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Structural anisotropy and annealing-induced nanoscale atomic rearrangements in metamict titanite

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Abstract

The structural state of metamict titanite was studied by Raman spectroscopy, complementary high-resolution transmission electron microscopy, and single-crystal X-ray diffraction. The results show that Raman scattering collected from metamict titanite is highly anisotropic, which is typical of single crystals. But surprisingly, the observed Raman-scattering dependence on the sample orientation is much more pronounced for heavily metamict than for weakly metamict titanite samples. These radiation-induced anisotropic effects are related to the specific atomic arrangements in metamict titanite. The Raman spectra collected in backscattering geometry from a plane nearly perpendicular to the chains of corner-sharing TiO_6 octahedra arise predominantly from phonon modes in crystalline nanoregions with radiation-induced defects, whereas the contribution of atomic vibrations in radiation-induced amorphous nanoregions is better pronounced in the Raman spectra collected from a plane containing TiO_6 chains. This difference provides a unique opportunity to study separately, the structural transformations of the crystalline and amorphous fractions in metamict titanite. The results show that the radiation-induced periodic faults in the crystalline matrix are related to the disturbance of SiO_4-TiO_6-SiO_4-TiO_6 rings comprising TiO_6 octahedra from different chains, whereas the radiation-induced amorphization is related to the partial change of Ti coordination from octahedral to pyramidal and/or tetrahedral, which in turn violates the Ti-O-Ti intrachain linkages. This indicates that the plane containing Si-O-Ti-O bond rings is less susceptible to a self-accumulation of radiation-induced defects resulting in the development of amorphous regions as compared to the perpendicular plane containing Ti-O bond chains. Sample-orientation-dependent Raman spectroscopy was further applied to annealed metamict titanite to give further insight into the temperature-driven recovery processes in the crystalline and amorphous nanoregions. Multistep annealing by 50 K for 2 h per step gradually suppresses the structural defects in the crystalline fraction as the improvement of the SiO_4-TiO_6 connectivity within planes nearly perpendicular to the TiO_6 chains reaches saturation near 900 K. The annealing-induced recrystallization of the radiation-induced amorphous nanoregions takes place in the temperature range between approximately 650 and 950 K, with a maximum near 750 K. Raman scattering shows that multistep annealing up to 1173 K is insufficient to recover the crystalline structure of the studied metamict titanite sample, which has an accumulated radiation dose of 1.2×10^{18} α-event/g.

Keywords: Metamict titanite, annealing, Raman spectroscopy, TEM