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Thermodynamic Properties of Complex, Ferrite $BiCa_3Fe_5O_{12}$

MUKHAMETKALI MUSAGALIEVICH MATAYEV[1]*, MOLDIR RASHIDOVNA ABDRAIMOVA[1], ZHANAR YLIASOVNA TURSINOVA[1] and ASSEL TAUPYKOVNA KEZDIKBAEVA[2]

[1]Kazakh State Women's Teacher Training University, 050000, Aiteke bi, 99, Almaty, Kazakhstan.
[2]Karaganda State University named by Y.A.Buketov, Universitetskaya 28, Karagandy, Kazakhstan.
*Corresponding author E-mail: mataev_06@mail.ru

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ABSTRACT

The compound $BiCa_3Fe_5O_{12}$ was synthesized by the solid-phase reaction method. For the first time, the thermodynamic properties were calculated using semi empirical methods: Standard enthalpy of formation, H^0298, Standard heat capacity, C^0_p, 298, Standard Gibbs energy, G^0298 and Standard entropy of formation, S^0298, coefficients in the equation of the temperature dependence of the heat capacity Cp(T). The temperature dependence of the specific heat was studied by dynamic calorimeter. Thus, in the temperature interval 298.15-673 K, the specific heats of the complex ferrite $BiCa_3Fe_5O_{12}$ were experimentally determined, and the polynomial equation of the temperature dependence of the heat capacity was derived. The comparative analysis of the experimental and calculated values of the specific heat was carried out.

Keywords: Thermodynamic properties, Ferrites, Heat capacity, Calorimeter.

INTRODUCTION

Investigation of the physico-chemical properties of ferrites formed in the Bi_2O_3-$Me^{II}O$-Fe_2O_3 (Me^{II}-alkaline-earths metal) systems is of definite scientific and practical interest for the directed synthesis of compounds with specified properties. The analysis of literature data shows that the most studied of ferrites are the $BiFeO_3$ orthoferrites, so-called multiferroics, which possess both electric polarization and magnetic ordering, recently there has been a significant increase in interest in these classes of compounds, their connection with promising applications as a working medium in devices of storage and information processing. On the basis of the most famous multiferroics, a wide search for new materials with ferroelectric properties is carried out by specific electronic and magnetic structures. The mixed result is based on bismuth ferrite which often combines ferroelectric and weakly ferromagnetic properties with the dominant antiferromagnetic ordering[1-2]. Experimental studies, as a rule, are time-consuming, expensive and do not always yield reliable results. An alternative source of obtaining new information and revising the availableis the use of computational methods, which are based on the idea of thermodynamic similarity connecting the physicochemical properties of the system with its composition[3].

In this paper, semi empirical calculations of the thermodynamic properties and the temperature dependence of the heat capacity of complex ferrite $BiCa_3Fe_5O_{12}$were carried out. The thermodynamic characteristics obtained are compared with the experimental data.

EXPERIMENTAL

The complex ferrite was obtained by the solid-phase synthesis method in an alundum crucible from pre-annealed and thoroughly grinded for 56 h. powders Fe_2O_3 (hp), $CaCO_3$ (bp) and Bi_2O_3 (bp).The composition of the obtained compound was confirmed by X-ray diffraction analysis using a RigakuMinilex 600 diffractometer.

The heat capacity of ferrites was studied by the method of dynamic calorimeter on a serial IT-S-400 instrument in the temperature range 298-673 K. The experiments were carried out in a monotonic regime, close to linear heating of the sample with an average rate of about 0.1 K per second. The maximum error in measuring the heat capacity on the S-400 IT device, according to the passport data, is ± 10%[9].

RESULTS

The compound $BiCa_3Fe_5O_{12}$ was synthesized by the solid-phase reaction method and for the first time, the thermodynamic properties were calculated using semiempirical methods. All the calculated properties of the compound are shown in Table 1.

DISCUSSIONS

Semiempirical calculation of thermodynamic properties: Information on the properties of simple oxides and Bi_2O_3 and Fe_2O_3, CaO was taken in[3].

Table. 1: Thermodynamic properties of $BiCa_3Fe_5O_{12}$ obtained by semiempirical methods

	$BiC\alpha_3Fe_5O_{12}$
ΔH^0_{298}(ox), kJ / mol	-192.582±61.74
$\Delta H^0_{298,}$ kJ / mol	-4443.5 ± 61.74
$S^0_{298,}$ kJ / mol	371.6±8
$C^0_{p,298,}$ kJ / mol	397.95 ±88.7
$G^0_{298,}$ kJ / mol	- 3684.94
α	82
b, 10^{-3}	775· 10^3T
c, 10^5	122 ·$10^{-5}T^{-2}$

1. Standard enthalpy of formation, H^0298

The standard enthalpy of formation is calculated by the formula used to estimate the heat of the compounds, which can be represented as pseudobinary or pseudotraic[4].

$$H^0298(j) = \sum ni\Delta H^0298(i) + \Delta H^0298(ox).$$

where ΔH^0298, n_i is the standard heat of formation and the number of moles of the i-th compound in the j-th complex; ΔH^0298 (ox) – SEO of a compound of simpler compounds.
In accordance with this formula, we can write

$H^0298(BiCa_3Fe_5O_{12})$=0,5.$\Delta H^0298(Bi_2O_3)$+3.ΔH^0298 (CaO)+2,5.$\Delta H^0298(Fe_2O_3)\Delta H^0298(0\chi)$

To estimate the value of ÄH⁰298 (ox) complex oxides, the empirical dependence was used[4].

$$H^0298(ox) \approx (-16{,}0485 \pm 5{,}145)\cdot m_0$$

where m_0 is the number of oxygen atoms in the compound formula.
As a result, we received:

$H^0298(ox) \approx 192{,}582 \pm 61{,}74 kJ/mol$ and
$H^0298(BiCa_3Fe_5O_{12}) \approx 4443{,}5 \pm 61{,}74 kJ/mol$

2. Standard entropy of formation, S^0298

The standard entropy of the formation of S^0298 is calculated by three methods: additively by the Kopp-Neumann rule using S^0298 simple oxides[5], the Latimer method[4] and the Kumok increments method[4]. The additive method for calculating S^0298 is based on the addition of S^0298 simple oxides that make up the compound in the molar ratio:

$$S^0298 = n\cdot S^0298(Bi_2O_3) + m\cdot S^0298(CaO) + r\cdot S^0298(Fe_2O_3)$$

$$S^0298 = (BiCa_3Fe_5O_{12}) = 419{,}2 J(mol\cdot K)$$

The Kumok increments method assumes the computation by equation

$$S^0298 = Sk\cdot nk + Sa\cdot na + Sl\cdot nl$$

where Sk and Sa, Sl are increments of cations and anions, respectively (values are taken in[4]), nk and na, nl is the number of cation and anion compounds making up a compound.

For $BiCa_3Fe_5O_{12}$ S°298, the Kumok increments method was 427.2 J/(mol·K). Using the Latimer method, it was 268.4 J/(mol·K). The average arithmetic value of the standard entropy of formation is 371.6 ± 8J/(Kmol).

3. Standard heat capacity, Ñ°ₚ, 298

The standard heat capacity was calculated according to the Kopp-Neumann rule[5]:

$$C^0P,298 = n \cdot C^0P,298(CaO) + k \cdot C^0P,298(Bi_2O_3) + 1 \cdot C^0P,298(Fe_2O_3)$$

and equaled 353.6 J/(mol"K), according to the dependence[5].

As per the Kumok increments method:

$$C^0P,298 = C^0P,298K \cdot nk + C^0P,298a \cdot na + C^0P,298a \cdot nc,$$

where C°p, 298K and C°p, 298a, C°p, 298a ·nc cation and anion increments, respectively, n·k and n·a, n·c is the number of cation and anion compounds making up the compound, the heat capacity is equal to 442.3J/(mol·K) .

The average value of 397.95 ± 88.7 is listed in Table 1.

4. Standard Gibbs energy, G°298

The standard Gibbs energy is calculated by the method of ion increments. Standard Gibbs energy of a solid salt according to this method is calculated according to the following formula:

$$\Delta_f G^0_{298} Me_m\left(X_\alpha O_\beta\right)_n = m\Delta G^0_{298} Me^{n+}_{(p-p;H_2O,cm.c..)} \cdot K + n \cdot \Delta G^i_{298}\left(X_\alpha O_\beta\right)^{m-}$$

WhereM^{n+} is a cation, X^{m-} is an anion, m, n- are indices of cations and anions. Using the alkaline, alkaline earth, transition, and rare-earth metal cations in standard aqueous solution and anions (ΔG°298), the standard Gibbs energies of the salts of the s, d, f elements in the solid state can be calculated[6-7].

Received $\Delta_f G^0_{298} = -3684{,}94 KJ/mol$

5. Temperature dependence of the heat capacity, Cp (T)

The temperature dependence of the heat capacity was calculated in the following ways: an additive method using data on simple oxides[5].

$$C(T)=(0.5\cdot\alpha Bi_2O_3+3\cdot\alpha C\alpha O+2.5\cdot\alpha Fe_2O_3)+(0.5\cdot bBi_2O_3)+3\cdot bC\alpha O+2.5\cdot bFe_2O_3+(0.5\cdot cBi_2O_3+3\cdot cC\alpha O+2.5\cdot cFe_2O_3)\cdot T$$

$$C(T) = 82 + 775\cdot 10^3 T - 122\cdot 10^{-5} T^{-2}$$

6. Experimental finding of heat capacity

Calorimetric methods for studying the thermodynamic properties of solids were used to measure the dependence of the heat capacity of solids on temperature and the change in energy during cation exchange. On anIT-S-400 calorimeter at the temperature interval 298.15-650 K, the comparative heat capacities of the synthesized $BiCa_3Fe_5O_{12}$ compounds were found experimentally. Fig. 1 shows that the heat capacity of substances increases with increasing temperature. One of the reasons for the increase in heat capacity with increasing temperature is the energy expenditure on the formation of a vacancy upon the transition of the nodes of crystal lattices to intermediate sites[8-9]. For $BiCa_3Fe_5O_{12}$, the temperature dependence of the heat capacity has the form shown in Figure. 1.

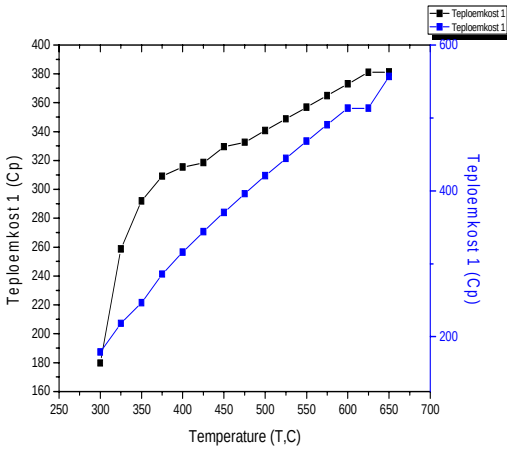

Fig.1. Temperature dependence of heat capacity of complex ferrite: 1 (black line) – calculated values; 2 (blue line) – experimental data;

CONCLUSION

The results of calculations of the thermodynamic properties of complex ferrite, carried out using semiempirical methods, are in satisfactory agreement with those values that could be obtained experimentally. Thus, for the first time in the temperature range 298.15-673 K, the specific heats of the complex ferrite $BiÑa_3Fe_5O_{12}$ were experimentally found, and the polynomial equation of the temperature dependence of the heat capacity was derived. A comparative analysis of the experimental and calculated values of the specific heat was carried out.

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