High-Temperature Compounds of Rare Earth Metals With Nonmetals

by

Grigorii Valentinovich Samsonov

Authorized translation from the Russian

HIGH-TEMPERATURE COMPOUNDS
OF RARE EARTH METALS WITH NONMETALS

TUGOPLAVKIE SOEDINENIYA
REDKOZEMEL'NYKH METALLOV S NEMETALLAMI

ТУГОПЛАВКИЕ СОЕДИНЕНИЯ
РЕДКОЗЕМЕЛЬНЫХ МЕТАЛЛОВ С НЕМЕТАЛЛАМИ

PREFACE

One of the most important conditions of the development of modern technology is the development of new high-temperature materials with special physical and technological properties—semiconductor, refractory, catalytic, heat-resistant and thermally stable, nuclear-physical, and corrosion properties, for supplying various fields of high-temperature technology.

Promising materials of this type are refractory compounds of the rare-earth metals (scandium, yttrium, and the lanthanides) with boron, nitrogen, carbon, silicon, and sulfur—the borides, nitrides, carbides, silicides, and sulfides. The necessity for the greatest possible expansion of both scientific research and the technological utilization of rare and rare-earth metals has thus become especially acute in recent years.

The investigation of refractory compounds of the rare-earth metals was begun in the second half of the 19th Century by the works of the French chemist and metallurgist Henri Moissan and his school. In prerevolutionary Russia practically no such investigations were conducted, and the first studies of refractory compounds of the rare-earth metals date from the beginning of the twenties, when the well-known Russian physical chemist N. N. Zhukov generalized for the first time the disconnected information on the nitrides of the rare-earth metals and gave a scientific substantiation for the methods of their production and the peculiarities of their physical and chemical properties. Investigations of refractory compounds of the rare-earth metals have achieved especially wide development in the USSR and abroad during the last 20 to 30 years. Here we should recall the works of Andrieux (France) on the production of these compounds by the method of electrolysis of fused media, the works of Lafferty (United States) and B. M. Tsarev (USSR) on the thermionic emission properties of the borides and silicides, the theoretical studies of Flodmark, Higgins, Yamazaki, G. S. Zhdanov, and N. N. Zhuravlev, investigations of the borides and silicides conducted by Post, Binder, Brewer, Krikorian, Eick, Parthe (United States), Bertaut and Blum (France), the works of Vickery, Spedding, Gschneidner, and Daane (United States, England) on the carbides of the rare-earth metals, the works of Klemm (German Federated Republic), Iandelli (Italy), Eick and Baenziger (United States) on the

nitrides, and the French school of chemists—Flahaut, Guittard, Patrie, Loriers, and Domange—on the sulfides of the rare-earth metals. An especially great contribution to the study of these theoretically interesting and practically important compounds has been made by Soviet researchers. In addition to the already-mentioned works of G. S. Zhdanov and N. N. Zhuravlev on the crystal chemistry of the borides, we should mention the works of V. A. Épel'baum on the synthesis and investigation of the borides, L. Ya. Markovskii on the study of the borides and carboborides, as well as a large series of studies conducted on all types of compounds of the rare-earth metals with nonmetals in the sector of Refractory Materials of the Institute of Problems of the Science of Materials, Academy of Sciences, Ukrainian SSR. These studies were used as the basis of this monograph, in which an attempt is made to generalize and systematize the accumulated information on the production and properties of refractory oxygen-free compounds of the rare-earth metals with nonmetals.

The monograph does not include data on the oxides of the rare-earth metals, since generalizations have been made on this problem in a number of monographs,* nor does it include data on the selenides and tellurides, which were included in a special monograph written by co-workers of our laboratory, V. A. Obolonchik and G. V. Lashkarev, and published by the Academy of Sciences, Ukrainian SSR Press, with the author as the editor. No information is cited on the phosphides, since a special monograph has been published on this problem.†

---

*For example, in the monograph of A. M. Cherepanov and S. G. Tresvyatskii, Highly Refractory Materials and Objects Made from Oxides, Metallurgy Press, Moscow, 1964, and the book of V. V. Serebrennikov, Chemistry of the Rare-Earth Elements, Vol. I, Tomsk University Press, Tomsk, 1959.

†G. V. Samsonov, and L. L. Vereikina, Phosphides, Press of the Ukrainian Academy of Sciences, 1961.

PREFACE TO THE AMERICAN EDITION

Refractory compounds of the rare-earth metals with boron, carbon, nitrogen, silicon, and sulfur are finding more and more use in technology, and at the same time represent interesting and important objects of scientific research, which is being intensively conducted in many countries of the world, especially in the USSR, United States, France, German Federated Republic, and Italy.

This monograph makes an attempt to generalize the scattered information on the methods of production, structure, properties, and fields of application of refractory compounds of the rare-earth metals. In comparison with the edition published in the USSR in Russian in 1964, the book is supplemented by materials of certain new studies, especially on the nitrides and sulfides of the rare-earth metals; in addition, certain refinements and corrections are introduced into certain diagrams and into the numerical data on the properties of refractory compounds of the rare-earth metals.

The author hopes that the book will be useful to American specialists working in the field of the rare-earth metals and their compounds and will serve as a supplement to the handbook, "Refractory Compounds," previously published in the United States.* The author would like to express his profound gratitude to Consultants Bureau and its subsidiary, Plenum Press, for their interest in his works on the generalization of data on refractory compounds.

---

*G. V. Samsonov, Handbooks of High-Temperature Materials, No. 2, Properties Index, Plenum Press, New York, 1964.

INTRODUCTION

Lanthanum, the lanthanides (elements Nos. 58-71), and the elements scandium and yttrium, which are close to them in position in the periodic system, properties, character of compounds formed, and geochemical features, are customarily assigned to the group of rare-earth metals. They are all transition metals with internal electron shells in the process of being filled. Moreover, scandium is a transition metal with an unfilled 3d-shell, and opens a new transition period, to which titanium, vanadium, chromium, manganese, and the metals of the iron triad also belong; yttrium is also a d-transition metal with an unfilled 4d-shell and begins the second transition period, being followed by zirconium, niobium, molybdenum, technecium, and the ruthenium triad, while lanthanum and the lanthanides are characterized by an unfilled 4f-electron level, having no 5f-shell at all, and the presence of one 5d-electron each in lanthanum, gadolinium, lutecium, and apparently in terbium.

The fact that they belong to the metals of the transition groups determines not only their properties in the metallic state, but also the properties of the compounds that they form — in particular, compounds with nonmetals: boron, carbon, nitrogen, silicon, and sulfur. In the formation of compounds of this type, the unfilled electron shells of the transition metals exhibit an ability to accept the valence electrons of the atoms of nonmetals,* which in the case of low ionization potentials of the nonmetal atoms (for example, of boron and silicon), leads to their positive (metallic) polarization, while in the case of difficultly ionized nonmetal atoms (for example, nitrogen), it leads to normal (negative) polarization, but with a certain displacement with respect to the maximum of the electron density in the direction of the transition metal atoms. At the same time, the atoms of readily ionized nonmetals manifest a tendency to form direct bonds with one another, leading to the

---

*The criterion $1/Nn$, where N is the principal quantum number of the unfilled electron level and n is the number of electrons on this level, proposed by the author (Dokl. Akad. Nauk, SSSR, 1953, Vol. 93, p. 689), can serve as a qualitative characteristic of the acceptor capacity of the atoms of d-transition metals.

appearance of structures consisting of nonmetal atoms in the lattices of the corresponding compounds of covalently bonded elements. Moreover, the atoms of nonmetals that possess small radii are capable of being inserted into the pores of the metallic lattices, forming the so-called interstitial phases, which also exerts an influence on the types of structures and on the properties of the compounds.

Consequently, compounds of the transition metals with nonmetals should be characterized primarily by a heterodesmic character of the chemical bond, i.e., by the superposition of various types of bonds, the relative fractions of which determine the character of the physical and chemical properties. However, in contrast to the d-transition metals, to which all the above pertains directly, lanthanum and the lanthanides possess deeply-lying unfilled 4f-electron shells, which cannot take direct part in the chemical bond (which is actually confirmed by measurements of the magnetic properties of lanthanum and the lanthanides and their refractory compounds), but can influence the character of the chemical bond formed by the external (valence) or shallow d-electron states. In particular, in view of the closeness of the 4f- and 5d-states, the latter can arise in compounds as a result of $f \rightarrow d$ transitions, the possibility and probability of which are determined by the number of possible terms. Thus, in the formation of compounds of the lanthanides with nonmetals, a unique "transformation" of the lanthanide atoms from f- to d-elements occurs, with the emergence of the possibility of utilizing the principles of formation of the chemical bond that have been rather well elucidated for compounds of the d-transition metals, for their consideration.

Considering the above, a mixed covalent-metallic bond can be ascribed to the borides and silicides of the rare-earth metals (the covalently bonded elements of the structure of boron or silicon atoms form metallic-type bonds with atoms of the rare-earth metals); another extreme case is represented by the nitrides of the rare-earth metals, which are characterized by negative polarization of the nitrogen atoms, with the resultant predominance of the ionic bond in the lattices, but with the simultaneous presence of elements of a metallic bond as well. The carbides and sulfides of the lanthanides occupy an intermediate position in this respect, between the silicides and borides, on the one hand, and the nitrides, on the other, so that, for example, in the crystal lattices of the sulfides with smaller values of the S/Me ratios, primarily metallic properties are manifested, while the phases in which the number of sulfur atoms is sufficient for the formation of covalent bonds among them are polymetallic and possess semiconductor properties.

The possibilities of wide variation of the character of the chemical bond in compounds of the rare-earth metals with nonmetals provide for the

corresponding possibilities of varying the physical and chemical properties of these compounds and producing compounds with preset properties—electrophysical, magnetic, optical, mechanical, refractory, and chemical, for various fields of the new technology, especially high-temperature technology.

CONTENTS

Chapter IV

Silicides of the Rare-Earth Metals

Chapter V

Sulfides of the Rare-Earth Metals

BORIDES OF THE RARE-EARTH METALS

1. Structures and Properties of Borides of the Rare-Earth Metals

Crystal Chemistry of the Borides. The borides of a number of alkaline-earth and rare-earth metals, as well as thorium, corresponding to the composition MeB_6, were produced first; the compounds of this type proved to be the most stable in the investigated metal-boron systems [1].

The independence of this composition from the normal valences of the metallic components of the compounds (from 2 to 4) made it possible to hypothesize [2] that all these substances possess the same structure, which is also responsible for their constant composition.

The first investigations of the structures of the rare-earth borides were conducted [2, 3] in 1932. It was established that the hexaborides of yttrium, lanthanum, cerium, praseodymium, neodymium, gadolinium, erbium, and ytterbium possess a monotypic structure.

The presence of systematic extinctions showed that the atoms of the metal are arranged in the points of a simple cubic lattice, while six boron atoms form a complex in which they are situated in the vertices of an octahedron, this complex centering the simple cubic lattice of the metal. The space group of this structure was established as O_h^1 — Pm^3m, and the positions of the metal (000) and boron ($\frac{1}{2}$ $\frac{1}{2} \pm u$ $\frac{1}{2}$ $\frac{1}{2}$; $\frac{1}{2} \pm u$ $\frac{1}{2}$) atoms were determined (Fig. 1).

Laves [4] investigated the crystal structure of a number of metal hexaborides, refined their parameters, and established the values of the interatomic distances. Pauling [5] gave a detailed crystal-chemical analysis of the structure of calcium boride CaB_6, according to the type of which all the hexaborides of the rare-earth metals are constructed.

It is crystal-chemically expedient to interpret this structure as a framework of octahedra, formed by boron atoms, in the vacancies of which the metal atoms are arranged. The general form of the structure of the compounds and (in a first approximation) the dimensions of the cell are determined
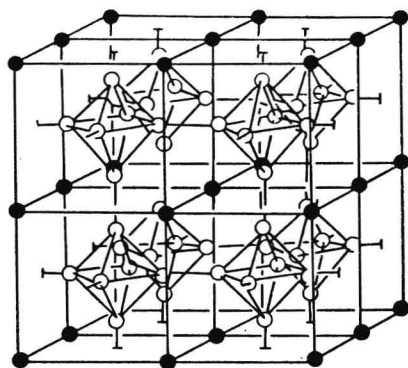
1

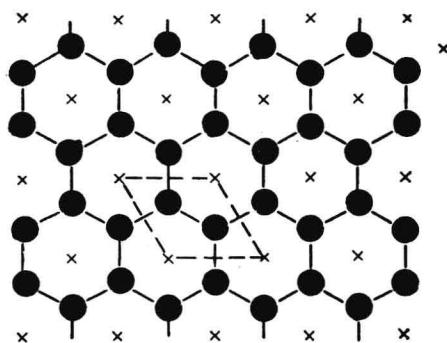Fig. 1. Crystal structure of the hexa-
borides MeB_6: $\bullet - Me$; $O - B$.

Fig. 2. Crystal structure of the diborides
MeB_2: $\times - Me$; $\bullet - B$.

chiefly by the framework of boron atoms. The metal in this case exerts less
influence, although the peculiarities of the properties are frequently related
to the metallic atoms. This is explained by the fact that the vacancies
among the boron octahedra are large enough so that the metal atoms can be
arranged in them without any great deformation, and in certain cases even
with free space left over [6-8].

The structures of the borides MeB_2 and MeB_4 were investigated
[9, 10, 177]. The borides MeB_2, detected for scandium and yttrium, and typi-
cal of transition metals with a d-electron level in the process of filling,
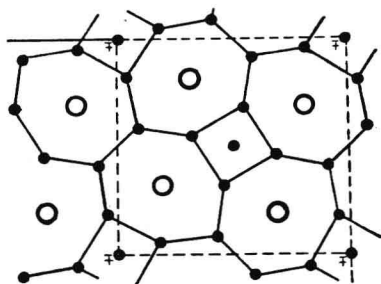
Fig. 3. Crystal structure of the te-
traborides MeB_4: $O-Me$; $\bullet-B$.

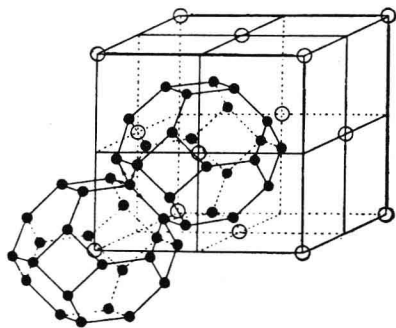Fig. 4. Crystal structure of the do-
decaborides MeB_{12}: $O-Me$; $\bullet-B$.

possess a structure representing a sequential alternation of hexagonal layers
of metallic atoms, situated in the points of a hexagonal close-packed lattice
with a small c/a ratio, and layers of boron atoms, forming a hexagonal two-
dimensional network (Fig. 2).

The tetraborides MeB_4, just like the hexaborides MeB_6, contain three-
dimensional frameworks of boron atoms, among which the metal atoms are
situated, arranged in the points of a tetragonal or cubic lattice.

The structure of the tetraborides can be represented as a combination
of the structures MeB_2 and MeB_6; the structure contains three-faced prisms
of the type of MeB_2, as well as four-faced prisms, analogous to somewhat
distorted cubes of MeB_6 (Fig. 3). Individual boron atoms are distributed in
the centers of the three-faced prisms, while the channels passing through the

3

four-faced prisms accommodate octahedra of boron atoms; these octahedra do not possess common vertices. The boron atoms from the square cross sections of the octahedra and the boron atoms in the three-faced prisms form flat networks of four- and seven-membered rings. Thus, the structural motif of MeB_4 is a combination of the motifs of MeB_2 and MeB_6 [6]. The elementary cell of this structure is tetragonal, with four molecules in the cell; space group $D_{4h}^6 - P4/mbm$.

Zalkin and Templeton [11-13] investigated the structure of this type in detail.

Dodecaborides MeB_{12} have been produced for yttrium, terbium, dysprosium, holmium, erbium, thulium, and lutecium [164, 168, 170]. They are isomorphous with the dodecaborides of zirconium and uranium and possess a face-centered cubic lattice, belonging to the space group $O_h^5 - Fm3m$ with four molecules in the elementary cell (Fig. 4). These structures are similar to a modified sodium chloride structure and are characterized by the presence of groups of 12 boron atoms (in contrast to the groups of six boron atoms in the structure of the hexaborides) occupying the positions of chlorine, and metal atoms occupying the positions of sodium. Thus, the metal atoms lie in the centers of cuboöctahedra, in the vertices of which 24 boron atoms are situated. A group of 12 boron atoms, forming icosahedra, is characteristic of certain boron compounds; in particular, it also exists in crystalline boron [167].

In the work of Post et al. [14], still another boride phase, detected for lanthanum, praseodymium, gadolinium, and ytterbium, is detected. The exact composition of this phase was not determined, but it corresponds approximately to the formula MeB_x with $x = 2 - 4$. The possibility of stabilization of this phase by carbon is not excluded, although in this case the amount of carbon should be extremely small. A study of the crystal lattice parameters of these compounds revealed an interesting variation of them with the atomic number of the metal forming the boride. These compounds possess a tetragonal lattice, but the ratio of the axes c/a in them decreases from 1.036 for LaB_x, passing through 1.000 for PrB_x, to 0.962 for GdB_x and 0.943 for YbB_x. A boride with a similar structure was also detected in alloys of yttrium with boron [15].

Borides of the composition MeB_4 have been established for yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium; the borides MeB_6 have been established for all the rare-earth metals (except for promethium).

On the basis of the high electroconductivity of the rare-earth hexa-borides, it was hypothesized that the metal gives its valence electrons to the complex B_6, which usually cannot accept them entirely [2]. The pres-ence of metal atoms in the hexaborides was considered demonstrated by magnetic measurements [16]. In this work it was shown that the magnet-ic properties of compounds of the rare-earth metals of different types are the same and correspond to the magnetic properties of tripositive ions (this conclusion was drawn in a measurement of the magnetic properties of the hexaborides of lanthanium, cerium, praseodymium, neodymium, and samar-ium, in which the effective valence of the metals is actually equal to three).

In principle, this hypothesis is correct—an increased electron density, belonging both to the metal and to the boron, is created between the core of the metal atom and the complex of boron atoms; the probability that these electrons will stay on the shells of both components is small [17], which is also responsible for the high electroconductivity of the hexaborides, the low electron work function in thermionic emission, the ability for auto-electronic (cold) emission of electrons, and other specific physical properties.

In the work of Zhdanov et al. [18]—one of the first studies devoted to the crystal chemistry of borides of the alkaline-earth and rare-earth metals—it is indicated that hexaborides are formed by the elements situated in Groups II, III, and IV of the periodic system; moreover, they all possess a cubic structure of the CaB_6 type, except for the hexaborides of beryllium and magnesium. It was established in this work that within the limits of the family of cubic hexaborides, there are several subgroups, the affilation to which is determined by the valence of the metal atom. An analogous viewpoint was expressed for the hexaborides of the rare-earth metals in [14], where correspondence of the curves of the effective atomic radii according to Klemm [19] and the lattice periods of the rare-earth hexaborides was detected. While for most of the rare-earth metals and their borides, the curves decrease with increasing atomic number of the metal, for europium and yttrium an anomalous variation is detected—a sharp increase in both curves, which, as is well known, for the atomic radii is related to the di-positive effective valence of europium and ytterbium, since the departure of one electron from an outer orbital to fill in a defect in an inner orbital produces an increase in the dimensions of these atoms. The closeness of the indicated curves shows, in the first place, that the effective valence of the metals in the hexaborides is close to the valence in crystals of the pure metals, and, in the second place, emphasizes the metallic character of the bond in the hexaborides. The variation of the ionic radii does not exhibit the indicated anomalies [20]; nor are they detected in the variation of the lattice periods of the phases MeB_4, to which, in accord with this, an
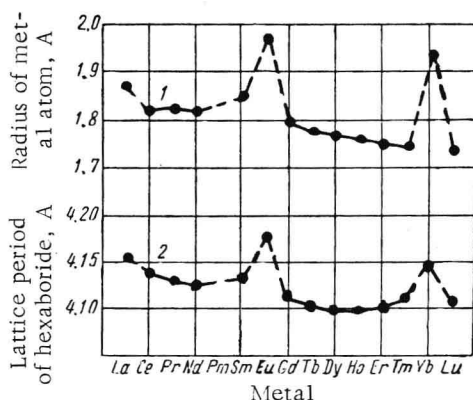
Fig. 5. Dependence of the atomic radii of the rare-earth metals (1) and lattice periods of their hexaborides (2) on the atomic number of the element.

ionic character of the bond between the metal and boron atoms is ascribed [14].

An analogous phenomenon is observed in the carbides of the rare-earth metals [21]. While the crystal lattice parameters of the dicarbides obey the same principle as the hexaborides of the corresponding metals (i.e., a metallic character of the bond is observed), in the case of carbides with the composition Me_2C_3, a different pattern appears, typical of the tetraborides, nitrides [22], and oxides [23, 24] of the rare-earth metals. After the values of the lattice periods of the hexaborides of europium [25, 26], terbium [27, 28], holmium, dysprosium, and lutecium [29, 30] were determined, the possibility emerged of refining the path of the curve of the lattice periods of the rare-earth hexaborides [25] (Fig. 5). In turn, the character of the arrangement of the curve, considering its interpretation outlined above, permits an interpolation of the approximate value of the lattice period of the still unknown hexaboride of promethium (a ≈ 4.128 A).

On the basis of the generally accepted concepts of the lanthanide compression in the series of rare-earth elements, we should have expected a continuous decrease in the crystal lattice periods of the hexaborides from CeB_6 to SmB_6, inclusively, then a maximum, in view of the change in the valence of europium in europium boride, and a further increase in the second half-period from GdB_6 to TaB_6, with a maximum at YbB_6. As precise measurements of the crystal lattice periods of the hexaborides showed, on

6