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# Thermodynamic properties of the rare earth borides and carbides in a wide temperature range

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**Abstract**

For the first time a systematic study was made of the heat capacity and enthalpy of the rare earth tetra- and hexaborides and sesqui- and dicarbides in the temperature range 60–2300 K.

## 1. Introduction

Rare earth compounds with boron and carbon are convenient and interesting model objects to ascertain the correlation between electronic structure and physical and thermodynamic characteristics. Up to now the heat capacity of the rare earth carbides and borides was studied only in the temperature range up to 30 K, except for La, Nd and Gd hexaborides, the heat capacity of which was measured up to 350 K [1]. The enthalpy of $LaB_6$ was measured in the temperature range 1100–2200 K [2] and those of $NdB_6$, $SmB_6$ and $EuB_6$ were studied in the temperature range 300–1200 K [3]. The present paper is concerned with a methodical study of the heat capacity and enthalpy of the rare earth borides and carbides of the cerium subgroup and gadolinium in the temperature range 60–2300 K.

## 2. Results and discussion

The heat capacity of borides and carbides in the temperature range 60–300 K were studied by the adiabatic technique with periodic heat supply, the error limit not exceeding 0.4% [4]. Enthalpy in the temperature range 400–2300 K was measured by the drop calorimetry method using vacuum calorimetric units with the error limit not exceeding 1.5% [5]. The units were calibrated using standard samples for the thermodynamic properties of $\alpha$-$Al_2O_3$ and Mo.

Rare earth carbides and tetraborides were prepared from the elements by arc melting in purified argon. The initial powders of hexaborides as well as gadolinium tetraborides were synthesized by borothermal reduction of the respective metal oxides in vacuum. Single crystals were grown from synthesized borides, except $EuB_6$ which was made by zone melting in purified argon. The results of chemical analysis of the samples are presented in Table 1.

Based on experimental data for the low temperature heat capacity the thermodynamic functions of the compounds at 298.15 K were calculated (Table 2). The heat capacity was extrapolated to 0 K [4] allowing for the phonon and electron component, while the Schottky contributions were taken into account implicitly. The values of the characteristic temperature possess an

TABLE 1. Chemical composition (wt.%) and lattice parameters (nm) of rare earth carbides and borides

| Compound | Metal | C | B | O | *a* | *c* |
|---|---|---|---|---|---|---|
| $LaC_2$ | 84.6 | 14.6 | – | 0.18 | 0.3933 | 0.6573 |
| $PrC_2$ | 85.0 | 14.5 | – | 0.22 | 0.3850 | 0.6431 |
| $NdC_2$ | 85.3 | 14.0 | – | 0.16 | 0.3819 | 0.6397 |
| $SmC_2$ | 85.2 | 14.0 | – | 0.24 | 0.3761 | 0.6317 |
| $GdC_2$ | 86.4 | 13.1 | – | 0.12 | 0.3712 | 0.6275 |
| $La_2C_3$ | 87.0 | 12.3 | – | 0.41 | 0.8816 | – |
| $Pr_2C_3$ | 87.8 | 11.8 | – | 0.95 | 0.8587 | – |
| $Nd_2C_3$ | 87.8 | 11.9 | – | 0.43 | 0.8542 | – |
| $Sm_2C_3$ | 87.7 | 12.0 | – | 0.27 | 0.8425 | – |
| $Gd_2C_3$ | 87.5 | 11.0 | – | 0.69 | 0.8332 | – |
| $LaB_4$ | 75.6 | 0.01 | 24.1 | 0.03 | 0.7323 | 0.4181 |
| $CeB_4$ | 77.2 | 0.01 | 22.4 | 0.5 | 0.7213 | 0.4106 |
| $PrB_4$ | 75.0 | 0.01 | 23.7 | 0.4 | 0.7236 | 0.4119 |
| $NdB_4$ | 75.9 | 0.01 | 22.3 | 0.3 | 0.7218 | 0.4102 |
| $GdB_4$ | 77.6 | <0.01 | 21.0 | <0.1 | 0.7150 | 0.4042 |
| $LaB_6$ | 68.2 | <0.2 | 31.7 | <0.2 | 0.4156 | – |
| $CeB_6$ | 68.1 | <0.2 | 31.4 | <0.2 | 0.4138 | – |
| $PrB_6$ | 68.1 | <0.2 | 31.1 | <0.2 | 0.4135 | – |
| $NdB_6$ | 68.7 | <0.2 | 31.4 | <0.2 | 0.4126 | – |
| $SmB_6$ | 69.6 | <0.2 | 30.1 | <0.2 | 0.4134 | – |
| $EuB_6$ | 70.1 | <0.2 | 30.0 | <0.2 | 0.4181 | – |
| $GdB_6$ | 70.7 | <0.2 | 29.3 | <0.2 | 0.4109 | – |

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TABLE 2. Heat capacity, entropy, free energy function (J $mol^{-1}$ $K^{-1}$) and enthalpy (J $mol^{-1}$) of the rare earth borides and carbides at 298.15 K

| Compound | $C_p$ | $S^0$ | $\Phi^0$ | $H^0$ (298.15 K) $-H^0(0)$ |
|---|---|---|---|---|
| $LaB_4$ | 79.07 | 64.9 | 27.3 | 11210 |
| $CeB_4$ | 73.95 | 66.4 | 29.4 | 11020 |
| $PrB_4$ | 72.84 | 74.1 | 34.9 | 11680 |
| $NdB_4$ | 72.71 | 71.6 | 36.6 | 11320 |
| $GdB_4$ | 68.75 | 62.4 | 27.2 | 10500 |
| $LaC_2$ | 66.30 | 72.6 | 34.3 | 11420 |
| $PrC_2$ | 78.00 | 76.7 | 34.1 | 12720 |
| $NdC_2$ | 73.91 | 80.8 | 36.3 | 13270 |
| $SmC_2$ | 67.22 | 84.0 | 44.1 | 11920 |
| $GdC_2$ | 59.25 | 71.3 | 35.4 | 10710 |
| $La_2C_3$ | 105.26 | 132.3 | 64.5 | 20230 |
| $Pr_2C_3$ | 120.77 | 157.8 | 82.0 | 22610 |
| $Nd_2C_3$ | 122.35 | 168.2 | 89.4 | 23520 |
| $Sm_2C_3$ | 125.08 | 154.3 | 75.8 | 23390 |
| $Gd_2C_3$ | 103.56 | 180.9 | 105.0 | 22620 |

TABLE 3. Temperature dependence parameters of the enthalpy (J $mol^{-1}$), heat capacity, entropy and free energy function (J $mol^{-1}$ $K^{-1}$) of the rare earth borides and carbides

| Compound | $T_m$ (K) | $A$ ($\times 10^3$) | $B$ | $C$ | $-D$ | $-E$ |
|---|---|---|---|---|---|---|
| $LaB_4$ | 2211 | 13.173 | 100.32 | 2587850 | 39762 | 529.08 |
| $CeB_4$ | 2254 | 22.396 | 85.63 | 2225388 | 34986 | 447.38 |
| $PrB_4$ | 2307 | 14.290 | 107.71 | 3522290 | 45198 | 573.26 |
| $NdB_4$ | 2307 | 10.522 | 116.55 | 4454762 | 50625 | 623.82 |
| $GdB_4$ | 2251 | 15.623 | 99.57 | 3567918 | 43042 | 534.26 |
| $LaB_6$ | 2296 | 14.926 | 138.15 | 4458324 | 57471 | 737.98 |
| $CeB_6$ | 2216 | 26.147 | 126.07 | 3773105 | 52568 | 657.23 |
| $PrB_6$ | 2115 | 27.104 | 123.82 | 3603537 | 51411 | 640.28 |
| $NdB_6$ | 2112 | 30.203 | 117.19 | 3207235 | 48382 | 600.20 |
| $SmB_6$ | 2157 | 28.341 | 129.99 | 3928009 | 54450 | 675.60 |
| $EuB_6$ | 2313 | 30.809 | 118.39 | 3558078 | 49969 | 605.87 |
| $GdB_6$ | 2309 | 21.823 | 131.86 | 4249919 | 55507 | 662.40 |
| $\alpha$-$LaC_2$ | 1369 | 1.575 | 71.84 | 575996 | 23491 | 340.95 |
| $\alpha$-$PrC_2$ | 1425 | 3.159 | 79.11 | 266373 | 24762 | 377.42 |
| $\alpha$-$NdC_2$ | 1436 | 2.410 | 78.48 | 533563 | 25401 | 370.60 |
| $\alpha$-$SmC_2$ | 1455 | 4.925 | 85.33 | 1870949 | 32154 | 415.63 |
| $\alpha$-$GdC_2$ | 1529 | 3.110 | 74.07 | 1482546 | 27334 | 380.98 |
| $\beta$-$LaC_2$ | 1900 | 10.714 | 61.49 | −3887632 | 6245 | 277.72 |
| $\beta$-$PrC_2$ | 2293 | 5.237 | 89.48 | −346340 | 25988 | 446.36 |
| $\beta$-$NdC_2$ | 2095 | 3.068 | 96.88 | 3666096 | 41454 | 495.76 |
| $\beta$-$SmC_2$ | 2067 | 4.930 | 97.55 | 453096 | 31041 | 492.10 |
| $\beta$-$GdC_2$ | 2278 | 3.676 | 91.02 | 3627838 | 39633 | 476.75 |
| $La_2C_3$ | 1633 | 20.107 | 104.35 | 985031 | 36203 | 479.73 |
| $Pr_2C_3$ | 1815 | 24.913 | 111.73 | 517188 | 37262 | 496.53 |
| $Nd_2C_3$ | 1892 | 23.328 | 112.04 | 320346 | 36554 | 485.83 |
| $Sm_2C_3$ | 1480 | 19.088 | 129.32 | 1388570 | 44910 | 601.75 |
| $Gd_2C_3$ | 1740 | 16.475 | 109.35 | 1387800 | 38721 | 459.80 |

"effective" behaviour. The coefficient of electron heat capacity $\gamma$ for the substances studied was taken to be $5\times10^{-3}$ J $mol^{-1}$ $K^{-2}$ as a mean value characteristic of the rare earth and transition carbide and boride phases [6]. The error limits for the entropy and enthalpy do not exceed 1% and 1.5% was the maximum error for the free energy function, except for $Gd_2C_3$. In this compound at about 130 K a heat capacity anomaly is observed that is not accompanied by changes in structure or magnetic susceptibility. The enthalpy of transition is 1.3 kJ $mol^{-1}$. For $Gd_2C_3$ the error limits are 2.1% and 2.9% respectively.

Experimental data for the enthalpy were approximated using the Mayer–Kelly equation:

$$H^0(T)-H^0\ (298.15\ \mathrm{K})=AT^2+BT+CT^{-1}+D \qquad (1)$$

The parameters in eqn. (1) were estimated by the least-square-root method with two boundary conditions: (1) $H^0(T)-H^0\ (298.15\mathrm{K})=0$ at 298.15 K and (2) the heat capacity values at 298.15 K. Since in the range 1350–1530 K for the rare earth dicarbides an uneven change in the enthalpy is observed resulting from the reversible $\alpha$–$\beta$ polymorphic transformation, for the $LaC_2$ $\beta$ modification the data were processed using only the first boundary condition. Proceeding from eqn. (1) the temperature dependences of heat capacity, entropy and the free energy function are as follows:

$$C_p(T)=2AT+B-CT^{-2} \qquad (2)$$

$$S^0(T)=2AT+B\ \ln T+0.5CT^{-2}+E \qquad (3)$$

$$\Phi(T)=AT+B\ \ln T-DT^{-1}-0.5CT^{-1}+E-B \qquad (4)$$

The parameters of eqns. (1)–(4) for the interval 298.15–$T_m$, where $T_m$ is the upper limit of the measurement for the compounds studies, are presented in Table 3. The error limit for the thermodynamic function determined using eqns. (1)–(4) does not exceed 1.5% for the enthalpy and 5% for the other characteristics.

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