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THORIUM CERAMICS DATA MANUAL

Volume IV — Borides

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ERRATA:

On page 39 of Vol. I, the callout of Ref. 72 should be changed to 97.

On page 67 of Vol. II, replace Fig. 7 with this illustration.

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Volume IV. Borides

Sigfred Peterson

ABSTRACT

Physical, chemical, and mechanical properties of thorium borides, alone and in combination with other borides, are compiled from the literature through November 1971. The compounds ThB_4 and ThB_6 and the solid solutions $(\text{Th,U})\text{B}_4$ are reasonably well characterized, although there are many gaps in the property data. Higher borides and boride-carbides are briefly described.

SYSTEM INFORMATION

A tentative phase diagram for the thorium-boron system has been proposed by Stecher *et al.*¹ and is shown in Fig. 1. Several investigations in this system have turned up only two important compounds, ThB_4

and ThB_6 . Evidence for ranges of nonstoichiometry in these compounds will be presented in the appropriate Sects. A1. Although lower borides have been reported in early work, modern examinations of thorium-rich samples^{2,3} show no borides below ThB_4 . Higher borides, proposed to be ThB_{18} and ThB_{66} were prepared by Etourneau and Naslain⁴ and characterized by x-ray diffraction. The formula of the latter was verified⁵ by x-ray diffraction by a single crystal obtained from a melt.

THORIUM TETRABORIDE SYSTEMS

A. Thorium Tetraboride

1. Composition

The lattice parameter did not vary for the ThB_4 phase in compositions ranging from 25 to 85 at. % B, indicating a very narrow range of composition for the tetraboride.² However, Matterson *et al.*^{6,7} report that on heating in vacuum at 2000°C, ThB_4 first becomes boron deficient with a 0.46% decrease in the c_0 lattice parameter before decomposing to metal. A similar difference in c_0 for boron-rich and thorium-rich specimens was reported by Stecher *et al.*¹

Fig. 1. Preliminary Phase Diagram of the Thorium-Boron System. Copied from Stecher *et al.*¹ with permission of Metallwerk Plansee AG.

2. Preparation

Thorium tetraboride has been prepared by many methods. Most of these have been reviewed by Matterson and coworkers,^{5,7} with references to the literature. Most modern preparations involve heating together powders of the elements; for example, Matterson and coworkers and Brewer *et al.*² Unfortunately, these powders are often contaminated, particularly with oxygen, so pure products are usually not obtained. Matterson *et al.*^{6,7} describe in detail a hot pressing technique that gave compacts of density near theoretical (1% porosity); they report impurity contents of 1 to 5% each of ThO₂ and ThB₆. First they cold pressed a nearly stoichiometric mixture of crystalline boron and thorium powder. The compacts were heated in argon; at 1000°C they reacted exothermally. After cooling, the compacts were crushed to -100 mesh. Thorium tetraboride bodies were formed from the powders by hot pressing in graphite dies. A thin layer of boron nitride was needed to prevent interaction at pressing temperatures over 1800°C. At pressing pressures of 2 tsi (30 MN/m²) the bulk density reached a peak at nearly theoretical for a pressing temperature of 1800°C. Brewer *et al.*¹ reported finding almost pure single crystals of ThB₄ in induction-heated mixtures of powders of the elements containing from 33 to 55 at. % Th. Griesenauer *et al.*⁸ prepared ThB₄ by arc melting stoichiometric proportions of the elements. Their castings cracked except when a preheated graphite mold was used.

3. Crystal Properties

Structure.⁹ – Tetragonal; space group D_{4h}^{5} , $P4/mbm$; isomorphous with UB₄ and CeB₄.

Lattice Parameters. – See Table 1.

Table 1. Lattice Parameters of ThB₄

Reference	Parameter (Å)	
	a_0	c_0
Zalkin and Templeton ⁹	7.256 ± 0.004	4.113 ± 0.002
Toth <i>et al.</i> ³	7.258	4.113
Matterson <i>et al.</i> ^{6,7}		
As prepared	7.258 ± 0.002	4.116 ± 0.002
Melted	7.257 ± 0.002	4.097 ± 0.002
Auskern and Aronson ¹⁰	7.245	4.11
Stecher <i>et al.</i> ¹		
Boron-rich material	7.258	4.113
Thorium-rich material	7.257	4.091

Theoretical Density.^{7,9} – 8.45 g/cm³.

Thermal Expansion. – Matterson *et al.*^{6,7} report a coefficient of $5.9 \times 10^{-6}/^{\circ}\text{C}$ for the range 25 to 1000°C. A constant coefficient of $9.9 \times 10^{-6}/^{\circ}\text{C}$ has been reported¹¹ for the range 1100 to 1900°C, increasing from lower values at lower temperatures.

Color. – Gray.^{1,6,10}

4. Thermodynamic Properties

Southern Research Institute¹¹ fits its enthalpy measurements on ThB₄ to an empirical equation that transforms to

$$H - H(0^{\circ}\text{C}) = 0.128t - 2.62 \times 10^{-5}t^2 + 31.14/(t + 18) - 17.51 \text{ cal/g} \\ = 0.535t - 1.10 \times 10^{-5}t^2 + 130/(t + 18) - 73.3 \text{ J/g},$$

where t is the centigrade temperature. From the slope of the enthalpy vs temperature plot, specific heats given in Table 2 were derived. Caution should be exercised in using these results. They appear to be from a screening program, in which several properties were measured hurriedly for a large number of materials, without any attempt to verify accuracy. Results from the same investigation on the enthalpy of zirconium diboride are inconsistent with additivity rules.¹² Other results from the same source may be similarly subject to question. They are quoted here in the absence of any other information on the same properties.

From high-temperature emf measurements, Aronson and Auskern¹³ found the standard free energy of formation at 850°C to be -52.0 kcal/mole or -218 kJ/mole. From a possibly uncertain consideration of the stability of ThB₄, Brewer and Haraldsen¹⁴ have estimated that the heat of formation is more negative than -54 kcal/mole (-226 kJ/mole).

5. Change of State

Matterson *et al.*⁷ report a melting point of 2210°C, but Stecher *et al.*¹ indicate congruent melting a little

Table 2. Specific Heat of ThB₄ from Southern Research Institute¹¹

Temperature (°C)	Specific Heat	
	(cal/g)	(J/g)
260	0.118	0.494
540	0.122	0.510
815–1925	0.124	0.519

below 2500°C. The lower melting point may have been due to contamination, since the material contained 1 to 5% each of ThO_2 and ThB_6 .

6. Electrical and Magnetic Properties

Several properties measured by Auskern and Aronson¹⁰ are collected in Table 3. Matterson *et al.*^{6,7} report a higher value of electrical resistivity of 200 $\mu\Omega\text{-cm}$, presumably at room temperature and uncorrected for porosity. High-temperature resistivity measurements¹¹ on a hot-pressed commercial specimen are shown in Fig. 2. The decrease with temperature contrasts with increases observed in the same investigation for other refractory borides. The sharp decrease is at the same temperature that dilatometric measurements in the same investigation showed deviations that may be an effect of sintering. (But see caution in Sect. 4 above.) The same investigators also measured thermoelectric voltages over the range 980 to 1750°C for ThB_4 specimens between contacts of ATJ graphite.

7. Heat and Mass Transport

Matterson *et al.*⁷ report a thermal conductivity of 0.13 $\text{W cm}^{-1} (\text{°C})^{-1}$ at 25°C for ThB_4 . High-temper-

ature thermal conductivity and total normal emittance are given in Figs. 3 and 4 for hot-pressed commercial specimens¹¹ (but see caution in Sect. 4).

Table 3. Electrical and Magnetic Properties of ThB_4 from Auskern and Aronson¹⁰

Property	Temperature (°K)	Value for ThB_4
Electrical resistivity ^a	300	$68 \pm 5 \mu\Omega\text{-cm}$
	78–700	$55 + 0.045T \mu\Omega\text{-cm}$
Hall coefficient ^a	78–350	$-1.6 \times 10^{-4} \text{ cm}^3/\text{C}$
Thermoelectric power ^b	300	$-5 \pm 1 \mu\text{V}/\text{°C}$
Magnetic susceptibility	300	$0.04 \times 10^{-6} \text{ cm}^3/\text{g}$
	70	$0.08 \times 10^{-6} \text{ cm}^3/\text{g}$

^aCorrected for porosity.

^bOver the range 100 to 325°K, values showed a scatter about values proportional to the absolute temperature.

Fig. 2. High-Temperature Electrical Resistivity of ThB_4 . Measured by Southern Research Institute.¹¹

Fig. 3. Thermal Conductivity of ThB_4 . Measured by Southern Research Institute.¹¹ The dashed portion of the curve is reported suspect because the specimen was found to be cracked after the measurement.

Fig. 4. Total Normal Emittance of ThB_4 . Reported by Southern Research Institute.¹¹

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8. Mechanical Properties

Matterson *et al.*⁷ report a modulus of rupture of 20,800 psi and a hardness of "1000 to 1200 V.P.N." (presumably a diamond pyramid hardness measured with a Vickers tester) for hot-pressed ThB₄ with a density of 8.4 g/cm³. The microstructure they show indicates a grain size of about 10 μ m.

9. Chemical Properties

Thermal Stability. — Matterson *et al.*^{6,7} found that ThB₄ loses boron on melting; on subsequent solidification the lattice parameter c_0 is decreased by 0.02 Å while a_0 is unchanged. On remelting, no further change occurs.

Reactions with Gases. — Matterson and coworkers^{6,7} measured the weight changes of hot-pressed ThB₄ specimens exposed to several gases for at least 40 hr at 600 to 1000°C. They observed no reaction with nitrogen in this range or oxygen at 600°C. Measured weight gains in O₂, CO₂, and dry H₂ are plotted in Fig. 5. Griesenauer *et al.*⁸ found that ThB₄ exposed at 515°C for 15 hr to carbon dioxide gained weight at the rate of 0.03 mg cm⁻² hr⁻¹.

Reactions with Liquids. — Thorium tetraboride is insoluble in water but soluble in nitric, hydrochloric, and hot sulfuric acids. It decomposes in acidic solutions of potassium iodate and cerous sulfate. Griesenauer *et al.*⁸ found that ThB₄ gains weight at the rate of 0.006 mg cm⁻² hr⁻¹ in water at 90°C and 0.016 mg cm⁻² day⁻¹ in sodium-potassium alloy at 650°C.

Reactions with Solids. — Brewer and Haraldsen¹⁴ considered ThB₄ unstable to graphite, probably because previous workers^{15,16} failed to obtain it by synthesis using reactions involving carbon or carbides. In agreement, Griesenauer *et al.*⁸ reported a thin reaction layer when ThB₄ was cast in a graphite mold. However, Matterson *et al.*⁷ reported no apparent reaction with carbon below 2000°C; this result is more consistent with knowledge of equilibria in the thorium-boron-carbon system (see part F below).

10. Surface Properties

No information is available.

Fig. 5. Reactions of ThB₄ with Gases. (a) O₂. (b) CO₂. (c) H₂. Copied from Matterson *et al.*⁷ with permission of Metallwerk Plansee AG.

B. Thorium-Uranium Tetraborides

1. Composition

Toth *et al.*³ have examined phases in the system thorium-uranium-boron. The only significant solid-state miscibility is between ThB_4 and UB_4 , and these form a continuous series of solid solutions. A phase diagram³ of the thorium-uranium-boron system is given in Fig. 6.

2. Preparation

Toth *et al.*³ prepared $(\text{Th,U})\text{B}_4$ solid solutions by hot pressing the appropriate mixtures of the elements and annealing 100 hr at 1500°C . Griesenauer *et al.*⁸ arc melted mixtures of the elements in proportions to give solid solutions of ThB_4 with 10 and 20 mole % UB_4 . The buttons cracked, and so did drop castings prepared from them, but the borides could be cast satisfactorily in heated graphite molds despite some reaction.

3. Crystal Properties

The solid solutions show the tetragonal structure of the components. The lattice parameters,³ shown in Fig. 7, show a positive deviation from Vegard's law. The thermal expansion of one composition, as determined by Griesenauer *et al.*,⁸ is given in Fig. 8.

Fig. 6. Phases in the System Thorium-Uranium-Boron. Section $\text{Th-UB}_2\text{-B}$ is for 1500°C , remainder for 800°C . The abbreviation MK represents the $(\text{Th,U})\text{B}_4$ solid solution. Copied from L. E. Toth *et al.*³

Fig. 7. Lattice Parameters of $(\text{Th,U})\text{B}_4$ Solid Solutions. Copied from L. E. Toth *et al.*³

Fig. 8. Thermal Expansion of $\text{ThB}_4\text{-10 at. \% UB}_4$. Based on Griesenauer *et al.*⁸

4. Thermodynamic Properties

No numerical values of functions are available.

5. Change of State

No information is available.

6. Electrical Properties

No information is available.

7. Heat and Mass Transport

Griesenauer *et al.*⁸ show graphically the thermal conductivity of arc-melted $\text{ThB}_4\text{-10 mole \% UB}_4$ from 200 to 900°C . Over this range their values can be fit by $0.239 + 0.000167t \text{ W cm}^{-1} (^\circ\text{C})^{-1}$, where t is the centigrade temperature.

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Fig. 9. Oxidation of ThB_4 -10 mole % UB_4 in Dry Air (Dew Point, -43°C). Copied from Griesenauer *et al.*⁸

8. Mechanical Properties

Griesenauer *et al.*⁸ report the following compressive fracture stresses for arc-melted ThB_4 -10 mole % UB_4 .

Temperature ($^\circ\text{C}$)	Fracture Stress	
	(psi)	(MN/m ²)
20	118,000	810
647	87,000	600
980	70,000	480

9. Chemical Properties

The oxidation behavior of ThB_4 -10 mole % UB_4 in dry air, as reported by Griesenauer *et al.*⁸ is given in Fig. 9. The same authors found no reaction of ThB_4 -10 mole % UB_4 or ThB_4 -20 mole % UB_4 with aluminum alloy 3003 or zirconium at 540°C with type 321 stainless steel, Inconel, Nb, Ta, Mo, or W at 815°C . The latter four metals also did not react in 100 hr at 1095°C , but in 1000 hr a slight reaction was observed with niobium and tantalum and a moderate reaction with molybdenum.

10. Surface Properties

No information is available.

C. Systems with Plutonium

No information is available.

D. Systems with Nonfuel Borides

Stecher *et al.*¹ found complete solid solutions between ThB_4 and CeB_4 . Their phase diagram for the system thorium-cerium-boron is shown in Fig. 10. The

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Fig. 10. System Th-Ce-B at 1600°C . Copied from Stecher *et al.*¹ with permission of Metallwerk Plansee AG.

lattice parameters of the solid solutions varied from $a_0 = 7.258$, $c_0 = 4.113$ for ThB_4 to $a_0 = 7.206$, $c_0 = 4.090$ for CeB_4 with a positive deviation from Vegard's law.

Pitman and Das¹⁷ report a ternary diagram for the system thorium-tungsten-boron, based on specimens fired at 1800°C and furnace cooled. No miscibility of tungsten with the thorium borides was detected, but a monoclinic compound ThWB_4 was formed.

E. More Complex Systems

No information is available.

F. Thorium Borocarbides

Toth *et al.*¹⁸ sintered and melted mixtures of thorium, boron, and carbon and determined by x-ray diffraction the phase relationships shown in Fig. 11. They found no solubility of boron in thorium carbides or carbon in thorium borides, but three borocarbide compounds were found with appreciable composition ranges: ThB_2C , ThBC , and Th_2BC_2 . The last of these was quite reactive toward air. The compound ThB_2C was hexagonal with lattice parameters $a_0 = 3.868 \text{ \AA}$, $c_0 = 3.810 \text{ \AA}$ for the carbon-rich composition limit and $a_0 = 3.860 \text{ \AA}$, $c_0 = 3.793 \text{ \AA}$ for the carbon-poor limit.

Fig. 11. Phase Fields in the System Thorium-Boron-Carbon. Copied from Toth *et al.*¹⁸

THORIUM HEXABORIDE SYSTEMS

A. Thorium Hexaboride

1. Composition

Stecher *et al.*¹ report a 0.002-Å difference in lattice parameter between thorium-rich and boron-rich preparations of ThB₆ and suggest that a narrow range of homogeneity is a possible cause. Etourneau *et al.*¹⁹ have verified this range of lattice parameters and with a study of x-ray diffraction, neutron diffraction, and density and have shown that it corresponds to a range of compositions from Th_{0.78}B₆ to stoichiometric.

2. Preparation

Thorium hexaboride is generally made from the powdered elements by pressing and sintering or hot pressing. Etourneau and Naslain⁴ report that the elements start forming the tetraboride on heating to 850°C, and that additional boron if present forms the hexaboride at 1000°C, reaching completion in 2 hr at 1300 to 1450°C. Aronson and Auskern¹³ report a similar experience. The material sinters readily to a density greater than 98% of theoretical. The material is usually prepared and fabricated in vacuum; sometimes a hydrogen atmosphere is used. Glaser¹⁵ prepared the hexaboride by hot pressing thorium, boron, and carbon at 1350°C or higher. Samsonov and Zorina¹⁶ reduced the oxide to hexaboride with B₄C and lampblack at 1800°C, and Post *et al.*²⁰ indicated that the hexaboride could be obtained by firing a mixture of oxide, boron, and carbon in hydrogen. Samsonov *et al.*²¹ prepared ThB₆ from B₄C and ThO₂ in 60 min at 1600°C and obtained 99.3%-dense compacts by hot pressing for 5 min at 2000°C and 20.7 MN/m².

Andrieux²² reduced ThO₂ electrolytically to ThB₆ in melts of B₂O₃ with alkali and alkaline earth metal oxides and fluorides.

3. Crystal Properties

Structure. — Thorium hexaboride has a cubic structure, isomorphous with several alkaline earth and rare earth hexaborides. The space group is O_h^1-Pm3m , with the thorium in a simple cubic lattice in a network of boron atoms. Stackelberg and Neumann²³ describe this structure, although they did not measure the thorium compound. Nonstoichiometry is accommodated by thorium vacancies.¹⁹

Lattice Parameter. — Table 4 lists several of the more recent values. Aronson *et al.*²⁶ give the following

Table 4. Lattice Parameter of ThB₆

Reference	Parameter (Å)
Etourneau and Naslain ⁴	4.1105 ± 0.0005
Matterson <i>et al.</i> ^{6,7}	4.111 ± 0.002
Auskern and Aronson ¹⁰	4.108
Toth ³	4.111
Post <i>et al.</i> ²⁰	4.110
Zhuravlev <i>et al.</i> ²⁴	4.101
Blum and Bertaut ²⁵	4.113 ₂
Aronson <i>et al.</i> ²⁶	4.106
Stecher <i>et al.</i> ¹	
Boron-rich material	4.110
Thorium-rich material	4.108
Etourneau <i>et al.</i> ¹⁹	
Stoichiometric material	4.110 ₅
Th _{0.78} B ₆	4.112 ₅

high-temperature parameters:

Temperature (°C)	Room	1010	1212	1420	1628
<i>a</i> ₀ (Å)	4.104	4.139	4.149	4.158	4.168

The difference in the room-temperature value here and by the same authors in Table 4 is attributed to less accuracy for the high-temperature apparatus.

Theoretical Density. — Etourneau and Naslain⁴ calculated 7.10 g/cm³ from their lattice parameter.

Color. — Red,⁶ red-violet,^{1,22} dark red powder.¹⁰ Etourneau *et al.*¹⁹ report that their powder samples varied from black to deep red through violet as the boron-to-thorium ratio decreased.

Thermal Expansion. — Zhuravlev *et al.*²⁴ give a coefficient of thermal expansion of 7.8×10^{-6} for the range 20 to 820°C. The expansion at higher temperatures, measured by Aronson *et al.*,²⁶ is shown in Fig. 4, p. 64, of Vol. II of this compilation.

4. Thermodynamic Properties

Etourneau *et al.*²⁷ give for the heat capacity of ThB₆ from 2 to 12°K

$$C = 4.8T + 0.3T^3 \text{ mJ mole}^{-1} (\text{°K})^{-1}.$$

From high-temperature galvanic cell measurements, Aronson and Auskern¹³ report the standard free energy of formation of ThB₆ to be -54.4 kcal/mole or 227.6 kJ/mole at 850°C. Brewer and Haraldsen¹¹ estimate a

heat of formation more negative than -54 kcal/mole (226 kJ/mole).

5. Change of State

Stecher *et al.*¹ indicate congruent melting of ThB_6 at about 2450°C . Earlier measurements, 2195°C (Lafferty²⁸) and 2150°C (Samsonov and Zorina¹⁶), may reflect the presence of free boron, since Stecher *et al.* show the ThB_6 -boron eutectic at 2050°C .

6. Electrical and Magnetic Properties

Reported values of several properties are collected in Table 5. Lafferty²⁸ measured the current density I of thermionic emission from 1160 to 1610°K ; he fit his data by $\log I/T^2 = \log A - 11600\phi/2.303T$, with the work function $\phi = 2.92$ V and the constant $A = 0.5$ A cm^{-2} $(^\circ\text{K})^{-2}$. Samsonov and Zorina¹⁶ reported a work function of 2.86 V.

Table 5. Electrical and Magnetic Properties of ThB_6

Property	Ref.	Temp ($^\circ\text{K}$)	Value for ThB_6
Electrical resistivity, $\mu\Omega\text{-cm}$	10	300	18^a
		78–700	$11 + 0.0225T^a$
	16	Room	37
Hall coefficient, cm^3/C	21	Room	14.8
	10	78–350	$-1.9 \times 10^{-4}^a$
	21	Room	-2.2
Seebeck coefficient, $\mu\text{V}/^\circ\text{C}$	10	300	-5 ± 1
		100–325	$-0.017T$
	27	300	-5
	21		-0.6
	16	293–373	2.5^b
Magnetic susceptibility, cm^3/g	10	70–300	-0.08×10^{-6}
	21		13×10^{-6}
	27	77–500	-1×10^{-5}

^aCorrected for porosity.

^bRelative to copper.

7. Heat and Mass Transport

Samsonov *et al.*²¹ report a thermal conductivity of 44.0 W m^{-1} $(^\circ\text{C})^{-1}$. They report a "radiation factor" (*koeff. izlucheniya* in Russian) of 0.74 at 655 μm . Presumably this is an emissivity, but no dictionary in either language available to the compiler would verify this.

8. Mechanical Properties

Matterson and Jones⁶ report a microhardness of "2590 V.P.N." (presumably a diamond pyramid hardness measured with a Vickers tester) for arc-melted ThB_6 with a density of 6.415 g/ cm^3 . Samsonov and Zorina¹⁶ reported a microhardness of 1740 ± 123 kg/ mm^2 with a load of 20 g for hot-pressed material.

9. Chemical Properties

Andrieux²² found that at room temperature thorium hexaboride is not attacked by hydrofluoric, hydrochloric, or dilute sulfuric acid or by alkalis. It is easily decomposed by hot concentrated sulfuric acid and by nitric acid. It is disintegrated by molten alkali carbonates and bisulfates. It reacts energetically with Na_2O_2 and PbO_2 . Lafferty²⁸ reports no reaction with moisture, oxygen, or hydrochloric acid, presumably at room temperature.

10. Surface Properties

No information is available.

B. Systems with Uranium

Toth *et al.*³ showed essentially no solubility of uranium borides (for example, UB_{12}) in ThB_6 (see Fig. 6). Apparently no one else has investigated mixtures of ThB_6 with uranium borides.

C. Systems with Plutonium

No information is available.

D. Systems with Nonfuel Borides

Since ThB_6 is isomorphous with several rare earth and alkaline earth hexaborides and the lattice parameters are not greatly different, complete solid solubility should be expected. This has been demonstrated for only one system: $\text{ThB}_6\text{-CeB}_6$. Andrieux²⁹ electrolytically reduced mixtures of CeO_2 and ThO_2 in a molten mixture of magnesium fluoride and borate. The result was a homogeneous mixed boride with color varying with composition from the red of ThB_6 to the violet of CeB_6 . Stecher *et al.*¹ found similar results for materials prepared by reactive sintering of the mixed elemental powders. Their equilibrium diagram is shown in Fig. 10, and they found lattice parameters varying from 4.109 for ThB_6 to 4.141 Å for CeB_6 , with a slight

negative deviation from Vegard's law. Lafferty²⁸ measured the thermionic emission of $\text{ThB}_6\text{-50% CeB}_6$ from 1180 to 1470°C; it was intermediate between those of the pure borides.

By electrolysis of appropriate melts, Andrieux and Barbetti³⁰ have substituted sodium for part of the thorium in the lattice of ThB_6 . Bertaut and Blum²⁵ have studied these products by x-ray diffraction. The lattice parameter increased from 4.113 Å for no sodium to 4.151 Å for 77 at. % substitution of sodium for thorium, the apparent limit.

E. More Complex Systems

No information is available.

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