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# Metamict Minerals: an Insight into a Relic Crystal Structure Using XRD, Raman Spectroscopy, SAED and HRTEM

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Metamict minerals are characterized by an amorphization of their crystal structure due to radiation damage, and they present an interesting challenge to the mineral and material scientist. The mechanisms of the crystal structure's metamictization and thermally induced recrystallization have been found not only to be of interest for solving mineralogical and geological problems, but also for helping with practical problems, like nuclear-waste storage. This paper gives an overview of the common problems and some analytical solutions involved in obtaining information about the crystal structure of metamict minerals.

## INTRODUCTION

Metamict minerals have been investigated for more than a century. A mineral is regarded as metamict when found in the amorphous state in nature, but assumed to have originally been crystalline. Thus, metamict minerals deviate from the generally accepted definition of minerals, which are normally considered to be crystalline.[1] Because of their unusual properties metamict minerals were known to scientists quite early. For instance, in 1815 the famous chemist Berzelius[2] reported on the pyrognomic behavior of gadolinite, a complex silicate frequently found in the metamict state. The term »metamict« was first used by Brøgger[3] in 1893 for a group of amorphous substances existing with two another: hyaline and porodine. Pyrognomic behavior, *i.e.*, a sudden glowing and subsequent shattering of a mineral upon heating, was also observed for some other metamict minerals, for instance, fergusonite.[4] The destruction of a mineral's crystal lattice is reflected in its physical properties. Usually this means a decrease in the density, the hardness, the birefringence and the refraction indices for metamict minerals. Although systematic investigations of metamict minerals using modern analytical techniques generally began during the second half of the 20th century, some theoretical fundamentals relating to the origin of the amorphous (metamict) state in minerals were postulated a little earlier. Thus, Goldschmit[5] defined the major structural preconditions for a mineral to become metamict:

I. the crystal structure should be weakly ionic and susceptible to hydrolysis;
II. it should contain ions with a variable »state of ionization«
III. it should be subjected to strong radiation.

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The last of these, the influence of the radiation on the crystal structure, was recognized previously by Hamberg[6] as a decisive factor in the processes leading to the amorphization of the crystal structure.

Metamictization, a term used synonymously for amorphization in minerals, is related to heavy-particle irradiation.[7] This irradiation emerges from the decaying nuclei of the radionuclides contained in the crystal structure of the mineral, mainly U and Th. The resulting metamict state is an almost inherent property of complex REE-Nb-Ta oxides, due to the frequent substitution of U and Th for large REE cations in the crystal structure. Examples include minerals such as pyrochlore, aeschynite, euxenite, and fergusonite. However, metamictization is not just limited to oxides, it also occurs in silicate minerals, like zircon, allanite or gadolinite, all of them containing substantial amounts of radioactive elements. Alpha decay is by far the most influential among the decay types for atoms when metamictization is considered. In the $\alpha$-decay series of U and Th, $\alpha$-particles and $\alpha$-recoil nuclei are ejected in opposite directions from the decaying nuclei (see Figure 1). Along their trajectories they transfer energy to the atoms in the crystal structure. This energy transfer occurs by two major processes: (a) ionization and electronic excitation, which almost always occur during the interaction of $\alpha$-particles with electrons, and (b) elastic collisions of both $\alpha$-particles and $\alpha$-recoil nuclei with the atomic nuclei.[8,9] The $\alpha$-particles have an energy of 4.5–5.8 MeV and can cause effects like self-heating, the formation of electron-hole pairs (responsible for bond rupture), charge defects, enhanced self-ion and defect diffusion, localized electronic excitations, and in some cases, defects from radiolysis.[10] Moreover, $\alpha$-particles can induce several hundred atomic displacements as a result of elastic atomic collisions, which form Frenkel defects over a range of 16–22 $\mu$m. However, although they are less energetic (70–100 keV), $\alpha$-recoil nuclei are much more effective, generating up to 2000 displacements that are highly localized in displacement cascades (30–40 nm).[10,11] As can be inferred from irradiation experiments, the final amorphization of heavily irradiated materials can be achieved by several mechanisms: point-defect accumulation (homogeneous amorphization),[12] interface-controlled amorphization,[13] cascade-overlap amorphization,[14] and in-cascade amorphization (heterogeneous amorphization).[15]

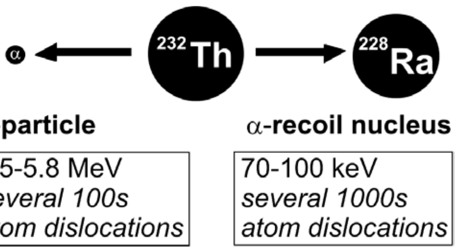

Figure 1. Alpha-decay of $^{232}$Th: schematic representation of the first $\alpha$-decay step.

There are a few good reasons why metamict minerals deserve to be investigated: (a) there is the intrinsic mineralogical interest in knowing more about its chemistry, crystal structure and the mechanism of crystal structure decay, which are very important for a proper mineral classification and nomenclature, (b) the suitability of some metamict minerals for age dating in geology, and (c) nuclear-waste storage, because an understanding of radiation's impact on the crystal structure of the storage matrices is crucial for the long-term immobilization of radionuclides from commercial nuclear plants.

The interactions during metamictization are usually considered in terms of the amount of radiation damage. A large number of experiments are performed using minerals and their synthetic analogues in order to study the effects of radiation on the crystal structure, but also to assess the resistance of certain structures to radiation damage and its healing, and the dependence on temperature. Oxide minerals, like pyrochlore, zirconolite, perovskite, and brannerite, are of special interest in this respect. Lumpkin and Ewing[16] studied the features and stages of the crystalline-metamict transition in natural pyrochlore samples with different degrees of metamictization, ranging from completely crystalline to completely amorphous. Upon ion irradiation, the pyrochlore structure transforms to a disordered fluorite structure prior to amorphization,[17] which after further irradiation results in the formation of amorphous nano-domains.[18] A later investigation by Lian *et al.*[19] confirmed the order-disorder transition in ion-irradiated pyrochlore, suggesting primary disordering in the anion array followed by cation disordering. Brannerite- and brannerite-type ceramics seem to be less resistant to heavy-ion irradiation; this is generally explained by their lower structural connectivity in comparison with that of pyrochlore.[20,21] Zirconolite and perovskite show the highest resistance to radiation damage among the oxides.[21,22] Additionally, the radiation resistance in natural minerals seems to be higher than in their synthesized ceramic analogues, amorphized in ion-beam facilities. This can be related to the thermal history of the minerals and the corresponding restoration of the crystal structure, as shown in zirconolite.[23]

Metamictization in silicate and phosphate minerals, especially those with monazite and zircon structures, has also been investigated. In principle, minerals with the monazite structure recrystallize more readily and are less susceptible to radiation damage than their silicate counterparts.[24–29] This stability of orthophosphates is likely to be related to the strength of the P-O bonds in the tetrahedral coordination, which is stronger than the Si-O bond in the same coordination, for example, in zircon.[30] Annealing experiments involving metamict zircon samples showed an enhanced rate of recrystallization when the experiments were performed in hydrothermal conditions.[31] This is related to the »catalytic« properties of wa-

TABLE I. Some common metamict minerals, their chemical formulae and symmetry

| Mineral | Chemical formula | Symmetry (space group) |
|---|---|---|
| *Oxides* | | |
| aeschynite-(Ce) | (Ce,Ca,Fe,Th)(Ti,Nb)$_2$O$_6$ | *Pbnm* |
| aeschynite-(Y) | (Y,Ca,Fe,Th)(Ti,Nb)$_2$O$_6$ | *Pbnm* |
| euxenite-(Y) | (Y,Ca,Ce,U,Th)(Nb,Ta,Ti)$_2$O$_6$ | *Pbcn* |
| polycrase-(Y) | (Y,Ca,Ce, U,Th)(Ti,Nb,Ta)$_2$O$_6$ | *Pbcn* |
| fergusonite-(Y) | (Y,Ca,Th,U)(Nb,Ta)O$_4$ | $I4_1/a$, *I2 (C2/c)* |
| samarskite-(Y) | (Y,Fe,U,Th)(Nb,Ta)O$_4$ | *Pbcn, P2/c (?)* |
| davidite-(Ce) | (Ce,La)(Y,U,Fe$^{2+}$)(Ti,Fe$^{3+}$)$_{20}$O$_{38}$ | *R-3* |
| brannerite | (U,Ca,Y,Ce)(Ti,Fe)$_2$O$_6$ | *C2/m* |
| pyrochlore | (Ca,Na,REE,U,Th)$_2$Nb$_2$O$_6$(OH,F) | *Fd-3m* |
| zirconolite | CaZrTi$_2$O$_7$ | *C2/c* |
| *Silicates* | | |
| allanite-(Ce) | CaCeFeAl$_2$(Si$_2$O$_7$)(SiO$_4$)O(OH) | $P2_1/m$ |
| gadolinite-(Y) | Y$_2$FeBe$_2$Si$_2$O$_{10}$ | $P2_1/a$ |
| perrierite | (Ca,Ce,Th)$_4$(Mg,Fe)$_2$(Ti,Fe)$_3$Si$_4$O$_{22}$ | *C2/m* |
| chevkinite | (Ca,Ce,Th)$_4$(Fe,Mg)$_2$(Ti,Fe)$_3$Si$_4$O$_{22}$ | *C2/m* |
| thorite | (Th,U)SiO$_4$ | $I4_1/amd$ |
| zircon | ZrSiO$_4$ | $I4_1/amd$ |

ter in structural recovery, with water diffusing into the amorphous regions and enhancing the solid-state recrystallization.[32] Hydrothermal conditions also proved to be efficient for the recrystallization of heavily metamictized samples of allanite and gadolinite.[33] The complexity of the crystal structure could also influence the metamictization of silicate minerals. The amorphization experiments performed for neptunite, titanite, gadolinite, zircon and olivine showed that the critical amorphization dose is lower if the structure is more complex.[34]

Detailed studies of the ion-beam-induced amorphization in oxides, silicates and phosphates have been performed in order to assess the critical amorphization dosages, and to study the amophization/recrystallization mechanisms. This is useful for the preparation of radiation-resistant ceramics used for the immobilization of actinides in nuclear-waste disposals. Recently, a very informative overview in this respect has been published by Lumpkin.[35]

Table I presents the most common metamict minerals with their chemical formula and symmetry, indicated by the space group. Note that the suffixes in parentheses following the mineral's name indicate the most abundant rare-earth element (REE). This notation is common for rare-earth minerals, *i.e.*, minerals that contain REEs as major constituents (Levinson's notation).[36]

There is a vast amount of data that has been collected from studies of metamict minerals. This, mainly mineralogical and geological information, is in addition to the results relating to possible applications, which are based on the structural properties and on the interaction between the crystal structure and the radiation. This overview is generally devoted to the problems of obtaining structural information about metamict minerals and the different approaches used to solve these problems.

## APPROACHES TO TREATING METAMICT MINERALS: HOW TO GET THE STRUCTURAL INFORMATION

The analytical techniques used to investigate metamict minerals have followed the development of standard mineralogical and structural analyses. The concise overview that follows will address only the approaches employing the most frequently used techniques for treating the problem of identifying the crystal structure in metamict minerals. The presented examples are based on the author's experience, and thus the choice of analytical methods is also limited in this respect. Our intention is to show the most typical examples of specific cases in the study of metamict minerals.

### *Approach No. 1: »Heat and X-ray«*

Although metamict minerals are, in general, X-ray amorphous, this has never prevented the use of X-ray-diffraction-based methods when investigating metamict minerals. However, recrystallization induced by annealing is a necessary step to follow in order to get some structural in-

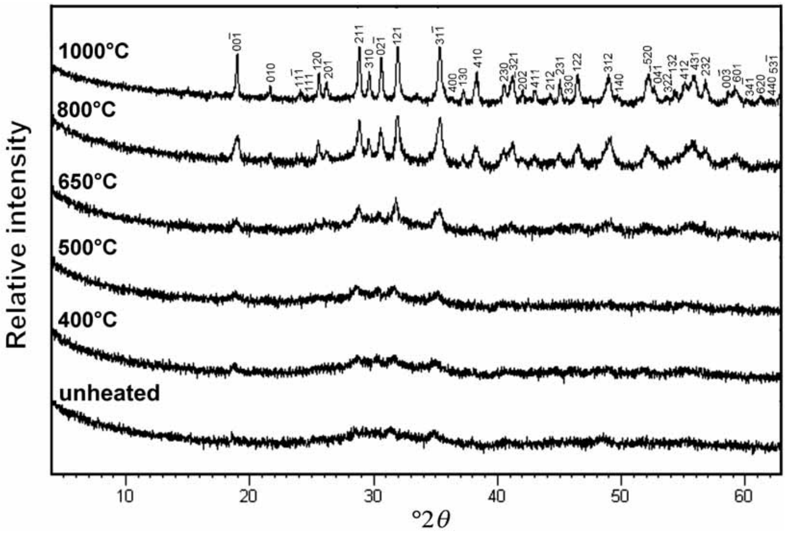

Figure 2. Gradual recrystallization of gadolinite-(Y), from Kåbuland, Norway, as observed by XRD.

formation about a mineral. Apart from diffraction data, the first systematic investigations employing X-rays brought about very useful guidelines for the thermal treatment of metamict minerals. Though they show some drawbacks, these combined heating and X-ray diffraction experiments have become a basic routine in the study of metamict minerals. In general, metamict minerals are heated for several hours up to one day (or, in some cases, even longer) at temperatures ranging from 400 °C to 1000 °C. This heat treatment can induce the recrystallization of the radiation-damaged crystal structure. At this point it is probably a good idea to mention some of the early researchers, like Arnott[37], Pabst,[38] Berman,[39] and Lima-de-Faria,[40,41] who were among the first to have systematically presented X-ray diffraction data obtained after the recrystallization of common metamict minerals, principally Nb-Ta-REE oxides like aeschynite, euxenite and samarskite, but also some metamict silicate minerals like allanite and perrierite.

In some cases the recrystallization of metamict minerals has proved to be strongly influenced by the atmosphere in the heating chamber. Thus, for example, Sugitani *et al.*[42] showed that samarskite can only be effectively recrystallized in a reducing atmosphere, for example, Ar/$H_2$. On the other hand, the recrystallization of euxenite does not depend on firing atmosphere.[43,44]

The described procedure for identifying metamict minerals using thermal treatments and X-ray powder diffraction has been employed for more than fifty years, and the drawbacks of this approach have been recognized from the very beginning of its application. Some of the key problems arising from this approach include:

(a) Does the recrystallized phase really represent the original pre-metamict structure? The problem is associated with the discrepancies in the crystallization conditions during the formation of the original mineral structure and the recrystallization induced during the heating experiments.

(b) The minerals are sometimes altered considerably during and after the metamictization process. In fact many studies have shown that some elements are preferentially leached out from their structural positions. Metamict minerals can be subjected to two kinds of alteration: a primary alteration occurring after the mineral's crystallization, and a secondary alteration occurring in the already-metamictized mineral.[45,46] Note that the minerals that are metamictized are chemically less resistant since their structure becomes more porous. The alteration processes influence the original chemistry of the mineral, *i.e.*, a change in the composition and the stoichiometry, which could prevent the original phase from recrystallizing.

(c) As a consequence of the uncertainties just postulated, recrystallization experiments frequently result in multiphase systems, which are inappropriate for the reliable identification of a metamict mineral and the extraction of structural data.

The following examples illustrate a few cases of metamict mineral identification. The procedure involves thermal treatments and X-ray diffraction analyses with variable success in the final phase/structure recognition.

*Straightforward Identification of Metamict Minerals.* – In some cases metamict minerals can be readily identified using this »classical« approach based on thermal recovery of the crystal structure. Figure 2 shows the gradual recrystallization of gadolinite-(Y), from Kåbuland, Norway. Although the mineral is heavily metamictized it shows a straightforward recrystallization from the lowest to the highest recrystallization temperature. The recrystallization path does not exhibit any phase transition or the occurrence of additional phases, which is otherwise very common for many metamict minerals. As the

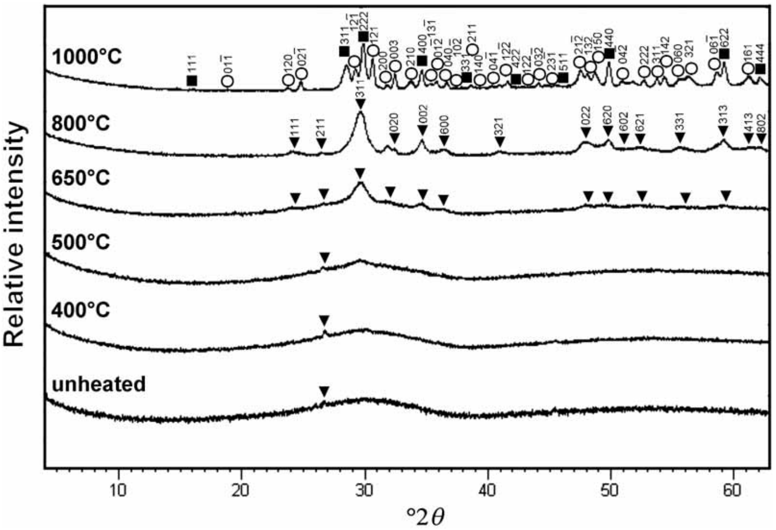

Figure 3. Gradual recrystallization of euxenite-(Y), from Lauvrak, Norway, as observed by XRD (▼ – euxenite, O – samarskite HT, ■ – pyrochlore).

temperature rises, the mineral gradually recrystallizes, increasing its degree of crystallinity, as measured by the decrease in the peak width and the intensifying of the diffraction maxima (Table II). The final diffraction pattern matches well with the expected pattern for gadolinite with the anticipated structure.[47]

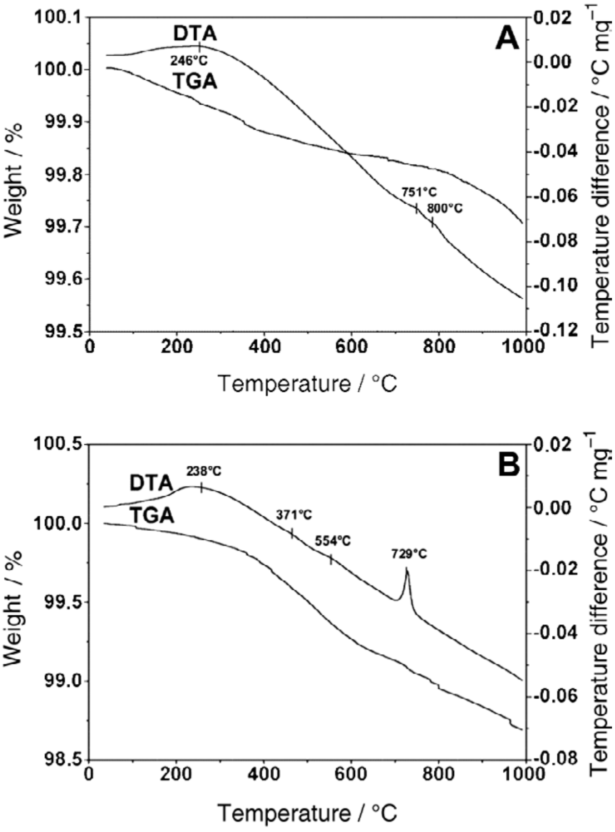

Figure 4. DTA-TGA curves for (A) gadolinite-(Y), from Kåbuland, and (B) euxenite-(Y), from Lauvrak.

*Complex Recrystallization Path: Phase Transition and the Occurrence of Additional Phases*. – In contrast to the previously presented example, the recrystallization of metamict minerals can result in a complex multiphase system. This tends to hinder the reliable identification of the metamict mineral, leaving the original (pre-metamict) structure unresolved. An example of a multiphase system that results from heating euxenite-(Y), from Lauvrak, Norway, in air is shown in Figure 3. Many factors can influence the response of a mineral to a thermal treatment. Two of them, already mentioned, seem to be most often responsible for the outcome of a recrystallization experiment: the chemical alteration of the mineral and the discrepancy between the original crystallization conditions and those simulated during the recrystallization experiments. Furthermore, water can play a significant role when the products of the thermal treatment are considered, since significant amounts can be absorbed by the mineral during and after the metamictization.

Due to the complex recrystallization, TGA-DTA analyses can be helpful in showing the critical temperatures that are accompanied by different chemical and physical processes, like dehydration, crystallization, oxidation, phase transitions and decomposition. Figure 4 shows the TGA-DTA curves for the two previous examples. The curves of gadolinite-(Y) (Figure 4a) depict a simple recrystallization path, evidenced only by two prominent processes: dehydration (mass loss and an endothermic maximum) and recrystallization (an exothermic maximum). On the other hand, the complex recrystallization path for euxenite-(Y) (Figure 4b) is evidenced by all the processes appropriate for gadolinite-(Y), further »interwoven« with multiple crystallization maxima at higher temperatures as the original phase disintegrates into a multiple-phase system.

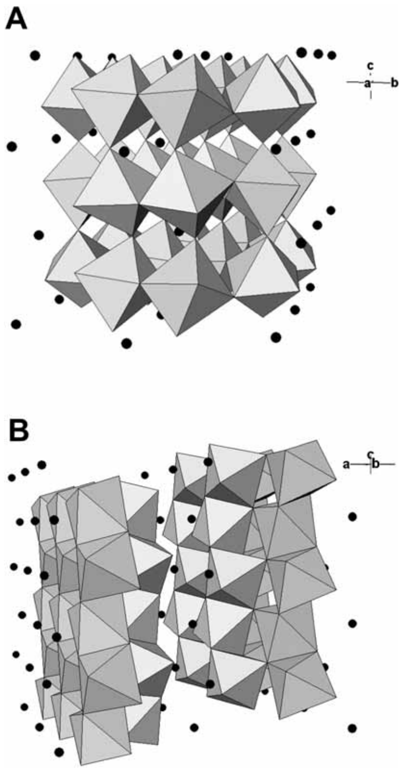

Figure 5. Crystal structure of aeschynite (A) and euxenite (B) after Alexandrov[56] and Aurissichio *et al.* [57], respectively. A-cations are represented by black spheres, and B-cations occupy distorted octahedra.

TABLE II. Temperature dependence of full width at half maximum (FWHM) and intensity of *112* reflection for gadolinite-(Y) from Kåbuland, Norway

| *t* / °C | FWHM / °2$\theta$ | Intensity / cts |
|---|---|---|
| 25 | 0.7810 | 18 |
| 400 | 0.8594 | 16 |
| 500 | 0.7374 | 19 |
| 650 | 0.6760 | 58 |
| 800 | 0.3748 | 145 |
| 1000 | 0.2022 | 365 |

### *Approach No. 2. »Heat and X-ray, but Chemistry Could Help«*

The example of samarskite has just shown that annealing experiments can produce ambiguous data regarding the identification of a metamict phase. In the absence of any other direct method for structural analysis, a thorough evaluation of the chemical composition and a statistical treatment thereof, can help to identify some structurally and chemically very similar metamict minerals. This approach could be called the »standard« approach for treating metamict minerals, especially when the mineral classification and the nomenclature are considered. The statistical approaches for dealing with chemical data have received particular attention for metamict oxide minerals. Ewing[48] used a canonical discriminant analysis to distinguish orthorhombic, frequently metamict minerals, with the $AB_2O_6$ stoichiometry (A = REE, Ca, U, Th; B = Ti, Nb, Ta). For a very long time these minerals had been difficult to distinguish from one another, which caused confusion resulting from a non-systematic nomenclature and classification. Thus, this approach proved to be useful for distinguishing and classifying minerals with the aeschynite and euxenite structures (Figure 5) into two independent mineral groups. The distinction between these minerals is further complicated by the transformation from the aeschynite to euxenite structure at higher temperatures, especially when the HREE-dominant mineral members are considered (HREE = lanthanides from Gd to Lu, including yttrium).[49] The ambiguity obtained with

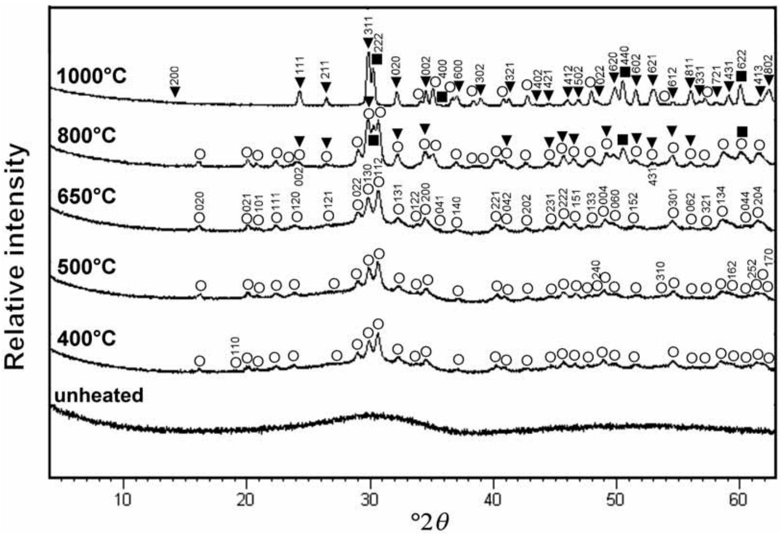

Figure 6. Gradual recrystallization of polycrase-(Y), from Ytterby, Sweden (○ – aeschynite, ▼ – euxenite, ■ – pyrochlore).

TABLE III. Chemical composition and cation assignment (six-oxygen basis) for polycrase-(Y), from Ytterby, Sweden

| | *w* / % | apfu |
|---|---|---|
| CaO | 2.98 | 0.204 |
| FeO | 1.93 | 0.103 |
| $UO_2$ | 8.27 | 0.117 |
| $Ce_2O_3$ | 0.06 | 0.001 |
| $Nd_2O_3$ | 0.76 | 0.017 |
| $Sm_2O_3$ | 0.77 | 0.017 |
| $Eu_2O_3$ | 0.03 | 0.001 |
| $Gd_2O_3$ | 1.17 | 0.025 |
| $Tb_2O_3$ | 0.22 | 0.005 |
| $Dy_2O_3$ | 1.97 | 0.041 |
| $Er_2O_3$ | 1.30 | 0.026 |
| $Tm_2O_3$ | 0.20 | 0.004 |
| $Yb_2O_3$ | 1.91 | 0.037 |
| $Y_2O_3$ | 19.45 | 0.661 |
| *A cations* | | 1.258 |
| $TiO_2$ | 21.95 | 1.054 |
| $Nb_2O_5$ | 28.15 | 0.812 |
| $Ta_2O_5$ | 1.57 | 0.027 |
| *B cations* | | 1.894 |
| Total | 92.69 | |

annealing and XRD experiments could be solved by calculating simple relations among the chemical components (*i.e.*, the variables), which are extracted using the canonical analysis. For instance, Ewing[48] extracted the following variables that influence the chemical and structural distinctions between the minerals: $TiO_2$, $Nb_2O_5$, $Ta_2O_5$, LREE, HREE, and $ThO_2$ and the sum of uranium oxides. Recently, this statistical approach has been further developed and extended to the fergusonite, pyrochlore and samarskite mineral groups with corresponding structures.[50]

In Figure 6 the recrystallization of polycrase-(Y), from Ytterby, Sweden, is presented. Polycrase-(Y) belongs to the euxenite mineral group, and thus it crystallizes with the euxenite structure and has more Ti than Nb on the B-site. The ambiguous identification emerging from the recrystallization experiments, where the mineral recrystallizes first with the aeschynite structure and then transforms to the euxenite structure, can be solved using the following relation:[47,49] LREE < 0.326Ti – 0.060Nb + 3.1, where the content of Ti and Nb is recalculated in oxide (*w*/%) (LREE = lanthanides from La to Eu). For the euxenite group minerals this inequality should be valid, and indeed, if it is solved using the chemical composition obtained for this mineral (Table III), the mineral should be identified as euxenite, *i.e.*, polycrase-(Y), since Ti > Nb (on the basis of cation assignment), and Y is the dominant cation on the A site.

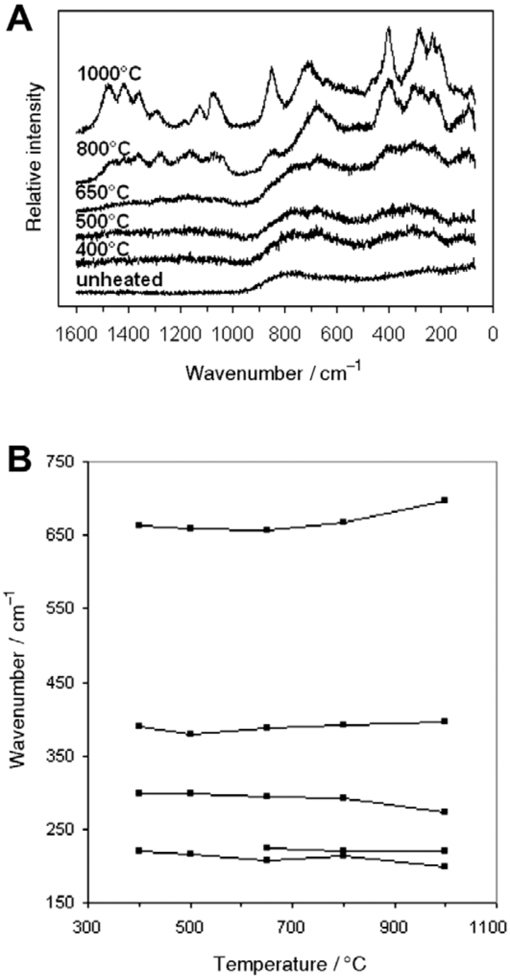

Figure 7. (A) Recrystallization of polycrase-(Y), from Ytterby observed by Raman spectroscopy, and (B) temperature evolution of Raman bands.

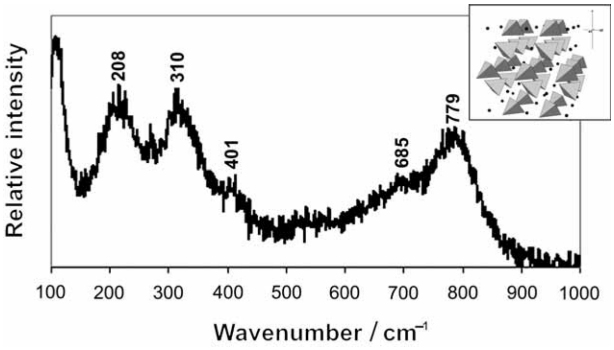

Figure 8. Relics of pre-metamict structure in fergusonite-(Y) traced by Raman spectroscopy. The inset image represents the crystal structure of α-fergusonite.[55] A-cations are represented by black spheres, and B-cations are tetrahedrally coordinated.

### *Approach No. 3: »Insight into the Metamict Structure«*

Intuitively, there is no better approach to reveal the original structure of a metamict mineral than to look directly into the »metamict structure«. This is because, in gen-

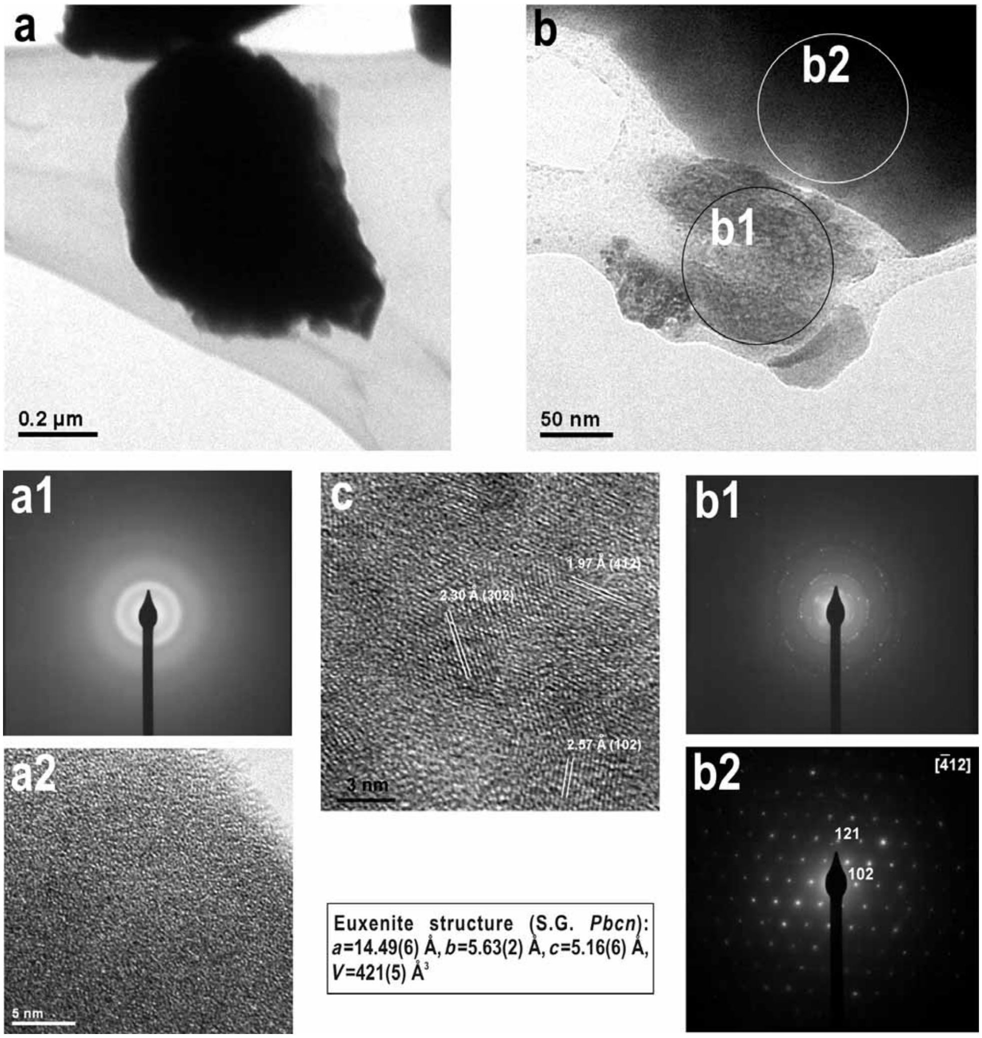

Figure 9. TEM images of metamict euxenite-(Y), from Lauvrak (thermally unheated): (a) amorphous grain showing no electron diffraction (a1) and no lattice fringes in the HRTEM image (a2); (b) a grain containing relics of the premetamict structure as indicated by electron diffraction images (b1, b2). The HRTEM image (c) shows randomly oriented crystallites (relics of the premetamict structure) with d-values corresponding well to the euxenite cell. The presented unit-cell parameters are calculated from image (b1).

eral, the metamict matrix always includes some tiny crystallites that can be considered as relics of the pre-metamict (*i.e.,* the original) mineral structure. These relics are usually very small and not very abundant, so they are not easy to observe with X-ray diffraction techniques. Partly metamictized minerals are an exception here, since they can be regularly identified by X-ray diffraction, although their diffraction patterns are characterized by broadened diffraction maxima, usually not very well resolved. However, this is usually sufficient to identify the mineral. In contrast, for heavily metamictized samples no diffraction maxima occur, thus preventing any proper mineral and structural identification. Therefore, analytical methods, like spectroscopic microprobes and transmission electron microscopy (TEM) techniques, have to be used to gain a direct insight into the structure of the metamict mineral, enabling a structural characterization based on the preserved relics of the original mineral structure.

*Spectroscopic Microprobes: Micro-Raman.* – Today, Raman spectroscopy is widely used as a powerful tool for solving various structural problems. For the study of metamict minerals it was introduced by Nasdala,[51] who showed how useful the technique is in an investigation of metamict zircon. Raman spectroscopy can be very sensitive for tracing the relics of mineral structures, represented by characteristic fundamental vibrations.[52] This effect is especially enhanced when the micro-Raman technique is applied, providing a better spatial resolution. Raman spectroscopy has also proved to be practical for monitoring the recrystallization of metamict minerals, showing a systematic decrease in the band width and an increase in the band intensity as the mineral recrystallizes.[51,53] This property could be applied for probing the tiny grains of metamict minerals to estimate the degree of metamictization, which can vary in different areas of the sample. Such a thorough characterization of metamict minerals like zircon is welcome because of its application for age dating.[54] The inhomogeneity of a single mineral grain in terms of crystallinity could significantly influence the accuracy of the obtained geological age. In Figure 7a the successive Raman spectra of polycrase-(Y), from Ytterby, demonstrated the change in the intensity and the width of vibration bands with an increase of recrystallization temperature. The influence is also observed to the vibration frequencies (Figure 7b). The stretching modes shift to higher frequencies, due to decrease of the metal-oxygen bonds in $BO_6$ (B = Nb, Ta, Ti) octahedra as the structure is recovered during the annealing experiments.

In Figure 8 the Raman spectrum of thermally untreated fergusonite-(Y) shows vibration bands corresponding to the stretching and bending modes of $NbO_4$ tetrahedra, characteristic for the $\alpha$-fergusonite structure.[55]

*TEM Techniques*. – The high spatial resolution of transmission electron microscopy promotes its wide application in the investigation of different materials on the nanoscale. The method is very suitable for investigating metamict minerals in many respects: (a) it can efficiently trace the relics of a pre-metamict structure, (b) it can focus on the radiation-induced defects, and (c) the changes of the mineral structure can be monitored more thoroughly during recrystallization, providing the opportunity to reveal the recrystallization mechanisms.[52]

The example of identifying the relics of the euxenite structure in the sample of euxenite-(Y), from Lauvrak, Norway, is presented in Figure 9. Selected-area electron diffraction (SAED) provides diffraction patterns from very tiny crystallites in a generally amorphous matrix (Figure 9a1, 9b1 and 9b2). For instance, by employing SAED one can obtain diffraction patterns, which are normally sufficient for a symmetry determination. Along with electron diffraction, high-resolution TEM (HRTEM) images can be useful in the identification of metamict phases (Figure 9a2 and 9c). HRTEM of highly metamict minerals shows a generally amorphous matrix in a metamict mineral, containing sparsely distributed nano-sized remnants of the preserved pre-metamict phase. Even without image filtering it is possible, by using Fourier transforms, to measure the interplanar distances very accurately. These data, together with spectroscopic data obtained from a thermally untreated mineral, can give a direct insight into the original structure. However, the information obtained from recrystallization experiments can still be useful. Although the recrystallized phases do not necessarily represent the original structure, they can at least give us some idea of that structure. This is frequently a good starting point in an analysis of electron diffraction patterns and HRTEM images. Namely, a conventional TEM study of metamict minerals is limited because nano-sized crystallites are difficult to orient. Therefore, the standard strategy is to try to index the electron diffraction pattern based on a few models emerging from the results of X-ray diffraction data and some chemical discrimination, as shown before. To speed up the procedure of indexing, some kind of software is always welcome. However, the calculations are simple and do not need much expertise; the main requirement being time and patience.

## CONCLUSION

An investigation of metamict minerals has shown the complexity often involved in determining their crystal structure. The routine application of X-ray-diffraction-based methods requires a previous recrystallization of heavily metamictized minerals. This recrystallization, usually performed by heating experiments, frequently results in multiphase systems, hindering a reliable and unambiguous identification of the metamict mineral. A direct insight into the original structure of the metamict mineral is possible with spectroscopic microprobes, like micro-Raman spectroscopy, or TEM techniques. Selected-area electron diffraction and high-resolution transmission electron microscopy provide a direct identification of the metamict mineral, since they can trace the relics of the mineral's original structure imbedded in the amorphous matrix. However, a combined application of analytical methods and approaches rather than a single method is preferable when studying metamict minerals, since the shortcomings of a single method can be avoided.

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## SAŽETAK

### Metamiktni minerali: uvid u ostatak kristalne strukture upotrebom rentgenske difrakcije, Ramanove spektroskopije, elektronske difrakcije i visokorazlučive elektronske mikroskopije

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Metamiktni minerali su obilježeni amorfizacijom kristalne strukture kao posljedicom oštećenja strukture uslijed radioaktivnog zračenja, te kao takvi predstavljaju stalni izazov mineralozima i drugim znanstvenicima koji proučavaju materijale. Mehanizmi metamiktizacije kristalne strukture te njene rekristalizacije potaknute zagrijavanjem, osobito su značajni u rješavanju mineraloških i geoloških problema, ali imaju i praktičnu primjenu, npr. u odlaganju radioaktivnog otpada. Ovaj rad daje pregled uobičajenih problema i nekih analitičkih rješenja pri prikupljanju informacija o kristalnoj strukturi metamiktnih minerala.