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

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Abstract

Graham and Thornber (1974b) have proposed a mechanism for metamictization in complex niobium-tantalum oxides in which complex compositions, rather than radiation damage, are the primary requirement. This note reviews the literature in support of radiation damage as a necessary condition for metamictization and suggests that the structural stability of the metamict "glass" relative to that of the crystalline pre-metamict material is an important consideration in predicting whether a substance will occur in the metamict state.

Introduction

Graham and Thornber (1974b) in an excellent study of complex niobium-tantalum oxides have proposed a new mechanism for the process of metamictization. Their model relies on the micro-exsolution of phases with similar structures in Nb-Ta oxides of complex compositions. The effect of radiation damage in the metamictization process is considered to only "accelerate the disproportionation." Although the process of metamictization is a complex one in which numerous factors must be considered, the purpose of this note is to reemphasize the importance of radiation damage in the metamictization process, particularly for the complex, orthorhombic, $AB_2O_r$-type Nb-Ta-Ti oxides, as well as to suggest that the structure of the metamict glass relative to that of the premetamict crystalline material is an important consideration in evaluating whether a substance may occur in the metamict state.

Metamictization in Complex, Orthorhombic $AB_2O_r$-type Nb-Ta-Ti Oxides

In Table 1, compositional data demonstrate the importance of uranium and thorium in the process of metamictization of complex $AB_2O_r$-type Nb-Ta-Ti oxides. Although the data in the literature are limited, in general those specimens of euxenite, fersmite, aeschynite, and lyndochite which are found in the crystalline state have distinctly lower uranium and thorium contents than their metamict euxenite and aeschynite counterparts. A similar relation has been demonstrated for zircons by Holland and Gottfried (1955). Graham and Thornber (1974b) have rightly pointed to structural and compositional mechanisms for metamictization in complex Nb-Ta oxides; but these models cannot be separated from the necessary catalytic effect of radiation damage. The heart of the difficulty in understanding the process of metamictization lies in evaluating the interaction of alpha particles with different structures and compositions.

Hamberg (1914) was the first to suggest that metamictization is caused by irradiation of substances by particles which originate in the decay of radioactive isotopes of the uranium and thorium series within a crystal structure. Later work by Mügge (1922), Von Stackelberg and Rottenback (1940), Morgan and Auer (1941), Kostyleva (1954), and Holland and Gottfried (1955) supports this theory, but the mechanism of the interaction of alpha particles with different structures and compositions.

Three effects are responsible for radiation damage: (1) a high velocity alpha particle may dissipate energy by excitation of electrons and ionization of atoms along its path, (2) a low velocity alpha particle may lose energy by collision, and (3) the energy of the alpha particle may be dissipated in the form of heat, resulting in a thermal spike which can reach temperatures of $10^5K$ for periods of $10^{-11}$ seconds along the path of the alpha particle. The last two effects are considered important in causing radiation damage (Chadderton, 1965). The collisions cause dislocations and Frenkel defects. Solidification of the material in the thermal spike area may result in: (1) a glass (Ueda, 1957); (2) finely crystalline component oxides (Ueda, 1957; Lipova, Kuznetsova, and Makarov, 1965; Makarov, 1970); (3) the original
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Weight percent

<table>
<thead>
<tr>
<th></th>
<th>$U_3O_8$</th>
<th>$ThO_2$</th>
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<tr>
<td><strong>Non-Metamict</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Euxenite (Nefedov, 1956)*</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Fersmite (Alexandrov, 1960)*</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>Aeschynite (Alexandrov, 1962; Zhabin et al., 1962)</td>
<td>0.08**</td>
<td>3.75***</td>
</tr>
<tr>
<td>Aeschynite (Čech et al., 1972)</td>
<td>0.25**</td>
<td>2.26**</td>
</tr>
<tr>
<td>Lyndochite (Gorzhevskaya and Sidorenko, 1962) *</td>
<td></td>
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* Metamict

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<tbody>
<tr>
<td>Euxenites (mean value of 28 analyses from the literature)</td>
<td>9.31</td>
<td>3.08</td>
</tr>
<tr>
<td>Aeschynites (mean value of 22 analyses from the literature)</td>
<td>1.21</td>
<td>10.73</td>
</tr>
</tbody>
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* Semi-quantitative analysis, no U or Th reported.
** Electron microprobe analysis by R.C.E.
*** Reported as $UO_3$.

Table 1. Uranium and Thorium Content of Non-Metamict and Metamict $AB_2O_4$-Type Nb-Ta-Ti Oxides

Because of the variation in the structure and bonding of geologic materials which caused early workers such as Goldschmidt (1924) and Faessler (1942) to note that the presence of uranium and thorium is a necessary but not sufficient condition for metamictization. There are minerals which maintain their structures against relatively high alpha-particle fluxes (e.g., xenotime, monazite, and thorianite) while others are found in a completely metamict state and yet contain trace amounts of uranium and thorium (e.g., gadolinite). The most striking example of this effect is seen in the dimorphous forms of $ThSiO_4$—thorite and huttonite. Tetragonal thorite is nearly always found in the metamict state (Pabst, 1952) while monoclinic huttonite has been reported only in crystalline form. Thus, radioactivity, while important, seems but a partial explanation of the process of metamictization; and any theory must account for the "disposition" of structures toward the metamict state. This "disposition" has previously been variously attributed to: (1) alteration involving hydrolysis (Broegger, 1890; Dana, 1892; Lacroix, 1922), (2) extensive isomorphism particularly of the rare earths (Faessler, 1942; Pyatenko, 1970), (3) the weakness of chemical bonds of the original phase as compared to the chemical bonds of the simple component oxides (Goldschmidt, 1924), (4) the degree of covalency (Slater, 1951; Pellis, 1954; Lipova, 1966), (5) auto-oxidation (Ellsworth, 1925, 1932; Tomkeieff, 1946; Hutton, 1950; Povarennykh, 1956), (6) instability at lower pressures (Vegard, 1927; George, 1949), and (7) alteration resulting in pseudomorphic replacement (Zhiev, 1952). Graham and Thornber (1974b) have proceeded one step further, considering that "the metamict state in niobium-tantalum oxide minerals is not due to radiation damage, but to their complex chemical compositions." This becomes a difficult question to resolve as the presence of uranium and thorium is usually indicative of complex compositions (e.g., they may be accompanied by REE). In either case, it is important to consider the compositional and structural features that may contribute to the "disposition" of the orthorhombic, rare earth $AB_2O_4$-type Nb-Ta-Ti oxides to metamictization.

Because minerals of the euxenite-polycrase and priorite-aeschynite series are nearly always found in the metamict state, structural data is available for only two non-metamict natural compositions—aeschnite (Alexandrov, 1962) and fersmite (Alexandrov, 1960). The general features of both structures have been summarized by Graham and Thornber (1974a), but certain specific features of the structures that may make these Nb-Ta-Ti oxides susceptible to radiation damage are:

1. Compositions are characterized by extensive isomorphous substitution in the A site which results in variable bond lengths and charge distributions for the individual coordination polyhedra. Although the A-site cations of fersmite and aeschnite are in 8-fold coordination (Alexandrov, 1960, 1962), the variation in A-site ionic radii causes distortion of the coordination octahedra and smaller cations ($Fe^{3+}, Y^{3+}$) are probably more stable in...
six-fold coordination. Also, the electrostatic charge
distribution is irregular. For fersmite (Alexandrov,
1960) the oxygens are overbonded or underbonded
by the following mean values:

\[ O_{I} = +1 \frac{1}{3} \]
\[ O_{II} = +2 \frac{1}{6} \]
\[ O_{III} = +2 \frac{1}{2} \]

This electrostatic imbalance is in part compensated
by differences in the mean cation-anion distances
(Alexandrov, 1960). As isomorphous substitutions
increase, the electrostatic charge balance may show
even wider deviations.

(2) Isomorphous substitutions in the \( A \) site of the

\[ 2(REE^{3+}) \rightarrow 3(Ca^{2+}) \]
\[ U^{++} \rightarrow 2(Ca^{2+}) \]

result in primary \( A \)-site deficiencies, and with hydration
and replacement of \( O^{2-} \) by \( (OH)^{-} \), secondary
\( A \)-site deficiencies are also formed (Pyatenko, 1959).
Primary deficiencies in the \( A \) site are about 15 percent
and may increase to 60 percent with alteration (Van
Wambeke, 1970).

(3) For fersmite and aeschynite the coordination
polyhedra of \( A \)- and \( B \)-site cations share edges as
well as apices, with a subsequent decrease in crystal
stability relative to structures in which only apices are
shared. Although this is an admitted simplification,
it may become an important factor when considering
the stability of a metamict structure relative to the
pre-metamict crystalline structure.

(4) The (Nb,Ta,Ti)-O bonds are not completely
ionic (Bouška, 1970; Alexandrov, 1962). Slater
(1951), Kinchin and Pease (1955), and Lipova (1966)
have pointed out that substances with covalent bonds
experience greater permanent radiation damage,
since the restoration of the bond requires a greater
activation energy than ionic bonds. As noted by Pel-
las (1954), the metamict state is characteristic only for
minerals with partially covalent bonds. This feature
agrees well with Smekal’s view (see summary by
Rawson, 1967) that “mixed” chemical bonds are re-
quired if a material is to form a glass. This correlation
can be quantified by considering electronegatives (see
Rawson’s summary of Stanworth’s work, 1967) or
the field strength. High values of field strength are
characteristic of glass forming oxides; and low values,
of oxides that do not form a glass (Lipova, 1966).

The Structure of the Metamict
“Glass” in Complex Nb-Ta-Ti Oxides

Another approach to the study of metamictization
is to consider the relative stability of the glass to the
crystalline structure and the kinetics of glass formation,
particularly as it relates to understanding the factors which determine whether or not a particular
substance is likely to form a glass. Here again the
discussion must remain qualitative as efforts at
developing a general theory of glass formation “are
usually more in the nature of tentative guesses”
(Rawson, 1967). Some substances readily form
glasses (e.g., SiO\(_2\), GeO\(_2\), B\(_2\)O\(_3\)) while others form
glasses only with the addition of oxides of restricted
compositional ranges (e.g., TeO\(_2\), SeO\(_2\), Al\(_2\)O\(_3\), V\(_2\)O\(_5\)).

Aside from compositional constraints, the formation
of a glass will depend on the rate of cooling and rate
of crystallization. Compositions, bond strengths,
melting point temperatures, rates of cooling, and
kinetics of crystallization all interact and provide a
complex picture of glass formation.

Modern ideas of the structure of inorganic glasses
developed from observations by Goldschmidt (1926)
who noted that the cation-anion radius ratio of
glasses lie in the range 0.2 to 0.4. Goldschmidt was
then led to the conclusion that a tetrahedral ar-
rangement of oxygens around the cation is neces-
sary for glass formation. Zachariasen (1932) ampli-
fied Goldschmidt’s observations, assuming that the
excess energy of the glass could not be much
greater than that of the crystalline structure (else
devitrification would occur). He envisioned the glass
structure as being similar to the crystalline structure
(e.g., composed of the same types of coordination
polyhedra joined in a similar manner) except with the
coordination polyhedra in random orientations and
without long range periodicity and without causing
an increase in cation-cation repulsion. These con-
siderations may be formalized, appropriately enough,
into Zachariasen’s Rules:

1. each oxygen atom is linked to not more than
two cations,
2. the number of oxygen atoms around cations
must be small, and
3. the oxygen polyhedra share corners with each
other, not edges or faces.

Zachariasen’s rules have been subject to criticism,
and oxide glasses may be formed that do not obey the
rules (Rawson, 1967), but there is an interesting
feature of the rules that seems to bear on the
metamict Nb-Ta-Ti oxides. Consider the general for-
mula of the commonly metamict Nb-Ta-Ti oxides,
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AB₂O₆ (euxenite, polycrase, priorite, aescynite, polymignite, kobeite) and A₁₋₂B₂O₇ (pyrochlore, betafite, and samarskite [note, the formula for samarskite may be included in either category; Nilsen, 1970]). In all of these cases the B-site cations are in octahedral coordination, with each octahedron sharing at least two edges with neighboring B-site octahedra. According to Zachariasen's rules, glasses of the general formulas AₙB₂O₆ and AₙB₂O₇ must have the B-site cation in octahedral coordination. Such a glass consists of a random three-dimensional framework of B-site octahedra joined along their apices. A-site cations occupy the "holes" in the three dimensional framework. Conforming to Zachariasen's nomenclature, where the general formula of a glass is given as AₙB₂O₆, the B-site cation would be the "network forming oxide" and the A-site cation the "network modifying oxide." Nb₂O₆ and Ta₂O₅ are listed as possible network forming oxides. Simplistically, the metamictization of Nb-Ta-Ti oxides of types AB₂O₆ and A₁₋₂B₂O₇ involves the disruption of the periodic arrangement of the B-site octahedra, which results in: (1) a transition from edge sharing of octahedra to corner sharing, (2) an increase in volume and decrease in density, (3) microfracturing if the increase in volume is constrained, and (4) distribution of A-site cations throughout "holes" of the glass structure as well as absorption of molecular water. The stability of the glass may be only slightly less than that of the crystalline structure, because the extensive isomorphous substitution and A-site deficiencies are easily accommodated in the glass structure. Thus, there is little driving force for devitrification, recrystallization, or self-annealing of radiation damage. In contrast, for structures of simple compositions (e.g., columbite) and no A-site deficiencies, the periodic arrangement of B-site octahedra is a much more stable configuration than the glass structure, and the driving force for continued self-annealing is greater. Although the argument here is qualitative, the important point is that structure of the glass may be as important as the structure of the crystalline material in determining why certain minerals persist in the metamict state (by a different line of reasoning, Primak (1954) has suggested a similar idea).

As with most qualitative pictures, detailed examination reveals inconsistencies. Zachariasen's rules have been criticized and exceptions documented (Rawson, 1967). In 1932, Zachariasen was not aware of the synthesis of glass-forming oxides of the type AO₃, A₂O₅, or AO₄ and therefore assumed, as Goldschmidt (1924) had, that network-forming oxides must have either trigonal or tetrahedral coordination, in contradiction with the suggested octahedral coordination of B-site cations in metamict Nb-Ta-Ti oxides. Additionally, although Zachariasen considered Nb⁵⁺ and Ta⁵⁺ as potential network-forming cations, he felt the network-modifying cations must be large and carry a small charge (e.g., Na⁺, K⁺, Ca³⁺). While this in part conforms to the composition of complex Nb-Ta-Ti oxides, one should note the presence of REE³⁺, U⁴⁺ and Th⁴⁺. Finally, although the complex Nb-Ta-Ti oxides of the general formula AB₂O₆ and A₁₋₂B₂O₇ conform to a model in which the coordination polyhedra of the crystalline structure form a random three dimensional framework in the glass structure, fergusonite (ABO₄) is an exception. According to Zachariasen's rules ABO₄ compositions should have the B-site network-forming oxides in octahedral coordination, but the B-site cations for fergusonite are in tetrahedral coordination. Thus, the transition from a crystalline to metamict state would involve a change in the coordination of B-site cations. A three dimensional glass could be formed from the B-site tetrahedra only for AₙBO₂ and AₙB₂O₅ compositions.

**Conclusions**

A substantial body of evidence supports the idea that metamictization is a result of radiation damage caused by alpha particles originating from constituent U and Th atoms within the crystalline structure. The main question lies in explaining why particular structures and compositions have a "disposition" toward the metamict state. The answer requires a consideration of the structural stability of the metamict material relative to that of the homogeneous crystalline pre-metamict material. Whether the metamict material consists of well ordered micro-domains as suggested by Graham and Thornber (1974b) or a three-dimensional random network of coordination polyhedra as suggested in this article, the catalytic role of the radiation damage cannot be discounted. Finally, one should note that the presence (Vance and Anderson, 1972; Lipova et al., 1965) or absence (Akhmanova and Leonova, 1961) of finely divided ZrO₂ in metamict zircons does not detract from the role of radiation damage as a mechanism for metamictization.

**Note Added in Proof**

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