The Crystal Structure of LaIr₄B₄, ThOs₄B₄, ThIr₄B₄ (NdCo₄B₄- Type) and URu₄B₄, UOs₄B₄ (LuRu₄B₄- Type) *

Peter Rogl

Institut für Physikalische Chemie, Universität Wien, A-1090 Wien, Austria

(Received 8 January 1979. Accepted 22 January 1979)

The crystal structure of LaIr₄B₄ has been refined from single crystal counter data. LaIr₄B₄ is tetragonal, P 42/n, Z = 2, isotypic with NdCo₄B₄, \( \frac{\sum |\Delta F|}{\sum |F_0|} = 0.039 \) for 312 independent reflections \(|F_0| > 2\sigma(F_0)\). ThIr₄B₄ and ThOs₄B₄ also belong to the NdCo₄B₄-type structure. URu₄B₄ and UOs₄B₄ were found to crystallize with LuRu₄B₄-type structure. The crystal chemistry of \((RE)T₄B₄\)-phases is discussed and simple geometric relations are shown to exist between them.

(Keywords: Crystal structure; Rare earth–noble metals–boron; Ternary metal borides)

Die Kristallstruktur von LaIr₄B₄, ThOs₄B₄, ThIr₄B₄ (NdCo₄B₄-Typ) und URu₄B₄, UOs₄B₄ (LuRu₄B₄-Typ)

Die Kristallstruktur von LaIr₄B₄ wurde an einem Einkristall bestimmt: tetragonal, \( P 42/n, Z = 2 \), isotyp mit NdCo₄B₄, \( \frac{\sum |\Delta F|}{\sum |F_0|} = 0.039 \) für 312 unabhängige Reflexe \(|F_0| > 2\sigma(F_0)\). ThIr₄B₄ und UOs₄B₄ gehören ebenfalls dem NdCo₄B₄-Typ an. URu₄B₄ und UOs₄B₄ kristallisieren im LuRu₄B₄-Typ. Die Kristallchemie der \((RE)T₄B₄\)-Phasen wird diskutiert und einfache geometrische Beziehungen werden zwischen ihnen aufgezeigt.

Introduction

In a recent study of \( RE \) (Rare Earth)—\{Os, Ir\}—B systems¹, two series of isotypic compounds have been observed: \{La, Ce, Pr, Nd, Sm\}Os₄B₄ and \{Y, La, Ce, Pr, Nd, Sm, Gd, Tb\}Ir₂B₄. All compounds were found to crystallize with the NdCo₄B₄-type structure, whereas for combinations of smaller \( RE \) atoms (Y, Gd, Tb, Dy, Er, Ho, Tm, Yb) with osmium and boron a new structure

* Dedicated to Prof. B. T. Matthias in celebration of his 60th birthday.
type was observed, closely related to NdCo₄B₄ but corresponding to an approximate formula \((RE)_{1.250}Os₄B₄\) (Ref.2).

However, only little information could be found from literature about actinide (Th, U)—noble metal—boron systems.

A CeCo₄B₄-type structure was reported by Vandenberg et al.3 for ThRh₄B₄ while ThRu₄B₄ has been found to crystallize with the recently described crystal structure of LuRu₄B₄ (Ref.4).

In view of a better understanding of the various decisive influences of size, electrochemical, and energy band factors among \((RE)M₄B₄\)-type structures, a study of the alloying behaviour of Th and U in combinations with noble metals and boron was carried out and is the subject of the present work.

Furthermore, single crystal counter data of LaIr₄B₄ have been analyzed in terms of precise atomic parameters, exact boron coordination, as well as boron—boron aggregation.

Arc melted alloys La—Ir—B confirmed the existence of LaIr₄B₄ (see Ref.1), samples however were poorly crystallized. To obtain single crystals, pellets of La(9)Ir(45)B(46) were heated at 1,600 °C for 10 minutes (well above melting) in a recrystallized alumina crucible sealed in a tantalum container. The mixture was then slowly cooled to 1,100 °C over a period of 20 minutes and finally radiation (argon) quenched. The crystal growth procedure was carried out in a purified argon atmosphere at a pressure of \(1.1 \times 10^5\) Pa.

A small crystal suitable for structure determination was obtained by mechanical fragmentation of the melted button.

Table 1. Crystallographic data for LaIr₄B₄, ThOs₄B₄ and ThIr₄B₄. Space group \(P4_2/n\) \((C_{4h}^{2}, \text{No.} \, 86)\), \(Z = 2\), NdCo₄B₄-type

<table>
<thead>
<tr>
<th></th>
<th>LaIr₄B₄</th>
<th>ThIr₄B₄</th>
<th>ThOs₄B₄</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (nm)</td>
<td>0.76719(4)</td>
<td>0.7668(2)</td>
<td>0.7579(2)</td>
</tr>
<tr>
<td>c (nm)</td>
<td>0.39739(2)</td>
<td>0.3972(1)</td>
<td>0.3999(1)</td>
</tr>
<tr>
<td>c/a</td>
<td>0.518</td>
<td>0.518</td>
<td>0.528</td>
</tr>
<tr>
<td>(D_x) kg/dm(^3)</td>
<td>13.50</td>
<td>14.84</td>
<td>14.98</td>
</tr>
<tr>
<td>(\mu) (MoK(\alpha))</td>
<td>1.176 cm(^{-1})</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Weißenberg photographs of the crystal fragment \((\sim 30 \times 30 \times 50 \mu m;\) axis [001]) proved the crystal to be tetragonal with Laue-symmetry \(4/m\). The extinctions \((hkl)\) with \(h + k \neq 2n\) and \((00l)\) with \(l \neq 2n\) * indicate \(P4_2/n\) (No. 86) as the only possible space group. Lattice parameters and intensities were measured with graphite monochromated Mo-\(K\alpha\) radiation on a PW-1100 computer controlled four circle diffractometer (Austrian Natural Science Research Council, Institute of Mineralogy, Technical University Vienna). Cell

---

* From automatic diffractometer intensity recordings.