

## 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  $\text{BiB}\alpha\text{Mn}_2\text{O}_{5.5}$  and ferrites  $\text{BiSrFe}_2\text{O}_{5.5}$ ,  $\text{BiCaFe}_2\text{O}_{5.5}\text{M}$  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  $^{\circ}\text{C}_p \sim f(T)$  of manganite  $\text{BiB}\alpha\text{Mn}_2\text{O}_{5.5}$  was determined. The values of the thermodynamic functions  $^{\circ}\text{C}_p(T)$ ,  $\text{H}^{\circ}(T) - \text{H}^{\circ}(298,15)$ ,  $\text{S}^{\circ}(T)$ ,  $\text{F}^{**}(T)$  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  $\text{Bi}_2\text{O}_3 - \text{Me}^{\text{II}}\text{O} - \text{Mn}_2\text{O}_3$ ,  $\text{Bi}_2\text{O}_3 - \text{Me}^{\text{II}}\text{O} - \text{Fe}_2\text{O}_3$  ( $\text{Me}^{\text{II}}$  - 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  $\text{Ln}_{1-x}\text{A}_x\text{MnO}_3$  ( $\text{Ln}=\text{La}^{3+}$ ,  $\text{Pr}^{3+}$ ,  $\text{Nd}^{3+}$  etc. and  $\text{A}=\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$  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  $\text{BiB}\alpha\text{Mn}_2\text{O}_{5.5}$  and ferrites  $\text{BiSrFe}_2\text{O}_{5.5}$  and  $\text{BiCaFe}_2\text{O}_{5.5}$ . Investigated manganites and ferrites were synthesized by solid-phase reaction of stoichiometrically appropriate mixtures of chemically pure oxides  $\text{Bi}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3$ ,  $\text{Mn}_2\text{O}_3$  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:  $\text{BiB}\alpha\text{Mn}_2\text{O}_{5.5}$  -  $a=3,79$ ,  $b=5,67$ ,  $c=23,2$  Å,  $V_{\text{un.cell.}}=498,6$  Å<sup>3</sup>,  $Z=4$ ,  $C_{\text{rad.}}=7,24$ ,  $C_{\text{picn.}}=7,23$  g/cm<sup>3</sup>,  $\text{BiCaFe}_2\text{O}_{5.5}$  -  $a=11,1$  Å,  $V_{\text{un.cell.}}=1382$  Å<sup>3</sup>,  $Z=8$ ,  $C_{\text{rad.}}=6,02$ ,  $C_{\text{picn.}}=3,03$  g/cm<sup>3</sup>,  $\text{BiSrFe}_2\text{O}_{5.5}$  -  $a=11,1$  Å,  $V_{\text{un.cell.}}=1364$  Å<sup>3</sup>,  $Z=16$ ,  $C_{\text{rad.}}=9,66$ ,  $C_{\text{picn.}}=9,60$  g/cm<sup>3</sup> [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  $K_\tau$ . 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:

$$K_\tau = \frac{C_{Cu}}{\tau_{Cu,t} - \tau_T^0} \quad (1)$$

where  $C_{Cu}$  - total heat capacity of the copper sample, J/K;  $\tau_{Cu,t}$  - the average delay of heat meter in experiments with copper sample, sec;  $\tau_T^0$  - 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:

$$C_{Cu,smpl} = C_{Cu,std} \cdot M_{smpl} \quad (2)$$

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

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

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

where  $K_T$  - thermal conductivity of a heat meter;  $m_0$  - mass of studied substance in kg;  $\tau_T$  - temperature delay on heat meter, sec;  $\tau_T^0$  - 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•K)) were calculated and for the average molar heat capacity values, the random errors ( $\Delta^\circ$ , J/(mol•K)) were also calculated [11].

The calorimeter was calibrated by measuring standard heat capacity of  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>. The obtained value of  $C^\circ(298,15)\text{Al}_2\text{O}_3$  [76,0 J/mol•K] satisfies the recommended value [79,0 J/mol•K] [12].

Table 1: The experimental data on the heat capacity

BiBaMn <sub>2</sub> O <sub>5,5</sub>		
Temperature, K	$C^\circ + \bar{\delta}$ (J/g•K)	$C^\circ + \Delta^\circ$ (J/mol•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<sub>2</sub>O<sub>5,5</sub>.

In the study of the heat capacity of lanthanum manganite within the temperature range from 548 K to 598K, the shifts of value  $C^\circ \sim f(T)$ , 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  $\Delta T$  (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 (~3%). Further, according to known experimental data on the  $C_p^\circ \sim f(T)$  and calculated values of  $S^\circ(298,15)$ , the temperature dependence of the thermodynamic functions  $C_p^\circ(T)$ ,  $H^\circ(T) - H^\circ(298,15)$ ,  $S^\circ(T)$ ,  $F^{**}(T)$  were calculated (Table 3).

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

Compound	$C_p = \alpha + BT + CT^{-2}$			$\Delta T, K$
	$\alpha$	$B \cdot 10^{-3}$	$C \cdot 10^6$	
BiBaMn <sub>2</sub> O <sub>5,5</sub>	71,24±5,5	415±0,03	0,132±0,01	298,15 - 673
BiCaFe <sub>2</sub> O <sub>5,5</sub>	180,81±11	321±0,02	0,152±0,03	298,15 - 673
BiSrFe <sub>2</sub> O <sub>5,5</sub>	294,94±22	92±0,06	0,262±0,02	298,15 - 673

Table 3: Thermodynamic functions of the manganites and ferrites in the temperature interval from 298,15 to 673 K.

Temperature, K	$C_p(T)$	$S^0(T)$	$F^0(T)$	$H^0(T) - H^0(298,15)$
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
BiSrFe <sub>2</sub> O <sub>5,5</sub>				
1	2	3	4	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
BiCaFe <sub>2</sub> O <sub>5,5</sub>				
1	2	3	4	5
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

## CONCLUSIONS

Thus, for the first time, the isobaric heat capacities for manganite  $\text{BiBaMn}_2\text{O}_{5.5}$  and ferrites  $\text{BiSrFe}_2\text{O}_{5.5}$ ,  $\text{BiCaFe}_2\text{O}_{5.5}$  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  $\text{BiBaMn}_2\text{O}_{5.5}$  at 573 K. The values of the thermodynamic functions  $C_p^\circ(T)$ ,  $H^\circ(T) - H^\circ(298,15)$ ,  $S^\circ(T)$ ,  $F^{**}(T)$  were calculated. The experimental results extend the thermodynamic data pool on complex inorganic crystalline compounds.

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