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Irradiation-induced stabilization of zircon ($ZrSiO_4$) at high pressure

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ABSTRACT

Zircon ($ZrSiO_4$), the most important accessory mineral in the Earth's crust, transforms under high pressure to reidite, a scheelite-structured polymorph. Recently, reidite was found in association with meteorite impact structures. Here, we show that the zircon-to-reidite transition, and thus the amount of reidite produced during high-pressure events, strongly depends on the microstructure of the initial zircon. Our results clearly demonstrate that radiation damage, present in natural zircon due to radioactive decay, dramatically modifies the phase stability of crystalline zircon at high pressure. By simulating this radiation damage with ion beams, we show that zircon, pre-irradiated with 1.47-GeV Xe ions, formed only minor amounts of reidite up to 36GPa; whereas, an unirradiated zircon was almost completely transformed to reidite under the same conditions. By means of Raman scattering, X-ray diffraction, and transmission electron microscopy, we confirmed that the stability field of the irradiated zircon is expanded to higher pressures as a result of the interplay between pressure, ion beam-induced amorphization, and the formation of nanoscale damage domains. These results provide insight into the formation-conditions of reidite in nature and illustrate how pressure-induced phase transitions may be affected by defects, in this case those caused by radioactive decay.

1. Introduction

Zircon ($ZrSiO_4$) is the most important accessory mineral in the Earth's crust. It is the main mineral used in U/Th/Pb age-dating and also provides geochemical and isotopic signatures of the Earth's earliest formed rocks (Hanchar and Hoskin, 2003). Among other remarkable properties (e.g., physical and chemical durability), zircon exhibits an anomalous phase-transformation to reidite at high pressure leading to a 10% denser phase with the scheelite structure (Liu, 1979; Kusaba et al., 1985; Knittle and Williams, 1993; Leroux et al., 1999; Glass and Liu, 2001; Glass et al., 2002; Gucsik et al., 2004; Ono et al., 2004; Van Westrenen et al., 2004). Based on the structural similarities between zircon and reidite, a special displacive mechanism has been proposed (Kusaba et al., 1986). This first-order transition is the result of simple shearing, followed by small atomic adjustments (Kusaba et al., 1986). At elevated temperatures (~ 1000°C), reidite begins to form at pressures above ~ 10 GPa (Ono et al., 2004). Due to hampered kinetics, the critical pressure at room temperature has to be significantly overstepped in excess of 20 GPa (Knittle and Williams, 1993; Van Westrenen et al., 2004). Above this threshold, the transformation takes place gradually, with both phases coexisting, up to pressures of 30 to 40 GPa (Gucsik et al., 2004; Van Westrenen et al., 2004). However, once the scheelite-structured phase is formed, it persists after pressure release and does not revert to zircon unless the temperature is above 1200°C (Kusaba et al., 1985). Recently, metastable reidite was found in naturally occurring shock-metamorphosed zircon in the vicinity of a meteorite impact structure (Glass and Liu, 2001; Glass et al., 2002). Thus, the zircon-reidite phase relation at elevated pressures has been proposed as a new peak-pressure indicator of such impact events (Kusaba et al., 1985; Leroux et al., 1999; Glass and Liu, 2001).

The zircon structure can incorporate and retain up to a few wt.% uranium and thorium (Finch and Hanchar, 2003). The decay of nuclides in the ^{238}U, ^{235}U, and ^{232}Th decay series leads to structural damage, the metamict state, mainly caused by alpha-decay events (Weber et al., 1994; Ewing et al., 2003). Hence, many natural zircons are partially amorphous or metamict. The use of zircon in geochronology and thermochronology (Davis et al., 2003; Reiners and Ehlers, 2005), as well as its possible application as a nuclear waste form for plutonium (Ewing, 1999), requires a detailed knowledge of the damage-formation process. For this reason, radiation-damage studies of zircon, particularly using ion irradiations, have been systematically completed using a variety of ion beams at different energies up to temperatures of nearly 1000°C (Weber et al., 1994; Ewing et al., 2000, 2003). Partially amorphous, natural zircons have recently been the subject of moderate (up to 9 GPa) compression experiments focusing on the structural details of the defective crystalline (Ríos and Boffa-Ballaran, 2003) and the amorphous phase (Trachenko et al., 2007).

The question of whether radiation effects may modify the phase stability of zircon under subsequent compression has never been addressed. Here, we report the first experiments that investigate the

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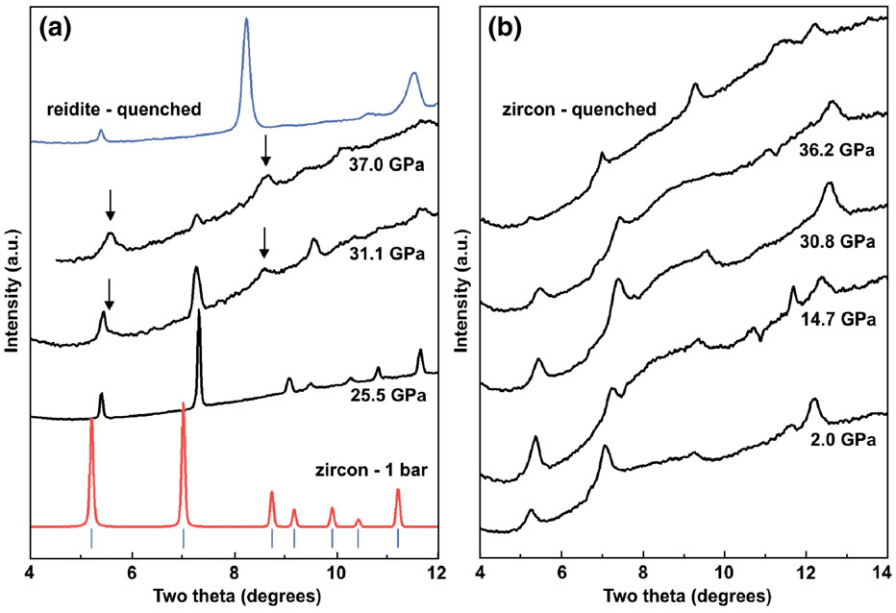

Fig. 1. XRD data of zircon pressurized in diamond anvil cells (a) unirradiated and (b) irradiated with 1.47-GeV Xe ions of fluence 5×10^{12} cm^{-2}. (a) The undamaged zircon gradually transformed to reidite above 25.5 GPa, as indicated by new peaks (arrows); the sample quenched from 37 GPa showed only reidite diffraction peaks. The vertical bars indicate the diffraction-peak positions of the zircon structure. (b) The irradiated specimen showed no phase transition up to 36.2 GPa; the quenched sample exhibited only typical zircon diffraction peaks.

effect of ion beam-induced damage prior to a high-pressure event. Up to now, phase-transition studies of zircon have only used undamaged, perfectly crystalline samples, not typical of zircon as it is found in nature. In a recent study, different solids, including zircon, were exposed simultaneously to high pressure and relativistic ion beams (Glasmacher et al., 2006). In these experiments, it was noted that reidite formed at ~ 14GPa rather than at 20 GPa, possibly due to kinetic effects, such as ion-induced pressure waves. In contrast, the results of this study show that pre-irradiation can stabilize the crystalline zircon structure to higher than expected pressures. This means that pre-existing, ion-induced modifications, similar to those that result from alpha-decay damage in natural zircon (Weber et al., 1994), significantly change the phase-transition behavior of zircon at elevated pressures. Our results not only contribute to an improved understanding of the formation conditions of reidite in nature (e.g., during meteorite impact), but also reveal the potential for ion-beam irradiation to form materials outside of their expected stability fields.

2. Experimental procedure

Two single-crystal samples of zircon synthesized by the flux method, a few mm in size, were polished without specific orientation down to 30μm thickness. One sample was entirely exposed to a defocused cm-sized ^{132}Xe-beam of energy 1.47 GeV with a calculated penetration depth of about 60 μm (SRIM, 2006), i.e., the ions completely penetrated the sample. The energy loss per unit path length dE/dx – the most crucial parameter for damage creation – was almost constant along the ion trajectory (25.8 ± 1.7) keV/nm. At 5×10^{12} ions/cm^2, the fluence was high enough to substantially damage the crystalline structure. Grains of both samples were mounted into a symmetric-type diamond anvil cell (DAC). A 16:3:1 mixture of methanol, ethanol, and H_2O served as a pressure-transmitting medium. Pressures up to 37 GPa at room temperature were applied and controlled via the fluorescence of several small ruby grains distributed throughout the sample chamber (Mao et al., 1986; Holzapfel, 2003). Besides Raman spectroscopy and transmission electron microscopy (TEM), samples were characterized by X-ray diffraction measurements (XRD) performed at the beam line X17C of the National Synchrotron Light Source of Brookhaven National Laboratory. Using powder XRD with a mono-energetic beam of 30.5 keV and a spot size of ~ 25 μm, the structure was monitored under compression, focusing on the onset of the transformation to reidite. After each compression step, typically 2 to 3 GPa, Debye diffraction rings were recorded with a Mar CCD detector. The duration of compression at each pressure value was identical for both samples and typically about 15 min. After compression, the pressure was

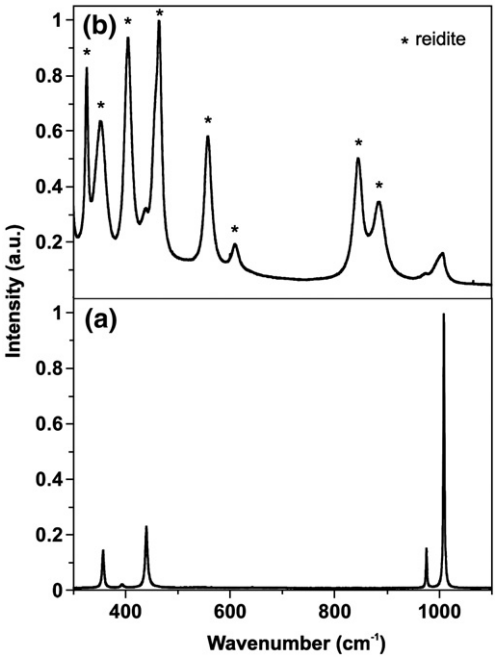

Fig. 2. Raman spectra of unirradiated zircon (a) before and (b) after applying a pressure up to 37 GPa, revealing an almost complete transformation to reidite. Only traces of zircon were observed in the quenched sample (b) as indicated by its SiO_4 antisymmetric stretching mode (at about 1000 cm^{-1}).