Preparation and Properties of Compact Cubic $\delta$-NbN$_{1-x}$

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Compact $\delta$-NbN$_{1-x}$ was prepared by heating niobium wire for several days in nitrogen at 4 MPa pressure and temperatures of 1723 to 1923 K. The samples obtained had compositions between NbN$_{0.924}$ and NbN$_{0.975} \pm 0.002$ and were coarse-grained. The lattice parameter increases with the nitrogen content from $a = 0.43884$ nm for NbN$_{0.924}$ to $a = 0.43913$ nm for NbN$_{0.975}$. From the determination of the lattice parameters up to 1073 K the coefficient of linear thermal expansion as a function of temperature was evaluated. The microhardness $H_V_{0.1}$ decreases from $1300 \pm 80 \cdot 10^7$ Nm$^{-2}$ for NbN$_{0.924}$ to $1080 \pm 60 \cdot 10^7$ Nm$^{-2}$ for NbN$_{0.975}$. The occupancies of both the niobium and the nitrogen sublattices were calculated using experimental density data. The occupancy of the niobium sublattice decreases linearly with increasing nitrogen content. An extrapolation gives $2.9 \pm 0.4\%$ vacancies in both sublattices for stoichiometric $\delta$-NbN.

(Keywords: B1 Niobium nitride; Microhardness; Thermal expansion; Vacancy concentration)

Herstellung und Eigenschaften von kompaktem, kubischem $\delta$-NbN$_{1-x}$

Kompaktes $\delta$-NbN$_{1-x}$ wurde durch mehrtägiges Erhitzen von Niobdraht in Stickstoff bei einem Druck von 4 MPa und Temperaturen von 1273 bis 1923 K hergestellt. Die dabei erhaltenen Proben hatten Zusammensetzungen von NbN$_{0.924}$ bis NbN$_{0.975} \pm 0.003$ und zeigten ein grobkörniges Gefüge. Der Gitterparameter steigt mit dem Stickstoffgehalt von $a = 0.43884$ nm für NbN$_{0.924}$ bis $a = 0.43913$ nm für NbN$_{0.975}$ an. Von einer Bestimmung der Gitterparameter bis 1073 K wurde der lineare thermische Ausdehnungskoeffizient erhalten. Die Mikrohärte $H_V_{0.1}$ sinkt von $1300 \pm 80 \cdot 10^7$ Nm$^{-2}$ für NbN$_{0.924}$ auf $1080 \pm 60 \cdot 10^7$ Nm$^{-2}$ für NbN$_{0.975}$ ab. Die Besetzung sowohl des Niob- als auch des Stickstoffteilgitters wurde unter Verwendung von experimentell gemessenen Dichten bestimmt. Die Besetzung des Niobteilgitters fällt mit zunehmendem Stickstoffanteil linear ab. Eine Extrapolation dieser Werte ergibt für stöchiometrisches $\delta$-NbN einen Leerstellenanteil von $2.9 \pm 0.4\%$ auf beiden Teilgittern.
The refractory mononitrides with the B1 type structure are of considerable interest since they combine a number of exceptional physical properties such as high superconducting transition temperatures, high melting points and high microhardness. They exist within a rather broad range of homogeneity whereas the physical properties change with composition within the limits of that range.

Many studies have been made of the niobium-nitrogen system; these were reviewed by Toth\textsuperscript{1}, Brauer, Elliot and Guard and their coworkers\textsuperscript{2–6} and recently Brauer and Kern\textsuperscript{7} have investigated the system Nb—N and several tentative constitution diagrams were proposed\textsuperscript{3,5–9}. Further, Storms et al.\textsuperscript{10,11} have derived several values for pure $\delta$-NbN by extrapolation from Nb$_{x}$C$_{y}$N$_{z}$O$_{z}$ phases. However, there are still some open questions about the stability of some phases with respect to the influence of oxygen, ordering of nitrogen within the nitrogen sublattice and phase relationships\textsuperscript{2,5,6,12–18}. The transition temperature\textsuperscript{7,18} as well as the exact nature of the $\gamma$-Nb$_{2}$N$_{3}$, $\delta$-NbN$_{1-x}$ phase transition have not been completely clarified, since X-ray, neutron and electron diffraction investigations as carried out by several investigators\textsuperscript{14,18–22} led to contradictory results.

Cubic $\delta$-NbN$_{1-x}$ crystallizes in the fcc sodium chloride structure and is considered to be a high-temperature modification\textsuperscript{3} which undergoes a phase transition to $\eta$-NbN and/or $\gamma$-Nb$_{2}$N$_{3}$ depending on the stoichiometry, at a temperature of 1 503–1 643 K. This high-temperature modification can be easily frozen in by cooling.

The niobium-rich phase boundary of $\delta$-NbN$_{1-x}$ is temperature dependent and is situated between NbN$_{0.86}$—NbN$_{0.88}$ at room temperature\textsuperscript{3,9}. Nitrogen-rich compositions have been reported up to NbN$_{1.06}$ by Brauer and Kirner\textsuperscript{23} by nitriding Nb powder at up to 16 MPa. Rögener\textsuperscript{24,25} was able to obtain compact samples of NbN$_{1.05}$ at 1 733 K and 4.2 MPa nitrogen pressure and Horn and Saur\textsuperscript{26} reported the formation of NbN$_{1.04}$ at 1 923 K and 10 MPa nitrogen pressure. The formation of films of $\delta$-NbN$_{1+x}$ with a nitrogen content even up to N/Nb = 1.5 prepared by reactive sputtering have also been reported\textsuperscript{13,27}.

Measurements of the nitrogen partial pressure as a function of composition of $\delta$-NbN$_{1-x}$ were carried out by Shchurik and Tomilin\textsuperscript{28}, Zhikharev and Kharina\textsuperscript{29}, and recently by Brauer and Kern\textsuperscript{7}. A log $p$(N$_{2}$) vs. N/Nb plot yields a straight line. The pressure ranges investigated in these studies were limited to those below atmospheric.

The melting point of $\delta$-NbN$_{1-x}$ was studied by Ettmayer et al.\textsuperscript{30} at nitrogen pressures up to 8.1 MPa. $\delta$-NbN$_{1-x}$ does not melt congruently even at 8.1 MPa but decomposes to $\beta$-Nb$_{2}$N$_{1-x}$. Similar observations were made during trial runs with the purpose of growing $\delta$-NbN$_{1-x}$ single crystals by zone melting\textsuperscript{31–34}.

The nitrogen content significantly influences the lattice parameter. According to Storms\textsuperscript{10} the lattice parameter of $\delta$-NbN$_{1-x}$ increases with increasing nitrogen content but levels off before reaching the stoichiometric composition, whereas Brauer and Kirner\textsuperscript{23} gave the vertex value of the lattice parameter close to N/Nb = 1.00.

The thermal expansion of NbN$_{1-x}$ was measured by Timofeeva and Shvedova\textsuperscript{35} on NbN$_{0.95}$ (from lattice parameters at 93 and 300 K, $\alpha = 4.3 \cdot 10^{-6}$ K$^{-1}$), by Bogdanov et al.\textsuperscript{36} on NbN$_{0.95}$ in the range of 293–1 173 K