Recrystallization effects in metamict titanite on progressive annealing

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The investigation of the long-term influence of nuclear radiation on crystalline material is very important in relation to nuclear waste disposal. For this reason, it makes sense to study natural metamict minerals which are exposed to nuclear radiation over geological timescales.

This study is focused on titanite. Titanite is an accessory mineral occurring in igneous and metamorphic rocks. The structure of the pure mineral titanite with chemical composition CaTiSiO$_5$ consists of corner linked TiO$_6$-octahedra, SiO$_4$-tetrahedra and sevenfold coordinated Ca positions. A well studied phase transition from A2/a – P2$_1$/a occurs near 500 K. In nature titanite often incorporates various impurities like the radiogenic elements U and Th. Through the resulting structural damage induced by $\alpha$-decay the titanite becomes metamict. This means over geological timescales recoil processes due to alpha radiation change the originally periodically structured material into a quasi-amorphous state with persisting short-range order but destroyed long-range order. [1, 2]

Progressive annealing studies on metamict titanite samples from the Cardiff uranium mine (Ontario, Canada) were carried out at beamline F1 (Hasylab/DESY) using a Kappa-diffractometer equipped with a CCD-detector (MarCCD165). The wavelength was 0.56 Å and the sample-to-detector distance 80 mm. Annealing for 15 minutes at each temperature step were done with a N$_2$ gas-stream heating device. Several samples with diameters of < 0.1 mm were prepared in quartz-glass capillaries and fixed with quartz-glass wool. Scans with a step width of 0.3° in different phi-positions were done for each temperature step and an exposure time of 15 s per frame.

Thermal annealing of metamict titanite leads via various steps to the recovery of the long-range order and to other phenomena such as dehydration and volume decrease [1,2]. We undertook this study to better understand the mechanism of recrystallization and structural recovery of metamict titanite on annealing.

The progressive annealing experiments with annealing temperatures from RT up to 950 K show an increasing of the correlation length in the sample with increasing annealing temperature, hence the metamict material recrystallizes. The integrated intensities of the (−1 3 −1) Bragg-reflection of the Cardiff titanite sample are shown in Figure 1 as functions of the rotation angle $\phi$ measured at RT before and after annealing at three expressive temperatures. There are only small changes visible between the integrated intensities measured at RT and 600 K. Annealing at 850 and 950 K show stronger influences on the degree of order of the highly metamict sample (Figure 1). The increasing degree of order in the system can be seen from the much better Lorentzian fits to the experimental data sets. The reduction of the FWHM (Figure 2) also shows the stronger recovery of the periodicity in the partially unordered titanite structure with higher annealing temperatures. Within the uncertainties, the FWHM of the (−1 3 −1) Bragg reflection measured after annealing at 600 K is the same as that for thermally non-treated Cardiff titanite, whereas the FWHMs for 850 K and 950 K are approximately smaller by a factor 2. [1]
Figure 1: Development of the integrated intensities around the (-1 3 -1) Bragg reflection in metamict titanite from Cardiff at 293 K and after annealing for 15 min at 600 K, 650 K, and 950 K. [1]

Figure 2: Reduction of the FWHM of the (-1 3 -1) Bragg reflection in metamict Cardiff titanite during annealing at 293 K, 600 K, 850 K and 950 K. [1]

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References