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Heat Capacity and Thermodynamic Functions of Complex Manganites and Ferrites in Temperature Range 298.15 - 673K

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Abstract: The isobaric heat capacities of polycrystalline manganites $BiB\alpha Mn_2O_{5,5}$ and ferrites $BiSrFe_2O_{5,5}$, $BiC\alpha Fe_2O_{5,5}M$ were experimentally studied by dynamic calorimetry in the temperature range 298,15 - 673 K. Mathematical treatment of experimental data derived to polynomial equations of temperature dependence of heat capacity of manganites and ferrites for appropriate temperature ranges and a shift in specific heats at 573 K related with the type II phase transitions in dependences ${}^{\circ}C_{p} \sim f(T)$ of manganite $BiB\alpha Mn_2O_{5,5}$ was determined. The values of the thermodynamic functions $C^{\circ}_{p}(T)$, $H^{\circ}(T) - H^{\circ}(298,15)$, $S^{\circ}(T)$, $F^{**}(T)$ were calculated. Standard values of the thermodynamic functions were determined by the method of ion increments. The experimental results extend the pool of thermodynamics data on complex inorganic crystalline compounds.

Key words: Manganites • Ferrites • Heat capacity • Thermodynamic functions • Calorimetry

INTRODUCTION

The study of physical and chemical properties of manganites produced in the systems Bi_2O_3 - $Me^{II}O$ - Mn_2O_3 , Bi_2O_3 - $Me^{II}O$ - Fe_2O_3 (Me^{II} - alkaline-earth metals) is scientifically attractive for the target synthesis of compounds with desired properties. This is related to the discovery of the effect of "giant" magnetoresistance (GMR) in manganites $Ln_{1-x}A_xMnO_3$ ($Ln=La^{3+}$, Pr^{3+} , Nd^{3+} etc. and $A=Ca^{2+}$, Sr^{2+} , Ba^{2+} etc.) and ferromagnetic properties in bismuth orthoferrites that stimulated intensive research of their physical and chemical properties [1-8].

The aim of this work is a calorimetric study of manganite BiBαMn₂O_{5,5} and ferrites BiSrFe₂O_{5,5} and BiCαFe₂O_{5,5}. Investigated manganites and ferrites were synthesized by solid-phase reaction of stoichiometrically appropriate mixtures of chemically pure oxides Bi₂O₃, Fe₂O₃, Mn₂O₃ and chemically pure carbonates of alkaline earth metals. The formation of the equilibrium phases of manganites was determined by X-ray scattering including the types of their symmetry and lattice parameters. It has been found that manganites crystallize in the orthorhombic symmetry and ferrites in a cubic structure

with the following parameters of the unit cells: $BiB\alpha Mn_2O_{5,5}$ - a=3,79, b=5,67, c=23,2 P, $V_{uncell}=498,6$ P³, Z=4, $C_{rad}=7,24$, $C_{picn}=7,23$ g/cm³, $BiC\alpha Fe_2O_{5,5}$ - $\alpha=11,1$ P, $V_{un.cell}=1382$ P³, Z=8, $C_{rad}=6,02$, $C_{picn}=3,03$ g/cm³, $BiSrFe_2O_{5,5}$ - $\alpha=11,1$ P, $V_{un.cell}=1364$ P³, Z=16, $C_{rad}=9,66$, $C_{picn}=9,60$ g/cm³ [9].

Experimental: The heat capacity of manganites and ferrites were investigated by dynamic calorimetry using IT-S-400 calorimeter in the temperature interval from 298 to 673 K. Experiments were carried out in a monotone regime close to the linear heating of the sample with an average heating rate 0.1 K per second. The maximum error of the heat capacity measurement on IT-S-400 calorimeter according to the manufacturer's certificate is \pm 10% [10]. The principle of the calorimeter is based on comparative method of dynamic C-calorimeter equipped by a heat meter. The investigated sample fixed in metal ampoule of measuring cell was continuously heated by heat flow continuously through the heat meter. The time delay temperature of ampoule in regard to the temperature of basis was measured after each 25°C of heating using microvoltammeter F -136 and SETs-100 stopwatch. Calibration of microvoltammeter was carried out before measurements which included determination of the thermal conductivity of the calorimeter K_{τ} . Then, the heat capacity of standard copper sample, specific and molar heat capacities of the studied substance have been determined.

The thermal conductivity of a heat meter was determined using the formula:

$$K_{\tau} = \frac{C_{Cu}}{\bar{\tau}_{Cu} - \bar{\tau}_{T}^{0}} \tag{1}$$

where C_{Cu} - total heat capacity of the copper sample, J/K; $\bar{\tau}_{Cu,t}$ - the average delay of heat meter in experiments with copper sample, sec; $\bar{\tau}_{T}^{0}$ -the average delay of heat meter in experiments with an empty ampoule, sec.

Total heat capacity of the copper sample was calculated according to the equation:

$$C_{Cu,smpl} = C_{Cu,std} . M_{smpl}$$
 (2)

where $C_{Cu,std}$ - standard value of the specific heat capacity of copper, $J / (kg \bullet K)$; M_{smpl} - the mass of the copper sample, kg.

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

$$C_{sh} = \frac{K_T}{m_0} \left(\tau_T - \tau_T^0 \right) \tag{3}$$

where K_T - thermal conductivity of a heat meter; m_0 - mass of studied substance in kg; τ_T - temperature delay on heat meter, sec; τ_T^0 - delay of temperature on

heat meter in experiments with an empty ampoule, sec.

Each sample was tested five times for each temperature interval. The results of the time delay on heat meter were averaged and statistically delivered. For an averages of the specific heats at each temperature, the standard deviations $(\bar{\delta}, J/(g \cdot K))$ were calculated and for the average molar heat capacity values, the random errors $(\Delta^{\circ}, J/(mol \cdot K))$ were also calculated [11].

The calorimeter was calibrated by measuring standard heat capacity of α -A1₂O₃. The obtained value of C°°(298,15)A1₂O₃ [76,0 J/mol•K] satisfies the recommended value [79,0 J/mol•K] [12].

Table 1: The experimental data on the heat capacity

	$BiB\alpha Mn_2O_{5,5}$		
Temperature, K	$C^{o}_{\delta} + \delta (J/g \cdot K)$	$C^{\circ}_{\delta} + \Delta^{\circ}(J/\text{mol} \cdot K)$	
298,15	0,379 + 0,01	206,10 + 8,5	
323	0,397 + 0,01	216,42 + 6,3	
348	0,420 + 0,03	228,07 + 5,2	
373	0,432 + 0,02	235,25 + 11,9	
398	0,436 + 0,01	237,05 + 7,6	
423	0,453 + 0,01	246,41 + 8,2	
448	0,473 + 0,02	257,73 + 10,0	
473	0,493 + 0,02	268,28 + 3,2	
498	0,473 + 0,03	273,67 + 4,0	
523	0,490 + 0,01	288,58 + 4,9	
548	0,534 + 0,02	290,70 + 5,2	
573	0,500 + 0,04	270,19 + 9,3	
598	0,538 + 0,03	292,93 + 2,2	
623	0,556 + 0,02	302,34+3,1	
648	0,571 + 0,01	310,86 + 4,2	
673	0,589 + 0,01	320,77 + 6,3	

Table 1 shows the results of calorimetric determination of the heat capacities for the manganite $BiSrMn_2O_{5.5}$.

In the study of the heat capacity of lanthanum manganite within the temperature range from 548 K to 598K, the shifts of value $C^{\circ\circ} \sim f(T)$, probably belonging to type II phase transitions have been identified. These transitions can be related with cation redistributions, the changes in the coefficients of thermal expansion and changes in the magnetic moments of the synthesized manganites.

The equations of temperature dependence of heat capacity of the manganite and ferrites for the appropriate temperature ranges ΔT (Table 2) were obtained by mathematical delivery of the experimental data.

The values of the standard entropies for compounds from experimental results according to the heat capacity data were calculated using the system of ion entropy increments what could not be achieved using IT-S-400 calorimeter [13]. The errors of the temperature dependence of the thermodynamic functions were calculated with the mean error of the heat capacity and entropy calculation accuracy (\sim 3%). Further, according to known experimental data on the $C^{\circ}_{p} \sim f(T)$ and calculated values ??of S°(298,15), the temperature dependence of the thermodynamic functions $C^{\circ}_{p}(T)$, $H^{\circ}(T) - H^{\circ}(298,15)$, $S^{\circ}(T)$, $F^{**}(T)$ were calculated (Table 3).

Table 2: The equations of temperature dependence of heat capacity of the manganite and ferrites.

Bibahn		$C_p = \alpha + BT + CT^{-2}$	1 2				
Bidish 100 1	Compound	α	B•10 ⁻³	c•10 ⁶	ΔT, K		
Bis Fisher Park	$BiBaMn_2O_{5,5}$	71,24±5,5	415±0,03	$0,132\pm0,01$	298,15 - 673		
Table 3: Thermodynamic functions of the manganites and ferrites in the temperature interval from 298, 15 to 673 K Temperature, K CyT(T) ST(T) Temperature, K CyT(T) Temperature, K CyT(T) Temperature, K Temper	BiCaFe ₂ O _{5,5}	· · · · · · · · · · · · · · · · · · ·	$321\pm0,02$				
Temperature, K. C, P(T) S(T) F(T) F(T) H(T)H(298,15) 1 2 2 3 4 5 300 206,10 413,96 209,20 413,06 3025 216,42 423,93 3516,63 411,11 3590 228,07 452,52 659,50 413,87 3755 235,25 439,92 9311,38 415,00 237,05 446,28 11859,24 416,63 425 246,41 451,71 14174,04 418,36 425 226,41 451,71 14174,04 418,36 420 257,73 456,31 16255,79 420,19 475 268,28 460,18 18104,46 422,07 475 208,28 460,18 18104,46 422,07 475 208,28 460,18 18104,46 422,07 475 208,28 460,18 18104,46 422,07 475 208,28 460,18 18104,46 422,07 475 208,28 460,18 18104,46 422,07 475 209,70 468,04 2251,93 425,55 510 290,70 468,04 2251,93 425,55 515 270,19 469,59 23168,21 429,31 600 292,93 470,70 23851,39 430,94 625 302,34 471,38 24301,47 432,49 625 310,34 471,38 24301,47 432,49 625 310,86 471,67 24518,43 435,94 625 320,77 471,60 24502,28 455,30 626 310,86 471,67 24518,43 435,94 625 320,77 471,60 24502,28 455,30 626 310,86 471,67 24518,43 435,94 627 300 319,63 224,39 534,82 233,62 325 327,88 224,49 534,82 233,62 325 322,36 224,49 534,82 233,62 325 322,36 224,49 534,82 233,62 325 322,36 224,89 332,21 224,39 335,49 340,41 2867,53 235,49 340 330,10 30,41 2667,53 225,49 340 330,10 30,41 2667,53 225,49 340 330,40 330,40 30,41 2667,53 225,49 340 330,40 330,40 30,41 2667,53 225,49 340 335,44 322,49 352,58 322,36 324,49 332,21 225,43 455 327,58 327,58 324,89 332,21 225,43 457 337,48 322,96 459,88,22 256,51 60 344,67 389,15 6492,78 271,89 600 349,41 410,14 7694,65 222,77 600 340,70 248,18 109,48 605 354,11 429,09 8846,64 229,99 605 344,67 389,15 6492,78 271,89 606 354,11 429,09 8846,64 229,99 607 340,70 248,81 109,56 222,27 607 340,70 248,81 109,56 222,27 607 340,70 248,81 109,56 222,27 607 340,70 248,81 109,56 222,27 607 340,70 248,81 109,56 222,27 607 340,70 248,81 109,56 222,27 607 340,70 248,81 109,56 222,27 607 340,70 248,81 106,57 222,27 607 340,70 248,81 106,57 222,27 607 340,70 248,81 106,57 222,27 607 340,70 248,81 106,57 222,27 607 340,70 248,81 106,57 222,27 607 340,70 248,81 106,57 222,27 607 340,70 248,81 106,57 222,27 607 340,70 248,81 106,57 222,27 607 340,7	BiSrFe ₂ O _{5,5}	294,94±22	92±0,06	0,262±0,02	298,15 - 673		
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1	Temperature, K	$C_p^{\circ}(T)$	S°(T)	F ^{õõ} (T)	H°(T)-H°(298,15)		
325	1		3	4	5		
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	675	397,15	247,76	9289,22	233,99		

CONCLUSIONS

Thus, for the first time, the isobaric heat capacities for manganite $BiB\alpha Mn_2O_{5,5}$ and ferrites $BiSrFe_2O_{5,5}$, $BiC\alpha Fe_2O_{5,5}$ in the temperature interval from 298,15 to 673 K were experimentally determined. The equations that describe their dependence on temperature have been obtained. The heat capacity shifts probably belonging to type II phase transitions were identified during measurements of the heat capacity of $BiB\alpha Mn_2O_{5,5}$ at 573 K. The values of the thermodynamic functions $C^{\circ}_{p}(T)$, $H^{\circ}(T)$ - $H^{\circ}(298,15)$, $S^{\circ}(T)$, $F^{**}(T)$ were calculated. The experimental results extend the thermodynamic data pool on complex inorganic crystalline compounds.

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