JOURNAL OF SOLID STATE CHEMISTRY **1**, 576–582 (1970)

Wadsley Defects and Crystallographic Shear in Hexagonally Close-packed Structures

STEN ANDERSSON AND JEAN GALY

Institute of Technology, Chemical Centre, Department of Inorganic Chemistry, Box 740, S-220 07 Lund 7, Sweden, and
Service de Chimie Minérale Structurale de la Faculté des Sciences de Bordeaux associe au CNRS, 33-Talence, France

Different shear structures are derived from the PdF_3, rutile, and α-PbO_2 structure types, which all have the anions in an approximately hexagonally close packed arrangement. Using the principles derived the corundum structure is described as a shear compound.

A new simple series M_nX_{3n-1}, with B–Nb_2O_5 as a known member ($n = 2$) is described as the high-pressure form of the series with known members Nb_3O_7F ($n = 3$) and R–Nb_2O_5 ($n = 2$).

Nonstoichiometry can be explained by Wadsley defects in these structures.

Introduction

The structural chemistry of a great number of compounds centered about Nb_2O_5 in composition have been recently reviewed (*1*). The structures of these compounds could all be derived by introducing one- or two-dimensional shear in the ReO_3 structure type. In this structure the anions are in a cubic close-packed arrangement except for the position $\frac{1}{2}\,\frac{1}{2}\,\frac{1}{2}$ which is empty. The ReO_3 structure is rather open and should not exist at elevated pressures. The structure of H–Nb_2O_5, by Gatehouse and Wadsley (*2*), contains ReO_3-blocks 3 × 4 and 3 × 5 octahedra in size. When a pressure of 20–30 kbar and a temperature around 1500 °C is applied to this substance, it transforms into the T form of H Nb_2O_5 (*3*). The structure of this modification has not been investigated, but it is clear from its relation to the U_3O_8 structure type that it contains some niobium in seven-coordination. The increase of coordination number is favoured by the high pressure. The density increase is approximately 10%. In the structure of B–Nb_2O_5 (*4*) there is only octahedral coordination of oxygens around niobium. However, the oxygens are in a hexagonally close-packed arrangement, and the density is 17% higher than that of H–Nb_2O_5. Preliminary studies at 900 °C and 120 kbar show that H–Nb_2O_5 transforms into B–Nb_2O_5 (*5*). Nb_3O_7F transforms at 20–30 kbar and 900 °C into a structure of the U_3O_8 (*7*) type with seven coordinated niobium (*6*).

From these investigations we now have the general picture that transition-metal oxide or similar systems with compositions above and below Nb_2O_5 (for example TiO–Nb_2O_5–WO_3) transform at moderate pressures to structures with an increase in coordination of the cation. At still higher pressures there is a decrease in coordination of the metal atoms (B–Nb_2O_5), but this is compensated by the close-packed arrangement of the anions.

We now wish to show with the geometrical principles of crystallographic shear how a great number of possible structures can be derived. All the structures have hexagonally close-packed anions, and octahedrally coordinated cations. Attempts to synthesize these hypothetical structures in form of compounds should be carried out under high pressure.

Crystallographic Shear in the PdF_3 Structure Type

Different ways of joining octahedra, formed by a hexagonally close-packed arrangement, are shown in Fig. 1. The projection axis is ~ 5 Å. Similarly to the ReO_3 structure, the PdF_3 structure is also formed by octahedra having corners in common (*8*), but it is denser than the ReO_3 structure. The anion arrangement in PdF_3 is, in fact, a hexagonally close-packed one, and we like to consider the PdF_3 structure type as the high pressure form of ReO_3. The PdF_3 structure is shown in Fig. 2. Analogously to the case for ReO_3, shear can be introduced in the PdF_3 structure type. Two of ways of doing this are shown in Fig. 3. In the left part of the figure, the shear is made so that a block of rutile structure is formed. In the right part, a block of the α-PbO_2 structure type is formed through the shear mechanism. In this way, the PdF_3 structure type might have two sets of intersecting shear planes, and block structures analogous to those of $TiNb_2O_7$ (*9*) and $Ti_2Nb_{10}O_{29}$ (*10*) can be designed. The concept of the simple rutile shear in the PdF_3 structure type will be expanded somewhat here. If the blocks are two octahedra wide, corresponding to $n = 2$ in the series M_nO_{2n-1}, the structure of B-Nb_2O_5 is obtained (Fig. 4). In Fig. 5 the PdF_3 blocks are expanded to become three octahedra wide, and the composition M_3O_8 ($n = 3$) is now obtained. Experiments are now being performed in order to find out if Nb_3O_7F can accept this structure at very high pressures.

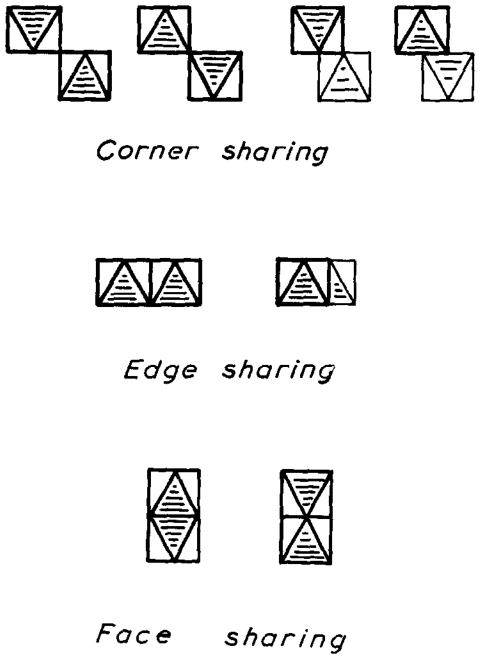

FIG. 1. Some different ways of joining octahedra when the projection axis is ~5 Å, corresponding to $a + b$ in the hexagonally close packed arrangement of atoms.

Crystallographic Shear in the Rutile and α-PbO_2 Structures, Giving Compositions MO_{2+x}

Nb_2O_5 has been reported to dissolve in small amounts in the rutile form of TiO_2 (*11*). In order

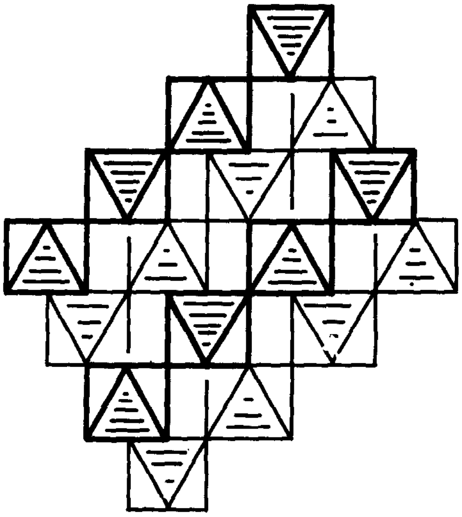

FIG. 2. The PdF_3 structure type.

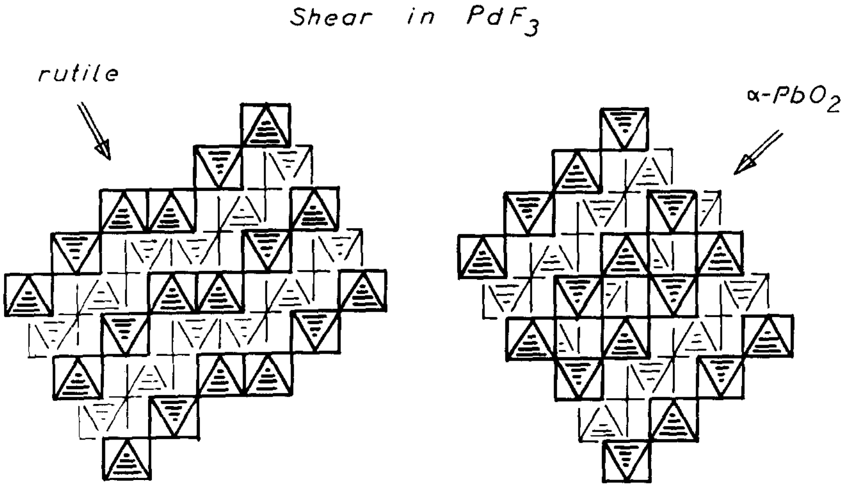

FIG. 3. Two different ways of producing shear in the PdF_3 structure type. Shear planes are in the direction of the arrows.

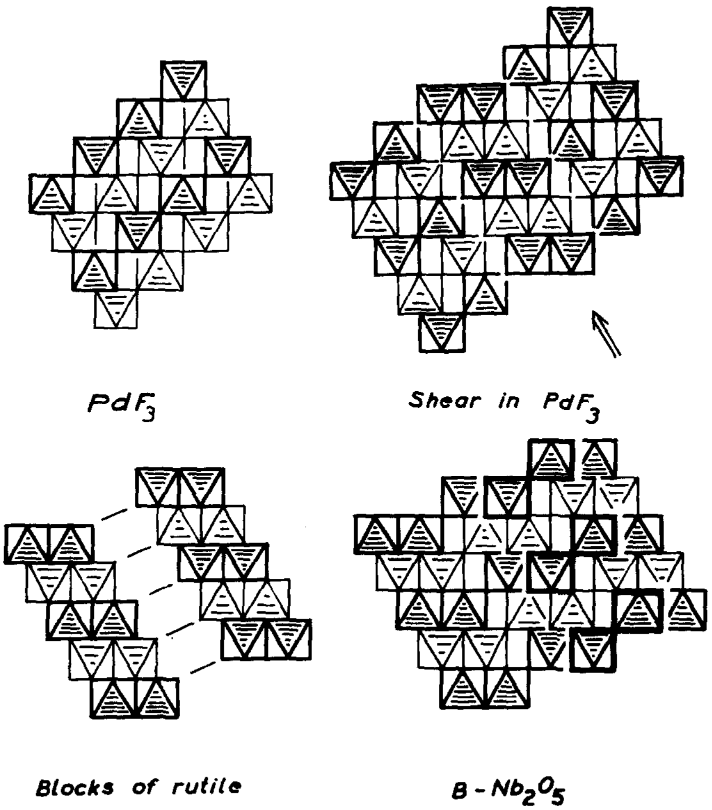

FIG. 4. The structure of $B-Nb_2O_5$ (bottom right) can be described as built of rutile blocks joined by corners (bottom left) or as blocks of the PdF_3 structure, joined by octahedra sharing edges in a shear plane.

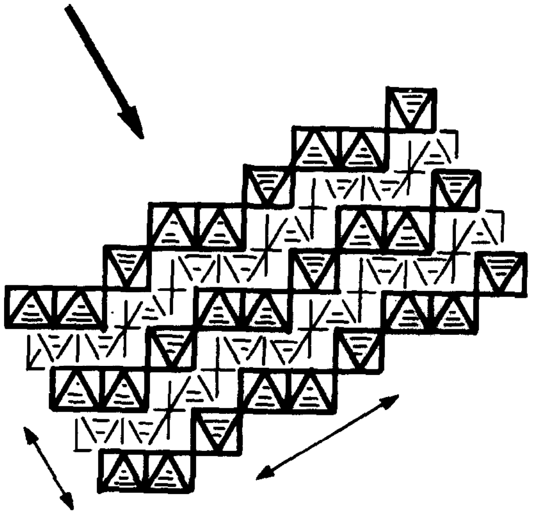

FIG. 5. Periodic shear in PdF_3, giving a hypothetical structure of the composition M_3X_8. The shear plane is in the direction of the heavy arrow.

to create Wadsley defects in this structure with a composition MeO_{2+x}, shear planes are introduced and this is demonstrated in Fig. 6b. The rutile structure is shown in Fig. 6a. The structure of the shear planes consists of parts of the PdF_3 structure with octahedra sharing corners. In the figure the shear planes occur regularly to produce a hypothetical structure M_3O_7.

The structures of rutile and α-PbO_2 are rather similar. The rutile structure with its straight strings of octahedra sharing edges, is not stable at high pressures. It transforms into the α-PbO_2 structure type, and a simple mechanism was recently given for this (*12*), which requires that every second metal atom in the strings jumps into a neighbouring empty octahedral position. This is shown in Fig. 7. It is easy to have shear planes as Wadsley defects in the α-PbO_2 structure type, to give a deviation from stoichiometry, MO_{2+x}. In Fig. 8 such shear planes are arranged to occur regularly to give a structure of

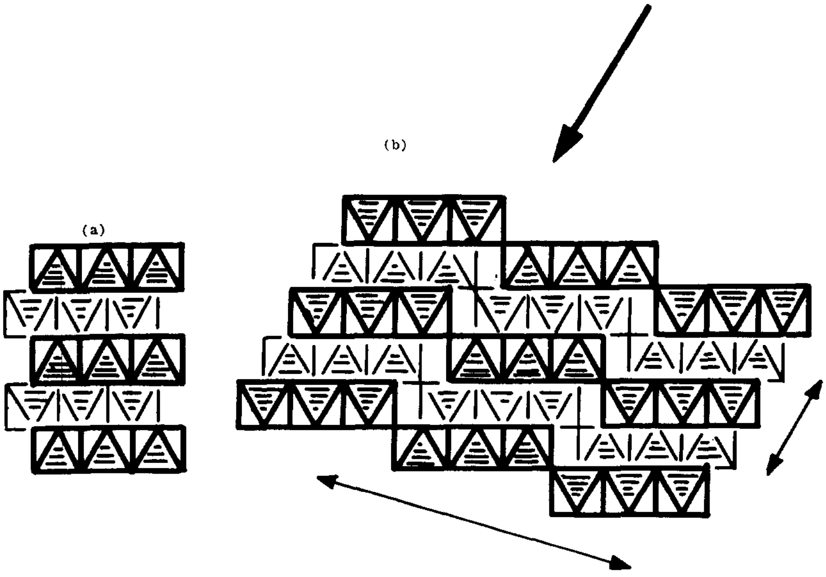

FIG. 6. (a) The rutile structure type. (b) Shear in rutile, giving compositions MX_{2+x}, here represented by a hypothetical structure M_3X_7.

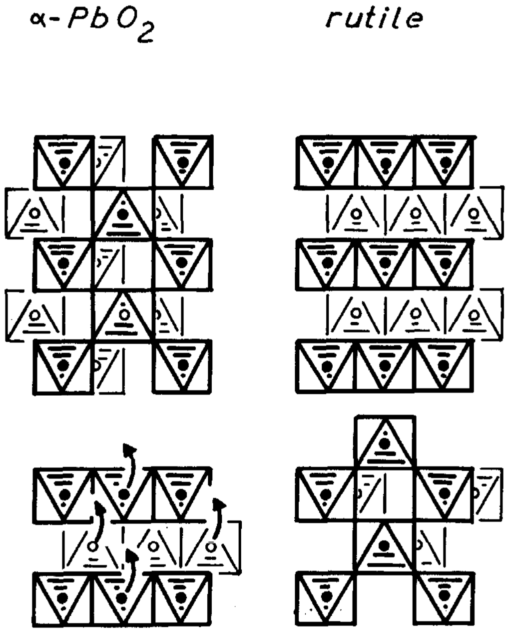

FIG. 7. Proposed mechanism for the transformation rutile → α-PbO_2.

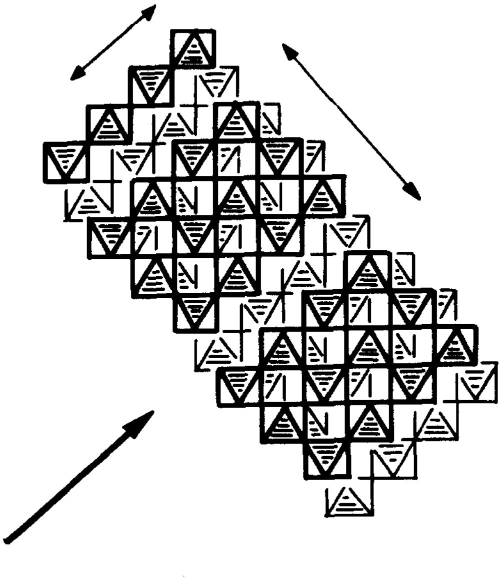

FIG. 8. Shear in α-PbO_2, giving compositions MX_{2+x}, here represented by a hypothetical structure M_3X_7.

the composition M_3O_7. This structure can thus be regarded as the high pressure polymorph of that one given in Fig. 6b.

Crystallographic Shear in the Rutile and α-PbO_2 Structures to Give Compositions, MO_{2-x}

If the rutile blocks in Fig. 4 are joined so that corner sharing occurs between the octahedra of the two blocks, the structure of B–Nb_2O_5 is formed. If the blocks join so that edge sharing occurs, the rutile structure is of course generated. A third possibility is that the blocks join so that face sharing occurs between octahedra, and this is demonstrated in Fig. 9. In this way, the corundum structure is formed, and it can thus be regarded as a shear structure—the shear planes going between the rutile

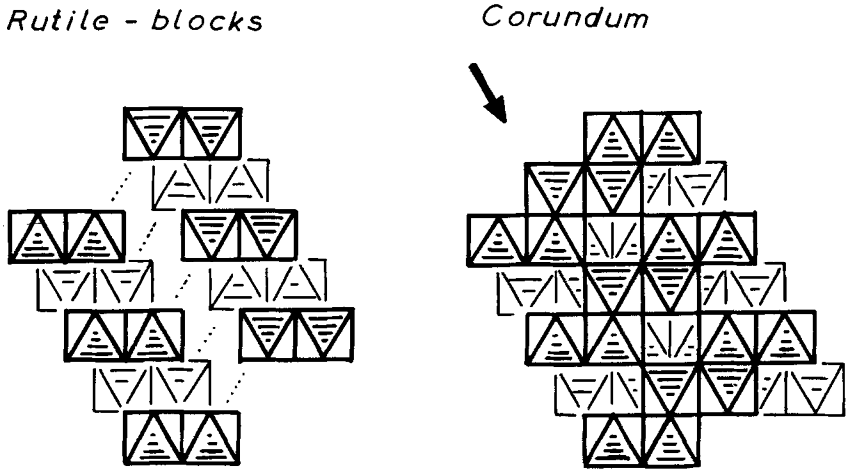

FIG. 9. The rutile blocks can join by octahedra sharing faces and the corundum structure is formed. The shear plane is in the direction of the arrow.

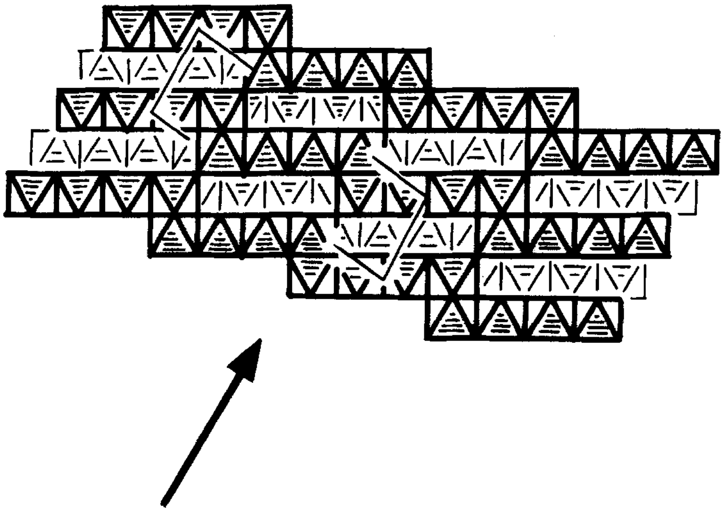

FIG. 10. Hypothetical structure M_4O_7 with shear planes of the same type as those present in corundum.

blocks where octahedra share faces. The corundum structure is geometrically a member of a series M_nO_{2n-1} with $n = 2$, and so far the only known member of this series. The structure of a hypothetical member, $n = 4$, is given in Fig. 10. It is interesting that Bursill, Hyde, Terasaki and Watanabe (*13*) have found Wadsley defects in slightly reduced rutile as disordered shear planes parallel to {132} and {101}, and their study made them suggest the existence of a family of ordered phases, Ti_nO_{2n-1} with $n = 15 \ldots \sim 36$, which can be derived from rutile by crystallographic shear on planes parallel to {132}. This is a new family of titanium oxides, related to but different from the one originally found for the oxides Ti_nO_{2n-1}, with $n = 4 \ldots 9$ (*14*). The {101} shear planes observed by Bursill et al. (*13*) are identical to the shear planes geometrically derived here, and which are present in the corundum structure type. Planar and extended defects in form of Wadsley defects can explain the changes in the corundum composition $M_2O_{3\pm x}$, which is achieved by making the rutile blocks larger or smaller.

Compositions MO_{2-x} in the α-PbO_2 structure type can also be obtained geometrically with Wadsley defects. It seems to us that the shear mechanism can act in two different ways, one of which is given in Fig. 11 for a hypothetical structure

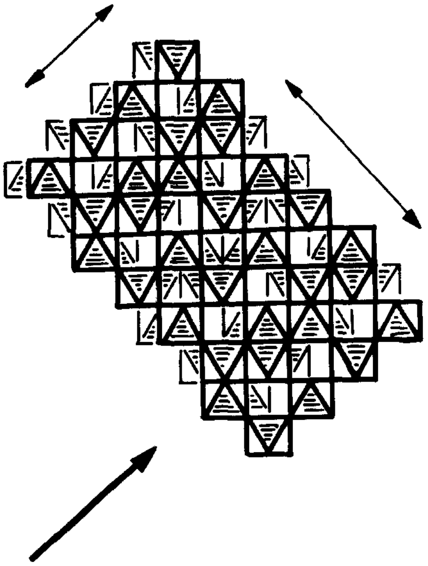

FIG. 11. Hypothetical high-pressure polymorph of Ti_4O_7.

of the composition M_4O_7. However, this shear mechanism is only possible for compositions M_nO_{2n-1} with n even. With n odd one arrives at the second shear mechanism, which for the composition M_3O_5 gives the V_3O_5 structure. Bearing in mind the transformation of rutile into an α-PbO_2 type structure at very high pressures, it seems likely that these structures, different for n odd or even in the series M_nO_{2n-1} based on the α-PbO_2 structure type, are the high-pressure polymorphs of the oxides Ti_nO_{2n-1} and V_nO_{2n-1}.

Some MX_2 Structures with Hexagonal Close Packing of the Anions

Ordering of different cations in the rutile and α-PbO_2 structure types, as for example, in trirutile, columbite, $MgWO_4$, $LiV_{0.5}W_{1.5}O_6$ (*15*) and also in $NaNbO_2F_2$ (*8*), is common. Li_2ZrF_6 (*16*) and the isostructural Li_2NbOF_5 (*17*) is another structure which can easily be described in this way (Fig. 12). Another hypothetical MX_2 structure, with the composition AM_3O_8, with the A atoms occupying octahedra marked with arrows in Fig. 13, has certain features from the Li_2NbOF_5 structure as well as from rutile and α-PbO_2.

AB_3O_8

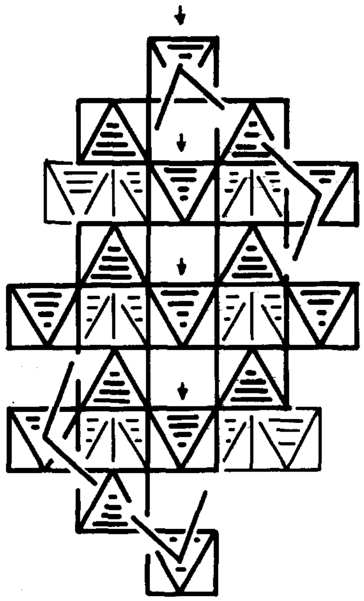

FIG. 13. Hypothetical structure AM_3O_8, the A atoms occupying octahedra marked with arrows.

In the brookite and topaz structures the anions are only partly in hexagonal close packing. Their structural principles and relationships to the α-PbO_2 structure can easily be described by the the methods used here, and will be published by us.

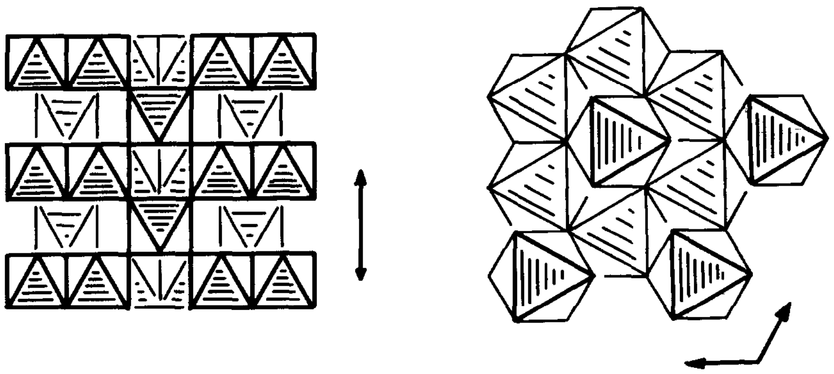

FIG. 12. The structure of Li_2NbOF_5.

References

1. A. D. Wadsley and S. Andersson, in "Perspectives in Structural Chemistry" (J. D. Dunitz and J. A. Ibers, Eds.), Vol. 1, John Wiley and Sons, Inc., New York, 1970.
2. B. M. Gatehouse and A. D. Wadsley, *Acta Cryst.* **17**, 1545 (1964).
3. K.-A. Wilhelmi and S. Andersson, unpublished work.
4. F. Laves, W. Petter, and H. Wulf, *Naturwissenschaften* **51**, 633 (1964).
5. A. F. Reid, A. E. Ringwood, and S. Andersson, unpublished work.
6. K.-A. Wilhelmi and S. Andersson, unpublished work.
7. B. O. Loopstra, *Acta Cryst.* **17**, 651 (1964).
8. S. Andersson and J. Galy, *Acta Cryst.* **B25**, 847 (1969).
9. A. D. Wadsley, *Acta Cryst.* **14**, 660 (1961).
10. A. D. Wadsley, *Acta Cryst.* **14**, 664 (1961).
11. R. S. Roth and L. W. Coughanour, *J. Res. Natl. Bur. Std.* **55**, 209 (1955).
12. S. Andersson and J. Galy, *Bull. Soc. Chim. France* 1065 (1969).
13. L. A. Bursill, B. G. Hyde, O. Terasaki, and D. Watanabe, to be published.
14. S. Andersson and L. Jahnberg, *Arkiv. Kemi.* **21**, 413 (1963).
15. J. Galy, to be published.
16. E. Hoppe and W. Dähne, *Naturwiss.* **47**, 397 (1969).
17. J. Galy, S. Andersson, and J. Portier, *Acta Chem. Scand.*, in print.