

The Crystal Chemistry of Complex Niobium and Tantalum Oxides IV. The Metamict State

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Abstract

Structural relationships and the effects of isomorphous substitution lead to a new interpretation of the phenomenon of metamictization for these minerals. It is proposed that many possible structures exist with about the same stability, each being favored by slight compositional differences. The metamict state is thus seen as the result of segregation into domains or microregions of different structure and/or composition.

Introduction

We believe, following Pyatenko (1970), that the metamict state in the niobium tantalum oxide minerals is due not to radiation damage, but to their complex chemical compositions. In discussing this thesis we will define the metamict state as "a state of lattice disorder and imperfection in externally well-crystallized natural minerals, which may be annealed out by moderate heating," leaving open the means by which this state is induced. Dobretsov *et al* (1968), for example, have been able to induce such a state by means of a shock wave.

Many synthetic phases of complex tantalum and niobium oxides show affinities with the various tungsten and molybdenum bronzes, and also with the low-temperature Ta₂O₅ structure. These, and the perovskite and other simpler structures, allow an extraordinary variety of closely related phases with slightly differing composition (Wadsley, 1964). A schematic phase diagram of part of the Ta₂O₅-WO₃ system from Roth and Stephenson (1970) is given as an example (Fig. 1). The phases represented by the dashed lines in this diagram have been deduced from structural principles and may not have been observed, and the way in which they decompose is largely hypothetical. But the diagram has a lesson for us with respect to the mineral structures and their crystallization.

Other examples include Nb₂O₅-WO₃ (Allpress, Sanders, and Wadsley, 1969), and Nb₂O₅-TiO₂ (Wadsley, 1964), in which each phase is directly related to the next by some simple alteration of a basic structure, forming a homologous series. Phase

transformations between these structures can be observed dynamically in the electron microscope (Bursill and Hyde, 1972). The phases are so similar that they may intergrow on a molecular scale without any appreciable effect on the X-ray diffraction pattern, and they can only be identified by selected area electron diffraction or imaging. The intergrown phases are the rule, rather than the exception.

The systems in which such closely spaced phases and homologous series have been observed are characterized by relatively highly charged cations, and the highly ordered state is an attempt to reduce unfavorable electrostatic interactions. The distortion of many of the coordination polyhedra from their ideal geometric configuration is usually due to such interactions, rather than to directional bonding (Baur, 1970).

Discussion

The structures we have been discussing are also similar in many respects and will be subject to the same kind of disproportionation and intergrowth. But there are many more opportunities for ordering on the basis of both metal content and metal-to-oxygen ratio, and it is highly likely that on cooling from a high temperature condition (whether single- or multi-phase) the structures will tend to segregate on a very small scale. If the domains are largely rutile, trirutile, wolframite, columbite, *etc.*, an oriented intergrowth of phases is likely to result, which will give an X-ray diffraction pattern corresponding to a more or less disordered rutile or columbite structure. If, however, there is an ap-

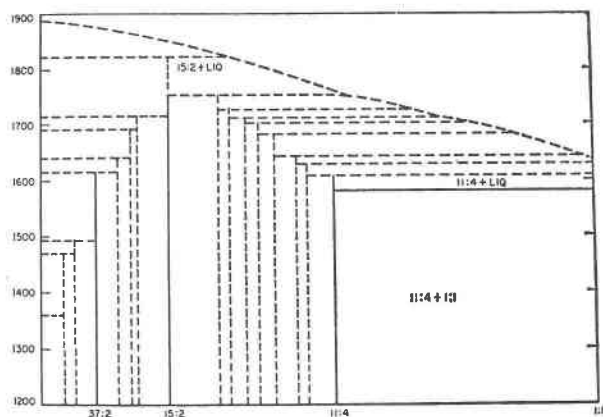


FIG. 1. Schematic representation of a portion of the phase equilibrium diagram of the Ta_2O_5 - WO_3 system (after Roth and Stephenson, 1970).

preciable proportion of larger ions, the coherency between the domains will be lost, and if the domains are <1000 Å, there may be no observable X-ray diffraction. Preliminary electron-diffraction work by Christ, Dwornik, and Tischler (1954) and by Bursill and McLaren (1966) showed such material to be well ordered on a micro-scale. Many samples of columbite-tantalite contain visible inclusions of other phases, often simple oxides such as SnO_2 and Ta_2O_5 (Fig. 2), and these have apparently taken up some of the deviations from stoichiometry of the complex phases. The precipitation and growth of these inclusions and inhomogeneous regions will be a complicated function of the composition and the cooling history. A recrystallization texture associated with a wodginite-tapiolite occurrence at Marble Bar in Western Australia has already been mentioned. The two phases are now relatively uniform in composition, and the low-temperature re-equilibration has allowed the formation of the well-ordered wodginite phase which now has no tendency to disproportionation.

A similar interpretation explains the order/disorder relationships of scandium ixiolite (Borisenko, Maksimova, and Kazakova, 1969). The composition deviates from the ideal $A^3B^5O_4$, and in fact seems to be oxygen deficient. The ordered form produced by heating cannot completely satisfy the ideal structural requirements, and is presumably stabilized by an entropy term; it therefore tends to disproportionate into other (α - PbO_2 related) phases on cooling. The ordered form is metastable at room temperature; the natural room temperature phase is only appar-

ently a disordered form of this structure, but in reality is probably an intimate mixture of *more* ordered forms. Order/disorder transformations for these structures and others previously discussed are only reversible for pure stoichiometric compounds, or after "activation" at a very high temperature (as in fergusonite). Structures of fairly fixed composition, such as the group I and group IV(C) structures cited in Part I, do not occur in a metamict form.

On the basis of microprobe and single crystal structural studies, Gasperin (1972) has recently proposed that in the partly metamict pyrochlore "neotantalite," the majority of the *B* cations and many oxygen ions are displaced to non-lattice posi-

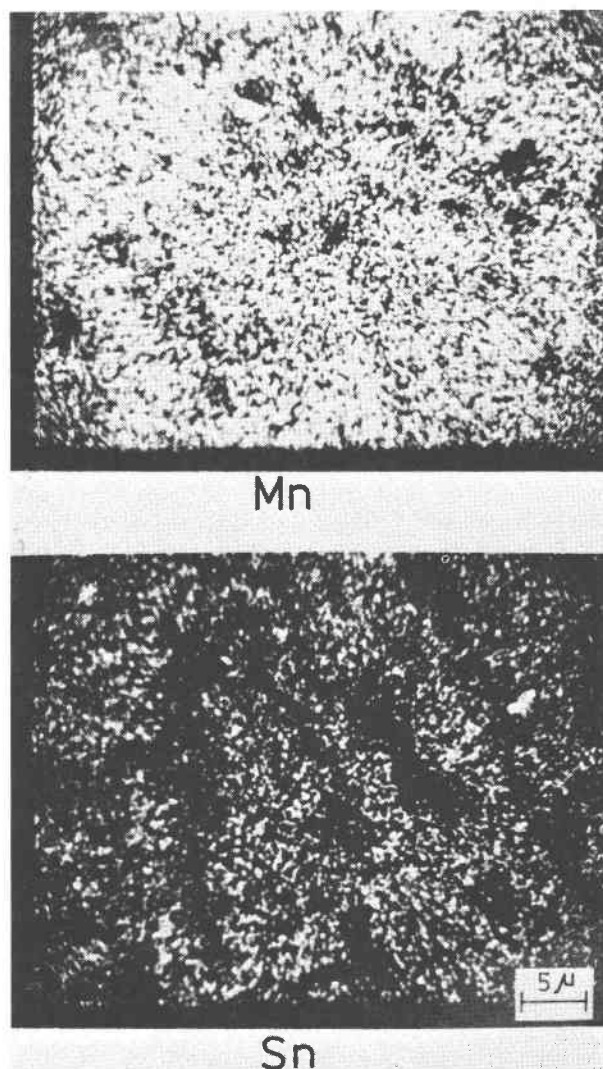


FIG. 2. Microprobe scanning picture of columbite. $SnK\alpha$ and $MnK\alpha$ radiation, showing fine-scale segregation.

tions, whereas all the *A* cations occupy lattice positions. However, a more likely interpretation is that amorphous $(\text{Ta,Nb})_2\text{O}_5$ is intergrown with a coherent skeleton of pyrochlore of composition approximately $\text{U}_{0.2}\text{Ba}_{0.2}(\text{Nb,Ta})_{2.3}\text{O}_6(\text{OH})$. Thus, Gasperin's microprobe analysis for her crystal 1 (on which the structure was done) may be fitted to a pyrochlore composition $A_2B_2O_6X$ to give the structural formula $(\text{U}_{0.074}\text{Ba}_{0.074}\text{Nb}_{0.481})_{0.629}(\text{Nb}_{0.015}\text{Ta}_{1.985})_2\text{O}_6(\text{OH})$, in which there is a large deficit of metals in the *A* site. By transferring Nb rather than Ta from the *B* site, the *A* and *B* scattering factors are adjusted to agree perfectly with the structural study. The metamictization in this case is aided by radioactivity, and probably consists of local areas of more or less disordered decomposition phases on an extremely fine scale (the crystal in question was clear and transparent). The crystals containing Ca instead of Ba seem to be even less stable because, when the uranium content is high, they are completely metamict and, when it is low, they disproportionate on a visible scale.

Conclusions

The observation of metamictization in the complex niobium-tantalum oxides may be explained then by the following postulates:

(1) *The disordered (high temperature) structure must be capable of accommodating a wide variety of ions without much tendency to distortion.* This corresponds to the "isodesmic structures" (without strong specific bonding) postulated by Holland and Kulp (1950), and is certainly true of the rutile/ α - PbO_2 structures shown in Figure 3, which also shows some of the more obvious disproportionation paths. On structural grounds, it also seems to be true of the other phases discussed in this paper. At least

the tantalum-niobium oxides are notorious among the pegmatite minerals for containing a wide variety of elements.

(2) *Ordering occurs to an intermediate phase at some elevated temperature;* cation ordering on the various sites is not complete because of non-ideal stoichiometry.

(3) *The further disproportionation into a number of ordered phases or simple oxides must be sluggish;* i.e., the difference in free energies between the ordered and partly ordered structures must increase slowly as the temperature decreases, so that by the time this difference is large enough to cause disproportionation, the diffusion rates are low or there is a high energy barrier against formation of the equilibrium phase mixture.

As the *A* cation size becomes larger, the probability of metamictization becomes greater. It is possible that the ionic mobility shifts from the cation to the anion under these conditions (compare Rhodes and Carter, 1966, and Simpson and Carter, 1966, who show the anion lattice to be mobile in oxide fluorites).

(4) *The presence of radioactive elements may be expected to accelerate the disproportionation.*

An idea rather similar to ours was expressed by Ueda (1957) in his abstract. "Radioactive minerals are melted, portion by portion, by the irradiation arising from disintegration of the radioactive elements contained in these minerals. The melted portion solidifies later on. The solidification occurs in two ways. One is that taking place in an original crystalline phase and in this case metamictization does not proceed, the other is that not doing and in this case metamictization proceeds." This suggests precipitation of submicroscopic regions of a phase

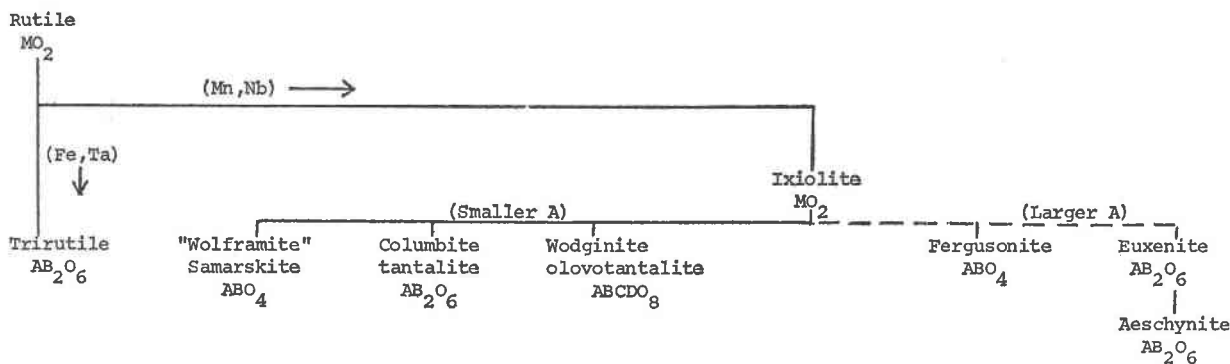


FIG. 3. Scheme of order-disorder and polymorphic transitions in some MO_2 oxides. Temperature increases upwards. Relationships indicated by broken lines have not been observed, but suggest that the larger ions in solution in ixiolite will tend to form these low temperature structures.

different from the matrix in a metamict phase. Ueda unfortunately ignored compositions in which more complicated phase precipitation occurred.

It should be borne in mind that when radioactivity is present, the phases formed are not necessarily the equilibrium ones for the temperature concerned—they are likely to be characteristic of a higher temperature (Mosley, 1971).

If our interpretation is correct, the usual heat treatment of a metamict specimen will restore the original high temperature form (provided the original conditions were not strongly reducing) and will result in a metastable room-temperature form. Without the opportunity for slow cooling under long-term geological conditions, this form may remain perfectly crystalline indefinitely, and may undergo reversible transformations with the high-temperature modification. For this, as for many other problems in geology, a reliable method of low-temperature synthesis would give invaluable information on true equilibria.

Occasional non-metamict occurrences of some of the typically metamict minerals may be due to a fortuitous correspondence between the overall composition of the high-temperature phase and that of one of the low-temperature phases, or to the occurrence of low-temperature recrystallization or other metasomatic or metamorphic processes.

It is worth noting that Pabst (1952), in his review on metamictization, dismissed isomorphous substitution as a cause because this would result in exsolution. We believe that it is just the attempted exsolution which results in a metamict structure. Some further support for our view is given by the common occurrence of finely divided ZrO_2 in metamict zircons (Vance and Anderson, 1972) and ThO_2 in thorite (Pabst, 1952). Pabst notes that many workers have elaborated on the theme of low structural stability, but in our view the metamict state represents an assemblage of structural alternatives which, in accommodating the compositional variations, are only marginally more stable than the original structure. Complete breakdown into the individual oxides as suggested by Goldschmidt (1933) is probably not necessary.

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