Metamictization and recrystallization of titanite: An infrared spectroscopic study

MING ZHANG,1,* EKHARD K.H. SALJE,1 ULRICH BISMAYER,2 LEE A. GROAT,3 AND THOMAS MALCHEREK4

1Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.
2Mineralogisch-Petrographisches Institut, Universität Hamburg, Grindelallee 48, D-20146 Hamburg, Germany
3Department of Earth and Ocean Sciences, University of British Columbia Vancouver, British Columbia, V6T 1Z4, Canada
4Institut für Mineralogie, Westfälische Wilhelms-Universität Münster Corrensstr. 24, D-48149 Münster, Germany

ABSTRACT

Radiation damage and the recrystallization of natural titanite (CaTiSiO5) were studied using infrared spectroscopy in the spectral range from 50 to 7500 cm⁻¹. The results show that radiation damage leads to systematic changes in spectral features: decreasing absorption and reflectivity, line broadening, and loss of orientational dependence. Strongly damaged titanite shows hydroxylate bands between 2200 and 3500 cm⁻¹. The band most affected by radiation damage is the Ti-O stretching band near 670 cm⁻¹. It shifts to 710 cm⁻¹ in the most damaged samples, possibly indicating the presence of TiO₅ complexes in metamict titanite. Titanite glasses (quenched melts of CaTiSiO₅) show spectral features different from those of radiation-damaged titanite, especially in the Ti-O and Si-O stretching regions.

Annealing radiation-damaged titanites at high temperatures results in the recovery of damaged crystalline regions. Recrystallization near 900 K is characterized by an increase in reflectivity, integrated absorbance, and line sharpening. Different infrared bands show recovery at different temperatures. The restoration of the Ti-O stretching band near 670 cm⁻¹ and an infrared band near 285 cm⁻¹ took place at temperatures of 1200–1400 K. Temperature-induced changes of the OH-absorption bands could be responsible for the previously reported differences in the temperature evolution of infrared spectra of OH species between in situ and quench experiments.

INTRODUCTION

The stabilization and immobilization of high-level radioactive waste in a solid form has become one of the most pressing industrial problems (Ahearne 1997a, 1997b; Ewing 1999; Weber and Ewing 2000). Titanite has been proposed as an actinide-bearing crystalline host for waste materials. Therefore, it is important to evaluate the effect of radiation on this crystalline phase, and to gain a better understanding of the mechanisms involved in radiation damage. The fundamental issues of particle-solid interactions and radiation-induced structural changes from a periodic-to-aperiodic state are an active and important area of research (Weber et al. 1998).

Pure titanite, with the general formula CaTiSiO₅, crystallizes with the space group P₂₁/a (Z = 4) (Speer and Gibbs 1976). Natural titanite occurs in igneous and metamorphic rocks and incorporates a variety of impurity ions such as U, Th, and the rare-earth elements (REE). In many cases, the structure of natural titanite is metamict (an aperiodic or amorphous state; Ewing 1994; Salje et al. 1999) as a result of self-radiation damage associated with the α-decay of the incorporated U, Th, and their daughter products. Metamictization in titanite is characterized by significant changes in physical properties. These include a broadening and decrease of X-ray Bragg diffraction (XRD) intensities, increasing cell parameters (Vance and Metson 1985; Fleet and Henderson 1985; Hawthorne et al. 1991; Chrosch et al. 1998; Paulmann et al. 2000), line-broadening and decrease of infrared (IR) signals (Vance and Metson 1985; Hawthorne et al. 1991; this study), absorption of hydrous species (Hawthorne et al. 1991; Zhang et al. 2000c; Salje et al. 2000; Zhang et al. 2001), the formation of recoil tracks (Lumpkin et al. 1991; Jonckheere and Wagner 2000), changes in NMR spectra (Hawthorne et al. 1991), the loss of anisotropy (Salje et al. 2000), and a change in density of more than 3% (Vance and Metson 1985; Hawthorne et al. 1991).

In this paper, we compare the metamict state of natural titanite with the glass state of its chemical analogue obtained through quenching titanite melts in order to clarify the relationship between the structural characteristics of these disordered states. Second, we discuss the local structural configurations of the metamict state of titanite in order to gain a better understanding of the processes of metamictization and recrystallization on the atomic scale. Third, we report on the question whether or not Ti-O stretching bands due to TiO₅ octahedra can be recovered through thermal annealing, because previous studies (e.g., Vance and Metson 1985; Hawthorne et al. 1991) showed that the Ti-O stretching bands were still weak after annealing at 1000 K for 1 h. Chemical impurities in metamict titanite samples may be connected with the observed lack of recovery of the Ti-O band after annealing, or may even cause the de-