fe_5O_{12}$ (სადაც R არის იშვიათმიწა მეტალი Sm-დან Lu-მდე) ქმნიან იზოსტრუქტურულ ნაერ-

თთა ჯგუფს, რომელთა საფუძველზე მუდმივად მიმდინარეობს ახალი, გაუმჯობესებული თვისებების მქონე მასალების ძიება. მრავალკომპონენტური ოქსიდური მასალების წარმოებისთვის მნიშვნელოვან საკითხს წარმოადგენს ოპტიმალური ტექნოლოგიური პროცესების შერჩევა და მისი ენერგეტიკული შეფასება სანდო თერმოდინამიკური პარამეტრების საფუძველზე. წარმოდგენილი ნაშრომის ძირითად მიზანს შეადგენს გრანატების ამ ჯგუფისათვის თერმოდინამიკური გათვლების ისეთი საკვანძო პარამეტრების დადგენა, როგორიცაა ენტროპია, ენთალპია და გიბსის ენერგია სტანდარტულ (298.15K) ტემპერატურაზე. ამ მიზნისთვის გამოყენებულია ჰემარიტი თბოტევადობის ტემპერატურული ფუნქციები. თბოტევადობა ექსპერიმენტულად შესწავლილია მაღალი სიზუსტის (0.25%) დაბალტემპერატურული კალორიმეტრული კვლევებით 20-300K ფარგლებში. ამ მონაცემების საფუძველზე დადგენილია ინტეგრალური თერმოდინამიკური პარამეტრები: ენტროპია $S(298.15)$, ენთალპია $H(298.15)$ და გიბსის ენერგია $G(298.15)$. შედეგები წარმოდგენილია ცხრილების სახით და განხილულია გრანატების კრისტალური სტრუქტურისა და მაგნიტური თვისებების თავისებურებების გათვალისწინებით.

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