Synthesis and Crystal Structure of Ordered, Orthorhombic α-NbBr₅

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Niobium Pentabromide, Crystal Structure, Band Gaps

Niobium pentabromide, NbBr₅, is prepared in the orthorhombic ordered (α)-form from the elements in sealed quartz ampoules (Nb powder, Br₂, I) at 973 K. The structure has been determined from single crystal data \(a = 1288.8(2)\), \(b = 1869.0(3)\), \(c = 614.9(1)\) pm; Pnma (No. 62); \(Z = 8; R = 0.055\). \(α\)-NbBr₅ forms dimeric \(\text{Nb}_{2}\text{Br}_{10}\) molecules with \(\text{d}(\text{Nb–Br}) = 271.5\) pm, \(\text{d}(\text{Nb–Br}) = 240.8\) pm and \(\text{d}(\text{Nb–Br}) = 246.1\) pm. \(α\)-NbBr₅ is a diamagnetic semiconductor with \(E_g(\text{NbCl}_5) = 2.74\) eV, \(E_g(α-\text{NbBr}_5) = 1.99\) eV, and \(E_g(\text{NbI}_5) = 0.99\) eV.

Introduction

During the preparation of chalcogenides and chalcogenide halides of niobium, we obtained several compounds like \(\text{NbS}_2\text{Cl}_2\) [1], \(\text{NbTe}_4\) [2], \(\text{Nb}_2\text{Te}_2\text{I}_4\), and others [3]. Especially in the experiments to prepare \(\text{Nb}_2\text{Te}_2\text{Br}_6\), both air-sensitive bromides and non air-sensitive compounds were observed. Further investigations of one of the air-sensitive compounds revealed similarities both with early data for \(\text{NbBr}_3\) [4], as well as the more recently reported \(\beta\)-NbBr₅ [5].

According to Rolsten [4], NbBr₅ crystallizes in the orthorhombic space group Pnma with \(a \sim 1292\) pm, \(b \sim 1860\) pm, \(c \sim 612.5\) pm, \(Z = 8\); a result later confirmed by Berdonosov, Lapitskii, Berdonosova, and Vlasov [7], However, Zalkin and Sands [6] found NbBr₅, crystallizing monoclinically in the space group C2/m with \(a \sim 1920\) pm, \(b \sim 1860\) pm, \(c \sim 600\) pm, \(\beta \sim 90°\), \(Z = 12\), and thus isomorphous with NbCl₅. The monoclinic modification of NbBr₅ was found later [9], and the finding is also supported by another work [8] on the basis of symmetry considerations on Nb NQR data. Crystal structure determinations of the orthorhombic and the monoclinic forms of NbBr₅ have not been reported, but both modifications are possible, and have been related crystallographically by group-sub-group relationships [10] by Müller [11].

The structure of \(\beta\)-NbBr₅ has been determined by Müller and Klingelhöfer [5]. \(\beta\)-NbBr₅ crystallizes orthorhombically in the space group Ccmm with \(a = 644\) pm, \(b = 1867\) pm and \(c = 615\) pm. The structure is characterized by an one-dimensional disordered stacking of \(\text{Nb}_2\text{Br}_{10}\) units in the \(b\)-direction. We report here on the crystal structure of orthorhombic, ordered \(α\)-NbBr₅, and the determination of the band gaps \(E_g\) of \(\text{NbCl}_5\), \(α\)-NbBr₅, and \(\text{NbI}_5\).

Experimental

Preparation

Crystals of the ordered orthorhombic form of \(α\)-NbBr₅ can be prepared by the reaction of niobium powder with liquid bromine at temperatures of 973 K in quartz ampoules. Freshly sublimed bromine was filled into a quartz ampoule (12 mm inner diameter, 16 mm outer diameter). After cooling with \(\text{N}_2\), the stoichiometric amount of niobium powder was added and the ampoule was sealed in vacuo. For safety purposes, the amount of bromine was limited to give a pressure within the ampoule not exceeding 35 atm at \(T \sim 970\) C, assuming all bromine being monatomic in the gas phase, and applying the ideal gas law. The ampoule was slowly heated in a slightly inclined position in a tubular furnace. After a reaction time of 2 d at 973 K the ampoule was cooled to room temperature over a period of 12 h by switching-off the furnace. The ampoule was opened in a glove box (M Braun, Munich, F.R.G., \(O_2 \leq 0.5\) ppm; \(H_2O \leq 0.5\) ppm) and the NbBr₅ collected in a Schlenk storage container.

\(\text{NbCl}_5\) was prepared according to [5]. The purity was checked by ICP-analysis and X-ray powder photographs (cf. below).

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**NbI₅** was prepared analogously to α-NbBr₅ from stoichiometric mixtures of the elements in sealed quartz ampoules at 1100 K [16]. ICP analysis as well as X-ray powder photographs (cf. below) confirmed a single-phased specimen. No attempt was made to get large single crystals of NbCl₅ and NbI₅.

**Properties**

α-NbBr₅ crystallizes as thick platelets with a black metallic luster. Thin crystals are ruby red in colour. α-NbBr₅ is sensitive towards moisture. It is a diamagnetic semiconductor with $\phi_{\text{cgs}}^{\text{mol}} = -72 \times 10^{-6}$ cm³/mol and a band gap $E_g = 1.99$ eV. NbCl₅ and NbI₅ both appear as microcrystalline powders. NbCl₅ is bright yellow, NbI₅ dark brown, sometimes black. Both are sensitive towards moisture under formation of oxide halides.

**Optical properties**

For the determination of the optical band gap $E_g$, the pentahalides are filled under inert conditions into a flat quartz container, which is sealed at atmospheric pressure of argon. The diffuse reflectivity was determined with a PERKIN-ELMER LAMBDA 9 spectrophotometer from 250 to 900 nm in the case of NbCl₅ and α-NbBr₅, and from 250 to 2700 nm in the case of NbI₅.

**Thermal properties**

For α-NbBr₅, DTA experiments in sealed quartz ampoules yield only an endothermic peak on heating at 534–538 K and an exothermic peak on cooling at 533 K. This agrees with the reported melting point of 538.4(2) K of Littke [17].

**Measurement of the electrical conductivity**

The electrical conductivity of α-NbBr₅ has been measured on a pressed pellet by a two contact method [15] in the region 300 ≤ T ≤ 500 K. Two values, namely 1.04 eV and 1.25 eV, respectively, are found for the activation energy.

**X-Ray crystallographic investigations**

X-Ray powder photographs were obtained by the Guinier-Simon technique [12] in a capillary of 0.3 mm diameter. The observed powder pattern shows good agreement with a diagram later calculated [13] on the basis of the result from the structure determination. Single crystals of α-NbBr₅ were isolated in a glove box under an integrated microscope, fixed with silicon grease (baked out 3 days under vacuum at 300 °C) in a quartz capillary which was sealed with an electrically heated Pt wire. The crystal quality was checked and determination of approximate lattice constants was performed with precession X-ray methods. The lattice dimensions agree reasonably well with those given for orthorhombic α-NbBr₅ [4, 7]. Overexposed photographs do not reveal any indication of a one-dimensional disorder, as observed in the cases of β-NbBr₅ and TaI₅ [5, 14]. The crystallographic data for orthorhombic ordered α-NbBr₅ are summarized in Table I. Table II gives the positional and thermal parameters and Table III bond lengths and bond angles.

**Discussion**

α-NbBr₅ crystallizes as dimeric molecules $\text{Nb}_2\text{Br}_5\text{Br}_4/2 = \text{Nb}_2\text{Br}_{10}$ (Fig. 1). The anions are arranged in hexagonal close packed layers, in which 1/5 of the octahedral holes are filled by the metal.
Table II. \(\alpha\)-NbBr\(_5\); positional and thermal parameters \(U_{ij}\) in pm\(^2\) (e.s.d.). The \(U_{ij}\) are expressed for 
\(\exp -2\pi^2(U_{11}h^2a^*+\cdots+U_{23}k1b^*c^*)\).

<table>
<thead>
<tr>
<th>Atom</th>
<th>(x)</th>
<th>(y)</th>
<th>(z)</th>
<th>(U_{eq})</th>
<th>(U_{11})</th>
<th>(U_{22})</th>
<th>(U_{33})</th>
<th>(U_{12})</th>
<th>(U_{13})</th>
<th>(U_{23})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>0.12459(8)</td>
<td>0.36156(4)</td>
<td>-0.0076(1)</td>
<td>237(3)</td>
<td>297(3)</td>
<td>124(4)</td>
<td>288(5)</td>
<td>1(4)</td>
<td>27(3)</td>
<td>-3(4)</td>
</tr>
<tr>
<td>Br(1a)</td>
<td>0.2023(3)</td>
<td>1/4</td>
<td>0.2226(3)</td>
<td>265(6)</td>
<td>361(14)</td>
<td>137(9)</td>
<td>297(8)</td>
<td>0</td>
<td>-81(6)</td>
<td>0</td>
</tr>
<tr>
<td>Br(1b)</td>
<td>0.0450(2)</td>
<td>1/4</td>
<td>-0.2366(2)</td>
<td>274(7)</td>
<td>329(14)</td>
<td>215(11)</td>
<td>278(8)</td>
<td>0</td>
<td>-48(6)</td>
<td>0</td>
</tr>
<tr>
<td>Br(2)</td>
<td>0.9708(1)</td>
<td>0.34865(9)</td>
<td>0.2249(2)</td>
<td>385(5)</td>
<td>348(9)</td>
<td>331(10)</td>
<td>395(7)</td>
<td>5(9)</td>
<td>104(5)</td>
<td>-10(5)</td>
</tr>
<tr>
<td>Br(3)</td>
<td>0.2202(1)</td>
<td>0.65253(9)</td>
<td>0.2620(2)</td>
<td>359(5)</td>
<td>350(10)</td>
<td>295(10)</td>
<td>431(7)</td>
<td>-4(9)</td>
<td>-112(5)</td>
<td>-22(5)</td>
</tr>
<tr>
<td>Br(4)</td>
<td>0.0407(2)</td>
<td>0.44248(10)</td>
<td>-0.2558(2)</td>
<td>374(6)</td>
<td>490(14)</td>
<td>235(10)</td>
<td>397(8)</td>
<td>62(10)</td>
<td>-42(5)</td>
<td>51(4)</td>
</tr>
<tr>
<td>Br(5)</td>
<td>0.7097(2)</td>
<td>0.44302(10)</td>
<td>0.2613(2)</td>
<td>375(6)</td>
<td>432(13)</td>
<td>289(11)</td>
<td>405(8)</td>
<td>-76(9)</td>
<td>39(4)</td>
<td>80(5)</td>
</tr>
</tbody>
</table>

Table III. \(\beta\)-Br\(_5\) Br distances [pm] and bond angles [°] (e.s.d.).

<table>
<thead>
<tr>
<th>Distance</th>
<th>Angles</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nb</td>
<td>Nb</td>
</tr>
<tr>
<td>Br(1a) – Br(1b)</td>
<td>100.5(1)</td>
</tr>
<tr>
<td>Br(1a) – Br(2)</td>
<td>100.2(1)</td>
</tr>
<tr>
<td>Br(1b) – Br(3)</td>
<td>93.4(1)</td>
</tr>
<tr>
<td>Br(1b) – Br(4)</td>
<td>93.6(1)</td>
</tr>
<tr>
<td>Br(1a) – Br(5)</td>
<td>93.9(1)</td>
</tr>
<tr>
<td>Br(1a) – Nb(a)</td>
<td>100.1(1)</td>
</tr>
</tbody>
</table>

Atoms (Fig. 2). The bridging \(\text{Nb}\)–Br bonds within the four-membered rings are much longer (271.5 pm) than the axial (246.1 pm) and equatorial (240.8 pm) ones. This significant difference between the two types of terminal bonds is present in all other \(\text{M}_2\text{X}_{10}\) compounds thus indicating a \textit{trans} effect for the equatorial terminal bonds. A further point of interest is the geometry of the four-membered ring, which is determined by the repulsion of the highly charged metal atoms, leading to a distinct deformation of the \(\text{Br}_5\)-octahedron with an angle \(\text{Br}(1a) – \text{Nb} – \text{Br}(1b)\) of 79.6° and 85.3° and \(\text{Nb} – \text{Br} – \text{Nb}\) angles of 100.5° and 100.2°. Analogous distortions are observed in \(\beta\)-NbBr\(_5\) [5].

Fig. 1. Molecular \(\text{Nb}_2\text{Br}_{10}\) unit with atomic labeling, mean bond distances and pertinent angles.
An interesting question is the existence of a monoclinic form of NbBr$_5$ [9] which is supposed to be isomorphous with NbCl$_5$. The orthorhombic form has a volume of 111.51 cm$^3$/mol, compared to 109.05 cm$^3$/mol for the monoclinic form. This indicates that the ordered orthorhombic NbBr$_5$ ($\alpha$-NbBr$_5$) is probably the high temperature modification, whereas the monoclinic form ($m$-NbBr$_5$) represents the low temperature form. DTA/DSC investigations, however, have so far been unsuccessful in proving phase transitions. The preparation temperatures of 973 K for $\alpha$-NbBr$_5$ and 523 K for $m$-NbBr$_5$ support this finding, but leaves the stability range of $\beta$-NbBr$_5$ with a volume of 111.34 cm$^3$/mol and a preparation temperature of $T \leq 498$ K (40 K below the melting point) to be explained.

Fig. 2 shows the stacking of the Nb$_2$Br$_{10}$ units in the unit cell. The stereo picture is directly comparable to the proposed structure in Pnma (Fig. 4 (h) in [11]). The observed band gaps (Fig. 3) $E_g$(NbCl$_5$) = 2.74 eV, $E_g$(a-NbBr$_5$) = 1.99 eV, and $E_g$(NbI$_5$) = 0.99 eV agree with values reported by Kepert and Nyholm [18] for $E_g$(NbCl$_5$) = 420 m$\mu$ ($\pm$ 2.85 eV) and $E_g$(NbBr$_5$) = 620 m$\mu$ ($\pm$ 1.99 eV). The somewhat higher values for NbCl$_5$ may be caused by admixtures of colourless oxide chlorides.

The diffuse reflection spectrum of $\alpha$-NbBr$_5$ shows two small additional humps at 456 and 493 nm, which are lying in the typical region for d-d transitions. They are present in all samples of $\alpha$-NbBr$_5$, investigated so far. For comparison, the pyridine adducts of Nb(IV) halides [19] give — in the case of NbBr$_4$ — two bands at 430 and 480 nm. This may lead to the conclusion, that our samples are contaminated with NbBr$_4$. However, our $\alpha$-NbBr$_5$ has been prepared by excess Br$_2$, so that the formation of NbBr$_4$ can be excluded. The observed activation energies from the conductivity measurement $E_1^\alpha = 1.04$ eV and $E_2^\alpha = 1.25$ eV are clearly related to “extrinsic” acceptor and/or donor levels, indicating an high degree of dopants present in the investigated samples of $\alpha$-NbBr$_5$.

Our thanks are due to W. Bauhofer and R. Kremer (both MPI, Stuttgart) for measurements of the conductivity and magnetic susceptibility, respectively.