

Local Phenomena in metamict Titanite

U. BISMAYER^{a,*}, C. PAULMANN^a, L. GROAT^b AND M. ZHANG^c

^aMineralogisch-Petrographisches Institut, Universität Hamburg

Grindelallee 48, 20146 Hamburg, Germany

^bDepartment of Earth and Ocean Sciences, University of British Columbia

Vancouver, British Columbia V6T 1Z4, Canada

^cDepartment of Earth Sciences, University of Cambridge

Downing Street, Cambridge, CB2 3EQ, U.K.

Pure titanite is a mineral with chemical composition CaTiSiO_5 . Its structure consists of corner linked TiO_6 -octahedra, SiO_4 -tetrahedra and sevenfold coordinated Ca positions. In nature various impurities like U and Th can be incorporated in the structure showing alpha and beta radiation. On metamictization, a process which occurs in nature when a mineral is exposed to radioactive irradiation, strong modifications of the structure are observed. Recoil processes due to alpha radiation change over geological time scales the originally periodically structured material into a quasi-amorphous state with persisting short-range order but destroyed long-range order. We report IR and Raman spectra as well as X-ray diffraction data of metamict and heat treated titanite from the Cardiff mine, Canada. IR as well as the Raman modes are strongly broadened in the metamict material and sharpen on annealing. The OH-stretching mode at 3486 cm^{-1} indicates strong changes in the local environment of OH in metamict titanite. The appearance of the Raman excitations between 620 and 750 cm^{-1} in metamict titanite, which in IR spectra are due to Ti-O stretching from TiO_6 octahedra, indicates the breakdown of the Raman selection rules. This points to the breaking of the octahedral symmetry of TiO_6 polyhedra.

PACS numbers: 23.60.+e, 61.43.-j, 62.23.-c, 78.30.-j, 81.40.-z

1. Introduction

The crystal structure of pure titanite had been studied previously using classical X-ray diffraction (XRD) [1] and synchrotron radiation [2]. Radiation-induced structural changes occur in the material if radionuclides are present in the structure and decay. The mineral becomes metamict. Various experiments like XRD, thermal gravimetric analysis (TGA), IR, magic angle spinning NMR (MAS NMR), high resolution transmission electron microscopy (HRTEM), extended X-ray absorption fine structure (EXAFS), X-ray absorption near-edge structure (XANES), Mössbauer spectroscopy had been applied to study such metamict titanites [3–6]. The local symmetry and the topology of polyhedra of metamict samples may be different from classical arrangements in the crystalline state and hence, local as well as macroscopic physical properties are modified in the irradiated material. Thermal annealing leads via various steps to a re-established long-range order and to other phenomena like dehydration and volume reduction [3, 5, 7]. The structural transformation behaviour of synthetic and natural crystalline titanite due to temperature is well known [2, 8, 9].

In this work we present local, mesoscopic and macroscopic behaviour of metamict titanite from Canada, Cardiff mine. In general, studies of metamict minerals provide a better knowledge on the damage and recrystallization processes of self-radiation damage which is relevant for the storage of high-level nuclear waste, a question of increasing importance with decreasing natural energy resources.

2. Experimental

The samples selected for this study were natural titanite from Rauris, Austria and dark metamict titanite from Cardiff mine, Ontario, Canada, both used for earlier experiments (Fig. 1). The chemical composition of the samples had been investigated previously [3, 10]. The Rauris sample was light green, well crystalline and contained Fe 1.8%, Al 3.8% as main impurities and a trace of Th [10]. The sample from Cardiff contained 7.9% Fe, 13.3% Al as well as 767 ppm U and 470 ppm Th [3]. For our measurements a synthetic, well crystalline sample was used as reference material [11].

Synchrotron studies were carried out using the Kappa-diffractometer, beamline F1 (HASYLAB/DESY) equipped with a CCD-detector (MAR). The wavelength was 0.07293 nm and the sample-to-detector distance 50 mm . Isothermal annealing experiments and progressive annealing for 15 min at each temperature step were done with a N_2 gas-stream heating device (Cryostream).

* corresponding author; e-mail:
ubis@mineralogie.uni-hamburg.de

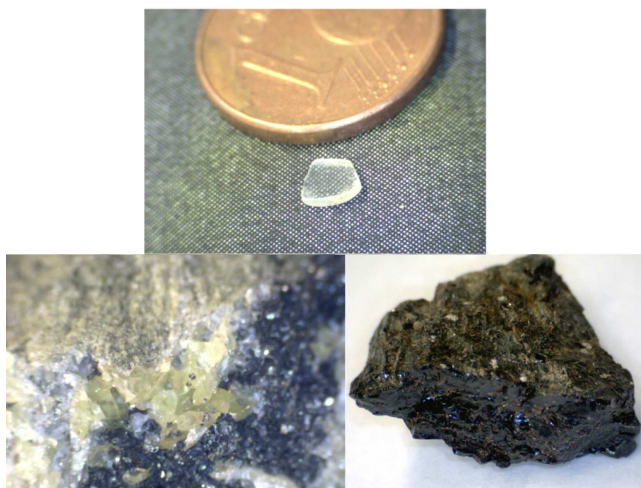


Fig. 1. Synthetic titanite from [11] (top). Crystalline titanite from Rauris, Austria (left bottom) and metamict titanite from Cardiff mine, Ontario, Canada (right bottom).

The heating device was calibrated using a NiCr/Ni-thermocouple prior to the experiment (giving a thermal stability ± 3.0 K). Data collection began with a scan step width of 0.5° (3.0 s/frame) and ended with 0.05° (1.0 s/frame) after the annealing cycles because of sharper diffraction peaks after heating.

Infrared spectra were measured using a Bruker IFS 113v and a Bruker IFS 66 V Fourier-transform spectrometer. A global light source, apertures of 0.5–2.5 mm, a KBr beamsplitter, and a wide-band MCT detector were used. 512 or 100 (for high temperature experiments) scans were accumulated for each spectrum. All spectra were recorded under vacuum. A KRS5 wire-grid polariser was used for polarized measurements.

The Raman spectrometric measurements were performed at room temperature using a triple monochromator system Jobin-Yvon T64 000 equipped with a liquid N_2 -cooled CCD camera. The unpolarised spectra were collected in backscattering geometry using the 514.5 nm line of an Ar^+ -ion laser with an output laser power of 100 mW. The exciting laser beam was focused through an Olympus BH2 20 \times microscope objective on the sample surface, correspondingly. The diameter of the laser spot on the sample surface was approximately 6 μm and the spectral resolution was about 2 cm^{-1} . From the synthetic titanite single crystal diagonal polarised Raman spectra were recorded.

3. Results and discussion

The progressive thermal behaviour of the Bragg-reflection (080) of Cardiff titanite is shown in Fig. 2. The (080)-reflection shows a gradually increasing integrated Bragg-intensity on annealing using 50 K steps between 473 and 623 K. Stronger changes take place at annealing temperatures above 623 K where the intensity increases

about one order of magnitude per 15 min heating. The thermal behaviour of the intensity is associated with a decrease in the full-width-at-half-maximum (FWHM) at temperatures below 623 K. Above this temperature, the FWHM decreases more rapidly and approaches values close to that of crystalline samples. Annealing at higher temperatures yields a faster kinetics. At 773 K, the peak intensity increases by almost one order of magnitude on the absolute scale within 90 min.

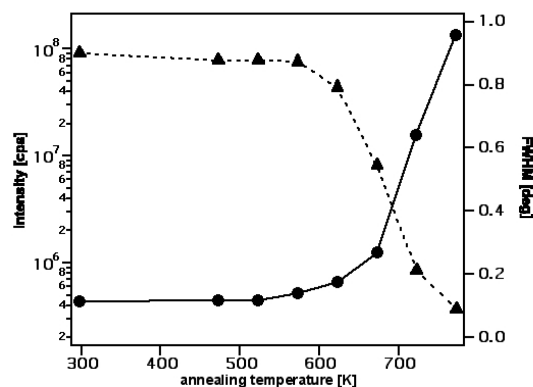


Fig. 2. Intensity (circles) and width (triangles) of the 080-Bragg reflexion in metamict titanite from Cardiff as a function of temperature and annealing time (15 min per temperature step at 298, 473, 523, 573, 623, 673, 723, 773 K). Lines are guides for the eye.

The crystal from Rauris shows IR absorption bands near 3486 cm^{-1} where the synthetic titanite shows only a very weak signal while the sample from Cardiff shows broad features between 2500 cm^{-1} and 3500 cm^{-1} (Fig. 3). The absorption at 3486 cm^{-1} in the metamict material is accompanied by a broad tail towards the low-energy side of the absorption. The absorption profile is in general unstructured in the spectrum of the metamict sample from Cardiff (Fig. 4). We found polarisation dependence of the 3486 cm^{-1} O–H stretching which indicates that the sample is anisotropic in the IR spectrum. The local structure is, thus, crystalline. The titanite from Rauris contains OH groups which are strongly bonded to specific crystallographic sites. Those OH groups are well aligned and their absorption spectra are polarised. Very similar OH groups also occur in metamict titanite from Cardiff (Fig. 3). In addition, a broad distribution of supplementary OH molecules can be observed. The vibrational frequencies of these additional molecules are characteristically shifted towards lower frequencies. This indicates that the effective oxygen–hydrogen bond, as seen by IR spectroscopy, is weaker than the structural bond OH in a well defined crystalline sample. As the weak O–H bonds appear only in metamict titanite we correlate their appearance with the defect structure of the sample. On annealing the IR excitations of the metamict sample from Cardiff (Fig. 5) show considerable sharpening and hence, the crystal structure recovers to a great extent on thermal treatment.

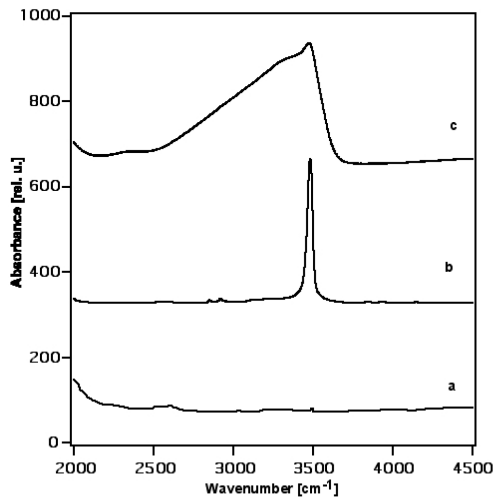


Fig. 3. Infrared spectra of synthetic titanite (*a*), titanite from Rauris (*b*) and from Cardiff (*c*) in the spectral region between 2000 and 4500 cm^{-1} .

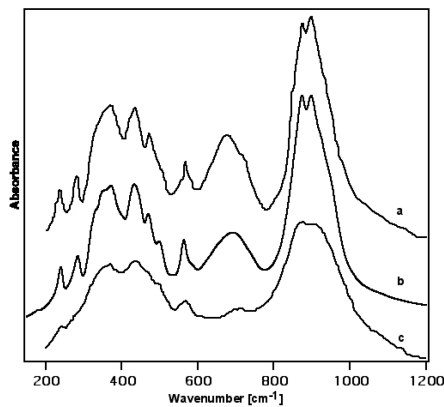


Fig. 4. Infrared spectra of synthetic titanite (*a*), titanite from Rauris (*b*) and from Cardiff (*c*) in the spectral region between 200 and 1200 cm^{-1} at 300 K.

The A_g polarised Raman spectra of synthetic titanite, Rauris titanite and unpolarised Raman spectra of the metamict Cardiff sample as well as the annealed Cardiff sample (30 min, 1123 K) are shown in Fig. 6. The metamict sample shows complete isotropy. According to group theoretical mode analysis of crystalline titanite (space group $P2_1/a$) 48 Raman active modes are expected at room temperature (RT) [12]. The Raman spectrum of synthetic titanite corresponds to that of the sample from Rauris. The modes of the Rauris crystal are lightly broadened perhaps due to impurities. The spectra of the metamict material show extremely broad excitations which sharpen considerably after annealing the sample. The strongest mode in synthetic titanite near 594 cm^{-1} shifts by 20 cm^{-1} to lower energies in the metamict material and remains there after annealing. The excitations around 520 cm^{-1} in the synthetic as well as in the Rauris sample do not appear in metamict

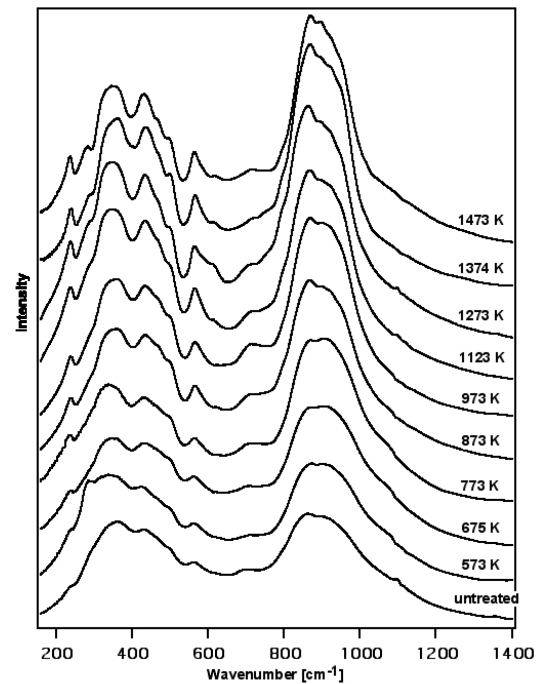


Fig. 5. IR spectra of Cardiff titanite measured at 300 K after annealing (annealing period 1 h) at the given temperatures.

Cardiff titanite even not after annealing. The mode near 109 cm^{-1} is visible only in the synthetic sample. Near 680 cm^{-1} there occurs a weak mode in the Raman spectrum of the metamict sample (Fig. 6d) which increases and forms a broad band on annealing (Fig. 6c).

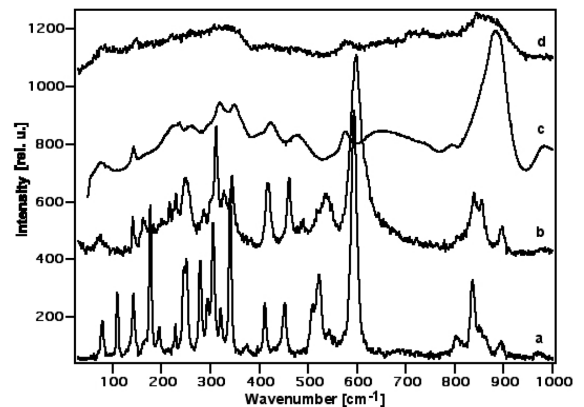


Fig. 6. Raman spectra of (*a*) synthetic titanite (A_g symmetry, 110 K), (*b*) Rauris titanite (95 K), (*d*) the metamict sample from Cardiff (unpolarised, RT), and (*c*) after annealing the Cardiff sample for 30 min at 1123 K.

The most relevant interaction between natural radiation of α -particles (He^{2+}) from radioactive impurities with atomic recoil processes are of mechanical nature. As a result of the recoil processes the structure ap-

pears to be damaged, however, short-range order persists and crystalline clusters occur in a quasi-amorphous matrix. A phenomenological theory of the crystalline-to-amorphous phase transition during self-irradiation describes the local effects [13]. In such damaged areas the vibrational properties of polyhedral modes are heavily modified because of their distortion and the influence of their surroundings. The coupling to phonons of the surrounding leads to further anharmonicity and our Raman spectra of metamict titanite suggest that the selection rules in such material may be broken. Therefore the suggestion by Farges [4] from XANES spectroscopy that five-fold coordinated Ti may occur in metamict titanite seems very reasonable and should be studied in more detail.

4. Conclusions

metamict titanite, CaTiSiO_5 occurs in nature as metamict material with radiation damage due to radioactive impurities. The mineral exposed to long-term radioactive irradiation shows strong modifications of its local atomic structure and can be transformed into a quasi-amorphous state with persisting short-range order but destroyed long-range order. Our IR and Raman spectra as well as X-ray diffraction data of metamict and heat treated titanite from the Cardiff mine, Canada show heavily broadened vibrational modes which sharpen on annealing. The results are compared with those from synthetic titanite and a sample from Rauris, Austria. The local environment of OH is affected by the radiation damage and the OH-stretching mode at 3486 cm^{-1} indicates structural changes in Metamict titanite. The appearance of the Raman signals between 620 and 750 cm^{-1} in metamict titanite, also seen in IR spectra are due to Ti-O stretching modes and may indicate a breakdown of

the Raman selection rules. The octahedral symmetry of TiO_6 polyhedra must be assumed to be broken.

References

- [1] J.A. Speer, G.V. Gibbs, *Am. Mineral.* **61**, 238 (1976).
- [2] S. Kek, M. Aroyo, U. Bismayer, C. Schmidt, K. Eichhorn, H.G. Krane, *Z. Kristallogr.* **212**, 9 (1997).
- [3] F.C. Hawthorne, L.A. Groat, M. Raudsepp, N.A. Ball, M. Kimata, F. Spike, R. Gaba, N.M. Halden, G.R. Lumpkin, R.C. Ewing, R.B. Gregor, F.W. Lytle, T.S. Ercit, G.R. Rossman, F.J. Wicks, R.A. Ramik, B.L. Sherriff, M.E. Fleet, C. McCammon, *Am. Mineral.* **76**, 370 (1991).
- [4] F. Farges, *Am. Mineral.* **82**, 44 (1997).
- [5] M. Zhang, E.K.H. Salje, U. Bismayer, L.A. Groat, T. Malcherek, *Am. Mineral.* **87**, 882 (2002).
- [6] C. Paulmann, U. Bismayer, L.A. Groat, *Z. Kristallogr.* **215**, 678 (2000).
- [7] R.C. Ewing, A. Meldrum, LuMin Wang, ShiXin Wang, *Rev. Mineral. Geochem., Min. Soc. America* **39**, 319 (2000).
- [8] T. Malcherek, C. Paulmann, M.C. Domeneghetti, U. Bismayer, *J. Appl. Crystallogr.* **34**, 108 (2001).
- [9] H.-W. Meyer, U. Bismayer, G. Adiwidjaja, M. Zhang, L. Nistor, G. Van Tendelo, *Phase Transit.* **67**, 271 (1998).
- [10] H.W. Meyer, M. Zang, U. Bismayer, E.K.H. Salje, C. Schmidt, S. Kek, W. Morgenroth, T. Bleser, *Phase Transit.* **59**, 39 (1996).
- [11] I. Tanaka, T. Obuchi, H. Kohima, *J. Cryst. Growth* **87**, 169 (1988).
- [12] U. Bismayer, *Rev. Mineral. Geochem.* **39**, 265 (2000).
- [13] P. Tolédano, U. Bismayer, *J. Phys., Condens. Matter* **17**, 6627 (2005).