The Canadian Mineralogist
Vol. 38, pp. 119-130 (2000)

DEHYDRATION OF METAMICT TITANITE: AN INFRARED SPECTROSCOPIC STUDY

MING ZHANG, EKHARD K.H. SALJE AND THOMAS MALCHEREK

Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, U.K.

ULRICH BISMAYER

Mineralogisch-Petrographisches Institut, Universität Hamburg, D-20146 Hamburg, Germany

LEE A. GROAT[§]

Department of Earth and Ocean Sciences, University of British Columbia, Vancouver, British Columbia V6T 1Z4, Canada

ABSTRACT

We carried out a study of dehydration in natural metamict and crystalline samples of titanite between 20 and 1060 K. Infrared absorption spectra of crystalline titanite show at least five O–H stretching bands in the region between 2000 and 4500 cm^{-1}. Metamict samples show a broad distribution of stretching modes between 2500 and 3700 cm^{-1}. The annealing of metamict titanite was studied by IR absorption spectroscopy under *in situ* and *ex situ* heating conditions. Heating a sample at high temperature leads to an irreversible decrease of the absorption signal of the O–H stretching bands, together with a significant sharpening of the band profile. The O–H bands in the metamict material show no preferential polarization. Annealing leads to a dramatic anisotropy of the IR absorption spectra. We believe that the recrystallization behavior of a metamict sample is correlated with its dehydration.

Keywords: titanite, metamict, dehydration, infrared spectroscopy.

SOMMAIRE

Nous avons étudié la déshydratation d'échantillons naturels métamictes et cristallins de titanite dans l'intervalle de 20 à 1060 K. Les spectres d'absorption infrarouge de titanite cristalline possèdent au moins cinq bandes dues à l'étirement du couple O–H dans la région entre 2000 et 4500 cm^{-1}. Les échantillons métamictes font preuve d'une distribution floue de modes d'étirement entre 2500 et 3700 cm^{-1}. Le recuit de la titanite métamicte a été étudié par absorption dans l'infra-rouge suite à un chauffage *in situ* et *ex situ*. Le chauffage d'un échantillon jusqu'à une température élevée mène à une diminution irréversible du signal dû à l'étirement O–H, en même temps qu'une définition accrue du profil des bandes d'absorption. Les bandes O–H du matériau métamicte ne montrent aucune polarisation préférentielle. Le recuit mène à une anisotropie dramatique des spectres infra-rouges. A notre avis, le comportement de la titanite métamicte au cours de sa recristallisation montre une corrélation avec sa déshydratation.

(Traduit par la Rédaction)

Mots-clés: titanite, métamicte, déshydratation, spectroscopie infra-rouge.

INTRODUCTION

Radiation damage in minerals is commonly accompanied by hydration. Synthetic titanite contains no H_2O molecules, whereas natural samples display a bewildering complexity of infrared (IR) absorption signals in the spectral region characteristic for hydrous molecules. Previous studies on the infrared absorption spectra of natural titanite show that protons in titanite are present as OH groups with a strong absorption band near 3485 cm^{-1} (Isetti & Penco 1968, Hawthorne *et al.* 1991, Hammer *et al.* 1996). Protons are bonded to the oxygen atom at the O(1) site in the titanite structure; the direction of the O–H dipoles is oriented in the (010) plane, approximately parallel to the direction of the index of refraction n_α (Isetti & Penco 1968, Beran 1970). Other

---

[§] *E-mail address*: lgroat@eos.ubc.ca

associations may occur, as indicated by complex IR band structures. No structurally bound H_2O has been reported, and its characteristic absorptions near 5200 and 1630 cm^{-1} have not observed in titanite (Hawthorne *et al.* 1991).

A question arises as to whether OH groups in titanite occur only because of the localization of protons on a specific structural site or, alternatively, whether OH groups can also be related to defect structures. The primary defect structures in metamict titanite are amorphous regions that are generated by radiation damage related to radiogenic impurities (Chrosch *et al.* 1998). Radiation damage produces defects that can be classified into two groups. Firstly, Frenkel defects are produced primarily by the collision of α-particles with atoms. Secondly, the recoil of the radiogenic impurity displaces a large number of atoms, which leads to amorphous areas in the crystal. The exact extent of the amorphous regions (per event) is not known in titanite. Comparing the radiation damage in titanite with that in zircon leads to a rough estimate of 10^3 Frenkel defects and 10^4 particles in the recoil areas per radiogenic event (Weber 1990, Ewing *et al.* 1987).

Our hypothesis is that impurities may well partition between the crystalline matrix and the damaged regions (Chrosch *et al.* 1998). In particular, we envisage OH groups to be enriched in the amorphous material. The next question concerns the way the OH groups are bonded to the structure. The amorphous parts of the material likely offer a multitude of sites that can anchor the OH groups. It is the purpose of this paper to show that the OH groups in the amorphous areas are more weakly bonded and disappear more readily under heating than the more strongly bonded OH groups that form part of the structure in crystalline titanite.

EXPERIMENTAL

Natural titanite samples “Cardiff”, B20323, “Rauris” and R17030, and a synthetic sample were used in this study. “Cardiff” titanite originates from the Cardiff mine near Bancroft, Ontario, Canada and was previously investigated by Vance & Metson (1985), Fleet & Henderson (1985), and Hawthorne *et al.* (1991). Sample B20323 is from the Smithsonian Institute in Washington, and “Rauris” is from the Rauris locality in Austria; both were previously studied by Meyer *et al.* (1996) and Zhang *et al.* (1997). Sample R17030 is from an unknown locality in Brazil. The synthetic sample was provided by Tanaka *et al.* (1988) and was previously investigated by Bismayer *et al.* (1992), Salje *et al.* (1993) and Zhang *et al.* (1995). Samples B20323, “Rauris” and R17030 are yellow-green and highly crystalline, whereas the “Cardiff” sample is black and strongly metamict; according to Hawthorne *et al.* (1991), microstructural features of the Cardiff titanite are consistent with damage on the order of 30 to 50% of that required to render the structure fully aperiodic. Electron-microprobe analysis was performed to characterize all natural samples using a Cameca SX–50 electron microprobe with a Link AN10000 energy-dispersion spectrometer. An accelerating voltage of 20 kV and a beam current of 20 nA were used. A beam size of 5 μm was used, and 20 points were analyzed on each sample. The following elements were sought: F, Al, Si, Ca, Ti, V, Mn, Fe, Ce, Nd, Gd and Th. The results of the chemical analysis of the samples are listed in Table 1. No attempts were made to determine the absolute H_2O content of the samples. The crucial changes upon annealing affect the absorption profiles, band positions and heights which were, hence, the focus of our investigations.

The crystallographic orientation of a section of titanite B20323 (1.001 mm thick) was determined by optical experiments and X-ray diffraction rocking-curve measurements (Chrosch *et al.* 1997). The results showed that the section is approximately parallel to (101), with an off-plane angle of 3°. The “Cardiff” sample was oriented by X-ray techniques, and then was sawn into slices of appropriate orientation. The oriented sections were subsequently polished using (in order) 12, 3 and 1 μm diamond pastes.

Infrared spectra between 500 and 7000 cm^{-1} were measured using Bruker IFS 113v and IFS 66v Fourier-

TABLE 1. CHEMICAL COMPOSITION OF THE TITANITE SAMPLES

		“Cardiff”	B20323	“Rauris”	R17030
SiO_2	wt.%	30.30	30.17	30.11	30.62
TiO_2		32.39	39.31	38.87	38.49
ThO_2		0.05	0.01	0.01	0.01
CaO		27.42	28.46	28.46	28.63
MnO		0.02	0.01	0.02	0.05
FeO		2.84	0.98	0.67	0.60
Al_2O_3		3.35	0.12	0.99	1.25
V_2O_3		n.d.	n.d.	0.24	0.18
Ce_2O_3		0.35	0.16	n.d.	n.d.
Nd_2O_3		n.a.	n.d.	n.d.	n.a.
Gd_2O_3		0.12	n.a.	n.a.	n.d.
F		1.43	0.09	0.13	0.11
$O \equiv F$		-0.60	-0.04	-0.05	-0.05
TOTAL		97.67	99.27	99.45	99.89
Si	*apfu*	1.004	0.992	0.984	0.994
Ti		0.807	0.972	0.956	0.940
Th		0.000	0.000	0.000	0.000
Ca		0.973	1.002	0.997	0.996
Mn^{2+}		0.001	0.000	0.001	0.001
Fe^{2+}		0.079	0.027	0.018	0.016
Al		0.131	0.005	0.038	0.048
V^{3+}		0.000	0.000	0.006	0.005
Ce^{3+}		0.004	0.002	0.000	0.000
Nd		0.000	0.000	0.000	0.000
Gd		0.001	0.000	0.000	0.000
F		0.150	0.009	0.013	0.011
O		4.804	4.962	4.955	4.955

Note: Oxides are in weight percent; compositions are normalized on 3 cations per formula unit; n.a. = not analyzed, n.d. = not detected.

transform spectrometers. A globar light source, apertures of 0.5 to 2.5 mm, a KBr beam splitter and a wideband MCT detector were used. Totals of 350 scans (for *in situ* high-temperature measurements), 512 scans (for measurements at room temperature and low temperatures) and 1000 scans (for selected experiments at room temperature) were accumulated for each spectrum. A spectral resolution of 2 cm^{-1} was used to record spectra at high temperatures. All spectra were recorded under vacuum. To record polarized spectra, a KRS5 wire-grid polarizer was used with a SPECA holder. The crystals were oriented with a polarizing microscope prior to insertion into the spectrometers.

Low-temperature measurements were collected with the samples mounted inside a closed-cycle liquid-nitrogen cryostat (Leybold) equipped with KRS5 window. The temperature stability was ±0.5 K. During the cooling sequences, samples were held at each temperature for 15 minutes to allow for thermal equilibration before collection of the infrared data.

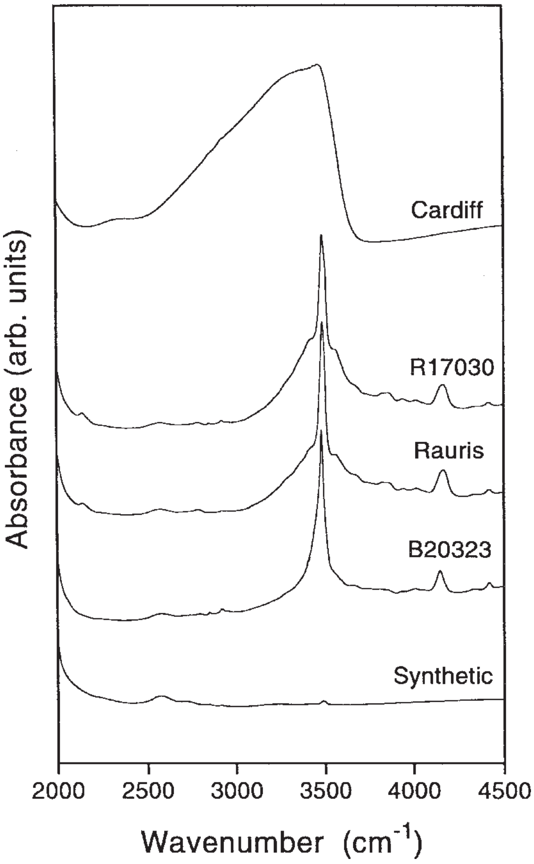

FIG. 1. Infrared spectra of titanite in the spectral region between 2000 and 4500 cm^{-1}.

Both *in situ* and stepwise heating experiments were performed. For the *in situ* heating measurement, sample crystals were sandwiched between two Pt-foil masks (0.05 mm thick), then were heated between 300 and 1060 K within a cylindrical platinum-wound furnace with a recycling cooling-water system (Zhang *et al.* 1996). The heating rate was 15 K/minute. Two thermocouples were used in the furnace. The temperature was controlled using a Pt–PtRh thermocouple located close to the heating wires and a Euro-815 temperature controller (accuracy ±1 K) The specimen temperatures were measured using a NiCr–NiAl thermocouple in contact with the samples. The thermocouple was connected to a Comark microprocessor thermometer and was calibrated against the α–β transition temperature of quartz and cristobalite. The uncertainty of the temperature of the sample was less than 5 K. Infrared spectra were recorded on both heating and cooling. Collection time per high-temperature spectrum was 6.5 minutes.

A stepwise experiment was performed on the "Cardiff" sample only. Three plates of "Cardiff" titanite were cut and ground with perpendicular crystallographic planes and similar thicknesses. The polished plates of "Cardiff" titanite were annealed for 15 minutes under N_2 gas at temperatures between 500 and 1500 K in a vertical Lenton furnace with a temperature interval of 100 K below 800 K and 50 K above 850 K. The samples were quenched in air. The annealed samples were measured at room temperature.

Profile analysis of the spectra was achieved by fitting of Lorentzian peak profiles with a linear baseline to the recorded absorption spectra using the program OPUS–IR II (Bruker). The same program was used to obtain integrated intensities. For resulting experimental errors of line positions, intensities and line widths, see Salje *et al.* (1989, 1992).

RESULTS

The infrared spectra of natural and synthetic samples of titanite in the frequency region 2000 to 4500 cm^{-1} are shown in Figure 1. The general features of the spectra are consistent with those reported by Beran (1970), Hawthorne *et al.* (1991), and Hammer *et al.* (1996). Our spectra show more spectral details with a better resolution and a larger spectral region than those previously published. Several characteristic features were found to differ strongly among the titanite samples. Firstly, the spectrum of the pure synthetic titanite is characterized by very weak absorption in the region of 3000 to 4000 cm^{-1}, which indicates low concentrations of OH. Secondly, the samples of natural titanite show different spectral details from that of synthetic titanite. Samples B20323, "Rauris" and R1730 have absorption bands near 3485 cm^{-1}, whereas the "Cardiff" sample shows broad features between ~2500 and ~3700 cm^{-1}. The peak profile of the bands at and below ~3700 cm^{-1} is strongly affected by radiation damage. The absorption profile is broadened to the low-energy side, and the spectrum of the untreated "Cardiff" sample is essentially isotropic for different directions of polarization. The polarized infrared spectrum of the annealed "Cardiff" crystal is dramatically different, with strong anisotropic behavior. It will be argued below that the spectral features between ~2500 and ~3700 cm^{-1} consist of various hydrous species at different structural sites. Thirdly, narrow but weak infrared absorption lines near 4200 and 4500 cm^{-1} occur in crystalline titanite B20323 (most obvious for $E \parallel b$ at 4156 cm^{-1}), "Rauris" and R17030, but not in "Cardiff". In natural quartz, similar infrared bands near 4200 and 4500 cm^{-1} were observed and assigned as Si–OH motions (Cordier & Doukhan 1991). Similar bands are also observed in hydrous glasses (Behrens *et al.* 1996).

Dependence of the O–H vibrations on polarization

Polarized infrared spectra were recorded for B20323 and the Cardiff sample at room temperature. The spectra of titanite B20323 exhibit a strong dependence on polarization (Fig. 2a). By varying the direction of polarization of the field vector $E \parallel b$ and $E \perp b$, the absorbance of the main feature near 3485 cm^{-1} varies significantly. Bismayer *et al.* (1992) gave an account of the geometrical relation of the indices of refraction and the crystallographic axes. In addition to the overall change in intensity, the absorption profile shows dramatic and systematic variation with θ, the angle of polarization (varied in steps of 10°). At $E \parallel b$, the band is sharp, and it becomes very broad at $E \perp b$ (apparently consisting of more than one band). At $E \perp b$, the main feature near 3485 cm^{-1} and the absorption at 4419 cm^{-1} reach their maximum intensities, whereas the signal near 4147 cm^{-1} is weak. The two minor bands may be combinations involving OH-stretching and two OH-bending modes. The various vibrational signals are better resolved at 20 K (Fig. 2b). In total, at least five absorption lines near 3470 cm^{-1} are resolved for $E \perp b$, whereas fewer are seen at $E \parallel b$. The bands at 3464 cm^{-1} are absent if $E \parallel b$. The absorption line near 4156 cm^{-1} reaches its maximum intensity for $E \parallel b$ and its minimum for $E \perp b$. Complete polarization of the infrared reflection spectra in the range between 40 and 2000 cm^{-1} was previously observed in a synthetic sample of titanite (Zhang *et al.* 1995). Our present results show that the O–H vibrations are equally well polarized in highly crystalline natural samples.

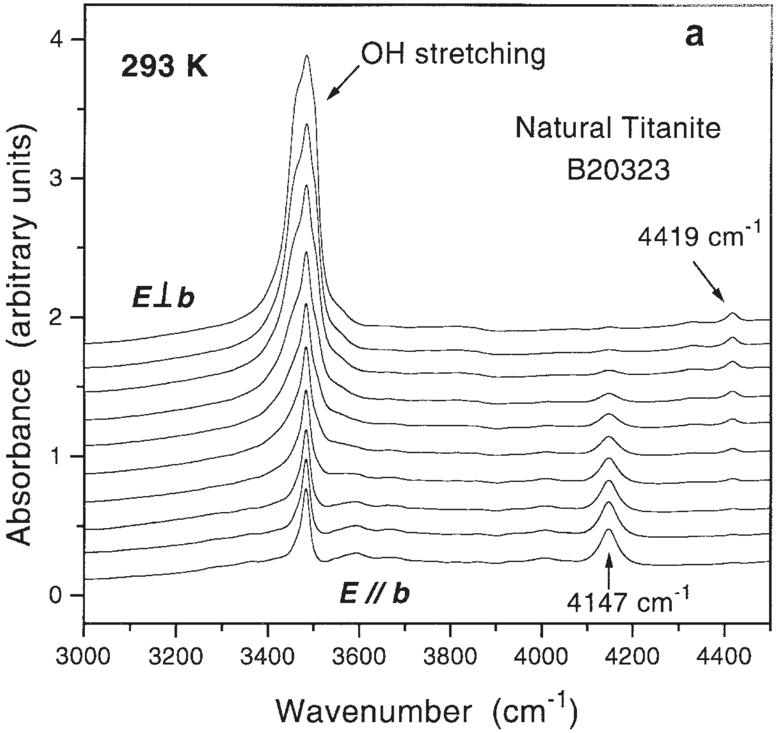

FIG. 2a. Angular dependence of the infrared spectra of crystalline titanite B20323 measured at room temperature. The rotation angle θ was varied in steps of 10°.

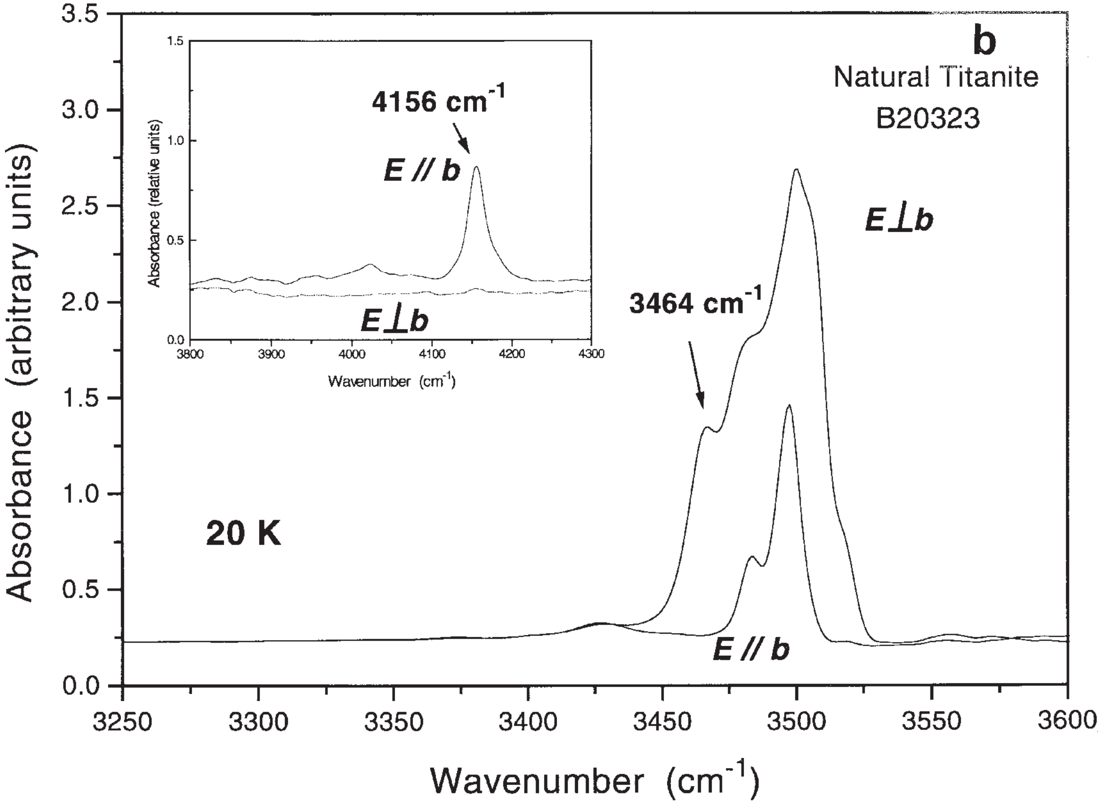

FIG. 2b. Angular dependence of the infrared spectra of crystalline titanite B20323 measured at 20 K.

The metamict "Cardiff" titanite exhibits a polarization behavior very different from that of crystalline titanite B20323. Figure 3 shows the spectra between 2000 and 5000 cm^{-1}. The damaged area of the metamict sample is almost isotropic (Fig. 3a). With changing orientation of E, the infrared spectra of "Cardiff" show weak variations in the region of 2000 to 5000 cm^{-1}. The O–H stretching bands near 3485 cm^{-1} appear as a weak local maximum, which merges with the wide low-frequency tail and cannot be clearly resolved. The weak dependence of the 3485 cm^{-1} O–H stretching band on polarization shows that the sample is weakly anisotropic in terms of the infrared spectrum, whereas it appears completely aperiodic and isotropic in transmission electron microscopy. The local structure, thus, is far from amorphous, but contains significant local order with weak correlation of orientation among the ordered parts of the sample.

The "Cardiff" sample was heated to 1000 K in vacuum and annealed for 90 minutes. Polarized infrared spectra, measured at room temperature, display a much stronger dependence on polarization than do spectra of the untreated sample (Fig. 3b). The O–H stretching mode near 3485 cm^{-1} shows a much more pronounced dependence of the intensity and line profiles on orientation than the untreated sample. Its maximum intensity occurs for $E \parallel a$, which corresponds to the directions of the chains of TiO_6 polyhedra. The spectra show that recrystallization does not occur as a random, isotropic process, but features strong correlations among different parts of the sample with orientation.

Temperature dependence at low temperatures

Figure 4 shows the temperature evolution of the infrared spectra (approximately $E \perp b$) of sample B20323 between 20 and 300 K. With decreasing temperature, the infrared bands become sharper, and the spectrum at 20 K shows well-resolved spectral details. At least five peaks (at 3426, 3464, 3482, 3497 and 3516 cm^{-1}) appear between 3400 and 3550 cm^{-1}. They can also be clearly seen in the polarized spectra at 20 K in Figure 2b. These signals are strongly polarized, and fewer bands appear for $E \parallel b$. The 3464 cm^{-1} absorption is

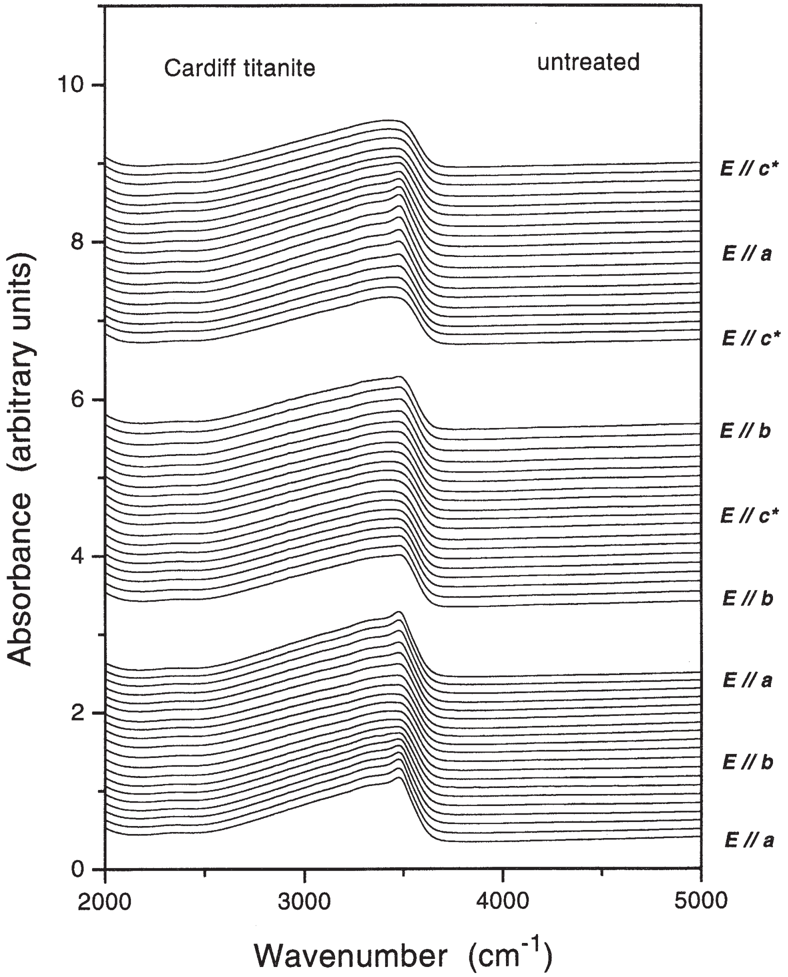

FIG. 3a. Polarization dependence of infrared spectra of untreated metamict "Cardiff" titanite along perpendicular crystallographic planes (thickness: 221, 238 and 225 μm from top to bottom). The spectra were measured at room temperature. The polarization angle was rotated in steps of 10°.

absent in the 20 K spectrum for *E* || *b*. The peak positions of these IR signals also show significant changes with increasing or decreasing temperature. The frequencies of the signals at 3482, 3507 and 3517 cm^{-1} (obtained from spectra at 20 K) exhibit considerable hardening (Salje & Bismayer 1997) with decreasing temperature and become saturated at around 50 K (Fig. 5). All thermal effects below room temperature are fully reversible.

In contrast to crystalline titanite, the metamict "Cardiff" samples show a very weak dependence on temperature between 20 and 300 K (Fig. 6). Changes between 20 and 300 K appear as a slight shift (*ca.* 2 cm^{-1}) to higher wavenumbers of the local maximum near 3485 cm^{-1} in contrast to hardening of about 23 cm^{-1} in spectra of sample B20323. The similarity between the spectra measured at 20 and 300 K also suggests a lack of H_2O and fluid inclusions, as these show strong dependencies of peak positions, band width and absorption cross-sections on temperature (Aines & Rossman 1984).

Dehydration at high temperatures

The temperature evolution of the infrared spectra of crystalline titanite R17030 between 2000 and 4500 cm^{-1} in the temperature region of 300 to 1020 K is shown in Figure 7. The spectra were recorded during both heat-

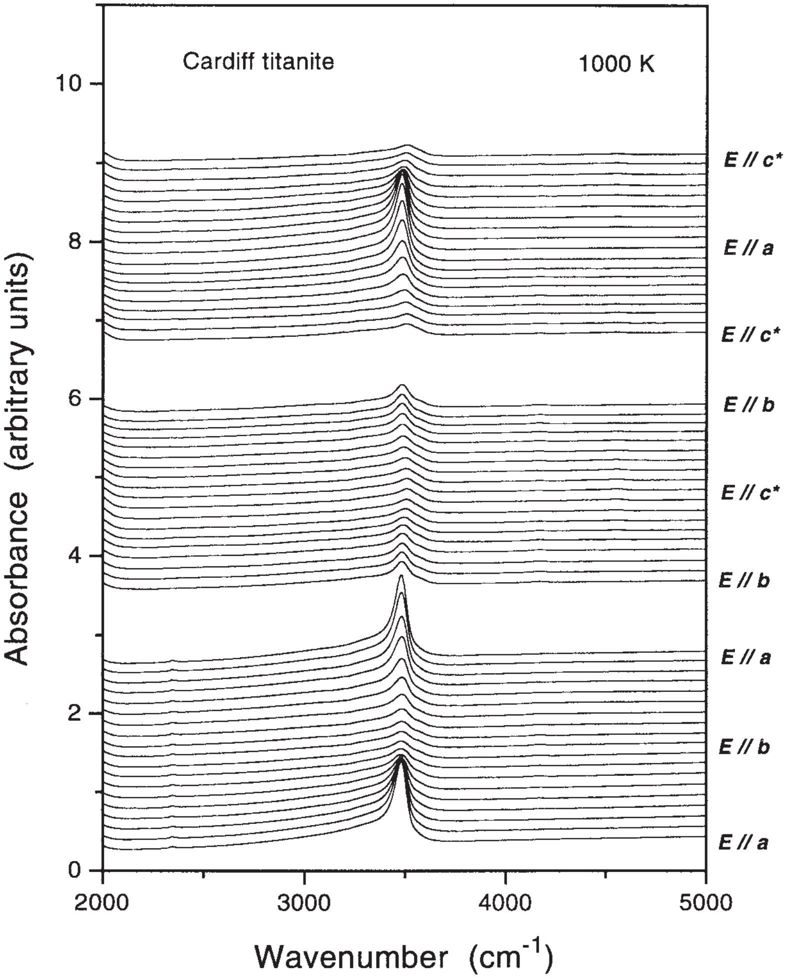

FIG. 3b. Polarization dependence of infrared spectra of metamict "Cardiff" titanite annealed stepwise to 1000 K.

ing and cooling of the sample. With increasing temperature, the infrared signals become broad, and the peak positions shift to lower frequencies. The main absorption band near 3487 cm^{-1} (300 K) shifts to 3439 cm^{-1} (1020 K), and the infrared active mode near 4165 cm^{-1} (300 K) shifts to 4106 cm^{-1} (1020 K). Peak-profile analysis was performed, as described above, to obtain band frequency, width and intensity. The temperature dependence of spectral parameters of the absorption bands near 3487 and 4165 cm^{-1} with heating and cooling are shown in Figures 8 and 9, respectively. The shift of the peak positions is fully reversible. After heating, the absorption of the 4165 cm^{-1} band is weaker owing to the loss of some OH at high temperatures. This result agrees qualitatively with the observation by Hammer *et al.* (1996), who noted that infrared spectra of single-crystal plates of titanite heated at 1273 K for 60 minutes showed a decrease of the integrated O–H band intensity to approximately one-sixth of its original value. After our heat treatment, the R17030 sample showed a decrease of the 4165 cm^{-1} height by approximately one-quarter.

Annealing behavior of metamict titanite

Heating the metamict "Cardiff" sample to 1060 K results in the spectra shown in Figure 10. The low-frequency tail near 3300 cm^{-1} disappears gradually. After annealing the sample at 1060 K for 90 minutes, infrared spectra were recorded at various temperatures (Fig. 10) while the crystal was slowly cooled to room temperature. The changes in the O–H vibrations during anneal-

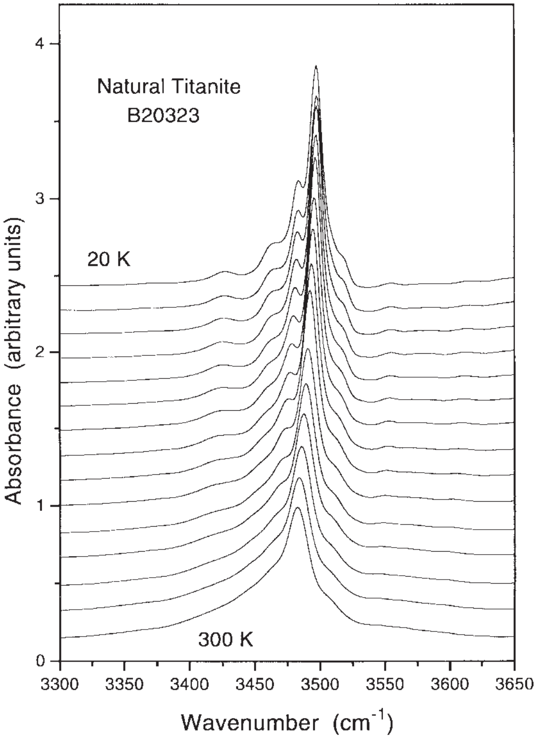

FIG. 4. Low-temperature spectra of B20323 in the spectral region of 3300 to 3650 cm^{-1} between 20 and 300 K. The temperature interval between spectra is 20 K.

ing are clearly irreversible. Cooling to room temperature leads to a sharpening of the O–H band near 3450 cm^{-1}. The temperature effects on hydrous species in metamict "Cardiff" titanite can be summarized as follows:

1. The absorption bands between 2500 and 4000 cm^{-1} show a systematic change of their profiles, namely a gradual loss of the low-frequency tail, with increasing temperature. This loss in absorbance is irreversible and related to dehydration.

2. The absorption near 3450 cm^{-1} shows almost constant height between 300 and 820 K (Figs. 10, 11). The intensity of the low-frequency tail decreases systematically in this temperature range. On the likely basis of unchanged or almost unchanged extinction-coefficients, this observation implies that below 820 K, no significant loss of the strongly bonded hydrous species with vibrational energy at 3450 cm^{-1} occurs.

3. A rapid decrease of the integrated intensity between 2300 and 3600 cm^{-1} occurs above 825 K during annealing, indicating that significant concentrations of the hydrous species are lost.

4. The infrared spectra recorded on cooling show a relatively sharp absorption feature near 3485 cm^{-1}. Its integrated intensity appears constant as a function of temperature.

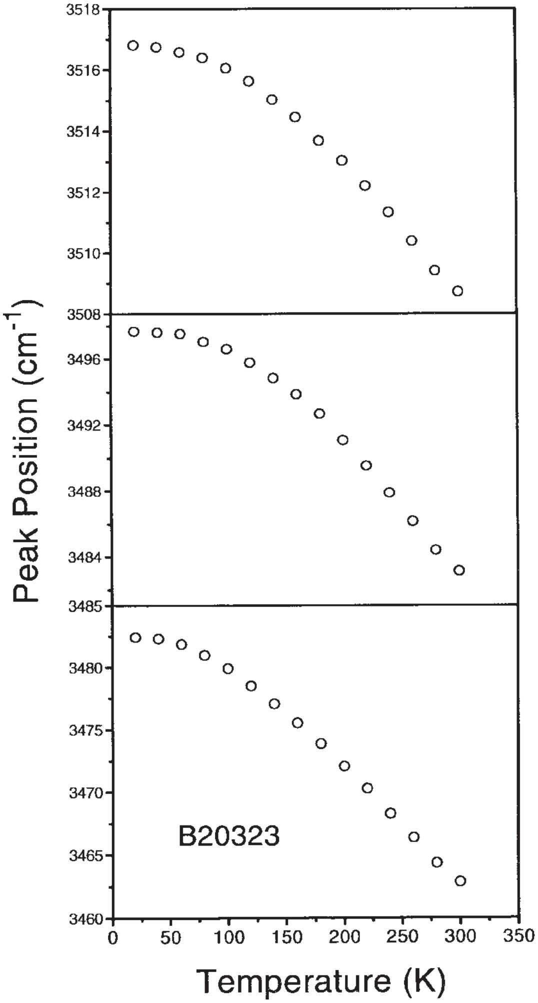

FIG. 5. Temperature dependence of band frequencies for B20323 between 20 and 300 K.

DISCUSSION

The band profiles of the O–H vibrations in titanite indicate the presence of two types of hydrous species. All natural samples of high-crystallinity titanite contain some OH groups, which are strongly bonded to specific crystallographic sites. These OH groups are well aligned, and their absorption spectra are highly polarized. At least five O–H stretching bands were observed in titanite.

The same (or very similar) O–H vibrations also exist in metamict titanite. In addition, a broad distribution

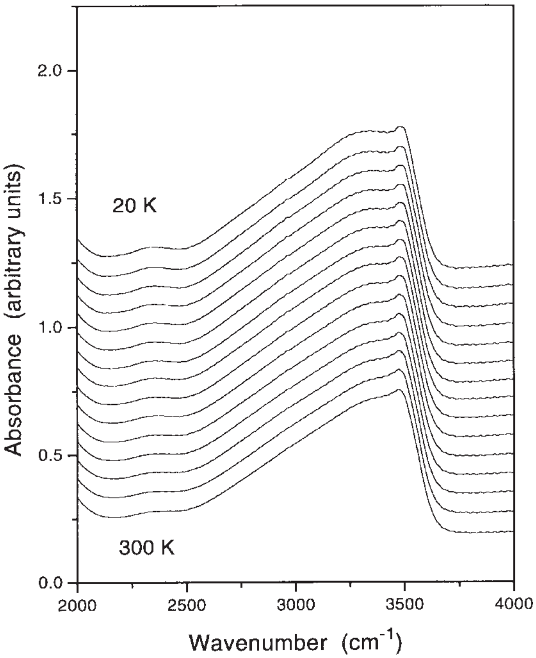

FIG. 6. Low-temperature spectra of “Cardiff” titanite (sample 230 μm thick) in the region 2000 to 4000 cm^{-1} at temperatures between 20 and 300 K. The temperature intervals are 20 K.

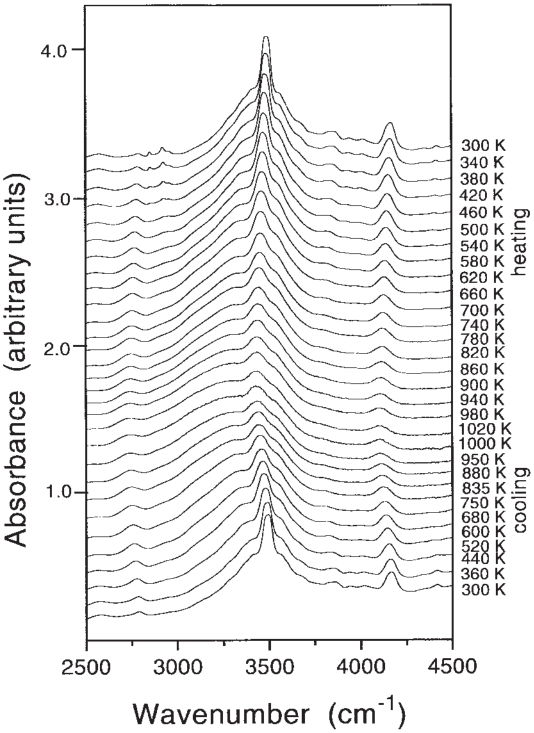

FIG. 7. Unpolarized infrared spectra of R17030 in the region 2500 to 4500 cm^{-1} at temperatures between 300 and 1020 K. Heating and cooling rates were 15 K/minute, and the samples were held at each temperature for seven minutes.

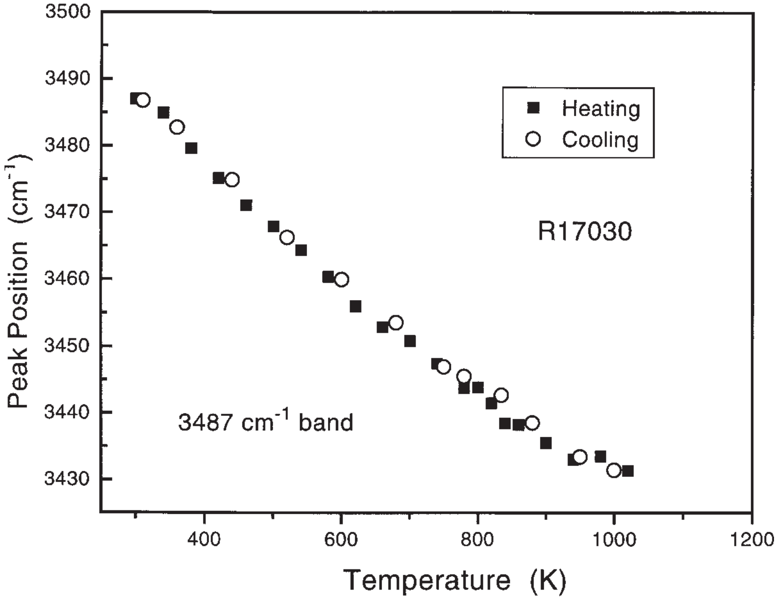

FIG. 8. Peak position of the 3487 cm^{-1} band as a function of temperature between 300 and 1020 K for R17030 with both heating and cooling.

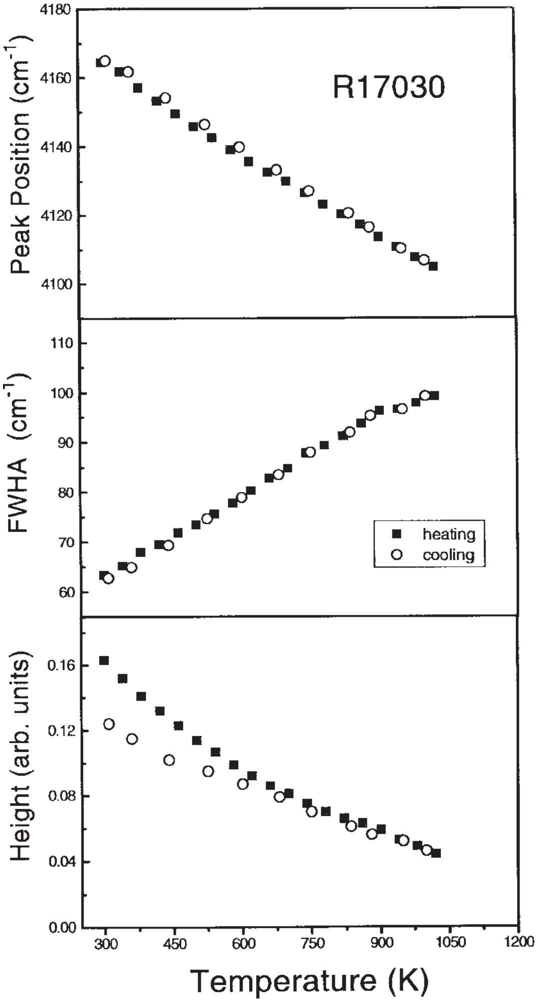

FIG. 9. Peak position, width and height of the 4165 cm^{-1} band as a function of temperature between 300 and 1020 K for R17030 with both heating and cooling.

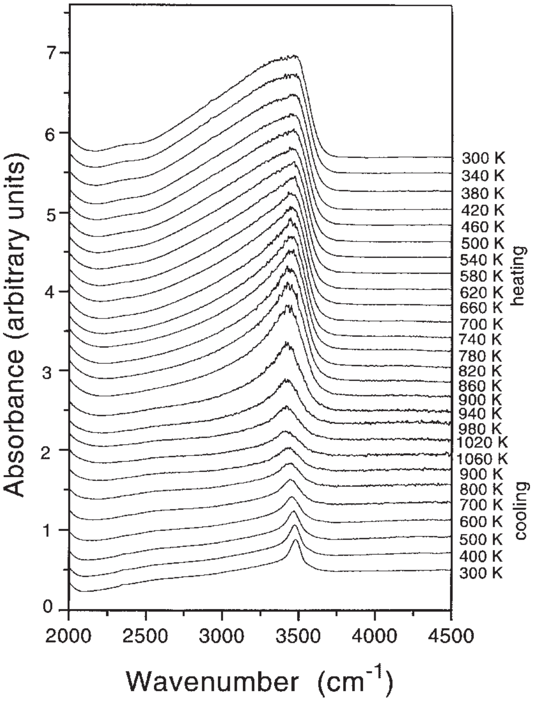

FIG. 10. Temperature evolution of unpolarized infrared spectra of the "Cardiff" sample [natural cleavage face (100), 462 μm thick] in the spectral region between 2000 and 4500 cm^{-1} measured with both heating and cooling. The heating and cooling rates were 15 K/minute, and the samples were held at each temperature for seven minutes.

of supplementary O–H bands is found. The vibrational frequencies of these additional OH groups are characteristically shifted toward lower frequencies. This shift indicates that the effective O–H bond, as seen by infrared spectroscopy, is "softer" than the structurally bonded OH in well-defined crystalline samples. As the weak O–H bonds appear only in metamict titanite, we correlate their appearance with the defect structure of the metamict "Cardiff" sample, namely Frenkel defects and recoil regions. Before we discuss their characteristics, we focus on the results of the heating experiments.

Crystalline titanite shows little dehydration at temperatures up to 1020 K, as seen by the reversibility (or nearly so) of the spectral changes in Figure 7. This observation is in stark contrast with the irreversible annealing behavior of metamict titanite, in which two thermal regimes are clearly identified (Figs. 10, 11). At temperatures between 300 and 900 K, only the most weakly bonded O–H is released, whereas the high-frequency signal of the strongly bonded O–H remains largely unchanged. This observation is now compared with the results of Vance & Metson (1985), who argued that thermal treatment at temperatures between 470 and 770 K primarily heals the Frenkel defects. This idea is supported by the observation that two structural modifications of titanite were found in untreated "Cardiff" samples by Chrosch *et al.* (1998). Both modifications structurally consist of the β-phase (*A*2/*a*), but differ systematically in their lattice parameters and their composition. One modification exhibits strong heterogeneous strain, whereas the other appears to be almost unstrained. The unstrained modification was found to consist of small nucleation centers in the damaged material. This modification grew when the sample was annealed at temperatures above 823 K.

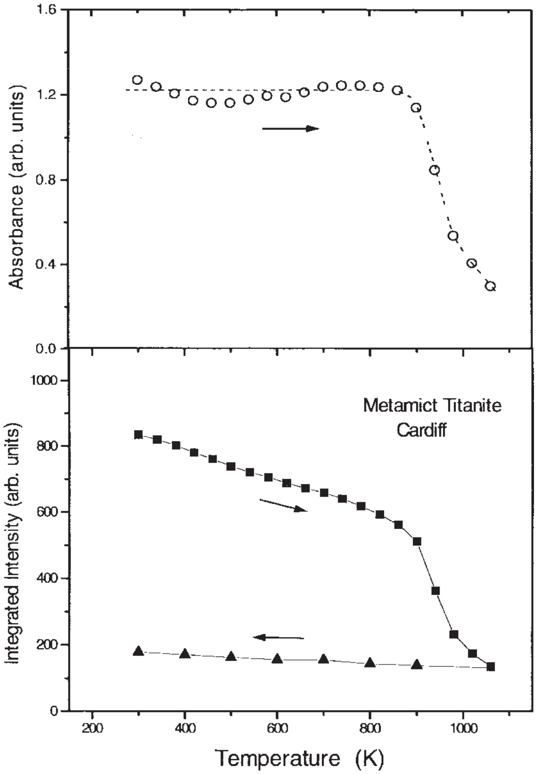

FIG. 11. Temperature dependence of the integrated intensity between 2300 and 3600 cm^{-1} for the "Cardiff" sample (black squares: heating, black triangles: cooling) and the temperature evolution of the absorbance near 3480 cm^{-1}. A horizontal background was used for integration at T above 400 K.

These observations are mirrored by the results of our infrared spectroscopy study. At room temperature, the loosely and strongly bonded OH groups exist simultaneously. Annealing at low temperatures removes the strain and also the weakly bonded OH groups. The strain is commonly related to the existence of Frenkel defects (Weber 1990), which supports the result of Vance & Metson (1985), namely that Frenkel defects are annealed in the same range of temperature ($\leq$700 K).

At higher temperatures, the recoil areas and all strongly stressed material recrystallize into strain-free titanite (Chrosch *et al.* 1997). This recrystallization seems to occur under the same conditions of annealing under which the main process of dehydration is observed in this study. During this dehydration process, virtually all the remaining weakly bonded OH leaves the sample. In addition, most (but not all) of the strongly bonded OH also is lost. The remaining OH groups have the same spectral characteristics as the OH groups encountered in well-crystallized titanite. Prolonged heating does not extend the dehydration process any further. Further experimental studies are necessary to explain the details of the OH kinetics in samples of metamict titanite. The remaining amount of OH is *ca.* 23% of the OH found in the natural sample prior to annealing. The dehydration of metamict titanite is therefore a multistage process: at low temperatures, the weakly bonded OH disappears under the same conditions as reported for the annealing of Frenkel defects and the strain relief of highly distorted titanite. At higher temperatures, the remaining weakly bonded OH leaves the sample, together with the majority of the strongly bonded OH. The annealing conditions are the same as used for macroscopic recrystallization, as seen in a powder X-ray-diffraction experiment (Hawthorne *et al.* 1991) Some strongly bonded OH remains in the sample, with characteristics similar to those of highly crystalline natural titanite.

ACKNOWLEDGEMENTS

We thank S.J.B. Reed for help with the electron-microprobe analysis, J. Chrosch for help with determination of the crystallographic orientation of sample B20323, and T. Abrahams for help in orienting the "Cardiff" sample. Financial support from ARC and EU network ERB–FMRX–CT97–0108 is gratefully acknowledged. UB acknowledges support from the BMBF (05647 GUA), and LAG from the Natural Sciences and Engineering Research Council of Canada. The comments of the referees led to significant improvements.

REFERENCES

AINES, R.D. & ROSSMAN, G.R. (1984): Water in minerals? A peak in the infrared. *J. Geophys. Res.* **89**, 4059-4071.

BEHRENS, H., ROMANO, C., NOWAK, M., HOLTZ, F. & DINGWELL, D.B. (1996): Near-infrared spectroscopic determination of water species in glasses of the system $MAlSi_3O_8$ (M = Li,Na,K): an interlaboratory study. *Chem. Geol.* **128**, 41-63.

BERAN, A. (1970): Messung des Ultrarot-Pleochroismus von Mineralen. IX. Der Pleochroismus der OH-Streckfrequenz in Titanit. *Tschermaks Mineral. Petrogr. Mitt.* **14**, 1-5.

BISMAYER, U., SCHMAHL, W., SCHMIDT, C. & GROAT, L.A. (1992): Linear birefringence and X-ray diffraction studies on the structural phase transition in titanite, $CaTiSiO_5$. *Phys. Chem. Minerals* **19**, 260-266.

CHROSH, J., BISMAYER, U. & SALJE, E.K.H. (1997): Anti-phase boundaries and phase transitions in titanite: an X-ray diffraction study. *Am. Mineral.* **82**, 677-681.

________, COLOMBO, M., MALCHEREK, T., SALJE, E.K.H., GROAT, L.A. & BISMAYER, U. (1998): Thermal annealing of radiation damaged titanite. *Am. Mineral.* **83**, 1083-1091.

CORDIER, P. & DOUKHAN, J.C. (1991): Water speciation in quartz: a near infrared study. *Am. Mineral.* **76**, 361-369.

EWING, R.C., CHAKOUMAKOS, B.C., LUMPKIN, G.R. & MURAKAMI, T. (1987): The metamict state. *Materials Res. Soc. Bull.* 58-66.

FLEET, M.E. & HENDERSON, G.S. (1985): Radiation damage in natural titanite by crystal structure analysis. *Materials Res. Soc., Symp. Proc.* **50**, 363-370.

HAMMER, V.M.F., BERAN, A., ENDISCH, D. & RAUCH, F. (1996): OH concentrations in natural titanites determined by FTIR spectroscopy and nuclear reaction analysis. *Eur. J. Mineral.* **8**, 281-288.

HAWTHORNE, F.C., GROAT, L.A., RAUDSEPP, M., BALL, N.A., KIMATA, M., SPIKE, F.D., GABA, R., HALDEN, N.M., LUMPKIN, G.R., EWING, R.C., GREGOR, R.B., LYTLE, F.W., ERCIT, T.S., ROSSMAN, G.R., WICKS, F.J., RAMIK, R.A., SHERRIFF, B.L., FLEET, M.E. & MCCAMMON, C. (1991): Alpha-decay damage in titanite. *Am. Mineral*. **76**, 370-396.

ISETTI, G. & PENCO, A.M. (1968): La posizione dell'idrogeno ossidrilico nella titanite. *Mineral. Petrogr. Acta* **14**, 115-122.

MEYER, H.W., ZHANG, MING, BISMAYER, U., SALJE, E.K.H., SCHMIDT, C., KEK, S., MORGENROTH, W. & BLESER, T. (1996): Phase transformation of natural titanite: an infrared, Raman spectroscopic, optical birefringence and X-ray diffraction study. *Phase Transitions* **59**, 39-60.

SALJE, E.K.H. & BISMAYER, U. (1997): Hard mode spectroscopy: the concept and applications. *Phase Transitions* **63**, 1-75.

________, GÜTTLER, B. & ORMEROD, C. (1989): Determination of the degree of Al, Si order Qod in kinetically disordered albite using Hard Mode Infrared Spectroscopy. *Phys. Chem. Minerals* **16**, 576-581.

________, RIDGWELL, A., GÜTTLER, B., WRUCK, B., DOVE, M.T. & DOLINO, G. (1992): On the displacive character of the phase transition in quartz: a hard mode spectroscopy study. *J. Phys.* **4**, 571-577.

________, SCHMIDT, C. & BISMAYER, U. (1993): Structural phase transition in titanite, $CaTiSiO_5$: a Raman spectroscopic study. *Phys. Chem. Minerals* **19**, 502-506.

TANAKA, I., OBUSHI, T. & KOJIMA, H. (1988): Growth and characterization of titanite ($CaTiSiO_5$) single crystals by the floating zone method. *J. Crystal Growth* **87**, 169-174.

VANCE, E.R. & METSON, J.B. (1985): Radiation damage in natural titanites. *Phys. Chem Minerals* **12**, 255-260.

WEBER, W.J. (1990): Radiation induced defects and amorphization in zircon. *J. Mater. Res.* **5**, 2687- 2697.

ZHANG, MING, SALJE, E.K.H. & BISMAYER, U. (1997): Structural phase transition near 825 K in titanite: evidence from infrared spectroscopic observations. *Am. Mineral*. **82**, 31-36.

________, ________, ________, UNRUH, H.G., WRUCK, B. & SCHMIDT, C. (1995): Phase transition(s) in titanite $CaTiSiO_5$: an infrared spectroscopic, dielectric response and heat capacity study. *Phys. Chem. Minerals* **22**, 41-49.

________, WRUCK, B., GRAEME BARBER, A., SALJE, E.K.H. & CARPENTER, M.A. (1996): Phonon spectra of alkali feldspars: phase transitions and solid solutions. *Am. Mineral*. **81**, 92-104.

Received January 14, 1999, revised manuscript accepted February 16, 2000.