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Abstract

Full Text

PHYSICAL CHEMISTRY

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ELECTRICAL PROPERTIES OF HEXABORIDES OF ALKALINE-EARTH, RARE-EARTH METALS AND THORIUM

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The study of the electrical properties of hexaborides of alkaline-earth and rare-earth metals, as well as of actinides, is of considerable interest both from the standpoint of understanding the nature of their physical properties and in connection with the practical use of these compounds as cathodes for powerful electronic generating devices ⁽¹⁾. In a number of works the electrical resistance ⁽²⁻⁴⁾, thermoelectric emf ^(4,5) of some of the indicated borides, and also the Hall coefficient of lanthanum and samarium borides ^(3,6) were determined. However, these data were not systematic; the determinations were carried out under different conditions, and the influence on the electrical properties of the porosity of the specimens, which sometimes reached 50%, was not always taken into account.

In the present work, simultaneous measurements of the specific electrical resistance, the Hall effect, the thermoelectric emf, and the thermal coefficient of electrical resistance were carried out on the same specimens. The specimens had the form of parallelepipeds measuring $12 \times 2.5 \times 0.5$ mm, which were cut by the electroerosion method from hot-pressed boride blanks. The porosity of the specimens ranged from 1.5 to 22%. To ensure reliable contacts, copper was electrolytically deposited on the ends of the specimens.

The Hall coefficient was measured in a field of 12,500 oersted. The absolute value of the thermoelectric emf was calculated taking into account the value of the thermoelectric emf of copper, with which the measurements were made as a pair ⁽⁷⁾.

The number of specimens of each compound ranged from 3 to 8, which made it possible to extrapolate with sufficient confidence the obtained values of electrical resistance and the Hall constant to zero porosity (using the method of least squares).

The values obtained are given in Table 1. In order to estimate the applicability of the one-zone model to the compounds under consideration, in accordance with work ⁽⁸⁾, the quantities

$$\delta = \frac{R}{e\rho^2} = n_+u_+^2 - n_-u_-^2$$

were determined (since, assuming charges of two signs, the Hall coefficient

$$R = \frac{1}{e} \cdot \frac{n_+u_+^2 - n_-u_-^2}{(n_+u_+ + n_-u_-)^2}$$

and the resistance

$$\rho = \frac{1}{e} \cdot \frac{1}{n_+u_+ + n_-u_-}$$

), also given in Table 1.

As can be seen, in all cases, with the exception of SmB₆, the absolute value of δ is sufficiently large, which indicates a very substantial role of electronic conductivity in the hexaborides. On this basis, within the one-zone model, the values of the concentration of effective current carriers n^* per metal atom and their mobility u^* were calculated. In all cases, again except for samarium hexaboride, the number of effective carriers for the hexaborides of trivalent rare-earth metals differs little from whole numbers, which confirms the possibility of using the one-zone model.

Table 1

Electrical properties of hexaborides

Boride	Specific electrical resistivity ρ , $\mu\Omega \cdot \text{cm}$	Hall coefficient $R \cdot 10^4$, cm^3/C	Thermoe.m.f., $\mu\text{V}/\text{deg}$	Thermal coefficient of electrical resistivity, $\alpha \cdot 10^3 \text{ deg}^{-1}$ (0–100°)	Concentration of current carriers n^* , el. per 1 Me atom	Mobility of carriers u^* , cm/sec per V/cm	$\delta \cdot 10^{23}$, $\text{cm}/(\text{V}^2 \cdot \text{sec}^2)$
Ca B ₆	222	−91.0	−32.8	+1.16	0.05	41.0	−11.5
Sr B ₆	111	−76.3	−30.3	+0.83	0.06	68.7	−38.7
Ba B ₆	77	−57.5	−26.2	+1.08	0.08	74.7	−60.5
Y B ₆	40	−4.56	−0.5	+1.24	0.96	11.4	−17.8

Boride	Specific electrical resistivity ρ , $\mu\Omega \cdot \text{cm}$	Hall coefficient $R \cdot 10^4$, cm^3/C	Thermo-e.m.f., $\mu\text{V}/\text{deg}$	Thermal coefficient of electrical resistivity, $\alpha \cdot 10^3 \text{ deg}^{-1}$ (0–100°)	Concentration of current carriers n^* , el. per 1 Me atom	Mobility of carriers u^* , cm/sec per V/cm	$\delta \cdot 10^{23}$, $\text{cm}/(\text{V}^2 \cdot \text{sec}^2)$
La	15.0	-4.96	+0.1	+2.68	0.90	33.1	-137.8
B ₆							
Ce	29.4	-4.18	+2.8	+1.00	1.06	14.2	-30.2
B ₆							
Pr B ₆	19.5	-4.33	-0.6	+1.92	1.02	22.2	-71.1
Nd	20.0	-4.39	+0.4	+1.93	1.00	22.0	-68.5
B ₆							
Sm	207.0	+1.54	+7.6	-0.42	2.86	0.74	+0.2
B ₆							
Eu	84.7	-50.2	-17.7	+0.90	0.09	59.3	-43.7
B ₆							
Gd	44.7	-4.39	+0.1	+1.40	0.94	9.8	-13.7
B ₆							
Tb	37.4	-4.57	-1.1	+1.31	0.94	12.2	-20.4
B ₆							
Yb	46.6	-83.6	-25.5	+2.34	0.05	179.4	-240.3
B ₆							
Th	14.8	-2.18	-0.6	+2.31	1.99	14.7	-62.1
B ₆							

Hexaborides of divalent metals—calcium, strontium, barium, europium, and ytterbium—have a very low concentration of free electrons, since the entire electron ensemble participates in the organization of bonds, i.e., the valence levels are filled. The comparatively low resistance of these compounds is explained by the high mobility of the carriers, which is, in turn, associated with their slight scattering in the filled band. An especially strong increase in mobility is observed for ytterbium hexaboride, which has a filled, high-lying $4f$ level.

The hexaborides of trivalent rare-earth metals are characterized by the presence of one free electron per metal atom, and that of tetravalent thorium by two free electrons. This agrees with the identical character of the bonds in all the isomorphous hexaborides.

The thermo-e.m.f. values of the hexaborides of trivalent metals and thorium are

very small, which is associated with the high concentration of free electrons. The thermo-e.m.f. of the borides of divalent metals is considerably higher; moreover, in the series CaB_6 – SrB_6 – BaB_6 it decreases somewhat.

The thermal coefficient of electrical resistivity in the interval 0–100° is positive, with the exception of samarium hexaboride (for which it is negative up to a temperature of 300°, above which the resistance again increases). It is interesting to note that metallic samarium also exhibits anomalous behavior in the temperature dependence of the Hall effect.

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