**Pb**+ irradiation of synthetic zircon (ZrSiO$_4$): Infrared spectroscopic investigation

MING ZHANG,1,* LYNN A. BOATNER,2 EKHANDR K.H. SALJE,1 S. HONDA,2 AND RODNEY C. EWING3

1Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, U.K.
2Center for Radiation Detection Materials and Systems, Materials Science and Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6056, U.S.A.
3Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109-1005, U.S.A.

**ABSTRACT**

The structural variations of synthetic zircon (ZrSiO$_4$) single crystals irradiated at room temperature by 280 keV Pb$^+$ ions (with fluences up to $1 \times 10^{15}$ ions/cm$^2$) were investigated using infrared (IR) spectroscopy. Like metamict zircon whose crystal structure is damaged and amorphized by naturally occurring $\alpha$-decay events, the Pb$^+$-irradiated zircon crystals show a dramatic decrease in reflectivity. However, no significant decrease in wavenumbers of the stretching vibrations of SiO$_4$ tetrahedra in zircon was detected. The Pb$^+$-implanted zircon exhibits new IR bands, indicating irradiation-induced new vibrations or domains, clusters or phases in addition to SiO$_2$ and ZrO$_2$. IR features consistent with those of Pb silicates (with a divalent state, i.e., Pb$^{2+}$) are also found in the irradiated sample. This finding implies that some of the radiogenic Pb in natural zircon might not actually reside in the zircon lattice or in ZrSiO$_4$ phases, but form new local domains or clusters. Infrared bands of OH-stretching vibrations were also detected in the irradiated synthetic zircon, which was originally free from OH features prior to the irradiation. These results indicate that H can easily diffuse into the irradiated layer or into irradiation-induced phases to form OH or and hydrous species after the irradiated material is damaged. The type and content of hydrous species vary with irradiation fluences.

**Keywords:** Infrared spectrum, zircon, irradiation, lead silicate, Pb, amorphization, OH species

**INTRODUCTION**

Zircon (ZrSiO$_4$) is a mineral commonly found in igneous, metamorphic, and sedimentary rocks. It has a tetragonal crystal structure ($I_4/1/amd$) that can incorporate minor amounts of actinides, such as U, Th, and Pu, as well as other rare-earth elements. Zircon has been proposed as a phase for the immobility of nuclear wastes (Anderson et al. 1993; Ewing et al. 1995; Weber et al. 1996). Recently, extensive studies have been reported on the impact of $\alpha$-decay radiation and heavy ion irradiations on the structure of zircon (Weber et al. 1998; Ewing et al. 2003 and references therein; Farnan et al. 2007). It has long been known that radioactive decay of naturally occurring radionuclides, such as $^{238}$U, $^{235}$U, and $^{232}$Th, and the daughter products in their decay series, can lead to radiation-induced structural damage (Holland and Gottfried 1955; Murakami et al. 1991; Rios et al. 2000; Zhang and Salje 2001; Balan et al. 2003; Ewing et al. 2003; Farnan et al. 2007), resulting in an aperiodic state, the so-called metamict state (Ewing 1994; Salje et al. 1999). High-energy ion-irradiations have been used to study damage mechanisms and to simulate the damage created by the recoil nucleus of the $\alpha$-decay event (e.g., Wang and Ewing 1992; Meldrum et al. 1998; Lian et al. 2003).

The key objective of the present study was to investigate the impact of the Pb$^+$-ion irradiation on the structure of zircon, as a continuation of our previous spectroscopic study on U ions in metamict zircon (2003). The present study was also motivated by the need to gain a better understanding of the behavior, localities, and valence states of radiogenic U and Pb ions in radiation-damaged zircon, an issue that is of considerable importance for geochemists and for radiogenic dating and is also poorly understood (e.g., Pidgeon et al. 1966; Cherniak et al. 1991; Watson et al. 1997; Zhang et al. 2003; Utsunomiya et al. 2004, 2007). The fundamental questions related to the occurrence and presence of Pb and U ions in natural zircon include the following: (1) How and to what extent can the radiogenic Pb and U ions be incorporated into the lattice of zircon and what are their oxidation states? (2) Where are the radiogenic Pb and U ions located and do they reside in crystalline or amorphous domains? (3) Do the radiogenic Pb and U ions in zircon react with other elements to form new domains or local clusters? (4) How do they respond to continued radiation or irradiation? And (5) what is the combined effect of radiation/irradiation, the presence of altering fluids and/or high temperatures on their valence states, localities, and motilities of the radiogenic Pb and U ions?

Investigations into some of these issues can offer not only a better understanding of the ballistic effect of the recoil nucleus of the $\alpha$-decay process, but also better insights into the diffusion behavior of Pb and U in zircon, and the possible causes for the discordant U-Pb zircon age—”a phenomenon only rarely observed in other minerals” (p. 127, Mezger and Krogstad 1997) and the “mysterious” Pb loss in natural zircon (Mezger and Krogstad 1997; Geisler et al. 2001). However, direct detection of possible Pb-related phases and the oxidation states of the Pb ion in natural zircon are not straightforward, because Pb concentrations in natural zircon crystals are commonly low. In the present study, IR spectroscopy was employed to analyze Pb$^+$-irradiated...