NOTATION. T_i and $\hat{T}_i$, temperature and mean temperature over the cross section for component i; q_{ij} heat flux density from component i to component j; c_i, ρ_i, λ_{ri}, λ_{zi} specific heat, density, and radial and axial thermal conductivities correspondingly; α_c and R_T, heat-transfer coefficient and contact thermal resistance between components; α_{g0} (α_{gH}), heat-transfer coefficient between gas and composite; T_{g0} (T_{gH}), gas temperature; R_f rod radius.

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SPECIFIC HEAT AND THERMODYNAMIC CHARACTERISTICS OF THE SYSTEM Bi—Sr—Ca—Mg—Cu—O IN THE TEMPERATURE RANGE 4.2-300 K

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Results are presented from an experimental study of specific heat of the superconductive metal oxide system Bi—Sr—Ca—Mg—Cu—O over the temperature range 4.2-300 K. Temperature-dependent components of entropy and enthalpy are calculated. A correlation is made between T_c and standard entropy and enthalpy values for high temperature superconductors of various classes.

There is a current trend toward deeper study of high temperature superconductor (HTSC) materials in order to accumulate information on this phenomenon, the physical nature of which is still unclear. In this respect the thermodynamic characteristics and their standard values are important for constructing phase diagrams in various coordinate systems, determining the character of phase transitions, etc. [1-3]. Such data are very lacking for HTSC materials [4-6].

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TABLE 1. Some Characteristics of Bi–Sr–Ca–Mg–Cu–O Specimens

Specimen No.	Composition	ρ, kg/m^3	Mass, g	Formula weight	T_c, K (R)	T_c, K (C_p)
1	$Bi_2Sr_2CaCu_2O_y$	4347	1,267	888,4	79	85
2	$Bi_2Sr_2Ca_{0,8}Mg_{0,2}Cu_2O_y$	5400	1,749	885,2	77	60
3	$Bi_2Sr_2Ca_{0,5}Mg_{0,5}Cu_2O_y$	5200	1,810	880,5	58	75,5
4	$Bi_2Sr_2MgCu_2O_y$	5400	1,707	872,6	<4,2	<4,2
5	$Bi_2Sr_2CaMg_{1,0}Cu_2O_y$	4000	1,210	912,7	75	74
6	$Bi_2Sr_2CaMg_{10,0}Cu_2O_y$	4400	1,562	1131	88	92

The present study will offer experimental results on the specific heat C_p of a system of superconductive metal oxides $Bi_2Sr_2Ca_{1-x}Mg_xCu_2O_y$ (x = 0, 0.2, 0.5, 1.0) and $Bi_2Sr_2CaMg_x$-Cu_2O_y (x = 1.0 and 10.0) and values of the thermodynamic functions calculated from C_p: the entropy $S^0(T)$ and enthalpy $H^0(T) - H^0(0)$. Separation of the total heat capacity into electron and phonon components permits calculation of the temperature-dependent portions of the entropy $S^0(T)_{el}$ and $S^0(T)_p$ and enthalpy $H^0(T)_{el} - H^0(0)_{el}$ and $H^0(T)_p - H^0(0)_p$.

Specimen synthesis was carried out with well dried finely dispersed powders of the oxides Bi_2O_3, MgO, CuO and carbonates $SrCO_3$ and $CaCO_3$ at a temperature of 800-870°C in air (specimens Nos. 1, 2, 3, 4, 5, Table 1). Specimen No. 6, containing magnesium in the amount x = 10, was synthesized at 1100°C over 1 hr, then annealed at 810°C for 24 hr in air. The superconductive properties, phase composition, and microstructural characteristics of these specimens were reported in [7-10].

Specific heat measurements were performed with the automated low-temperature calorimetric apparatus of [11] in an adiabatic regime with periodic introduction of heat with an uncertainty of not more than 1% over the temperature range 5-50 K, 2% over 50-80 K, and 0.3% for 80-300 K. The characteristics of the specimens studied are presented in Table 1. Figure 1 shows the experimental data for $C_p(T)$ for the six compositions studied.

Estimates of the Sommerfeld coefficients and Debye temperature at T = 0, characterizing the electron and phonon components of the heat capacity in the low temperature limit (4.2-14 K) showed that for specimens which are superconductive in this range (specimens Nos. 1, 2, 3, 5, 6) $\gamma(0)$ can be considered equal to zero. For specimen No. 4, in which all the calcium atoms were replaced by magnesium, and which does not enter the superconductive state at 4.2 K, $\gamma(0) = 0.032$ J/(kg·K^2). For specimens Nos. 1, 2, 3, 5, 6 γ was evaluated from the change in heat capacity at T_c in the Bardeen–Cooper–Schrieffer theory approximation. Results are presented in Table 2. The electron state density at the Fermi level $N(E_F)$ was also calculated in the BCS weak bond approximation with the expression: $N(E_F) = (3/(2\pi^2 k_B^2))\gamma$, where k_B is Boltzmann's constant.

Considering the temperature dependence of the electron component of the heat capacity C_p for the normal state in the form γT and for the superconductive state in the form of an exponential with exponent $2\Delta/T_c = 4$ [12], C_p was separated into electron and phonon components and the temperature-dependent portions of the electron and phonon entropy $S^0(T)_{el}$, $S^0(T)_p$ and

TABLE 2. Values of $\Delta C_p/T_c$, γ, $N(E_F)$, Θ_D (0), Θ_D (100 K) Θ_D (200 K) and Θ_D (300 K) for System Bi–Sr–Ca–Mg–Cu–O

Specimen No.	$\Delta C_p/T_c$, J/(kg·K^2)	γ, J/(kg·K^2)	$N(E_F)$ states/eV·atom	Θ_D (0), K	Θ_D(100 K) K	Θ_D(200 K) K	Θ_D(300 K) K
1	0,071	0,049	0,55	220	432	513	510
2	0,058	0,041	0,51	230	434	512	532
3	0,050	0,035	0,44	230	440	513	541
4	0,000	0,032	0,40	250	453	570	604
5	0,067	0,047	0,57	240	430	460	365
6	0,040	0,028	0,27	220	515	550	516

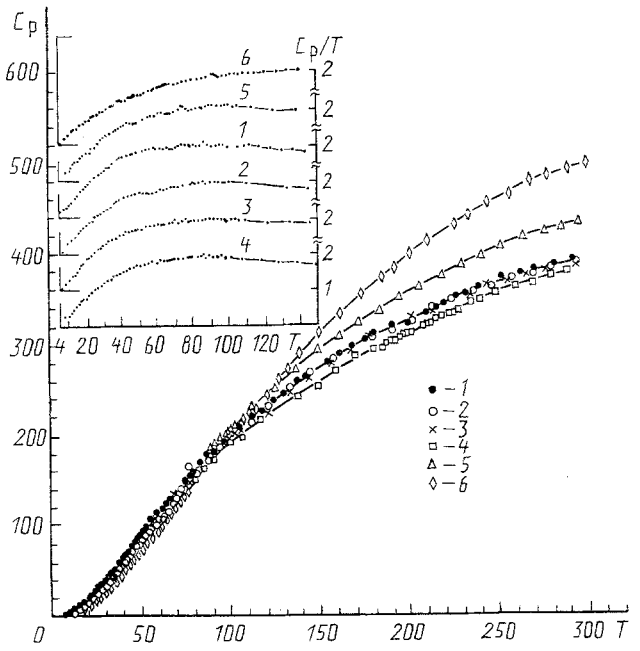

Fig. 1. Temperature dependence of specific heat C_p (J/(kg·K)) of Bi–Sr–Ca–Mg–Cu–O over interval 4.2-300 K; insert shows C_p/T (J/(kg·K²)) vs. T (numerals 1-6 correspond to specimen Nos. in Table 1).

enthalpy $H^0(T)_{el} - H^0(0)_{el}$, $H^0(T)_p - H^0(0)_p$ were calculated for the HTSC's studied. Figure 2 shows temperature dependences of total entropy $S^0(T)$ and total enthalpy $H^0(T) - H^0(0)$ for the system Bi–Sr–Ca–Mg–Cu–O. Table 3 presents standard values of total and phonon entropy, as well as total and phonon enthalpy ($S^0_{298,15}$ and $H^0_{298,15}-H^0_0$).

The results of calculating the thermodynamic functions reveal that in the system $Bi_2Sr_2Ca_{1-x}Mg_xCu_2O_y$ partial replacement of calcium atoms by magnesium, accompanied by intense degradation of superconductive properties [8], followed by complete replacement of Ca by Mg, leads to a decrease in standard values of entropy and enthalpy, both total and phonon values. On the other hand, upon addition of magnesium to $Bi_2Sr_2CaMg_xCu_2O_y$ in the quantity x = 1.0 and 10.0 $S^0_{298,15}$ and $H^0_{298,15}-H^0_0$, total and phonon, increase.

For comparison of the present standard entropy and enthalpy values for a basic $Bi_2Sr_2CaCu_2O_y$ specimen (Table 3) we present data from [5] for the composition $Bi_2Sr_2Ca_{1,2}Cu_{1,8}O_{8+\delta}$: $S^0_{298,15}$ = 458 J/(kg·K), $H^0_{298,15}-H^0_0$ = 70920 J/kg and for the composition $Bi_2Sr_{2,3}Ca_{0.7}Cu_2O_{8+\delta}$: $S^0_{298,15}$ = 449 J/(kg·K) and $H^0_{298,15}-H^0_0$ = 68000 J/kg. One may note the completely satisfactory agreement of the results. Figure 3 shows the dependence of standard total entropy and enthalpy values on superconductive transition temperature T_c for various compositions and classes of HYSC material. As is evident from the figure, there is a definite correlation between T_c and $S^0_{298,15}$, T_c and $H^0_{298,15}-H^0_0$: HTSC compounds having higher values of the standard thermodynamic functions correspond to higher T_c values also.

To summarize, we may conclude that with replacement of calcium atoms by magnesium in $Bi_2Sr_2CaCu_2O_y$, high temperature superconductive metal oxides $Bi_2Sr_2Ca_{1-x}Mg_xCu_2O_y$ are formed with small teamperature-dependent energy functions, while the functions decrease with increase in magnesium content; in contrast, addition of Mg to $Bi_2Sr_2CaCu_2O_y$ leads to formation of a system with higher thermodynamic parameter values. A correlation has been established between T_c and standard entropy and enthalpy values for HTSC materials.

NOTATION

C_p, total specific heat at constant pressure; $S^0(T)$, $S^0_{298,15}$, total entropy and standard value thereof; $S^0(T)_{el}$ and $S^0(T)_p$, electron and phonon entropy; $H^0(T)-H^0(0)$, $H^0_{298,15}-H^0_0$, temperature-dependent portion of total entropy and its standard value; $H^0(T)_{el} - H^0(0)$,

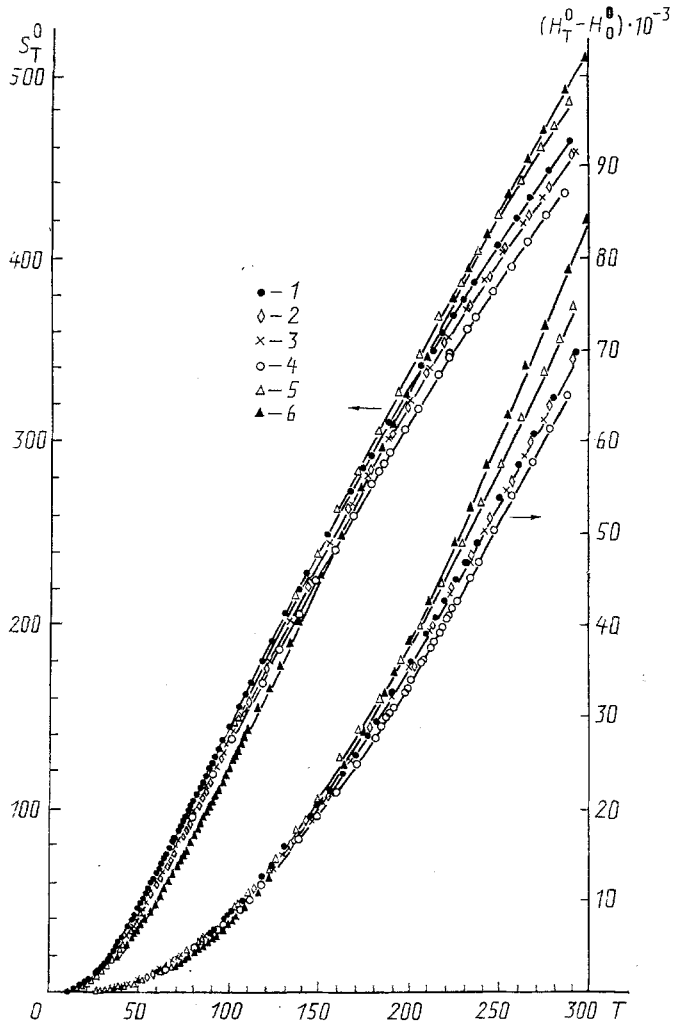

Fig. 2. Temperature dependence of thermodynamic functions S_T^0 (J/(kg·K)) and $H_T^0 - H_0^0$ (J/kg) for specimens Nos. 1-6 (Table 1).

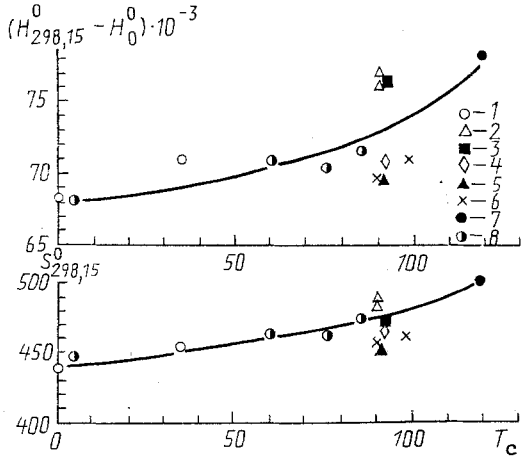

Fig. 3. Correlation between T_c (K) and the standard values of entropy $S_{298,15}^0$ (J/(kg·K)) and enthalpy $H_{298,15}^0$ (J/lg) for HTSC materials of various classes: 1) La-system [6], 2) Y [6], 3) Gd [6], 4) Ho [6], 5) Yb [6], 6) Bi [5], 7) Tl [5], 8) Bi—Mg (our data).

TABLE 3. Standard Entropy and Enthalpy Values for System Bi–Sr–Ca–Mg–Cu–O

Specimen No.	$S^0_{298.15}$ (total)	$S^0_{298.15}$ (phonon)	$H^0_{298.15}-H^0_0$ (total)	$H^0_{298.15}-H^0_0$ (phonon)
	J/(kg·K)		J/kg	
1	472	459	71480	69470
2	463	451	70880	68820
3	462	452	70340	68820
4	448	437	68060	66430
5	494	480	76780	74645
6	508	500	82930	81660

$H^0(T)_p - H^0(0)$, temperature-dependent portions of electron and phonon enthalpy; ρ, density; T_c, temperature of transition to superconductive state; $T_c(R)$, T_c determined by resistance measurements; $T_c(C_p)$, T_c determined from calorimetric measurements; γ, Sommerfeld constant; Θ_D (0), Θ_D (100 K), Θ_D (200 K) and Θ_D (300 K), characteristic Debye temperatures at 0, 100, 200, and 300 K respectively; $N(E_F)$, electron state density at Fermi level.

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