Elastic softening of metamict titanite CaTiSiO$_5$: Radiation damage and annealing

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ABSTRACT

We have measured the elastic response of radiation-damaged titanite, CaTiSiO$_5$, as a function of thermal annealing. We estimate the bulk modulus of the damaged samples (~24% amorphous) to be 85 GPa, which is much softer than for undamaged crystalline titanite [131.4 GPa; Angel et al. (1999)]. Conversely, the lowest shear modulus of the radiation-damaged material is 52–58 GPa, which is harder than that of the undamaged titanite, 46–52 GPa. The bulk and shear moduli of the radiation-damaged materials are close to those of thermal titanite glass, $B_{\text{glass}} \approx 75$ GPa and $G_{\text{glass}} \approx 47$ GPa, and are much smaller than expected based on other radiation-damaged materials such as zircon (ZrSiO$_4$). Surprisingly, annealing of the damaged titanite in the range $600 < T < 1000$ K leads to additional massive softening of the shear moduli. During annealing the shear modulus of titanite sample 1 softened from 58 to 29 GPa, and sample 2 softened from 52 to 19 GPa. The temperature range for the softening coincides with that found for crystallization of the amorphous regions, as measured previously by diffraction and spectroscopic methods. In contrast to the huge softening of the ultrasonically measured shear modulus, the calorimetrically measured Debye temperature $\theta_D$ increases by ~5%, suggesting a small intrinsic hardening of the acoustic shear modes. Additional heating to 1473 K leads, in one titanite sample, to a steep increase of the shear modulus to values much larger than that of the initial, radiation-damaged material. Theoretical models are discussed to rationalize the massive softening due to both radiation damage and subsequent anneal.

Keywords: Titanite, resonant ultrasound spectroscopy, elastic moduli, metamict, Kramers-Kronig, heat capacity

INTRODUCTION

The investigation of ceramic matrices for the encapsulation of high-level nuclear waste may be exemplified by the comparison between two possible matrix materials, namely zircon (ZrSiO$_4$) and titanite (CaTiSiO$_5$). While the research on zircon has reached maturity with a detailed understanding of the radiation-damage mechanism and the recrystallization process, the equivalent research on titanite is much less advanced (Weber et al. 1998; Rios et al. 2000a, 2000b; Zhang et al. 2000a, 2000b, 2001, 2002, 2003; Farman and Salje 2001; Trachenko et al. 2001; Capitani et al. 2000; Geisler et al. 2003; Lang et al. 2008; Ewing 2001, 2007; Ewing et al. 2003; Hawthorne et al. 1991). One reason is the greater chemical complexity of titanite where a recoil cascade may not only break Zr-Si or Ca-Si bonds and allow polymerization of Si-O clusters, but also involves one more element, namely Ti. Titanium tends to form polymeric clusters similar to Si and shows great structural flexibility even in otherwise well-defined structural environments (e.g., Goncalves-Ferreira et al. 2008). This may be the reason for the observed tendency of titanite to amorphize and re-crystallize more readily than zircon. The concentration of U and Th is lower in titanite than in zircon (<0.1 wt%), so that the radiation damage is in general milder in titanite. Based on the estimates of Vance and Metson (1985), the calculated doses for Cardiff titanite lie in the range of $1.3-2.8 \times 10^{18} \alpha$-events/g, whereas our sample, E2335 titanite, shows roughly half the radiation damage so that we may estimate a dose of approximately $10^{18} \alpha$-events/g. It also appears that the amorphized areas in titanite contain significantly more short-range order (Bismayer et al. 2010) than amorphized regions in zircon, where the dose required for full amorphization is $\sim 13 \times 10^{18} \alpha$-events/g.

More complexity is added when we consider phase transitions in these minerals. Zircon shows two percolation transitions as a result of radiation damage (Salje et al. 1999). Titanite in addition undergoes structural transitions between the crystalline phases $\alpha$, $\beta$, and $\gamma$ (Salje et al. 1993; Zhang et al. 1995, 1997; Chrosch et al. 1997; Meyer et al. 1996; Hayward et al. 2000). These transitions are a consequence of the inherent structural instabilities of the titanite crystal structure. The structure consists of chains of corner-sharing TiO$_6$-octahedra parallel to the a axis, cross-linked by edge-sharing chains of Ca-O polyhedra parallel to [101].