OH species, U ions, and CO/CO$_2$ in thermally annealed metamict zircon (ZrSiO$_4$)

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ABSTRACT

Metamict zircon crystals have been thermally annealed between 500 and 1800 K and analyzed using infrared and optical spectroscopy in the spectral region of 1400–7000 cm$^{-1}$. Recrystallization and dehydroxylation via complex proton/OH diffusion, redistribution, and incorporations of additional hydrogen-related species within the crystal structure of zircon occur at temperatures above 700 K in partially metamict zircon and above 1200 K in heavily amorphized material. Thermally induced changes in O-H stretching spectra are different between $E\|\epsilon$ and $E\perp\epsilon$ in weakly metamict zircon. The O-H stretching band near 3342 cm$^{-1}$ (with $E\perp\epsilon$) in an untreated sample shifts to 3277 cm$^{-1}$ at 1200 K, where the frequency of O-H stretching bands with $E\parallel\epsilon$ increases. Conversions of hydrogen-related species were observed and extra OH bands were found at temperatures between 1200 and 1600 K. A dramatic change of OH spectra was recorded between 1600 and 1800 K in partially metamict crystals, resulting in additional absorption features (near 3098 and 2998 cm$^{-1}$ along $E\perp\epsilon$). U$^{4+}$ and U$^{5+}$ related spectra are also affected by high-temperature annealing. For highly metamict zircon, the U$^{3+}$ band near 4830 cm$^{-1}$ shows an increase in intensity above 1200 K. Additional IR bands at 2146 and 2344 cm$^{-1}$ appear in the spectra of metamict zircon annealed at high temperatures. Their frequencies are consistent with stretching vibrations of CO and CO$_2$.

Keywords: Infrared spectroscopy, zircon, high temperature, hydroxyl species, metamictization, uranium, CO, CO$_2$, dehydroxylation and recrystallization

INTRODUCTION

A detailed picture on what happens to hydroxyl and uranium ions during high-temperature annealing has not yet emerged despite extensive studies undertaken to investigate structural recovery and recrystallization of metamict zircon (e.g., Vance 1975; Weber 1991; Murakami et al. 1991; Ellsworth et al. 1994; Colombo et al. 1999; Capitani et al. 2000; Zhang et al. 2000a, 2000b; Geisler 2002; Ewing et al. 2003). OH spectra of heated zircon (e.g., Aines and Rossman 1986; Woodhead et al. 1991b; Nasdala et al. 2001), U-ion absorption of heated metamict zircon (Zhang et al. 2003), and structural and chemical variations of hydrothermally treated metamict zircon (e.g., Geisler et al. 2001, 2003). The disappearance of U$^{4+}$ absorption was observed in a partially metamict zircon sample heated between 1400 and 1600 K (Zhang et al. 2003), whereas it is not clear how hydroxyl/hydrous species behave in the same temperature region. The present work was also inspired by the fact that natural zircon crystals have large variations of OH spectra in contrast to some other nominally anhydrous minerals (e.g., titanite). The causes for this are unclear, but geological thermal processes could be one of them. In addition, recent research on crystalline and metamict titanite (Salje et al. 2000; Zhang et al. 2000d, 2001, 2002) has shown that thermally induced dehydroylation is not a simple process involving recrystallization and migration of protons from damaged to crystalline regions. We undertook this study to compare the changes in metamict titanite and zircon and to see if a similar behavior occurred in heat-treated metamict zircon.

SAMPLES AND EXPERIMENTAL METHODS

Gem-quality crystals of metamict zircon (samples Cam25, Z3, 157, and SD4) with different degrees of radiation damage were used for annealing experiments. The samples were characterized previously (Zhang et al. 2000a, 2000b, 2000c, 2003; Capitani et al. 2000). OH contents or “water” concentrations in these samples were estimated to range from 0.032 to 0.101 H$_2$O wt% using the calibrations of Paterson (1982). The calibration diagram reported by Paterson (1982) is considered acceptable for an estimate of water in metamict substances, as Paterson (1982) used also glasses for the calibration. This diagram has been used to determine OH contents in metamict zircon (e.g., Woodhead et al. 1991b; Salje and Zhang 2006) and metamict titanite (Zhang et al. 2001). The thicknesses of the treated samples ranged from 80 to 905 µm. Sample Cam25 is partially metamict (self-radiation dose of $-3.5 \times 10^{10}$ $\alpha$-event/g), sample Z3 (with a self-radiation dose of $-7-8 \times 10^{10}$ $\alpha$-event/g) has a higher degree of damage, and samples 157 and SD4 were highly metamict (with doses of $-13.1$ and $-15.9 \times 10^{10}$ $\alpha$-event/g, respectively). Sample Cam25 was oriented using a polarized optical microscope and cut into thin plates with the $c$ axis parallel to the largest surfaces of the plate. The other three crystals were analyzed using unpolarized radiation. Two types of thermal annealing (stepwise annealing of the same crystal at various temperatures and annealing of untreated grains for each designated temperature) were carried out. During the stepwise annealing experiment, the sample was heated in a Lenton (UAF 16/5) furnace for 1 h in air and then quenched in air. After being measured at room temperature, the samples were further annealed at a higher temperature. In the second type of experiments, untreated grains were annealed at each temperature in N$_2$ atmosphere in a vertical furnace for the specified time and then quenched in air.

Mid-infrared (MIR) and near-infrared (NIR) absorption spectra were recorded using Bruker IFS 66v and IFS 113v spectrometers. The data from samples Cam25, Z3, and SD4 were recorded with the IFS 66v system under vacuum. KBr and CaF$_2$ beamsplitters, Globar and tungsten lamps and a liquid-nitrogen cooled mercury