Hydrous species in crystalline and metamict titanites

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ABSTRACT

The content of hydrous species in crystalline and metamict titanite (CaTiSiO₅) have been investigated using polarized infrared spectroscopy. The effects of metamictization are a decrease of intensity and a broadening of Ti-O and Si-O stretching overtones, accompanied by development of the isotropic spectral features of hydrous species. Metamict and partially metamict titanites show OH contents up to 0.73 wt% H₂O on the basis of previously reported calibrations. On heating, crystalline and metamict titanite showed a different temperature evolution of their OH content. Thermal annealing of crystalline titanite at temperatures above 1100 K for 15 min resulted in dehydration, characterized by a dramatic decrease in the intensity of the OH signal near 3486 cm⁻¹, in contrast to a two-stage dehydration process in metamict titanite. The results show that the high OH contents in metamict titanites are probably due to hydrogen diffusion during and after metamictization. The results also show that the recrystallization in metamict titanite at high temperatures involves epitaxial growth of crystalline domains.

INTRODUCTION

Titanite (CaTiSiO₅) is a common mineral in crustal igneous, metamorphic and sedimentary rocks, mantle xenoliths, and tektites. Pure synthetic titanite is monoclinic, P2₁/a (Z = 4) with unit-cell parameters a = 7.057, b = 8.707, c = 6.555 Å, β = 113.8° (Taylor and Brown 1976). The crystal structure consists of chains of corner-sharing TiO₆ octahedra along [100] that are cross-linked by chains of edge-sharing CaO₇-polyhedra parallel to [101]. SiO₄-tetrahedra are linked by corners to both structural units (Taylor and Brown 1976; Speer and Gibbs 1976). The twenty O atoms per unit cell are in three different kinds of sites. Among these, only O1 is not bound to SiO₄ tetrahedra and can be substituted by OH or F.

Due to radioactive decay of naturally occurring radionuclides and their daughter products in the ²³⁸U, ²³⁵U, and ²³²Th decay series, titanite can be heavily damaged over geologic time, resulting in loss of translational and orientational correlations and the formation of amorphous domains (Fleet and Henderson 1985; Vance and Metson 1985; Hawthorne et al. 1991; Lumpkin et al. 1991; Ewing 1994; Chrosch et al. 1998). Metamict minerals commonly contain relatively higher concentrations of H₂O or OH than undamaged crystals. There are pervasive studies of hydrous species in metamict minerals (Hofmeister and Rossman 1985; Caruba et al. 1985; Aines and Rossman 1986; Woodhead et al. 1991; Zhang et al. 2000d; Salje et al. 2000; Gu et al. 2000). Several important questions have been raised regarding the roles of hydrous species in metamictization and recrystallization, e.g., whether hydrous species stabilize the metamict state, and why metamict minerals are generally “wet,” even for some normally anhydrous minerals.

The aim of this work is to report new data on hydrous species in crystalline titanite and characteristics of OH species in metamict titanite, to gain some understanding of OH behavior during high-temperature thermal annealing, and to compare thermal behaviors of crystalline and metamict titanite through high-temperature annealing.

EXPERIMENTAL METHODS

Titanite samples used in this study (Table 1) have been extensively analyzed previously (for samples E2312 and M28173, see Hawthorne et al. 1991; for the Cardiff sample, see Hawthorne et al. 1991; Chrosch et al. 1998; Zhang et al. 2000d; and Salje et al. 2000; for samples No12 and No15, see Hammer et al. 1996). Cardiff, M28173, and E2312 are black or dark brown in thin section, whereas titanates No12 and No15 are light green. Infrared powder absorption spectra (150–1600 cm⁻¹) and polarized reflection spectra (650–1400 cm⁻¹) show that samples M28173, E2312, and Cardiff are damaged by radiation, due to α-decay, because they have broad spectral features as reported by Hawthorne et al. (1991). Samples No12 and No15 are highly crystalline titanites: they show high reflectivity, well-resolved reflection bands between 650 and 1400 cm⁻¹, and anisotropic Si-O overtone bands.

The crystallographic orientation of each crystal was determined using X-ray precession photography. The crystal was