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A Thermodynamic Analysis of Lanthanum Hexaboride Crystal Preparation from Aluminum Flux with the Use of Compound Precursors

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The temperature dependencies of the change in Gibbs energy for a series of probable reactions in the aluminothermic reduction of La_2O_3, $LaCl_3$, and B_2O_3, borothermic reduction of La_2O_3, and synthesis of LaB_6 in an aluminum flux using compound precursors of the boride components have been plotted on the basis of thermodynamic data from the literature. It has been shown that under the experimental conditions of the growth of rare earth boride single crystals by crystallization from high-temperature solutions in molten aluminum, a rare earth oxide and B_2O_3 should be used as precursors instead of the corresponding elements. © 1997 Academic Press

INTRODUCTION

The growth of single crystals of refractory borides has attracted the attention of many scientists for many years. This is mainly due to the necessity of obtaining reliable information on the structure, the properties, and some specific applications of these borides. Methods for the growth of boride single crystals from melts, from vapor phase, and from high-temperature solutions (flux growth) have been developed (1). The most usual of these groups of methods are those using high-temperature solutions. This concerns both the number of published investigations and the variety of crystals grown.

In flux growth crystallization proceeds at temperatures considerably lower than the melting points of the substances, which allows the growth of high-quality crystals of incongruently melting borides. Abundant data concerning the growth of boride single crystals from high-temperature solutions (HTS) are summarized in several review papers (1–5).

Since the chemical bond of metallic character prevails in refractory borides, practically only metals can be used as high-temperature solvents for flux growth of these substances. A significant number of requirements are to be met by an ideal solvent, but a study on the applicability of 18 metals as possible solvents for the growth of boride single crystals has shown (6) that it would hardly be possible to find a solvent meeting all these requirements. For a large number of borides it has been established that molten aluminum and germanium offer the best compromise. In the case of aluminum, this conclusion has been confirmed by the experiments of a series of authors during the past two decades.

In boride single crystal preparation from an aluminum flux, usually boron and the corresponding metal are dissolved in molten aluminum. Crystals are obtained during slow cooling of saturated solutions from temperatures on the order of 1700–1800 K at which the volatility of aluminum becomes measurable.

A very important characteristic of aluminum is its great reducing power with respect to a large number of metal compounds. This property is the basis of many aluminothermic processes of metal recovery (7). This allows assuming that the precursors used for the preparation of boride single crystals from high-temperature solutions in aluminum might be chemical compounds, e.g., oxides or salts of the elements participating in the borides, instead of the elements themselves if the conditions needed for eliminating the aluminum compounds appearing during the reduction are present (8–11).

The possible application of lanthanum and boron oxides and lanthanum trichloride to the preparation of lanthanum hexaboride (LaB_6) single crystals from high-temperature aluminum solutions has been considered in the present work. A thermodynamic analysis has been made in order to estimate the probability for various reactions to proceed between the precursors and aluminum. On the basis of the close properties of the rare earths and their compounds, the general conclusions of this analysis are expected to be, to a great extent, valid for the growth processes of all rare earth boride crystals.

THERMODYNAMIC CALCULATIONS

An approximate estimation of the probability for one or another reaction to take place in the system for preparation of LaB_6, as well as of the expected reduction mechanism at

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298–2000 K, was performed thermodynamically by calculation of the temperature dependence of Gibbs energy according to the well-known equation

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 - T\int_{298}^{T}\frac{dT}{T^2}\int_{298}^{T}\Delta C_\mathrm{p}\,dT, \quad [\mathrm{I}]$$

where ΔG_T^0 is the change in Gibbs energy (kJ/mol), ΔH_{298}^0 denotes the standard change of the reaction enthalpy (kJ/mol), ΔS_{298}^0 is the standard change of the reaction entropy (J/mol degree), T is the temperature (K), and C_p, the molar heat capacity (J/mol degree).

Using data from the literature on the enthalpy of formation, ΔH_{298}^0, and the entropy S_{298}^0 under standard conditions, as well as data on the temperature dependence of the molar heat capacity ($C_\mathrm{p} = A + B\cdot 10^{-3}T + C\cdot 10^5T^2 + D\cdot 10^{-6}T^2$) for each of the substances participating in the reaction (see Table 1), we calculated the change of the Gibbs energy by the method of Temkin and Schwartzmann, according to which the above equation can be written as

$$\Delta G_T^0 = \Delta H_{298}^0 - T\Delta S_{298}^0 - T(M_0\Delta A + M_1\Delta B + M_2\Delta D + M_{-2}\Delta C). \quad [\mathrm{II}]$$

The values of the constants M_0, M_1, M_2, and M_{-2} for the different temperatures investigated have been tabulated (12).

RESULTS AND DISCUSSION

1. Aluminothermic Reduction of La_2O_3

If La_2O_3, instead of elemental La is used for the growth of LaB_6 single crystals, the first stage presupposes reduction of the oxide by aluminum which plays the role of a high-temperature solvent. This interaction can proceed according to the reaction

$$0.5La_2O_3 + Al = La + 0.5Al_2O_3. \quad [1]$$

TABLE 1
Thermodynamic Data on the Substances Participating in the Reactions Investigated

				$C_\mathrm{p} = A + B\cdot 10^{-3}\,T + C\cdot 10^5\,T^{-2} + D\cdot 10^{-6}\,T^2$ (J/mol·deg)					
No.	Substance	ΔH_{298} (kJ/mol)	S_{298} (J/mol deg)	A	B	C	D	Temperature range (K)	Reference
1.	La	0	56.9	25.83	6.70	—	—	298–1141	13
				33.9	—	—	—	1141–1193	13
				34.8	—	—	—	1193–3693	13
2.	Al	0	28.34	17.75	12.39	—	—	298–932	13
				– 68.580	– 4.2	—	51.58	932–2723	13
3.	B	0	5.874	27.834	– 0.699	– 32.192	5.213	298–800	14
				21.386	4.723	– 12.117	—	800–1500	14
				32.117	0.071	– 96.816	—	1500–2450	14
				30.56	—	—	—	2450–3200	14
4.	La_2O_3	– 1794.5	128.1	120.83	12.90	– 13.73	—	298–1171	13
5.	Al_2O_3	– 1674.7	51.1	144.84	12.81	– 35.46	—	298–1800	13
6.	AlO (g)	69.1	218.43	35.366	1.398	– 4.601	—	298–2000	13, 15
7.	Al_2O (g)	– 134.0	257.11	55.182	1.517	– 9.244	—	298–2000	13, 15
8.	B_2O_3	– 1271.28	53.88	102.845	– 84.959	– 24.392	145.43	298–723	14
				245.979	– 145.61	– 171.28	48.198	723–1400	14
				127.865	—	—	—	1400–2316	14
9.	B_2O_2 (g)	– 456.4	242.67	57.32	—	—	—	298	15
10.	BO (g)	0.4	203.48	29.22	—	—	—	298	15
11.	$LaCl_3$	– 1071.4	144.4	97.26	21.48	—	—	298–1128	13
				125.6	—	—	—	1128–2085	13
12.	$AlCl_3$	– 706.10	109.36	64.98	87.9	—	—	298–454	14
13.	$AlCl_3$ (g)	– 584.9	314.504	82.007	0.624	– 9.914	—	298–2000	14
14.	Al_2Cl_6 (g)	– 1296.34	475.817	181.04	1.05	– 20.419	—	298–2000	14
15.	LaB_6	– 129.8	83.23	90.98	85.4	—	—	298–1483	16, 17

However, it has been known for a long time (18, 19) that at high temperatures liquid aluminum reacts with Al_2O_3, forming unstable aluminum suboxides which disproportionate into Al and Al_2O_3 on cooling or rapid quenching. It has been established that the stability of the suboxides and especially that of Al_2O increases with temperature, significant aluminum losses, probably as volatile suboxides, being observed (20) in the system during aluminothermic production of metals. On the basis of the foregoing it may be assumed that the reduction of La_2O_3 by Al can proceed not only by reaction [1] but also according to the following reactions in which gaseous AlO and Al_2O are formed:

$$0.5La_2O_3 + 1.5Al = La + 1.5AlO \qquad [2]$$

and

$$0.5La_2O_3 + 3Al = La + 1.5Al_2O. \qquad [3]$$

Figure 1 illustrates the change of the Gibbs energy with rising temperature for reactions [1]–[3]. The shapes of the curves allow the conclusion that from a thermodynamic viewpoint up to 1400 K the reduction of the lanthanum oxide by aluminum would most probably occur with formation of Al_2O_3. However, the homogenization processes of the high-temperature solution and the growth of the boride crystals are performed usually at 1700–1800 K when proceeding of reaction [3] is most probable. In contrast to the assumptions made in some papers (21), reduction could hardly be expected to proceed by reaction [2] with formation of AlO. The change in slope of the curves at 932 K is associated with the phase transition $Al_{solid} \rightarrow Al_{liquid}$.

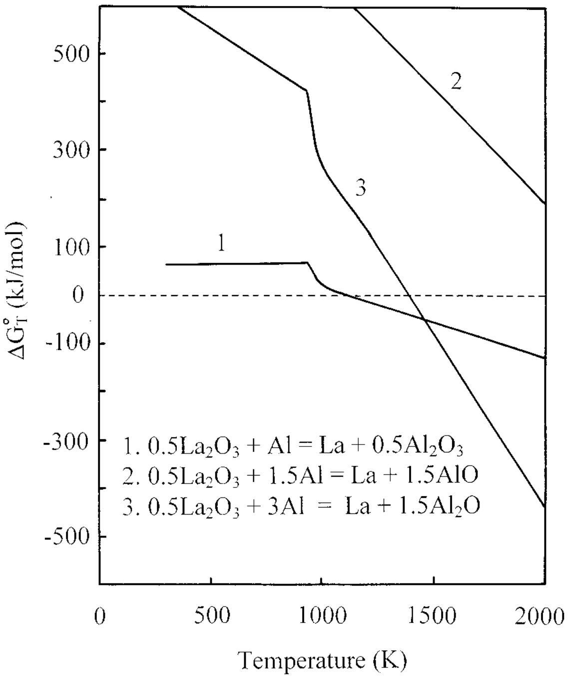

FIG. 1. Gibbs free energy vs temperature plots for reactions of aluminothermic reduction of La_2O_3.

The flux growth of boride crystals usually takes place in an inert gas flow or under dynamic vacuum, the volatile Al_2O formed being constantly removed from the system. This circumstance and the presence of a large excess of aluminum in which the lanthanum appearing during the reduction is dissolved contribute to a complete shift of the reaction to the right at considerably lower temperatures than is the case of the classical aluminothermic processes in metallurgy (7).

2. Borothermic Reduction of La_2O_3

Reduction at high temperatures of oxides with excess boron is one of the general methods for the synthesis of metal borides (22). For that reason it was worth checking whether boron might compete with aluminum as a reducing agent for La_2O_3 in the system for flux growth of LaB_6 crystals which contains lanthanum oxide, elemental boron, and aluminum as a high-temperature solvent. The reduction with boron may occur by one of the following three reactions:

$$0.5La_2O_3 + B = La + 0.5B_2O_3, \qquad [4]$$

$$0.5La_2O_3 + 1.5B = La + 0.75B_2O_3, \qquad [5]$$

and

$$0.5La_2O_3 + 1.5B = La + 1.5BO. \qquad [6]$$

On the basis of Fig. 2, where the dependence $\Delta G^0_T = f(T)$ for these reactions is presented and after comparison with Fig. 1 it may be concluded that at temperatures up to 2000 K elemental boron could not act as a reducing agent for La_2O_3 in the presence of aluminum. This conclusion is not unexpected since it is known that borothermic syntheses of rare earth borides proceed at temperatures above 2000 K with formation of lower boron oxides (22), which is in agreement with the shape of the curves in Fig. 2. The sharp change in slope of curve 1 at 723 K is caused by the phase transition $B_2O_{3\,solid} \rightarrow B_2O_{3\,liquid}$. Since in the literature there are no data on the temperature dependence of C_p for the lower oxides of boron, the plots $\Delta G^0_T = f(T)$ for reactions [5] and [6] are obtained assuming that ΔC_p = const = O.

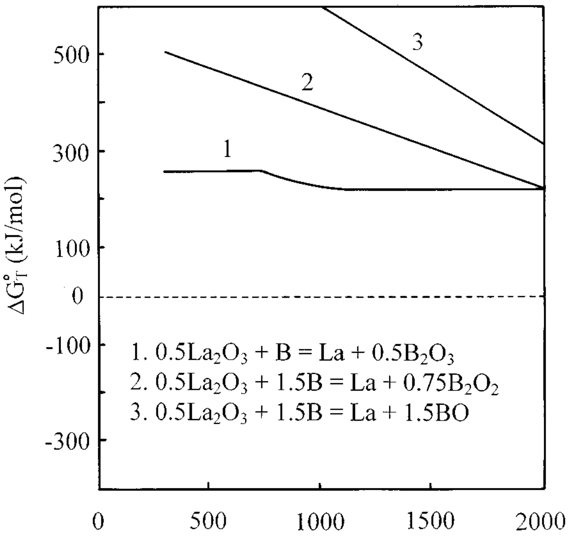

FIG. 2. Gibbs free energy vs temperature plots for reactions of borothermic reduction of La_2O_3.

3. *Aluminothermic Reduction of $LaCl_3$*

A lanthanum halide might be used as a compound precursor instead of lanthanum oxide for the growth of LaB_6 crystals from high-temperature solutions in molten aluminum. If the halide is $LaCl_3$, its reduction with aluminum may proceed according to one of the reactions

$$LaCl_3 + Al = La + 0.5Al_2Cl_6 \qquad [7]$$

and

$$LaCl_3 + Al = La + AlCl_3, \qquad [8]$$

as a result of which a dimer or a monomer of the aluminum trichloride will be obtained in addition to lanthanum. From the $\Delta G_T^0 = f(T)$ dependence for these two reactions, which is shown in Fig. 3, it may be concluded that reaction [7] is more probable at low temperatures, whereas above the temperatures of the solid → liquid transition of Al and $LaCl_3$, reaction [8] should predominate. Under the conditions of homogenization of a real high-temperature solution, the thermodynamic equilibrium of this reaction has been attained. The possibility of easy elimination of the reaction product ($AlCl_3$), which sublimes already at very low temperatures, should be considered an advantage of $LaCl_3$ as a precursor. However, this advantage is significantly reduced by the necessity of obtaining absolutely anhydrous $LaCl_3$ and the precautions associated with its use (23).

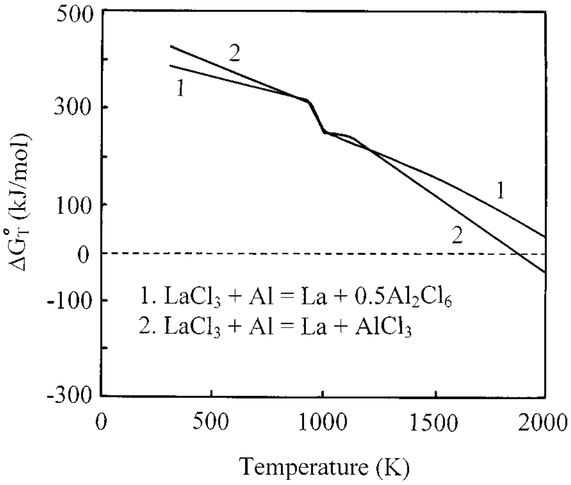

FIG. 3. Gibbs free energy vs temperature plots for reactions of aluminothermic reduction of $LaCl_3$.

4. *Aluminothermic Reduction of B_2O_3*

When boride single crystals are grown from Al fluxes, one should use compound precursors not only for the metal but also for the boron. Precursors for boron are very restricted in number and the choice is reduced practically to B_2O_3 alone. The reduction of this oxide with aluminum might proceed according to one of the following reactions:

$$0.5B_2O_3 + Al = B + 0.5Al_2O_3, \qquad [9]$$

$$0.5B_2O_3 + 1.5Al = B + 1.5AlO, \qquad [10]$$

and

$$0.5B_2O_3 + 3Al = B + 1.5Al_2O. \qquad [11]$$

From the data in Fig. 4 it is obvious that from a thermodynamic viewpoint the aluminothermic reduction of B_2O_3 should proceed much more easily than that of La_2O_3, and prevalence of Al_2O among the reaction products should be expected at the practically important temperatures above 1500 K.

5. *Synthesis of LaB_6 in the High-Temperature Solution Using Compound Precursors of Lanthanum*

The thermodynamic analysis of the reduction of La_2O_3 and $LaCl_3$ by aluminum has established that the most probable reactions for the synthesis of LaB_6 are those associated with the presence among the reaction products of Al_2O and $AlCl_3$, respectively. However, this synthesis would proceed after the introduction of the necessary amount of

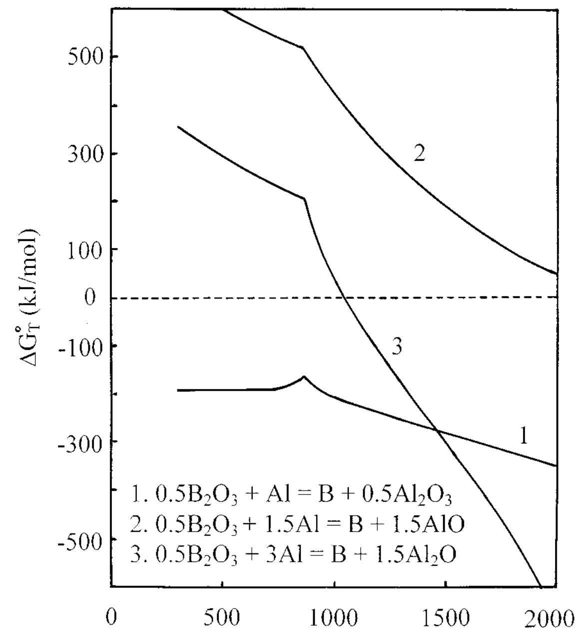

FIG. 4. Gibbs free energy vs temperature plots for reactions of aluminothermic reduction of B_2O_3.

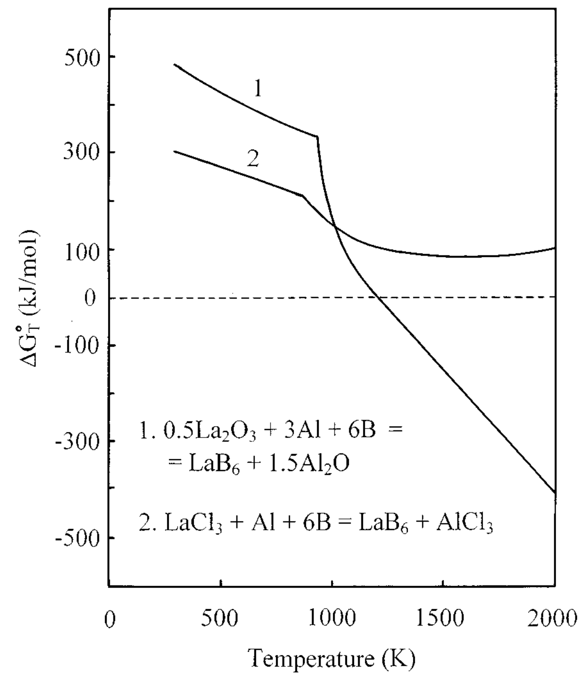

FIG. 5. Gibbs free energy vs temperature plot for the synthesis reaction of LaB_6 in a high-temperature solution using La_2O_3 or $LaCl_3$ as a precursor.

boron into the respective systems. In this case, the following reactions might take place:

$$0.5La_2O_3 + 3Al + 6B = LaB_6 + 1.5Al_2O \quad [12]$$

and

$$LaCl_3 + Al + 6B = LaB_6 + AlCl_3. \quad [13]$$

The shapes of the $\Delta G_T^0 = f(T)$ curves for these two reactions presented in Fig. 5 indicate that in the presence of La_2O_3 as a precursor the synthesis of LaB_6 in the high-temperature solution should proceed easily. In contrast, $LaCl_3$ is a very inappropriate precursor and above 1200 K even the probability for the synthesis to take place decreases.

6. Synthesis of LaB_6 in the High-Temperature Solution Using Oxide Precursors of Lanthanum and Boron

In the present investigation it has been established that in molten aluminum the oxides of both lanthanum and boron should be reduced relatively easily at moderate temperatures. The dissolution of the elements in aluminum and the elimination of the volatile Al_2O from the reaction contribute to the shift of the reaction equilibria to the right. The synthesis of LaB_6 from La_2O_3 and B_2O_3 with the participation of aluminum as a high-temperature solvent can be presented by the equation

$$0.5La_2O_3 + 3B_2O_3 + 21Al = LaB_6 + 10.5Al_2O. \quad [14]$$

The $\Delta G_T^0 = f(T)$ dependence for the simultaneous reduction reaction is presented in Fig. 6. Evidently, the thermodynamic equilibrium for this reaction is attained at about

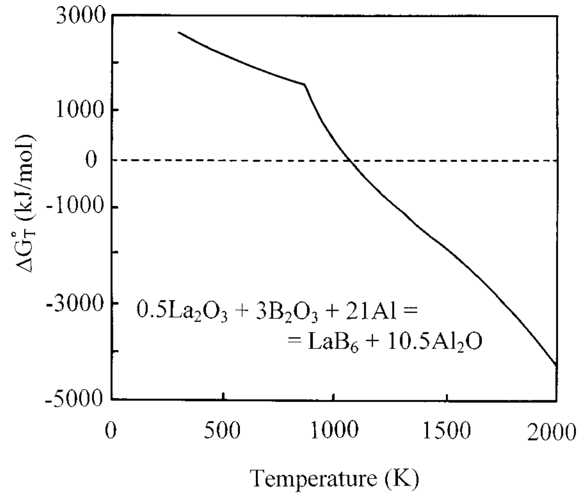

FIG. 6. Gibbs free energy vs temperature plot for the synthesis reaction of LaB_6 in a high-temperature solution using La_2O_3 and B_2O_3 as precursors.

1100 K, i.e., at an even lower temperature than is the case of the reaction when only lanthanum is introduced into the system as an oxide (reaction [12]).

CONCLUSION

The results from the thermodynamic calculations presented in this work have shown that under the conditions of the real experiments on the growth of rare earth (lanthanum) boride single crystals by crystallization from high-temperature solutions in molten aluminum, a rare earth oxide and B_2O_3 might be used instead of the corresponding elements. The corroboration of this basic conclusion by experiments would allow a simplified preparation of lanthanum hexaboride crystals at a reduced price. It would also be of interest to establish the real mechanism of the aluminothermic processes and to compare them with the assumptions formulated in this work.

The evaluation has been made without taking into account the probability for side processes to take place along with those under investigation. Two such possibilities deserve being considered:

1. Interaction of the lanthanum formed during oxide (or chloride) reduction with the excess aluminum and the resulting formation of aluminides. As was shown recently (24), during reduction of Nd_2O_3 by Al at 1073 K, a mixture of NdAl and $NdAl_2$ phases appears. Due to the great similarity of the *Ln*–Al phase diagrams (25, 26), formation of such phases of aluminum with lanthanum and with the other rare earths is possible. However, this occurs at relatively low temperatures. At the temperatures of the flux growth processes these phases are not stable (25, 26).

2. Dissolution of the elements (La or B) obtained during the reduction in molten aluminum, which would in principle cause changes in value of the Gibbs energy. A rough estimation of the concentration dependence of ΔG might be made assuming that the solutions being obtained are ideal (12). When making this estimation one has to take into account that at the real temperatures (1700–1800 K) of LaB_6 flux growth the saturated solution contains about 3–3.5 at.% B (22, 27); i.e., a huge excess of aluminum is needed. The necessity of maintaining a stoichiometric boron/lanthanum ratio, similar to that in LaB_6, presupposes working with solutions containing only 0.5–0.6 at.% La. The evaluation has shown that the corrections of the Gibbs energy values for such solutions are very small and can be neglected.

REFERENCES

1. P. Peshev, *in* "Proc. 9th Int. Symp. Boron, Borides and Related Compounds" (H. Werheit, Ed.), p. 72. University of Duisburg Press, Duisburg, 1988.
2. M. M. Korsukova and V. N. Gurin, *Zh. Vses. Khim. Obshch.* **26** (6), 79 (1981).
3. V. N. Gurin and M. M. Korsukova, *Progr. Crystal Growth Charact.* **6,** 59 (1983).
4. T. Lundström, *J. Less-Common Met.* **100,** 215 (1984).
5. M. M. Korsukova and V. N. Gurin, *Usp. Khim.* **56,** 3 (1987).
6. P. Peshev, *Bulg. Chem. Commun.* **24,** 235 (1992).
7. N. P. Lyakishev, Yu. L. Pliner, G. F. Ignatenko, and S. I. Lappo, "Aluminothermic Processes." Metallurgiya, Moscow, 1978. [In Russian]
8. G. H. Olsen and A. V. Cafiero, *J. Crystal Growth* **44,** 287 (1978).
9. A. Iltis and P. Maestro, *Eur. Pat.* No. 341106, 08. 11. 1989.
10. S. Okada, K. Kudou, Y. Yu, and T. Lundström, *in* "Proc. 11th Int. Symp. on Boron, Borides and Related Compounds, Tsukuba 1993," Jpn. J. Appl. Phys. Series 10, p. 136. 1994.
11. V. Gurin, *in* "Proc. 11th Int. Symp. Boron, Borides and Related Compounds, Tsukuba 1993," Jpn. J. Appl. Phys. Series 10, 138. 1994.
12. M. Kh. Karapet'yants, "Chemical Thermodynamics," Khimiya, Moscow, 1975. [In Russian]
13. I. Barin and O. Knacke, "Thermochemical Properties of Inorganic Substances." Springer-Verlag, Berlin/Heidelberg/New York, 1973.
14. I. Barin, O. Knacke, and O. Kubaschewski, "Thermochemical Properties of Inorganic Substances. Supplement." Springer-Verlag, Berlin/Heidelberg/New York, 1977.
15. R. D. Srivastava and M. Farber, *Chem. Rev.* **78,** 627 (1978).
16. V. P. Glushko (Ed.), "Thermodynamic Constants of Substances," Vol. VIII. VINITI, Moscow, 1978. [In Russian]
17. G. V. Samsonov and I. M. Vinitskii, "Handbook of Refractory Compounds." Plenum Press, New York, 1980.
18. L. Brewer and A. W. Searcy, *J. Am. Chem. Soc.* **73,** 5308 (1951).
19. M. Hoch and H. L. Johnston, *J. Am. Chem. Soc.* **76,** 2560 (1954).
20. G. N. Kozhevnikov and V. V. Efremkin, *Izv. Akad. Nauk SSSR, Metally* **3,** 42 (1972).
21. G. V. Samsonov and V. A. Podergin, *Dopovidi Akad. Nauk Ukr. RSR* **12,** 1609 (1963).
22. T. I. Serebryakova, V. A. Neronov, and P. D. Peshev, "High-Temperature Borides." Cambridge International Science, Cambridge, 1995.
23. F. E. Block and T. T. Campbell, *in* "The Rare Earths" (F. H. Spedding and A. H. Daane, Eds.), Chap. 7. Wiley, New York/London, 1961.
24. G. A. Lebedev, T. S. Lebedeva, and V. S. Volkov, *Izv. Vyssh. Uchebn. Zaved., Chern. Metall.* **7,** 74 (1993).
25. C. E. Lundin, *in* "The Rare Earths" (F. H. Spedding and A. H. Daane, Eds.), Chap. 16. Wiley, New York/London, 1961.
26. V. S. Sinel'nikova, V. A. Podergin, and V. N. Rechkin, "Aluminides." Naukova Dumka, Kiev, 1965. [In Russian]
27. M. Hansen and K. Anderko, "Constitution of Binary Alloys." McGraw Hill, New York/Toronto/London, 1958.