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The Preparation and Nonstoichiometry of Samarium Hexaboride

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Samarium hexaboride was prepared by the borothermal reaction; $2\,Sm_2O_3+(6+4x)B=4\,SmB_x+3\,B_2O_2$. The residual oxygen content amounted to less than 0.03 w/o under optimum reaction conditions heating at 1650°C for 2 hr under a high vacuum. It was found by X-ray intensity and density measurements that the samarium hexaboride stayed stable over a large nonstoichiometric region from $Sm_{0.68}B_6$ to SmB_6. These extensive nonstoichiometric properties of samarium hexaboride can be explained in terms of the required electron numbers of the SmB_6 network in hexaboride.

In recent years the rare earth elements and their high-temperature compounds have been intensively investigated since their applications range over an extensive area of new technology, including radio engineering, electronics, metallurgy, machine construction, and electrical engineering. In particular, the hexaborides of the rare earth elements have become a subject of increasing importance and interest because of their high melting points, low electric resistivities, low values of the electron work function, high emission-current densities, and thermal stabilities.

All the rare earth metals, as well as scandium, strontium, barium, and plutonium, form isostructural hexaborides. The crystal structure of hexaborides was first determined by Stackelberg and Neuman.[1] According to them, the crystal structure is cubic and of the cesium chloride type, in which the metal atom is held in the center of a cage of boron atoms (just as the cesium atom is held in the CsCl crystal); six boron atoms in the octahedral form are located at the corners of the cell, in the same position as the chloride ion in cesium chloride.

The theoretical treatments by Longuet-Higgins and Roberts,[2] Eberhardt[3] and Yamazaki[4] have led to the conclusion that each boron octahedron requires 20 electrons, of which 18 come from the boron atoms and 2 from the metal atom. Out of the total of 20 electrons, 14 supposedly form bonds within the octahedron, and 6 enter into the external two-electron covalent bonds connected with neighboring octahedra. Therefore, it is possible that the rare earth hexaborides have a

1) Stackelberg, M. Von, and F. Neumann, *Z. Phys. Chem.*, **B19**, 314 (1932).

2) H. C. Longuet-Higgins and M. Dev. Roberts, *Proc. Roy. Soc. (London)*, **A223**, 336 (1954).

3) W. H. Eberhardt, B. L. Crawford, and W. N. Lipscob, *J. Chem. Phys.*, **22**, 989 (1954).

4) M. Yamazaki, *J. Phys. Soc. Japan*, **12**, 1 (1957).

relatively wide range of homogeneity, for the rare earth metals have three valence electrons.

The present study has been carried out so as to investigate the nonstoichiometric properties of pure samarium hexaboride. The results show that the study of nonstoichiometric propeties of the hexaboride will also provide useful information on the electronic configuration.

Experimental

Materials. Samarium sesquioxide, Sm_2O_3,[5] was separated from a crude rare earth mixture at this laboratory by replacement chlomatography, using the EDTA solution as the solvent. The Sm_2O_3 obtained by this method was over 99.9% pure, and other rare earth elements were found to be negligible in quantity by mass spectrography and radioactivation analysis.

The crystal boron, 99.9% pure and containing 0.11% oxygen. was obtained from Wako Pure Chemical Industries, Ltd, Tokyo.

Preparation of Samples. The hexaboride was prepared by the borothermal reduction[6-10] of samarium oxide, Sm_2O_3, according to the following equation:

$$2Sm_2O_3 + (6 + 4x)B = 4SmB_x + 3B_2O_2 \quad (1)$$

The lower volatile suboxide of the boron, B_2O_2, was removed upon reduction under a vacuum.

The samarium sesquioxide and boron were mixed in the desired mole proportions and ground carefully in a sardonyx mortar for complete homogenization. Samples weighing 4—5 g were heated at 1650°C in a tantalum crucible placed in an electric-resistance heater in a vacuum of 10^{-4}—10^{-6} mmHg at several temperatures for different times. The temperature was read with a W-WRe thermocupple and an optical pyrometer, corrected for window and prism absorptions.

X-Ray Diffraction. X-ray photographs of the products were taken using CuK_α and FeK_α radiations and a Debye-Scherrer X-ray powder camera (114.8 mm diameter). The precise lattice constants for the cubic hexaboride samples were calculated by extrapolating a plot of lattice constants *vs.* $\cos^2\theta$ to $\theta=90°$. The X-ray intensity ratio between the particular diffraction planes for the hexaboride was measured using an X-ray diffractometer equipped with a monochrometer.

Chemical Analysis. The boride samples were dissolved in Na_2CO_3 aq., and then their pH values were adjusted to 5.2 with $(CH_2)_6N_4$. After adding the XO indicator, analyses of the samarium were performed by titration with a 1/100 mol EDTA standard aquasolution. Boron analyses were performed by titration with a 1/10 N NaOH aquasolution after dissolving the samples in Na_2CO_3, adjusting their pH to 6.9, and adding Mannitol. Oxygen analyses were performed by the inert-gas-fusion coulonic titration method.

Density Measurements. The powdered specimens of 325—400 mesh were prepared by grinding them carefully in the sardonyx mortar. The density was determined at 20.5°C by a flotation technique using CCl_4.

Resistivity Measurements. For the resistivity measurements, a current of about 0.04 to 0.5 A was passed through the specimens and a standard resistance connected in series. A simple two-point apparatus and a standard potentiometric method were used. The resistivity measurements were carried out from the temperature of liquid nitrogen to 1000°K. The specimens used were $3\times5\times16$ mm blocks which were cut from annealed pellets using a diamond cutter.

Results and Discussion

Determination of Reaction Conditions. The samarium sesquioxide-boron compacts mixed at a 1 : 15 mol ratio were heated in a vacuum at 900—1900°C for 30 min. A loss weight results from the vaporization of the lower volatile oxide of boron, B_2O_2. The loss weight percentage after the heating reaction is plotted against the reaction temperature in Fig. 1. The dotted line indicates the theoretical loss weight percentage when the reaction is performed according to Equation (1).

Figure 1 shows that the borothermal reaction begins at about 1350°C and exceeds the theoretical weight loss at 1600°C. Figure 2 shows the oxygen content *vs.* the reaction time when the samarium sesquioxide-boron compact was reacted in a vacuum at 1650°C for different times. From Fig. 2 it is clear that the products contain only 300 ppm oxygen when reacted at 1650°C for 2 hr in a high vacuum.

From the results shown in Fig. 1 and Fig. 2, it can

TABLE 1. THE ANALYSES OF THE PRODUCTS

Nominal composition B/Sm_2O_3	B/Sm			Phases
	Theo.[a]	Theo.[b]	Analyses	
9	3.0	3.5	5.54	SmB_6+SmB_4
9.5	3.3	3.8	5.65	SmB_6+SmB_4
10	3.5	4.0	5.71	SmB_6+SmB_4
11	4.0	4.5	5.88	SmB_6+SmB_4
12	4.5	5.0	5.93	SmB_6+SmB_4
13	5.0	5.5	5.96	SmB_6
14	5.5	6.0	6.02	SmB_6
15	6.0	6.5	6.13	SmB_6
16	6.5	7.0	6.51	SmB_6
17	7.0	7.5	7.01	SmB_6
18	7.5	8.0	7.49	SmB_6
18.5	7.75	8.25	7.82	SmB_6
19	8.0	8.5	8.13	SmB_6
20	8.5	9.0	8.52	SmB_6
21	9.0	9.5	8.86	SmB_6
22	9.5	10.0	9.27	SmB_6+B (trace)
23	10.0	10.5	9.62	BmB_6+B
24	10.5	11.0	10.41	SmB_6+B
25	11.0	11.5	11.02	SmB_6+B
26	11.5	12.0	12.28	SmB_6+B

a) Calculated values on the assumption of formation of B_2O_2 during reaction.
b) Calculated values on the assumption of formation of B_2O_3 during reaction.

5) S. Yajima, K. Sasaki, and M. Noro, *Kogyo Kagaku Zasshi*, **72**, 1213 (1969).
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9) B. Post, S. Moskowitz, and F. W. Glaser, *ibid.*, **78**, 1800 (1956).
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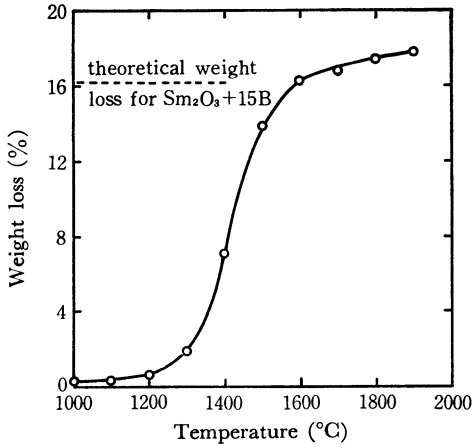

Fig. 1. The effect of temperature on the weight loss of Sm_2O_3+15B mixtures after 30 min.

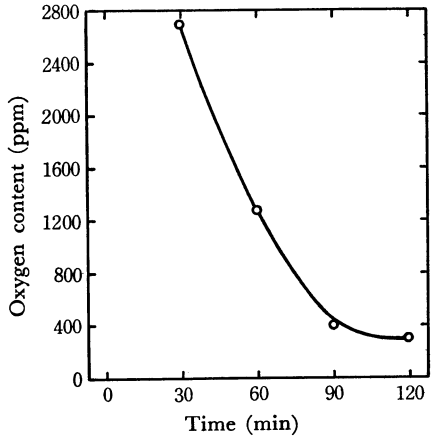

Fig. 2. The effect of time on the oxygen content after heating Sm_2O_3+15B mixtures at 1650°C in 10^{-4}—10^{-6} mmHg.

be seen that the borothermal reaction is almost completed by heating at 1650°C for 2 hr in a vacuum.

Preparation of Samarium Hexaboride. The samarium sesquioxide-boron compacts mixed at various ratios were heated under a vacuum of 10^{-4}—10^{-6} mmHg at 1650°C for 2 hr. The results of chemical and X-ray analyses are summarized in Table 1. In the regions of 13—21 and 9—12 in the nominal composition ratio, B/Sm_2O_3, only samarium hexaboride, SmB_6, and both samarium tetraboride, SmB_4, and samarium hexaboride, SmB_6, were observed, respectively. In the region of 22—26 in the nominal composition, SmB_6 and a trace of boron were observed. In this region, samarium dodecaboride, SmB_{12}, was not detected at all. If the borothermal reaction takes place according to Eq. (1), the boron-samarium atomic ratio, B/Sm, must agree with the theoretical values shown in the second column in Table 1. Felten *et al.*[6] have reported that boric anhydride, B_2O_3, vaporizes during the reaction. If the boric anhydride, B_2O_3, vaporizes during the reaction, the B/Sm ratio in the region of 14—26 in the nominal composition is in good agreement with the theoretical values shown in the third column. However, the observed values coincide well with the theoretical values in the second column. From this fact, it may be concluded that, during the reaction, not boric anhydride, B_2O_3, but a volatile suboxide of the B_2O_2 boron is formed in the region of 15—26 in the nominal composition. In the region of 9—14, the analytical values of B/Sm are considerably different from the theoretical values. It is reasonable to think the borothermal reaction takes place in this region following these equations.

$$Sm_2O_3 + (15 - 2x)B = (2 - x)SmB_6 + xSmB_4 + (3/2)B_2O_2(g) \quad (2)$$

$$SmB_4 = SmB_6 + Sm(g) \quad (3)$$

Samsonov[11,12] has reported that an approximate thermodynamic calculation of either the suboxide of the B_2O_2 boron or boric anhydride, B_2O_3, but that SmB_4 is decomposed into SmB_6 and Sm(g) according to Eq. (3).

Nonstoichiometric Properties. As can be seen from Table 1, the samarium hexaboride is stable in the nonstoichiometric composition of 5.96—9.27 at the boron-samarium atomic ratio. The variation in the lattice parameter of the cubic hexaboride *vs.* B/Sm is shown in Fig. 3. The lattice parameter decreases with an increase in the B/Sm ratio in the region of the monophase hexaboride.

If the nonstoichiometric properties of samarium hexaboride are related to the position of samarium metal, the X-ray diffraction intensity will vary considerably because the magnitude of the atomic scattering factor of samarium is much larger than that of boron. The diffraction of the 100 and 110 planes is sensible for the position of samarium metal. The variation in the X-ray intensity ratio of the 100 diffraction plane *vs.* the 110 plane is plotted against the B/Sm ratio in Fig. 4. The dotted line shows the value of the calculated X-ray intensity ratio. These calculated values are obtained according to Eq. (4), supposing that is the formation of $Sm_{1-x}B_6$, the excess boron does not enter into interstitial sites in unit cells, but vacancies form at random in the sites of the samarium metal:

$$I \alpha |F|^2 p \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta}$$

$$\frac{I_{100}}{I_{110}} \alpha \frac{|F_2|^2 p_2 \dfrac{1 + \cos^2 2\theta_2}{\sin^2 \theta_2 \cos \theta_2}}{|F_1|^2 p_1 \dfrac{1 + \cos^2 2\theta_1}{\sin^2 \theta_1 \cos \theta_1}} \quad (4)$$

where p is the permutation factor.

The variation in the density against B/Sm=1+y in SmB_{1+y} or 1−x in $Sm_{1-x}B_6$ is plotted in Fig. 5. The solid line (a) shows the experimental values, both the closed circles (b) and the open circles (c) being the theoretical values. The values of the closed circles and open circles are calculated on the assumption that the nonstoichiometric composition can be indicated by the $Sm_{1-x}B_6$ formula or the SmB_{6+y} formula respectively. The experimental results are in good

11) G. V. Samsonov, *Uspekki Khim.*, **28**, 189 (1959).

12) G. V. Samsonov, Boride of the rare earth metals. "High temperature compounds of the rare earth metals with nonmetals," Edited by G. V. Samsonov, Consultants Bureau, New York (1965), p. 56.

agreement with the values of the closed circles. From the variations in the lattice parameter, the X-ray intensity ratio, and the density, it seems probable that the samarium hexaboride phase is stable from SmB_6 to $Sm_{0.68}B_6$. Johnson and Daane[13] have found that the lantanum hexaboride phase is stable from LaB_6 to $LaB_{7.8}$. It is probably more exact to refer to the latter as $La_{0.76}B_6$.

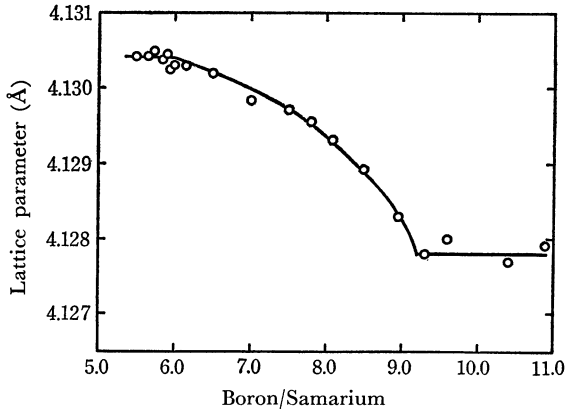

Fig. 3. The variation in the lattice parameter of samarium hexaboride.

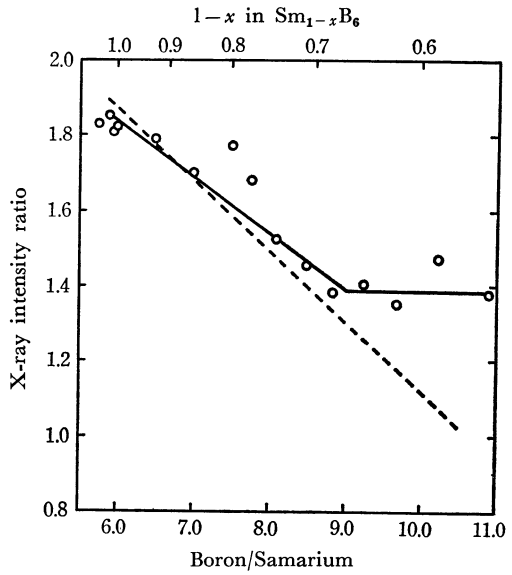

Fig. 4. The variation in the X-ray intensity ratio, $I(100)/I(110)$, against nonstoichiometric composition of samarium hexaboride.
-○-: experimental values, ----: calculated values.

Relationship between a Wide Homogeneity Range and Bonding. The wide range of homogeneity in samarium hexaboride can be explained in terms of the required electron numbers of the boron network and the availability of such electrons in the valence band of the metal atom. Calculations by Longuet-Higgins and Roberts[2] and Lipscomb and Britton[3] indicate that two electrons must be transferred to each boron octahedron in the hexaboride structure to ensure its

13) R. W. Johnson and A. H. Danne, *J. Phys. Chem.*, **65**, 909 (1961).

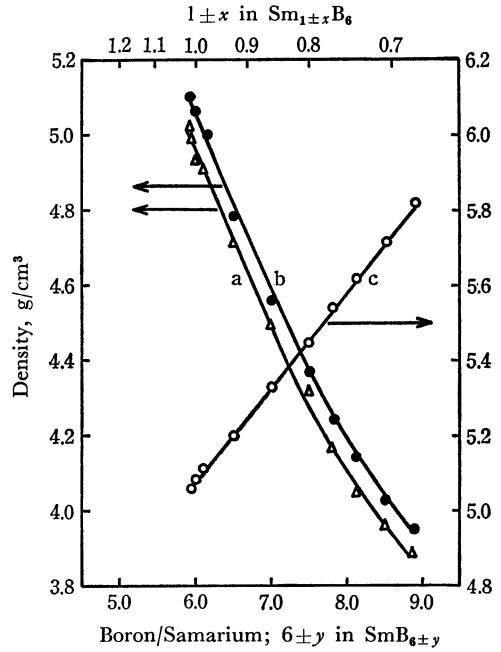

Fig. 5. The variation of density against nonstoichiometric composition of samarium hexaboride.
a(-Δ-): experimental values, b(-●-) and c(-○-) are X-Ray density calculated on the assumption that $Sm_{1-x}B_6$ or SmB_{6+y} respectively.

stability. In stoichiometric SmB_6 there is, therefore, one excess valence electron for each samarium atom because the rare earth metals generally have three valence electrons. This excess metal valence electron is responsible for the metallic properties. The lower limit of $Sm_{0.67}B_6$ is theoretically possible, with each samarium atom contributing all three valence electrons to the boron net; at that composition, the phase is presumably an electrical insulator.

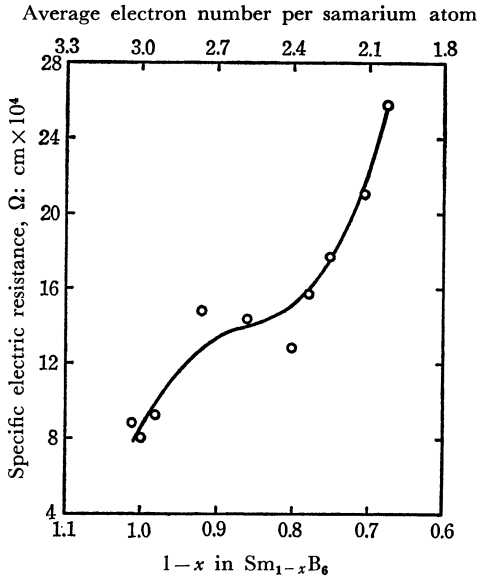

Fig. 6. The plot of specific electric resistivity *vs.* $1-x$ in $Sm_{1-x}B_6$ or average electron number per samarium metal atom.

Generally the temperature dependence of the electric resistance of a number of hexaborides of the rare

earth metals[12,14,15] showed a positive value of the temperature coefficient of the resistance, just as we should have expected for a substance with metallic conductivity. An exception is the hexaboride of samarium, which possesses a negative value of the thermal coefficient of the resistance. This fact can be explained by the change in the ratio of divalent and trivalent samarium with the temperature.[16-18] In the present work, $Sm_{1-x}B_6$ possessed a negative value of the temperature coefficient of resistance, very small in absolute magnitude at temperatures above 500°C. The variation in the electrical resistivity at 25°C against the electron number to be transfered to each boron octahedron is shown in Fig. 6. The electrical resistivity varies from 8×10^{-4} to $26\times10^{-4}\,\Omega\cdot$cm with an increase in the number of samarium-metal atom vacancies. At the lower limit of the homogeneity range, $Sm_{0.68}B_6$ (electron number, 2.04), the electrical conductivity is relatively large, probably due to: (a) impurities, (b) the effect of the d band of samarium metal, and (c) more few electrons being required to form the B_6 net.

Referring to (c) among these three factors, $Ba_{0.57}Na_{0.43}B_6$ and $Th_{0.23}Na_{0.77}B_6$ are stable in the $(NaMe)B_6$ system[19,20] and correspond to 1.60 electrons per metal atom. If the formation of the bond of boron in the SmB_6 phase requires 1.60 electrons, a somewhat smaller electron number per metal atom than two, the remaining electrons ($2.04-1.60=0.44$) per samarium atom in $Sm_{0.68}B_6$ can enter into the conduction band and its electrons can be responsible for the comparatively high electroconductivity at the lower limit of the nonstoichiometric composition.

From this standpoint, the limit of the homogeneity range existing between SmB_6 and $Sm_{0.53}B_6$ can be explained theoretically. The lower limit observed in this study was $Sm_{0.68}B_6$. It seems that the lower limit may be determined by the onset of mechanical instability in the boron lattice due to the large number of metal-atom vacancies. This point is still open to question, though, and further work is called for.

The author would like to thank Professor Seishi Yajima for his guidance and encouragement, and Mr. Masahiko Sase for his chemical analyses.

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19) F. Bertant and P. Blum, *Compt. Rend.*, **234**, 265 (1952).
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