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Thermodynamic study of ferrites $LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr)

New ferrites $LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr) were obtained by high-temperature synthesis on ceramic technology. By powder X-ray diffraction established that compounds crystallize in the tetragonal singonia, the parameters of its crystal lattices are determined. The heat capacity of ferrites has been defined by dynamic calorimetric method at 298.15–673 K and detected the presence of phase transitions of type II. The equations describing the dependence in the range 298.15–673 K are derived taking into account the phase transitions.

Key words: heat capacity, temperature dependence of the heat capacity, phase transitions, ferrites, perovskite.

Introduction

Oxides of variable valence metals with the perovskite structure are a class of materials that exhibit a number of interesting and important effects for practical applications: metal-insulator transitions, magnetic ordering of different nature (ferromagnetism and antiferromagnetism), superconductivity. Therefore, they are of interest among scientists around the world, carrying out the theoretical researches aimed to understanding the nature of these physical effects, and applied studies in the field of technology of perovskite oxides. It is possible to create variety of devices based on them due to the electronic properties of oxides. This direction of study has been called oxide electronics [1].

The aim of this work is calorimetric study of ferrites' heat capacity $LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr) in the range of temperature 298.15–673 K. New ferrites synthesized by solid-phase reaction at high temperature at presence of oxides La_2O_3, Fe_2O_3, magnesium carbonate, calcium and strontium.

There were established by the method of radiography that ferrites crystallize in the dimetric system with the next lattice parameters: $LaMg^{II}_3Fe_5O_{12}$; $a = 11{,}105$ Å; $c = 17{,}1$ Å; $V^o = 2109{,}3$ Å^3; 263,66 Å^3; 8; $\rho_{roentgen} = 4{,}3$ g/cm^3; $\rho_{picn} = 4{,}45 \pm 0{,}09$ g/cm^3, $LaCa^{II}_3Fe_5O_{12}$; $a = 11{,}005$ Å; $c = 16{,}91$ Å; 2047,89 Å^3; 255,99 Å^3; 8; $\rho_{roentgen} = 4{,}74$ g/cm^3; $\rho_{picn} = 4{,}82 \pm 0{,}04$ g/cm^3, $LaSr^{II}_3Fe_5O_{12}$; $a = 11{,}1$ Å; $c = 16{,}98$ Å; 2076,57 Å^3; 259,57 Å^3; 8; $\rho_{roentgen} = 5{,}58$ g/cm^3; $\rho_{picn} = 5{,}61 \pm 0{,}07$ g/cm^3.

Experimental part

Isobaric heat capacity of ferrites was investigated in the temperature range 298.15–673 K on ITS-400 calorimeter. Duration of the measurements over the all temperature range with the processing of the experimental data was not more than 2.5 hours. Maximum permissible error of the instrument on passport data was ±10.0 %. Calibration of the device was carried out by determining the thermal conductivity of K_T heat meter [2, 3]. Several experiments carried out with a copper pattern and an empty ampoule for this purpose. Lag time to achieve the desired temperature was recorded using microvoltampermeter F136 and digital stopwatch with a step of 25 K. The heat capacities of samples were also measured at 25 K. At each temperature five parallel experiments were carried out, the results were averaged due to method [4], then were calculated random components of error (Δ) for $C_{p(sp)}$ (specific) and C°_p (mol) of the specific heats values.

By method of powder radiography there were established that compounds crystallize in the dimetric system, the parameters of their crystal lattices are determined. By method of dynamic calorimeter at 298.15–673 K the heat capacity of ferrites has been defined, wherein the presence of phase transitions of type II revealed. The equations describing the dependence at 298.15–673 K temperature were derived taking into account the phase transitions. There are results of the calorimetric studies in Table 1 below.

Table 1

The experimental values of the heat capacity of compounds $LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr)

T, K	$C_p \pm \delta$	$C°_p \pm \Delta$	*T*, K	$C_p \pm \delta$	$C°_p \pm \Delta$
$LaMg_3Fe_5O_{12}$					
298	0,73±0,01	495,69±4,88	498	0,60±0,03	411,09±21,60
323	0,94±0,06	645,37±38,26	523	0,58±0,04	396,44±25,64
348	0,87±0,05	594,43±36,85	548	0,51±0,03	350,16±17,72
373	0,79±0,05	539,65±34,37	573	0,42±0,02	288,60±14,71
398	0,69±0,14	471,78±96,09	598	0,35±0,02	242,05±14,09
423	0,61±0,04	419,21±24,19	623	0,34±0,03	234,12±17,80
448	0,54±0,03	368,02±21,88	648	0,35±0,02	240,96±14,51
473	0,55±0,03	376,73±20,75	673	0,40±0,03	271,60±17,38
$LaCa_3Fe_5O_{12}$					
298	0,39±0,30	285,62±218,95	498	0,56±0,06	407,69±45,08
323	0,87±0,05	636,52±34,21	523	0,60±0,04	439,24±30,84
348	0,82±0,13	596,31±94,01	548	0,70±0,05	510,10±38,83
373	0,73±0,30	534,79±220,48	573	0,53±0,05	387,46±34,97
398	0,66±0,03	479,87±21,46	598	0,37±0,03	270,55±21,97
423	0,57±0,03	416,94±25,18	623	0,28±0,05	207,94±35,37
448	0,53±0,65	385,18±473,80	648	0,24±0,30	178,86±220,92
473	0,49±0,04	359,00±30,53	673	0,22±0,02	158,54±12,55
$LaSr_3Fe_5O_{12}$					
298	0,70±0,00	610,86±3,04	498	0,51±0,02	444,51±17,17
323	0,88±0,05	769,09±47,92	523	0,47±0,02	409,61±18,10
348	0,83±0,05	724,18±45,57	548	0,42±0,12	370,43±103,96
373	0,70±0,04	613,67±31,84	573	0,38±0,02	330,44±13,55
398	0,61±0,03	535,80±22,22	598	0,35±0,02	304,52±13,18
423	0,55±0,04	480,56±33,48	623	0,35±0,02	304,89±17,56
448	0,49±0,03	426,17±25,00	648	0,37±0,16	322,95±143,05
473	0,43±0,03	375,97±24,30	673	0,40±0,18	350,93±159,62

Results and discussion

The equation of temperatures dependence of the heat capacity is derived (Table 2). The dependence heat capacity on temperature is depicted taking into account the experimental data on $C_p°(T)$ (Fig. 1–3).

Table 2

Equations of the temperature dependence of the specific heats of ferrites $LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr)

Compounds	Coefficients of the equation $C^0_p = a + b\cdot T + c\cdot T^{-2}$, J/(mol·K)			ΔT, K
	a	*b*	$c\cdot 10^{-5}$	
$LaMg_3Fe_5O_{12}$	–1500,24	6,45	64,0877	298,15–323,0
	1059,98	–1,70	140,6381	323,0–448,0
	–4617,36	7,34	3407,81	448,0–498,0
	7062,98	–8,89	–5517,27	498,0–573,0
	–6783,18	7,49	9136,514	573,0–673,0
$LaCa_3Fe_5O_{12}$	–3262,26	12,70	–212,122	298,15–323,0
	718,25	–1,00	250,4178	323,0–473,0
	–933,34	2,46	291,1446	473,0–548,0
	–7580,43	7,67	11675,89	548,0–673,0
$LaSr_3Fe_5O_{12}$	17089,38	–33,06	–5886,57	298,15–348
	46,12	–0,13	876,2147	348,0–473
	20615,07	–26,82	–16894,6	473,0–523,0
	–4252,29	5,01	5590,562	523,0–673,0

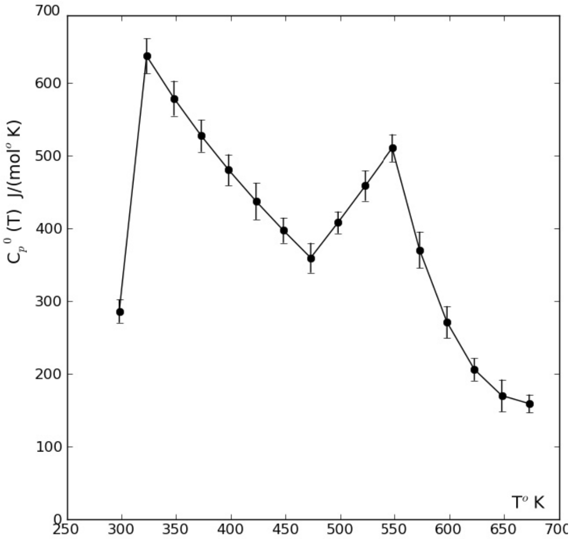

Figure 1. Dependence of the heat capacity $LaCa_3Fe_5O_{12}$ on temperature

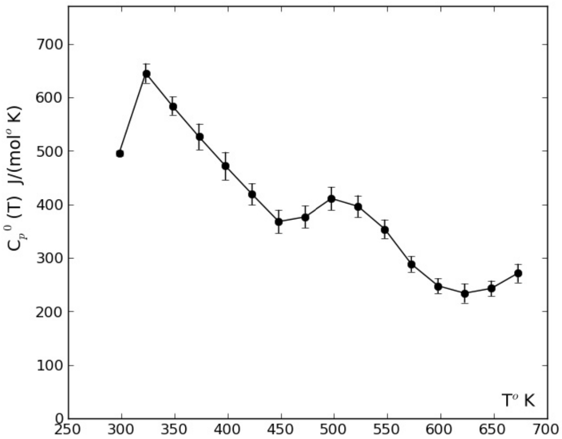

Figure 2. Dependence of the heat capacity $LaMg_3Fe_5O_{12}$ on temperature

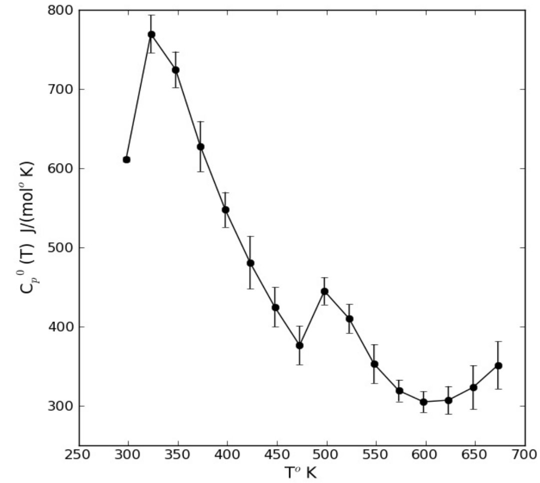

Figure 3. Dependence of the heat capacity $LaSr_3Fe_5O_{12}$ on temperature

Data from Table 1 shows that the error of measurement of the heat capacity fit within permissible accuracy of the calorimeter. It is found out that a number of ferrites has a sharp jumps in the dependence curve of the heat capacity $C_p°\sim f(T)$. This fact occurs probably due to the presence of phase transitions type-II. These transitions may be caused by cationic redistributions, changes of the coefficients of thermal expansion, the advent of the Curie and Neel [5], etc.

It is known that in compounds containing paramagnetic transition metal ions, often occur heat capacity anomaly connected with the Schottky effect.

Since the possibilities of calorimeter IT-400 do not allow to calculate the standard entropy of the studied ferrites directly from the experimental data on $C_p°(T)$, it was estimated using the method of ion entropy increments [6]. Also coefficients of the temperature dependence of the heat capacity are determined (Table 2):

$$H^0(T) - H^0(298.15) = \int_{298.15}^{T} C_p^0 dT\ ; \quad (1)$$

$$S^0(T) = S^0(298.17) + \int_{298.15}^{T} \frac{C_p}{T} dT\ ; \quad (2)$$

$$\Phi^{xx}(T) = S^0(T) - \frac{H^0(T) - H^0(298.15)}{T}\ . \quad (3)$$

In continuation of our studies there were calculated temperature dependence of thermodynamic functions ($S°(T)$, $H°(T) – H°(298,15)$) using the ratios 1, 2, 3 and the experimental data of $C_p°\sim f(T)$ was applied. $S°(T)$, $H°(T) – H°(298,15)$ and $\Phi^{xx}(T)$ ferrites (Table 3).

Table 3

Thermodynamic functions $LaM^{II}{}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr). ($C^0{}_p(T)$, $S^0(T)$, $\Phi^{xx}(T)$, $H^0(T) – H^0(298,15)$)

T, K	$C^0{}_p(T)$	$S^0(T)$	$\Phi^{xx}(T)$	$H^0(T) – H^0(298,15)$
$LaMg_3Fe_5O_{12}$				
298	495,7±4,9	365,3 ± 11	365,3 ± 11	–
323	645,4±38,3	410,9 ± 41	367,0 ± 37	14172,4 ± 891
348	594,4±36,9	456,7 ± 46	371,8 ± 37	29533,0 ± 1858
373	539,7±34,4	495,2 ± 50	378,9 ± 38	43411,2 ± 2731
398	471,8±96,1	527,6 ± 53	387,2 ± 39	55886,0 ± 3515
423	419,2±24,2	554,8 ± 55	396,3 ± 40	67017,8 ± 4215
448	368,0±21,9	577,4 ± 58	405,8 ± 41	76853,3 ± 4834
473	376,7±20,7	597,5 ± 60	415,4 ± 42	86103,4 ± 5416
498	411,1±21,6	617,7 ± 62	425,1 ± 43	95903,2 ± 6032
523	396,4±25,6	637,6 ± 64	434,8 ± 43	106060,9 ± 6671
548	350,2±17,7	655,2 ± 66	444,4 ± 44	115494,2 ± 7265
573	288,6±14,7	669,6 ± 67	454,0 ± 45	123570,8 ± 7773
598	242,1±14,1	681,0 ± 68	463,2 ± 46	130216,6 ± 8191
623	234,1±17,80	690,8 ± 69	472,2 ± 47	136190,7 ± 8566
648	240,9±14,5	700,1 ± 70	480,8 ± 48	142112,4 ± 8939
673	271,6±17,4	709,8 ± 71	489,1 ± 49	148508,9 ± 9341
$LaCa_3Fe_5O_{12}$				
298,15	285,62±21,9	411,9 ± 12	411,8 ± 12	–
323	636,52±34,2	448,7 ± 45	413,1 ± 41	11517,8 ± 724
348	596,31±94,0	494,0 ± 49	417,3 ± 42	26688,4 ± 1679
373	534,79±22,5	532,3 ± 53	423,8 ± 42	40489,9 ± 2547
398	479,87±21,5	564,9 ± 56	431,6 ± 43	53062,8 ± 3338
423	416,94±25,2	592,9 ± 59	440,4 ± 44	64514,7 ± 4058
448	385,18±47,8	616,8 ± 62	449,5 ± 45	74928,9 ± 4713
473	359,00±30,5	637,3 ± 64	458,9 ± 46	84371,4 ± 5307
498	407,69±45,1	657,0 ± 66	468,4 ± 47	93950,9 ± 5910
523	439,24±30,8	678,2 ± 68	477,9 ± 48	104770,7 ± 6590
548	510,10±38,8	700,8 ± 70	487,6 ± 49	116871,2 ± 7351
573	387,46±34,9	720,3 ± 72	497,3 ± 50	127779,4 ± 8037
598	270,55±21,9	733,9 ± 73	506,9 ± 51	135708,0 ± 8536
623	207,94±35,4	743,5 ± 74	516,2 ± 52	141592,7 ± 8906
648	178,86±22,9	750,8 ± 75	525,2 ± 53	146224,9 ± 9198
673	158,54±12,6	756,9 ± 76	533,7 ± 53	150278,2 ± 9453
$LaSr_3Fe_5O_{12}$				
298,15	285,6±21,95	444,8 ± 13	444,8 ± 44	–
323	636,5±34,21	501,5 ± 50	446,9 ± 45	17632,9 ± 1109
348	596,3±24,01	558,3 ± 56	452,9 ± 45	36662,8 ± 2306
373	534,8±22,48	605,1 ± 61	461,6 ± 46	53514,1 ± 3366
398	479,9±21,46	643,1 ± 64	471,9 ± 47	68163,7 ± 4287
423	416,9±25,18	674,4 ± 67	482,9 ± 48	80987,5 ± 5094
448	385,2±47,80	700,4 ± 70	494,4 ± 49	92277,6 ± 5804
473	359,0±30,53	722,1 ± 72	505,9 ± 51	102264,0 ± 6432
498	407,7±40,08	743,7 ± 74	517,2 ± 52	112757,9 ± 7092
523	439,2±30,84	765,0 ± 76	528,6 ± 53	123628,9 ± 7776
548	510,1±38,83	782,7 ± 78	539,8 ± 54	133102,5 ± 8372
573	387,5±34,97	797,6 ± 80	550,7 ± 55	141449,3 ± 8897
598	270,6±21,97	810,8 ± 81	561,3 ± 56	149203,2 ± 9385
623	207,9±35,37	823,3 ± 82	571,6 ± 57	156812,2 ± 9863
648	178,9±22,92	835,6 ± 84	581,5 ± 58	164655,1 ± 10357
673	158,5±12,55	848,3 ± 85	591,2 ± 59	173054,5 ± 10885

Errors of the temperature dependence of the thermodynamic functions were calculated based on an average error of the heat capacity and entropy calculation accuracy (3 %).

Conclusion

1. Isobaric heat capacity of iron $LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr) was measured at temperature 298.15–673 K for the first time.
2. It is revealed a sharp jumps in the heat capacity connected with the presence of phase transitions of type II.
3. Equations of the temperature dependence of the heat capacity have been calculated taking into account the temperatures of phase transitions type II.
4. The functions $S°(T)$, $H°(T) – H°(298,15)$ and $\Phi^{xx}(T)$ were calculated in the certain temperature interval.

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$LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr) құрамды ферриттердің термодинамикалық зерттеулері

Мақалада керамикалық технология әдісі бойынша жоғары температуралық синтезбен жаңа ферриттер алынған $LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr). Қосылыстардың тетрагоналды сингония бойынша кристалданатыны ұнтақты рентгенография әдісі арқылы дәлелденді, олардың кристалл торларының параметрлері анықталды. Ферриттердің жылусыйымдылықтары 298,15–673 К температура аралығында динамикалық калориметрия әдісімен зерттелді және бұл жағдайда 2-ші реттік фазалық ауысу орын алатыны көрсетілді. Фазалық ауысуларды ескере отырып, 298,15–673 К температура аралығында тәуелділікті сипаттайтын теңдеулер қорытылып шығарылды.

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Термодинамические исследования ферритов состава $LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr)

В статье высокотемпературным синтезом по керамической технологии получены новые ферриты $LaM^{II}_3Fe_5O_{12}$ (M^{II} — Mg, Ca, Sr). Методом порошковой рентгенографии установлено, что соединения кристаллизуются в тетрагональной сингонии, определены параметры их кристаллических решеток. Методом динамической калориметрии в интервале 298,15–673 К определены теплоемкости ферритов, при этом выявлено наличие фазовых переходов II рода. С учетом фазовых переходов выведены уравнения, описывающие зависимость, в интервале 298,15–673 К.