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Calorimetric and Thermodynamic Studies of Complex Ferrites in the Temperature Range of 298,15-673K

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ABSTRACT

By method of dynamic calorimetry, in the temperature range between 298,15 and 673 K, isobaric heat capacity of polycrystalline ferrites $Bi_2CaFe_4O_{10}$, $BVMgFe_2O_{5.5}$, $BiMgFe_4O_{10}$ was experimentally studied. Mathematical processing of experimental data made it possible to derive polynomial equation of temperature dependence of ferrites heat capacity for respective temperature ranges, in dependencies C^0_p~f(T) of ferrite $Bi_2CaFe_4O_{10}$ a jump was detected in heat capacity at 625K associated with phase transitions of type II. The values of the thermodynamic functions $C^0_p(T)$, $H^0(T) - H^0(298,15)$, $C^0(T)$, $F^{hh}(T)$ have been calculated. Standard values of thermodynamic functions were determined using the method of ion increments. The results obtained broaden thermodynamic data bank for complex inorganic crystalline compounds.

Key words: oxides, ferrites, heat capacity, thermodynamic functions, calorimetry.

INTRODUCTION

Study of physico-chemical properties of ferrites formed $Bi_2O_3 – Me^{II}O – Fe_2O_3$ (Me^{II} - alkaline earth metals) systems is of certain scientific and practical interest for directed synthesis of compounds with desired properties. Analysis of the published data shows that among ferrites, the most studied ones are orthoferrites BiFeO3, the so-called multiferroics having both electric polarization and magnetic ordering. In recent years interest to these classes of compounds has significantly increased due to perspective of their use as a working environment in information storage and processing devices. On the basis of the most known multiferroic, new materials with ferroelectric properties of the specific electronic and magnetic structures were searched for. Substituted perovskites based on bismuth ferrite often combine ferromagnetic and weak ferroelectric properties under the dominant anti-ferromagnetic ordering[1-6].

The purpose of this work is a calorimetric study of $Bi_2CaFe_4O_{10}$, $BVMgFe_2O_{5,5}$, $Bi_2MgFe_4O_{10}$ ferrites. The tested ferrites have been synthesized by solid phase interaction of stoichiometrically matching oxide mixtures Bi2O3, Fe2O3 of chemically pure grade, and carbonates of alkaline-earth metals of essential purity. Formation of equilibrium phases of ferrites was detected by X-ray diffraction method and types of their symmetry and lattice constants[7,8] were identified. It has been determined that ferrites crystallize into a tetragonal and cubic structure with the following lattice cell parameters: $Bi_2Ca0Fe_4O_{10}$ –a=5.56, C=8.12 Å, $V_{el.cell.}$=251.0 Å3, Z=1, $\rho_{rent.}$=6.56, $\rho_{pikn.}$=6.93g/cm^3: BiMgFe2O5,5 – a=11,1 Å, $V_{el.cell}$= 1382 Å3, Z=8, ρ_{rent}.= 6,02, ρ_{pikn}.=3,03 g/ cm^3: Bi2MgFe4O10– a=11,1 Å, $V_{el.cell}$= 1364 Å3, Z=16, ρ_{rent}.= 9,66, ρ_{pikn}.=9,60 g/ cm^3[9].

MATERIALS AND METHODS

Heat capacity of ferrites was investigated by dynamic calorimetry method using a serial device IT-400 in the temperature range between 298 and 673 K. Experiments were performed in the mode of a monotonous close to linear heating of the sample at the average heating rate of about 0.1 K per second. The maximum error of measurement of specific heat capacity using the IT-400 device according to the datasheet is ± 10% [10,11]. Principle of calorimeter operation is based on comparative method of a dynamic c-calorimeter with a heat meter. The tested sample placed in a metal vial of the measuring cell was heated up continuously by heat flow through a calorimeter. After every 25 °C of heating, time lag of the vial temperature was measured against temperature of the base, using a micro voltamperemeter -136 V and a stopwatch SEC-100. The meter had been pre-calibrated, i.e., thermal conduction of the K_T calorimeter was defined. After that, specific heat of a standard copper sample was defined, as well as specific and molar heat capacities of the substance. Thermal conductivity of the heat meter was defined by the following formula:

$$K_\tau = \frac{C_{copper.sample}}{\bar{\tau}_{T.M.} - \bar{\tau}_T^0}, \qquad ...(1)$$

where $C_{copper.sample}$ is the total heat capacity of a copper sample in J/K, $\bar{\tau}_{T.M.}$ is the average lag time at the heat meter in experiments with copper sample in seconds, $\bar{\tau}_T^0$ is the average lag time at the heat meter in experiments with an empty vial.

Table 1: Experimental values of heat capacity

T, K	$Bi_2CaFe_4O_{10}$	
	C0p + δ (J/g·)	C0p + Δ°(J/mol)
298.15	0,429±0,02	360,81±11,9
323	0,439±0,01	369,73±5,86
348	0,450±0,01	378,92±5,71
373	0,464±0,01	390,25±5,41
398	0,469±0,01	394,63±5,48
423	0,486±0,02	408,71±10,5
448	0.491±0.01	412,99±5,24
473	0,505±0,02	425,31±10,1
498	0,512±0,02	430,45±10,0
523	0,524±0,01	441,12±4,9
548	0,535±0,02	450,83±9,61
573	0,544±0,02	458,06±9,45
598	0,552±0,01	464,86±4,66
623	0,549±0,01	360,81±11,9
648	0,557±0,01	369,73±5,86
673	0,592±0,01	378,92±5,71

Table 2: Equation of temperature dependence ferrites hear capacity

Compound	Cr =a+bT+cT-2			ΔT, K
	a	b 10-3	c·10^6	
$Bi_2CaFe_4O_{10}$	266,36±18	334±0,02	0,293±0,02	298,15 - 673
$BiMgFe_2O_{5,5}$	148,77±10	198±0/01	0,101±0,01	298,15 - 673
$Bi_2MgFe_4O_{10}$	255,19±18	403±0,03	0,565±0,04	298,15 - 673

Table 3: Thermodynamic functions of ferrites in temperature range between 298.15 and 673 K

T, K	C_P^0 (T), J/mol K	S^0 (T) J/mol K	F^{hh}(T),J/mol K	H^0 (T) H^0 (298.15) kJ/mol
		$Bi_2CaFe_4O_{10}$		
1	2	3	4	5
300	206,10	413,96	269,80	413,06
325	216,42	423,93	3516,63	413,11
350	228,07	432,52	6530,50	413,87
375	235,25	439,92	9311,38	415,09
400	237,05	446,28	11859,24	416,63
425	246,41	451,71	14174,04	418,36
450	257,73	456,31	16255,79	420,19
475	268.28	460,18	18104,46	422,07
500	273,67	463,38	19720,05	423,94
525	288,58	465,98	21102,54	425,79
550	290,70	468,04	22251,93	427,58
575	270,19	469,59	23168,21	429,31
600	292,93	470,70	23851,39	430,94
625	302,34	471,38	24301,47	432,49
650	310,86	471,67	24518,43	433,94
675	320,77	471,60	24502,28	435,30
$BiMgFe_2O_{5,5}$				
300	319,63	234,39	534,82	323,62
325	322,36	255,49	7189,14	233,37
350	325,00	274.87	13786,05	235,49
375	327,58	292,78	20325,53	238,59
400	330,10	309,41	26807,55	242,39
425	332,58	324,89	33232,11	246.71
450	335,04	339,38	39599,21	251,38
475	337,48	352,96	45908,82	256,31
500	339,89	365,73	52160,96	261,41
525	342,29	377,77	58355,62	266,62
550	344,67	389,15	64492,78	271,89
575	347,05	399,92	70572,46	277,19
600	349,41	410,14	76594,65	282,49
625	351,76	419,85	82559,34	287,76
650	354,11	429,09	88466,54	292,99
675	356,46	437,91	94316,24	298,18
$Bi_2MgFe_4O_{10}$				
300	275,42	222,18	169,94	221,62
325	283,69	228,51	2181,83	221,80
350	291,92	233,78	3993,44	222,37
375	300,10	238,15	5604,47	223,21
400	308,26	241,73	7014,90	224,20
425	316,39	244,61	8224,73	225,26
450	324,50	246,88	9233,95	226,36
475	332,61	248,59	10042,56	227,45
500	340,70	249,81	10650,56	228,51
525	348,78	250,58	11057,94	229,51
550	356,86	250,94	11264,70	230,46
575	364,93	250,93	11270,85	231,33
600	372,99	250,58	11076,37	232,12
625	381,05	249,92	10381,28	232,83
650	389,10	248,97	10085,55	233,46
675	397,15	247,76	9289,22	233,99

The total heat capacity of the copper sample was calculated according to the following equation:

$$C_{copper.sample} = C_m \cdot m_{sample}, \quad ..(2)$$

where C_m is the tabular value of specific heat capacity of copper in J/(kg·K), and M_{sample} is the mass of the copper sample in kg.

The value of specific heat capacity of the substance tested was calculated by the following formula:

$$C_{ud.} = \frac{K_T}{m_0}(\tau_T - \tau_T^0), \quad ...(3)$$

where K_T is the thermal conductivity of the heat meter, m0 is the mass of the tested substance in kg, Tt is the time lag of temperature at the heat meter in seconds, and τ_T^0 is the time lag of temperature at the heat meter in experiments with an empty vial in seconds.

Five experiments were made for each sample temperature range. The obtained results of the lag time at the heat meter were averaged and processed by methods of mathematical statistics. For the average values of specific heat capacities at each temperature, standard deviations ($\overline{\delta}$, J/(g·K)), average values for molar heat capacities, and random error components (∆°, J/(mol K)) were calculated[10].

RESULTS AND DISCUSSION

Calibration of the instrument was made by measuring standard heat capacity Q-A12O3. The obtained value of C^0_p (298.15) A12O3 [76.0 J/mol K] satisfactorily aggrees with the recommended one - [79.0 J/mol K][11].

Table 1 shows results of calorimetric definition of the $BVSaFe_4O_{10}$ ferrite heat capacities.

In studying the heat capacity of $BiCaFe_4O_{10}$ ferrite within the limits between 598K and 648K, jumps of value C°p~f(T) were found, probably related to phase transitions of II kind. These transitions may be caused by cationic rearrangements, changing coefficients of thermal expansion and changes of magnetic moments of synthesized ferrites.

Mathematical processing of experimental data was used to derive equations of temperature dependence of ferrites heat capacity for respective temperature ranges ∆T (Table 2)[12,13].

Due to the fact that specifications of IT-400 calorimeter do not allow calculation of values of the standard entropy of compounds from experimental data about heat capacity, they were assessed using the system of ion entropy increments[14]. Errors of temperature dependence of the thermodynamic functions were calculated basing on the average error of the heat capacity and accuracy of entropy calculation (~3%). Next, by the known relations of the experimental data on C^0_p~f(T) and the calculated values of S°(298.15), the temperature dependencies of the thermodynamic functions $C^0_p(T)$, $H^0(T) - H^0298.15)$, $C^0(T)$, F **(T) (Table 3) were calculated.-

CONCLUSION

Thus, for the first time, in the temperature range 298.15 - 673 K, the isobaric heat capacities of $Bi_2CaFe_4O_{10}$, $BiMgFe_2O_{5,5}$, $Bi_2MgFe_4O_{10}$ ferrites were experimentally determined. Equations that describe their dependence on temperature have been made. In course of changing the heat capacity of $Bi_2CaFe_4O_{10}$ at 625 K, heat capacity jumps were discovered, probably related to phase transitions of II kind. Values of thermodynamic functions $C^0_p(T)$, $H^0(T) – H^0(298,15)$, S°(T), $F^{hh}(T)$ have been defined. The results obtained increase thermodynamic database about complex inorganic crystalline compounds.

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