Triniobiumoctabromide, Nb_3Br_8, Revisited

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Z. Naturforsch. **2010**, *65b,* 770 – 772;
received March 31, 2010

A facile route to single crystals of Nb_3Br_8 by the reaction of $NbBr_5$ with the wall of the niobium reaction vessel at 800 °C is reported. The crystal structure (a = 707.87(5), c = 3895.7(6) pm, $R\bar{3}m$, Z = 6) was determined from diffractometer data; the crystal data are compared with those obtained from film data in 1966 which were of already high precision. Triangular $\{Nb_3\}$ clusters with Nb–Nb distances of 288.6(2) pm are surrounded by 13 bromide ligands which bridge them to double layers, $\{Nb_3\}(\mu_3\text{-Br4})^{i}{}_{1/1}(\mu_2\text{-Br1})^{i}{}_{(3/2)\cdot 2}(\mu_1\text{-Br2})^{a\text{-}a}{}_{6/2}(\mu_1\text{-Br3})^{a\text{-}a\text{-}a}{}_{3/3}$ that are stacked to a 12R structure.

Key words: Niobium, Bromide, Cluster, Crystal Structure

Introduction

The systems Nb/X with X = Cl, Br, I contain, as stoichiometric phases, halides of the composition $NbX_{2.67} = Nb_3X_8$. These were thought to be the lower end of a homogeneity range, for example for $NbCl_x$ with $2.67 \leq x \leq 3.13$ [1], but none of the halide-richer phases have been characterized by diffraction methods so far. There are two crystal structure types, called α and β, for the composition Nb_3X_8 [2]. In both crystal structures, closest packed double layers of X atoms are present between which 3/8 of the octahedral voids are occupied by niobium atoms such that these build triangular clusters. Both structures were first determined from single crystal X-ray diffraction data (film techniques), in 1961 for the example of Nb_3Cl_8 (= α) [3] and in 1966 for the examples of Nb_3Br_8 and Nb_3I_8 (= β) [2]. The crystal structure of Nb_3Cl_8 has been refined with modern precision in 2001 [4]. Diffractometer data for Nb_3Br_8 are missing although the electronic structure of Nb_3Br_8 has been evaluated previously [5].

As part of a broader study of niobium and tantalum halides [6] we now have not only obtained $RbNb_4Br_{11}$ [7] but also found a facile route to grow single crystals of Nb_3Br_8.

Table 1. Comparison of atomic and displacement parameters for Nb_3Br_8 of the present study (upper line) with those of the first structure determination carried out in 1966 [2].

Atom	W.-position	x	z	U_{eq}	B
Nb	18h	0.46922(11)	0.08219(4)	0.0140(4)	
		0.469	0.0826		−1.16
Br1	18h	0.16682(13)	0.12687(4)	0.0183(4)	
		0.167	0.1269		−1.32
Br2	18h	0.83630(13)	0.04534(4)	0.0174(4)	
		0.837	0.0455		−1.21
Br3	6c	0	0.21495(7)	0.0158(6)	
		0	0.2152		−1.19
Br4	6c	0	0.36531(7)	0.0162(6)	
		0	0.3648		−1.21

Results and Discussion

Single crystals of Nb_3Br_8 were obtained by reduction of $NbBr_5$ with the wall of the niobium reaction vessel at 800 °C. The crystal structure is that of the previously reported β form, first determined from film data and published in 1966 [2]. Table 1 compares present and previous results and attests to the high precision of the structure as determined from film data.

In the crystal structure of Nb_3Br_8, two closest packed layers of bromide ions form a double layer in which three out of four octahedral voids are occupied by niobium atoms, in such a way that triangular niobium clusters with Nb–Nb distances of 288.6(2) pm occur (Fig. 1). The double layers are stacked in a rather complicated manner, with six double layers stacked in the [001] direction to give a 12R structure (Fig. 1). Thereby, one double layer has a height of 649.3 pm, as compared with 611.6 pm in Nb_3Cl_8 (α, 2T) [4] and 695.3 pm in Nb_3I_8 (isostructural with Nb_3Br_8) [2]. The thicknesses of the double layers correlate very well with the sizes of the halide ions, when for example Shannon's ionic radii [8] are taken into account. A reason for the different stackings – two double layers in Nb_3Cl_8, six double layers in Nb_3Br_8 and in $Zn_3Mo_3O_8$ [9], or three in $Na_2Ti_3Cl_8$ [10] – is not known. It is also unclear if the α and β forms are truly low- and high-temperature modifications and whether other polytypes/polymorphs exist or not.

An alternative description of the crystal structure of Nb_3Br_8 starts with Nb_3Br_{13} building units (Fig. 1) in which Br4 caps the triangular face of the Nb_3

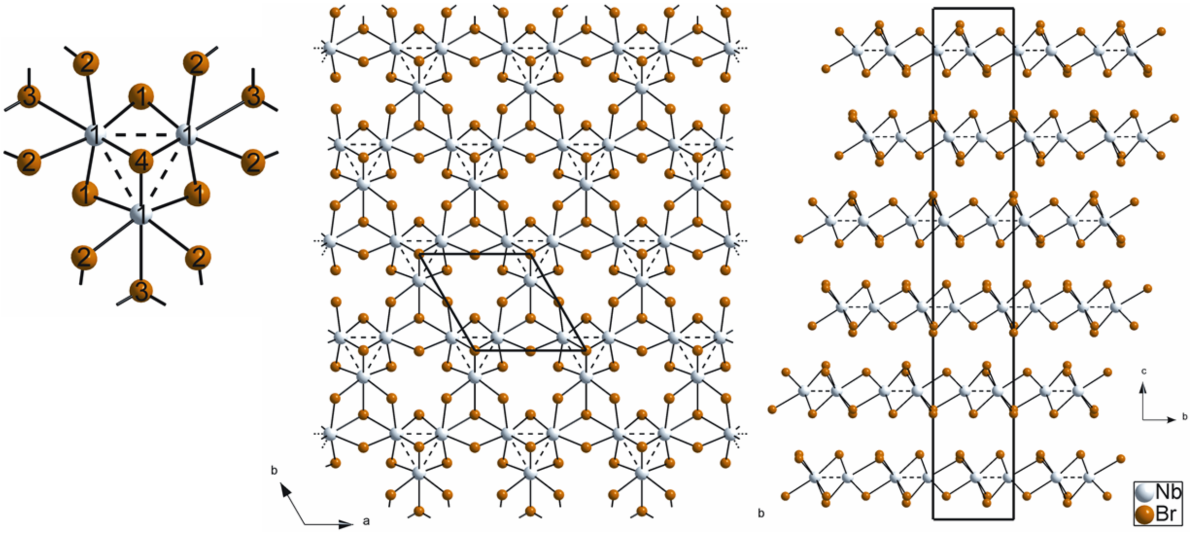

Fig. 1. The crystal structure of Nb_3Br_8 (β, 12R); middle: one double layer is shown with the triangular niobium clusters highlighted by dashed lines; left: a blow-up shows the building unit $\{Nb_3\}Br_{13}$ with the crystallographic atomic numbering scheme; right: stacking of the double layers in the [001] direction.

cluster on one side (μ_3 bridging), three Br1 cap the three edges of the triangle (μ_2 bridging), six Br2 (μ_1) are connecting to six surrounding clusters *via* a-a bridges, and three Br3 (μ_1) to three neighboring clusters *via* a-a-a bridges. This may be put in the formulation $\{Nb_3\}(\mu_3\text{-Br4})^{i}{}_{1/1}(\mu_2\text{-Br1})^{i}{}_{(3/2)\cdot 2}(\mu_1\text{-Br2})^{a\text{-}a}{}_{6/2}(\mu_1\text{-Br3})^{a\text{-}a\text{-}a}{}_{3/3}$ (for the nomenclature, one may consult refs. [11, 12]). The connectivity of the $\{Nb_3\}Br_{13}$ units leads to the double layers mentioned above, which are then stacked without any further occupation of voids between them. In compounds like $Na_2Ti_3Cl_8$ and $Zn_3Mo_3O_8$, or in intercalated derivatives of Nb_3Cl_8 such as $Na_xNb_3Cl_8$ [13], voids between the double layers are occupied.

Experimental Section

$NbBr_5$ was prepared following the route described in Brauer's Handbook [14] from niobium powder and bromine in a sealed niobium ampoule at 300 °C. The crude product was sublimed for purification. For the synthesis of Nb_3Br_8, 0.2 g $NbBr_5$ was sealed by He-arc welding in a niobium ampoule. The niobium container was jacketed with a silica ampoule and heated at 800 °C for two days. All manipulations were carried out under conditions that strictly excluded air and moisture, mostly in an argon-filled drybox (MBraun, Garching).

Single crystals of Nb_3Br_8 were obtained as black plates in an approximately 25 % yield. They were selected in a dry box and sealed in thin-walled glass capillaries. The crystal quality was checked by Laue patterns, and the best specimen was transferred to a Stoe Image Plate Diffraction System (IPDS-I). A complete intensity data set was collected using graphite-monochromatized MoK_α radiation (λ = 71.073 pm). A numerical absorption correction based on crystal shape optimization was applied for all data (X-SHAPE), and the data set was merged to 578 unique reflections using the X-AREA program suite [15]. For structure solution and refinement the WINGX suite of programs [16] including SIR-92 [17] and SHELXL-97 [18] was used. The last refinement cycles included anisotropic displacement parameters for all atoms.

Crystal data for Nb_3Br_8: 918.0 g mol^{-1}; trigonal, $R\bar{3}m$ (no. 166), a = 707.87(5), c = 3895.7(6) pm, V = 1690.5(3) $10^6 \cdot pm^3$, Z = 6, ρ_{calc} = 5.41 g cm^{-3}, μ = 31.3 mm^{-1}, $F(000)$ = 2418 e, T = 293(2) K; φ-scan, 200 images, index range: $-9 \le h \le 9$, $-9 \le k \le 9$, $-51 \le l \le 51$, $2\,\theta_{max}$ = 56.3°, 5454 measured reflections of which 403 were symmetrically independent, R_{int} = 0.1150; 26 refined parameters, R values: R_1 / wR_2 for 403 reflections with $[I_0 \ge 2\,\sigma(I_0)]$: 0.048 / 0.116, for all data: 0.074 / 0.129, S_{all} = 1.027, $\Delta\rho_{fin}$ (max / min) = 2.22 / −2.26 e Å^{-3}.

Further details of the crystal structure investigation may be obtained from Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: +49-7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fiz-informationsdienste.de/en/DB/icsd/depot_anforderung.html) on quoting the deposition number CSD-421609.

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Nachdruck – auch auszugsweise – nur mit schriftlicher Genehmigung des Verlags gestattet
Druck: AZ Druck und Datentechnik GmbH, Kempten