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Crystal Chemistry of Complex Niobium and Tantalum Oxides
III. Relationship Between M, T, and M′ Fergusonite Structures

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Abstract

T and *M′* fergusonites are related by a regular rotational twinning for which a simple transformation mechanism does not seem to exist. This fact is used to explain why the *M* phase is formed metastably in most circumstances.

Introduction

Since the introduction of the concept of "crystallographic shear" by Wadsley (1958), a new awareness of geometric crystallography has become evident, and recent ideas such as "rotational faults" (Bursill and Hyde, 1972) and "continuous topological distortions" (Hyde *et al,* 1972) have resulted in an understanding of relationships between apparently unrelated structures.

Structural Relationships

An exceptionally interesting example of such geometrical ideas is the relationship between the three forms *M*, *T*, and *M′* of fergusonite ($YNbO_4$), shown in Figures 1**a** and 1**b**, which have been redrawn from Part I. Again, the corners of the net represent oxygen atoms, which in these structures are closely coplanar. Figure 1**a** is a slightly idealized representation of *M′* fergusonite, in which niobium atoms in octahedral coordination occur below the heavy triangles, forming chains parallel to [100]. Yttrium atoms are situated above the shaded squares in approximately cubic or square antiprismatic coordination.

The next oxygen layer up is a mirror image of the one shown and, in order to provide the correct coordination for yttrium, is shifted slightly to the right, giving the observed monoclinic symmetry. Direct vertical stacking of the layers is not possible without the niobium atoms reverting to tetrahedral coordination, or the yttrium atoms taking a lower coordination number.

Figure 1b represents both *M* and *T* fergusonite to a slightly less satisfactory approximation. The figure has the ideal dimensions for a planar oxygen net, and the angle between pairs of adjacent rectangles is 150°. In *M* and *T* fergusonite, the layer is more or less rumpled, and the corresponding angles are 176° and 143° respectively. Niobium atoms above the plane are represented by the symbol Nb; the unshaded squares and remaining diamonds have yttrium and niobium below the plane.

Direct vertical stacking of these layers with their mirror images (*T* fergusonite) results in coordination figures in which niobium is tetrahedrally coordinated and yttrium is in somewhat irregular 8-coordination. A slight reduction in volume is achieved in the transition to the monoclinic *M* form by moving each oxygen net to the right parallel to [100] until the 2-fold axis of the tetrahedron is vertical. It is a property of this net that octahedral coordination of niobium cannot be achieved without distorting the net beyond recognition. The transition between *M* and *T* fergusonite can evidently be effected quite easily by small movements of atoms, the major change being merely a uniform shear parallel to [100], accompanied by an extension parallel to [010].

The vibrational spectrum of niobium and tantalum in these structures (Blasse, 1973) is consistent with the above suggestion that the tetrahedral coordination is due rather to an external mechanical constraint than to any inherent stability of the NbO_4^{3-} tetrahedron; the bond stretching and bending constants are exceptionally low.

Besides the change in niobium coordination between the structures of Figures 1**a** and 1**b**, a major difference is that in the former, niobium and yttrium are in separate layers parallel to (001), whereas the latter has equal numbers of niobium and yttrium

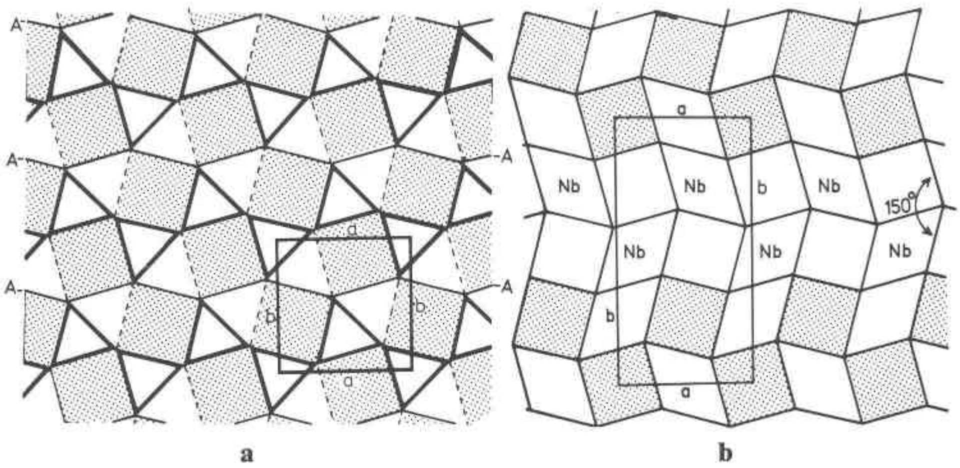

FIG. 1. The structures of *M′*fergusonite (**a**) and *M* and *T* fergusonite (**b**). For explanation, see text. The angle between rectangles in **b** is the ideal value of 150°. In *M* fergusonite this becomes 176°, and in *T* fergusonite 143° (Wyckoff parameters) or irregular (Komkov parameters).

in each layer. A consideration of Figure 1 will show that the shaded squares in **b** form slabs parallel to (010) which are identical with the corresponding slabs in **a**, except that the niobium atoms have shifted a short distance from the octahedral to the tetrahedral sites. If now the intermediate slabs of **a** are removed, and reinserted with the *c* axis pointing into the paper instead of out, the structure of **b** is duplicated. The reader may verify this relationship by duplicating Figure 1**a** and cutting along the zigzag lines **A-A.** The pattern must be traced through onto the back of the copy.

Each structure may thus be considered as a regularly twinned version of the other. The rotational twinning relationship also introduces anti-phase boundaries which break up the niobium and yttrium layers of the *M′* structure.

Since there is no simple mechanism to produce rotation twins spontaneously in a crystal, the transition from *T* to *M′* is a difficult one to accomplish; instead, a metastable phase of intermediate energy, *M*, is formed, reducing the driving force and making the equilibrium phase *M′* even more difficult to realize. The reverse transition from *M′* to *T* is aided by temperature and is probably reconstructive.

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