Thermodynamic Approach of Lanthanide-Iron Double Oxides Formation

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Abstract—Standard Gibbs energy of formation $\Delta G_{for}(298.15)$ of lanthanide-iron double oxides of garnet-type crystal structure $R_3Fe_5O_{12}$ - RIG (R – are rare earth ions) from initial oxides are evaluated. The calculation is based on the data of standard entropies $S_{298.15}$ and standard enthalpies $\Delta H_{298.15}$ of formation of compounds which are involved in the process of garnets synthesis. Gibbs energy of formation is presented as temperature function $\Delta G_{for}(T)$ for the range 300-1600K. The necessary starting thermodynamic data were obtained from calorimetric study of heat capacity – temperature functions and by using the semi-empirical method for calculation of $\Delta H_{298.15}$ of formation. Thermodynamic functions for standard temperature – enthalpy, entropy and Gibbs energy - are recommended as reference data for technological evaluations. Through the structural series of rare earth-iron garnets the correlation between thermodynamic properties and characteristics of lanthanide ions are elucidated.

Keywords—Calorimetry, entropy, enthalpy, heat capacity, gibbs energy of formation, rare earth iron garnets.

I. INTRODUCTION

THERMODYNAMIC analysis of chemical reactions is important preliminary procedure for indicating the optimal thermal conditions of corresponding technological processes.

The thermodynamic analysis of high temperature chemical reactions mainly bases on well-known equation:

$$\Delta G = \Delta H_{298.15} - \Delta S_{298.15}T + \int_{298.15}^{T}\Delta Cp\, dT - T\int_{T298.15}^{T}\Delta Cp\, dlnT \quad (1)$$

where ΔG, $\Delta H_{298.15}$, $\Delta S_{298.15}$ and ΔC_p are respectively the changes of Gibbs energy, enthalpy, entropy and heat capacity in result of chemical reaction. Therefore, for achieving the accurate estimation when using (1) the reliable data of thermodynamic parameters for reagents and products of chemical processes are to be employed. For this purpose the numerous Data Books and computer Data-Banks are used for today, as well as many scientific works are published permanently in order to refill and renew the thermodynamic data.

Standard enthalpy of formation $\Delta H_{298.15}(for)$ and standard entropy of chemical compounds $(S_{298.15})$ are the most required values at thermodynamic evaluation of chemical processes. The reliable data of standard entropy (as well as temperature

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functions of entropy and enthalpy) are usually determined by calorimetric measurements of heat capacity for wide temperature region and using the following expressions:

$$S_T = \int_0^T C_p\, d\,lnT + \Sigma\left(\frac{\Delta H_i}{T_{tr}}\right);$$

$$H_T - E_0 = \int_0^T C_p\, d\,T + \Sigma(\Delta H_i); \quad (2)$$

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

For recent years the special interest of specialists has been directed to the complex inorganic oxide systems, because many of them revealed very valuable properties from the point of view both of fundamental and applied sciences. Most of these multi-component oxides mainly are produced by high temperature solid state reactions of starting oxides – "ceramic" method. Therefore, the preliminary thermodynamic analyses on the base of temperature dependences of Gibbs energy of related chemical reactions are very important, and for this purpose the reliable thermodynamic properties (including the data of standard entropy, enthalpy of formation, phase transitions, and others) of compounds are to be employed.

Among a various complex oxide systems the rare-earth iron double oxides with garnet structure $R_3Fe_5O_{12}$ (in which R varies from *Sm* to *Lu*) are the object of continuing interest, because they are used as basic compositions for working out a new multicomponent materials with advanced electric, magnetic and other physical properties.

The objective of the present study is to suggest the data of Gibbs energy of formation of lanthanide-iron garnets from starting oxides and the values of standard entropy $S_{298.15}$ of lanthanide-iron double oxides $R_3Fe_5O_{12}$ (RIG) as reference data for thermodynamic estimations of technological processes.

For today a great deal of information about structural, Compositions garnet-type compounds are published [5]. The thermal properties are also the object of permanent interests [1]-[9], and estimation of thermodynamic parameters of rare-earth is actual problem still. From this point of view the special interest has to be directed for investigation of heat capacity function in the low temperature (T<298.15K) and high temperature (T>298.25) regions, that gives possibility to calculate entropy, enthalpy and Gibbs energy in wide temperature intervals. All these parameters create the informational basis for relevant thermodynamic evaluations of processes with participation of rare earth-iron garnets, including the processes of their manufacturing by high

temperature synthesis of starting oxides.

In the present work the standard entropy ($S_{298.15}$) of investigated garnets are determined based on calorimetric study of low temperature heat capacity in the wide temperature interval 20(50)-320K. Combined them with literature data for the temperature domain 0.4-20K [2], [3] and our previous measurements [6], [7] the reference data of entropy, enthalpy and Gibbs energy been calculated, which are relevant for using at calculation of Gibbs energy of formation by (1). For evaluation the enthalpy of formation $\Delta H_{298.15}$(for) at standard temperature, the semi-empirical method of calculation have been used.

II. Experimental

The samples of garnets were synthesized by high temperature solid state reaction. The starting materials were Fe_2O_3 and R_2O_3 oxides of high purity (99.9%). Passing two stages of intermediate grindings and calcinations at 1300K the final syntheses of pressed tablets was carried out at 1650K for about 40-45 hours in air.

Characteristics of the products of synthesis (chemical composition, crystal structure parameters, magnetic moments, Curié temperatures) show a good agreement with literature data [5]. All samples have garnet–type crystal structure, they exhibit a ferromagnetic properties and their Curie temperatures decrease in the direction of reducing of lanthanide ions radius.

The data of standard entropy $S_{298.15}$ of RGI were obtained on the base of calorimetric investigation of temperature dependence of heat capacity by using the low-temperature adiabatic vacuum micro-calorimeter [4] in the range 20(50)-300K. High temperature drop calorimeter (300-1200K) and differential scanning calorimeter DSK-111 (for 300-900K) were used to study enthalpy and heat capacity above standard temperature. The accuracy of the measurements is ±0.3, 0.5 and 1.0 respectively. The data of all temperature intervals are overlapped in accordance of accuracy of their settings.

For calculating the derived integral thermodynamic properties (entropy, enthalpy, Gibbs energy) and their values at standard temperature (298.15K) the following procedures were carried out: smoothing the raw experimental heat capacity data and representing them as temperature functions; extrapolating the heat capacity function below temperature of lowest experimental determination (T_{min}) to 0.K; to calculate entropies and thermodynamic properties by (2).

The first procedure has been carried out using spline-fittings. The values of entropy and enthalpy for T_{min} were determined proceeding from the literature heat capacity data of lanthanide-iron garnets for temperature interval 0.4-20K which are given in publications [2] and [3] and using numerical or graphical integration. The entropy (and enthalpy) at standard temperature are found as the sum of experimental ($T>T_{min}$) and extrapolated ($T<T_{min}$) temperature intervals. Above the highest experimental temperature ($T>1200K$) the data were calculated by extrapolation enthalpy equations which were obtained experimentally for the interval $T<1200K$.

III. Results

A. Thermodynamic Properties

For estimation the values of entropy at standard temperature by (2), experimental investigation of heat capacity of $Sm_3Fe_5O_{12}$, $Gd_3Fe_5O_{12}$, $Tb_3Fe_5O_{12}$, $Dy_3Fe_5O_{12}$, $Er_3Fe_5O_{12}$ and $Lu_3Fe_5O_{12}$ were fulfilled in the temperature range 20(15) – 320K, while for $Eu_3Fe_5O_{12}$ and $Tm_3Fe_5O_{12}$ the experimental temperature domain was 50-320K. Consequently, the procedures of extrapolation to 0.K are different for these two groups of garnets.

The value of entropy at standard temperature was calculated as the sum of entropy changes for the investigated temperature range $S(298.15-T_{min})$ and for the domain below the lowest experimental determination ($T<T_{min}$) as: $S_{298.15}=S(T_{min})+S(298.15-T_{min})$. Therefore, we should consider two different occasions:

For the first group the heat capacity data of 0.4-20K interval are published in [2] and [3]. The tests on overlapping experimental area (15-25K) show that the agreement between our and literature data is ~ 1.5-2.0%. This gives the possibility to calculate the values of standard entropy as the sum: $S_{298.15}=S_{20}+(S_{298.15}-S_{20})$.

Heat capacity of another group of garnets is not known below 20K yet. Only very low temperature interval (0.4 - 4.5K) is reported for $Eu_3Fe_5O_{12}$ in [3]. The entropy for this domain is found to be: $S_4 = 0.418$ J/K.mole. The interval between 4 and 50K we expressed by using the equation composed by Debye, Einstein functions and ferromagnetic increment. Standard entropy of $Eu_3Fe_5O_{12}$ is found as the sum of these three temperature domains: $S_{298.15}=S_4+(S_{50} - S_4) + (S_{298.15} - S_{50})$. The same procedure has been carried out for $Tm_3Fe_5O_{12}$.

TABLE I
THERMODYNAMIC PROPERTIES OF RARE EARTH IRON GARNETS (RIG) AT STANDARD TEMPERATURE

RIG	Entropy $S_{298.15}$ (J/K.mole)	Heat Capacity $Cp(298)$ (J/K.mole)	Enthalpy $H_{298.15}$ (J/mole)	Gibbs Energy $(G_{298.15}-H_0)/T$ (J/K.mole)
Sm	447.0	462.2	74295	219.9
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

TABLE II
HIGH TEMPERATURE HEAT CAPACITY C_p OF $R_3Fe_5O_{12}$ (J/K.MOLE)

T,K	SmIG	EuIG	GdIG	TbIG	DyIG	ErIG	TmIG	LuIG
300	456	464	435	450	447	451	455	437
400	517	527	497	506	504	510	503	495
Tc	623	617	590	600	590	598	590	580
600	559	555	525	532	526	533	527	530
800	574	577	532	546	535	540	532	537
1000	588	582	545	560	547	550	542	549
1200	606	590	560	579	549	560	549	563
1400*	615	598	568	590	550	564	553	570
1600*	617	599	570	592	552	566	555	572
Curie temperature T,K	565	563	560	556	552	541	539	539.5

*Extrapolate

The results are listed in Table I. Comparing our data with [1] and [8] we can observe some disagreements, especially in the case of low-temperature entropy values, though heat capacity data which was used in [1] and [8] do not differ significantly from ours. As the cause of these differences it can be named the fragmental temperature intervals of experimental investigations of heat capacity, on the base of which the entropy values have been calculated in the indicated above works [1] and [8].

Lanthanide-Iron garnets form the series of structural analogs.According to the Neel's ferrimagnetic theory, the complex crystal structure of garnets are composed by combination of three sub-lattices (tetrahedral - *d*, octahedral-*a*, and dodecahedral- *c*). Antiferromagnetic exchange interactions between sublattices cause peculiar magnetic properties of garnets [5]. In result of observation of crystal structure of garnets and electronic structure of lanthanide ions one can see that their entropy (as well as heat capacity) is an additive quantity and can be expressed as the sum of regular (S_{reg}), ferromagnetic (S_f) and Schottky (S_{sh}) contributions: $S=S_{reg}+S_f+S_{sh}$. Crystal parameters, volumetric properties and Debye characteristic temperatures of these compounds differ very slightly from each other [2], [3]. Therefore, we can assume that the regular parts of heat capacity and entropy (C_{preg}, S_{reg}) also varies negligibly through the isomorphic group of garnets. Besides, magnetization of iron *(a)* and *(d)* sub-lattices in low-temperature region (T<200K) is very weak function of temperature and cannot affect the heat capacity significantly. At the same time the different magnetic and electronic structures of rare-earth sub-lattices of the members of this group can cause the different types of excess heat capacity and entropy increments, both of cooperative and non-cooperative magnetic origin, especially below 298.15K. The first one is connected with destroying of magnetic order in rare-earth sub-lattices of garnet structure *(S_f)*, while the second one - s. c. Schottky-type heat capacity anomaly *(S_{sh})* is connected with redistribution of exited electrons over Stark levels of lanthanide ions [6], [7] and [9]. The observation of entropy data given in Table I reveals that *LuIG* has the lowest heat capacity and entropy values in the garnet group. Lutetium-iron garnet contains diamagnetic *Lu(III)* ions in the ground state S_0. Therefore neither "low-temperature magnetic heat capacity anomaly", nor Schottky effect is typical for this compound.

The *EuIG* also has comparatively small standard entropy, which is result of following factors: a) the "low-temperature magnetic heat capacity anomaly" don't present in *EuIG* because of small magnetic moment of *Eu(III)*, which is in addition very weak function of temperature, b) redistribution of exited electrons in *Eu(III)* begins at comparatively higher temperatures (from T>150K) than it happens in other garnets, and this gives relatively small value of Schottky anomaly. As to *SmIG*, though the "low-temperature magnetic heat capacity anomaly" has no place in this garnet too, but the Schottky effect appears from very low temperatures. In result, the standard entropy of samarium-iron garnet is higher than for *EuIG*. The other members of the series reveal both types of magnetic anomalies from very low temperatures. Hence, the increased values of heat capacity and entropy of these compounds are due to the excess effects.

B. Gibbs Energy of Formation

For nowadays the simplest and most convenient way for manufacturing the lanthanide-iron garnets is high temperature synthesis of oxides -"ceramic method" by reaction: $1.5R_2O_3 + +2.5\ Fe_2O_3 = R_3Fe_5O_{12}$. Thermodynamic analysis of relevant chemical processes is based on estimation of equilibrium constant of reaction – K_p via determination of Gibbs energy of formation of garnets.

For calculating by (1) it is essential, together with entropy, enthalpy and entropy functions, to have also the values of enthalpy of formation at standard temperature $\Delta H_{for}(298.15)$. No reliable experimental data for $\Delta H_{for}(298.15)$ can be found in literature for rare-earth garnets. Taking in view the lack of experimental values, we applied to the semi-empirical calculation method which is recommended in [11]. The method is valid for calculation of $\Delta H_{for}(298.15)$ of double oxides type xA_cO_d-yB_nO_m. The advantage of the method is its simplicity and possibility to use the most available data. As the basic parameters for calculation the characteristics of structure forming cations (ions radius–*r*, electronegativity -*e*, and oxidation rate-*l*) are applied. These data we have used from [5], [11] and [12]. The details of the method are presented in [11].

Using evaluated $\Delta H_{for}(298.15)$, thermodynamic functions (enthalpy, entropy, heat capacity) given in Tables I and II, and published data for starting oxides [10], we calculated

ΔG_{for}(298.15) and ΔG_{for}(T) for lanthanide-iron double oxides by (1) and (2). The results are presented in Table III. The data of enthalpy and Gibbs energy of formation at standard temperature for lanthanide-iron oxides are presented on Fig. 1. As the example, on Fig. 2 the temperature dependence of Gibbs energy of formation ΔG_{for}(T) of gadolinium-iron garnet is demonstrated, which is typical for the whole isomorphic series.

We can see that above standard temperature the reaction of garnets formation is an exothermic process. The values of ΔG_{for}(T) differ from each other negligibly, though we can state that the trend of increasing of ΔG_{for}(298.15) from the "cerium" subgroup (Sm,Eu IG) to the "yttrium" (Gd-Lu IG) subgroup is evident. For synthesis the most recommended temperatures is the region above 1200K.
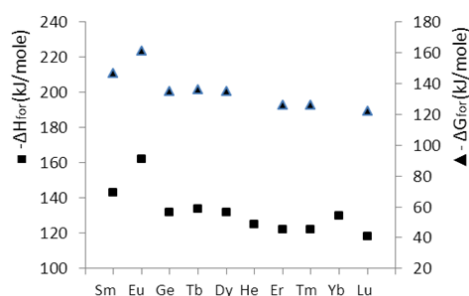

Fig. 1 Enthalpy and Gibbs energy of formation of lanthanide-iron double oxides
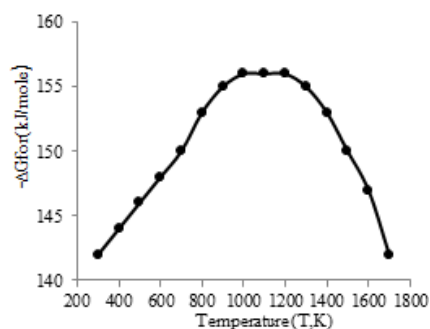

Fig. 2 Gibbs energy of formation of gadolinium-iron garnet

TABLE III
GIBBS ENERGY OF FORMATION OF RARE-EARTH IRON GARNETS $R_3Fe_5O_{12}$ FROM OXIDES (- ΔG_{FOR} KJ/MOLE)

T,K	SmIG	EuIG	GdIG	DyIG	ErIG	TmIG	LuIG
298,15	150	165	142	140	135	135	130
400	153	168	144	144	140	138	133
600	157	171	148	148	147	145	140
800	165	174	153	153	156	152	148
1000	170	175	156	156	163	157	155
1200	174	173	156	155	167	159	158
1400	176	168	153	150	168	156	159
1600	174	159	147	141	165	150	156

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