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Abstract

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STUDY OF THE α-, β-, AND γ-PHASES OF THE NIOBIUM–TELLURIUM SYSTEM

The formation of phases of variable composition is characteristic of transition-metal chalcogenides.

Among niobium chalcogenides only the sulfides have been studied. Biltz and Köcher ([1]), who studied the niobium–sulfur system, found that niobium forms the sulfide Nb_2S_3, which can dissolve sulfur up to the composition NbS_4, and the monosulfide NbS, which forms a solution with excess niobium up to the composition $NbS_{0.5}$. Hägg and Schönberg ([2,3]) found in the niobium–sulfur system two phases with narrow homogeneity ranges, close to the compositions NbS and NbS_2. The structure of composition NbS belongs to the WC type with parameters: $a = 3.32$ Å; $c = 3.83$ Å; $c/a = 0.97$; $z = 1$. With excess sulfur it transforms into the NiAs structural type ($a = 3.32$ Å; $c = 6.46$ Å; $c/a = 1.95$, $z = 2$). The NbS_2 phase crystallizes in a lattice of the $CdCl_2$ type with parameters $a = 6.24$ Å; $\alpha = 30.95°$; $z = 3$.

In studying the niobium–tellurium system by X-ray phase analysis and on the basis of measurements of electrical conductivity, we established ([4]) the existence of three phases of variable composition: the α-phase, whose homogeneity range lies between the compositions $NbTe_{0.18}$ and $NbTe_{0.82}$; the β-phase in the composition interval $NbTe_{1.0}$ to $NbTe_{1.70}$; and the γ-phase, whose composition can vary from $NbTe_{2.33}$ to $NbTe_{4.00}$.

In the present work, the results of an X-ray investigation of the indicated phases are reported in greater detail.

The preparations were made by prolonged (750 h) sintering at 900° of ground powders of niobium and tellurium in quartz ampoules sealed under vacuum. The preparation of niobium tellurides was described in more detail in ([4]). The prepared specimens were studied by the powder method; for some compositions single crystals were obtained, which were studied by the oscillation method.

In our work we used RKD and RKU cameras with diameters of 57.3 and 86 mm, respectively. Loading of the film was carried out by the asymmetric method. Single crystals were studied in an RKOP camera with a cassette diameter of 57.3 mm*. Radiation from a copper anode was used without a filter. Powder patterns

were measured on a comparator with an accuracy of 0.02 mm. The intensity of the diffraction lines was estimated visually on a decadic scale. Calculations were carried out allowing for absorption corrections (by the Gadding formula). Specimens for recording powder patterns were prepared by applying ground powders, with the aid of liquid tsapon lacquer, to a thin Pyrex glass fiber.

The α-phase ($NbTe_{0.18}$–$NbTe_{0.82}$) crystallizes in a primitive cubic lattice with parameter $a = 8.418 \pm 0.005$ Å. This value of the parameter remains unchanged, within the limits of measurement error, throughout the entire homogeneity range.

X-ray patterns of preparations belonging to this phase are distinguished by well-resolved CuK_{α_1} and CuK_{α_2} doublets (beginning from $\theta = 53^\circ$) and

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* All cameras were made at the Scientific Research Institute of Physics of Moscow State University.

clarity of the lines not only at small angles, but also at large ones (up to 80°). Particularly clear radiographs, with well-resolved CuK_{α_1} and CuK_{α_2} doublets, were given by specimens corresponding to the compositions $NbTe_{0.25}$ and $NbTe_{0.82}$.

Indexing of the powder patterns of the specimen of composition $NbTe_{0.82}$ gave the lattice-parameter value with still greater accuracy: 8.419 ± 0.001 Å. A pycnometric determination of the density of this specimen gave the value 6.00 ($t = 20^\circ$), which agrees well with the calculated X-ray density: 6.036 for $z = 1$.

β-phase ($NbTe_{1.00}$–$NbTe_{1.70}$). The radiographs obtained are indexed in a hexagonal lattice with parameters $a = 5.16 \pm 0.01$ Å; $c = 7.62 \pm 0.05$ Å; $c/a = 1.477$ for the composition $NbTe_{1.00}$.

The specimen containing 50 at. % tellurium ($NbTe_{1.00}$) was studied in a Unicam high-temperature X-ray camera[5] at 700°. The powder specimen, placed in a quartz sealed capillary, was photographed at temperatures of 20°, 700°, and, after cooling, again at 20°. Visual comparison of the powder patterns obtained did not show the presence of any polymorphic transformation. The indistinctness of the lines and the presence of a large background due to the quartz did not permit any sufficiently accurate measurements.

γ-phase ($NbTe_{2.33}$–$NbTe_4$). An X-ray study of single crystals of composition $NbTe_3$ by the oscillation method showed that the γ-phase crystallizes in a tetragonal body-centered lattice with axial parameters $a = 9.10 \pm 0.05$ Å, $c = 21.35 \pm 0.05$ Å, $c/a = 2.346$. The powder patterns obtained for specimens of the γ-phase are well indexed in this tetragonal lattice.

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References Cited

[1] W. Biltz, A. Köcher, Zs. anorg. Chem., **237**, 369 (1938).
[2] N. Schönberg, Acta Metallurgica, **2**, 427 (1954).
[3] G. Hägg, N. Schönberg, Arkiv Kemi, **7**, 371 (1954).
[4] A. V. Novoselova, L. A. Grigoryan, Yu. P. Simanov, DAN, **134**, No. 6 (1960).
[5] H. Lipson, A. Wilson, J. Sci. Instr., **18**, 144 (1941).

Note: Figure translations are in progress. See original paper for figures.