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Preparation of Single Phases and Single Crystals of Niobium—Germanium Compounds

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Niobium-germanium compounds were prepared by floating zone melting of niobium-germanium mixtures. Compounds with a β-W-like structure (A15) and composition Nb_xGe were prepared as single phases for $6 \geq x \geq 4$. Small single crystals were found. Single crystals of Nb_5Ge_3 of volume 30 mm^3 were prepared by peritectic melting. Sintering of niobium-germanium mixtures leads to formation of both an A15 phase and of Nb_5Ge_3 also at compositions where one of the phases disappears on melting and resolidification.

The formation of niobium-germanium compounds has been investigated by several authors. Carpenter and Searcy[1] reported a compound of stoichiometry Nb_3Ge and of A15 structure. They also described a compound $NbGe_2$. Geller[2] pointed out that the lattice constant for Nb_3Ge reported in Ref. 1 indicated a deviation from stoichiometry. Reed *et al.*[3] found that the stability range of the A15 structure is from $Nb_{6.29}Ge$ to $Nb_{4.52}Ge$. They found transition temperatures for superconductivity from 4.9 K to 5.5 K. Carpenter[4] also studied the composition range of the A15 structure. His results agree with those of Reed *et al.* Matthias *et al.*[5] achieved a more stoichiometric Nb_3Ge A15 phase with a critical temperature of 17 K by rapid quenching of a melt of Nb and Ge. Gavaler[6] used sputtering techniques to fabricate films of Nb_3Ge which exhibit superconductivity above 21.4 K. Müller[7] published a phase diagram for NbGe covering the region 60 – 100 atomic % Nb. Heller[8] gave a slightly more complete phase diagram.

In the composition range 50 – 100 atomic % Nb the phase of A15 structure and one other niobium-germanium compound, Nb_5Ge_3, are generally encountered. Nb_5Ge_3 crystallizes in the tetragonal system. Nowotny *et al.*[9] determined its structure from powder photographs. Jagner and Rasmussen[10] redetermined the structure using single crystal X-ray diffraction, and Larsen and Rasmussen[11] confirmed their results by single crystal neutron diffraction.

As most structural investigations in the Nb – Ge system have been carried out using powder methods the present work aims at investigating the possibilities of producing single crystals of Nb – Ge compounds in order to get improved crystallographic description of these compounds. As a first attempt to grow single crystals, the conditions for producing single phase samples were investigated.

EXPERIMENTAL

Powder mixtures of nominally 99.8 % Nb and 99.99 % Ge were pressed into nearly cylindrical rods of 12 mm diameter and 100 – 130 mm length by isostatic pressing at a force of 4×10^5 N. The rods were sintered in an A.D. Little model MP furnace in a helium atmosphere at 1000 – 1300 °C by inductive heating. Afterwards a molten zone of width ~10 – 15 mm was passed through the sample at a speed of about 10 mm/h. All operations were crucible free. The temperature of the molten zone was estimated at intervals using a pyrometer. Fairly large crystals (30 mm^3) of nominal composition Nb_5Ge_3 were grown in the following manner: Rods of compositions Nb_5Ge_3 and NbGe were sintered in the usual way. A piece of NbGe of width 15 mm was inserted in the Nb_5Ge_3 rod and melted, and the molten zone was passed through the sample. Samples of NbGe composition melt peritectically, the melt being in equilibrium with solid Nb_5Ge_3.

Table 1. Phases observed in experiments of sintering and/or zone melting mixtures of niobium and germanium.

Initial composition	Phases after sintering	Phases after zone melting Surface layer	 Core
12Nb+Ge	Nb+unknown phase		
12Nb+Ge			A15,Nb
9Nb+Ge	Nb_5Ge_3,Nb		
9Nb+Ge		Nb,NbO	A15,Nb_5Ge_3
6Nb+Ge	Nb_5Ge_3,A15,Nb		A15,Nb_5Ge_3,Nb
6Nb+Ge			A15
5Nb+Ge			A15
4.5Nb+Ge			A15
4Nb+Ge			A15
5Nb+3Ge+(Nb+Ge)	Nb_5Ge_3		Nb_5Ge_3,A15
Peritectic melting			Nb_5Ge_3
3Nb+Ge	A15,Nb_5Ge_3	A15,Nb_5Ge_3	A15,Nb_5Ge_3

Although helium of high purity was used, a thin layer of NbO was invariably formed at the surface of part of the sample, always on the part which was melted first.

After the zone melting we cut the rods perpendicular to the cylinder axis in several pieces and took samples partly from the surface and partly from the interior by filing with a diamond file. The powder obtained was examined using a Guinier-de Wolff powder camera. The plane surfaces of a number of samples were ground and polished and examined by metallographic methods. The chemical composition was established by X-ray fluorescence analysis. Typical results are given in Tables 1 and 2.

The formation of Nb – Ge phases was also examined using a high temperature X-ray powder diffractometer, PW 1158. Tantalum sample holders were employed and the samples were surrounded by a helium atmosphere.

Diffractograms were taken at temperatures ranging from 25 °C to 1800 °C. A surface layer of NbO and NbO_2 was invariably formed during heating and as the linear absorption coefficient for Nb towards Cu*Kα* radiation is 1277 cm^{-1} even a thin oxide layer obscures observations of reactions in the bulk of the sample. The lattice constant of Nb was determined as a function of temperature. When a vacuum of $P \leq 2 \times 10^{-5}$ Torr was obtained and the temperature was above 1000 °C, the formation of niobium oxides was avoided. The following lattice constants were found for Nb: $a = 3.3027$ Å (296 K), 3.329 Å (1268 K), 3.345 Å (1738 K).

Table 2. X-Ray fluorescence analysis for niobium at various sections in a rod after zone melting. Initial composition: 5Nb+Ge: 86.49 wt % Nb.

Zone travel (mm)	Wt % Nb
12	86.8
14	86.9
38	86.1
40	87.0
61	88.8
63	86.9

RESULTS AND DISCUSSION

According to the phase diagram by Müller and Heller [8] the A15 phase melts peritectically at 1910 °C and Nb_5Ge_3 is formed by incongruent melting. It is also reported that Nb_5Ge_3 melts congruently at 2065 °C. We have not been able to confirm this supposition. Nb_5Ge_3 should also be formed at peritectic melting of phases of composition NbGe. The latter observation is in agreement with the way in which we prepared large crystals of Nb_5Ge_3. This compound has a narrow composition range as shown by the X-ray single crystal analysis of Jagner and Rasmussen [10] on a crystal formed from an experiment where the initial composition was 3Nb + Ge and a neutron crystallographic investigation by Larsen and Rasmussen [11] on a large crystal from the peritectic formation as described in EXPERIMENTAL. In both investigations excellent agreement was found between observed and calculated structure factors assuming a stoichiometric composition. The Nb_5Ge_3 phase is formed readily at sintering processes also in concentration ranges where

Table 3. Phases identified by powder diffractometry at various temperatures. The sample holder was a tantalum boat.

Initial composition	T/K	Phases identified	Lattice constants (Å)
3Nb, Ge	1278	Nb_5Ge_3 (NbO, NbO_2)	
3Nb, Ge	1483	A15 Nb_5Ge_3 (NbO, NbO_2)	5.169
6Nb, Ge	787	Nb, Ge	
6Nb, Ge (a)	2000	hexagonal phase	a=5.346 c=5.021
6Nb, Ge (a) after cooling	296	hexagonal phase	a=5.286 c=4.977
6Nb, Ge after heating to 2473 K	296	hexagonal phase	a=5.292 c=4.972

it is not stable at equilibrium conditions. The lattice constants vary slightly according to the composition of the matrix in which the compound is formed (Table 4).

According to the evidence from the X-ray powder diagrams, the A15 phase is formed as a single phase or at least nearly so at the zone melting process when the compositions of the rods are in the interval Nb_6Ge to Nb_4Ge. For a given rod, *e.g.* of initial composition Nb_5Ge, the X-ray fluorescence analysis showed that no significant change in composition accompanied the travel of the molten zone. It is therefore probable that equilibrium was established during the zoning process. Single crystals of volume $\sim 10^{-3}$ mm^3 were found in runs where initial compositions were Nb_4Ge. Nb_5Ge and Nb_6Ge, respectively. These crystals have been subject to single crystal X-ray investigations which will be reported in a forthcoming publication in collaboration with R. G. Hazell. For compositions $5/3 \leq x \leq 3$ of Nb_xGe the A 15 phase is formed together with Nb_5Ge_3. The latter compound is formed in smaller or greater amounts by sintering processes at temperatures between 500 °C and the melting points in the range $5/3 \leq x \leq 9$.

In the sintering processes the A15 phase was invariably formed together with the Nb_5Ge_3 phase. It is therefore unlikely that a pure A15 phase of stoichiometry Nb_3Ge can be formed by sintering. The A15 phase of this composition is not stable and apparently it has to be prepared by techniques which prevent equilibrium from being established (Matthias *et al.*[15], Gavaler [16]).

Table 4. Lattice constants of A15 compounds and of Nb_5Ge_3.[a]

Initial comp.	Phases after zone melting	A15 a Å	Nb_5Ge_3 a, Å	c, Å
12Nb, Ge	A15, Nb	5.177		
9Nb, Ge	A15, Nb_5Ge_3	5.178		
6Nb, Ge	A15 (Nb_5Ge_3)	5.167		
5Nb, Ge	A15	5.170		
4.5Nb, Ge	A15	5.170		
4Nb, Ge	A15	5.170		
3Nb, Ge	A15, Nb_5Ge_3	5.166	10.162	5.144
5Nb, 3Ge	Nb_5Ge_3, A15	5.167	10.173	5.141
Peritectic melting	Nb_5Ge_3		10.170	5.139

[a] Average standard deviation ~1 part in 2000.

Because of the presence of niobium oxides in the samples examined by high temperature X-ray diffractometry, it is difficult to draw definite conclusions from these experiments except in one case. When a mixture of composition 6Nb + 1Ge is heated in a tantalum sample holder, a hexagonal phase is formed which remains on cooling (Table 3). We checked that it was not due to a thin surface layer by taking a Guinier diagram of the bulk of the sample. We did not observe this hexagonal phase in any of the experiments using the crucible free technique.

The lattice constant of the A15 phase depends to some extent on the composition of the matrix in which it is formed (Table 4). The variation is so small, however, that the lattice constant cannot be used for estimating analytical compositions. The precision of our measurements is not high enough for this purpose.

T. Claeson *et al.*[12] measured critical temperatures of superconductivity of Nb_5Ge_3 crystals. Similar measurements were carried out on A15 phases too. We hope to report on these measurements later.

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