Structural transitions and electron transfer in coffinite, USiO$_4$, at high pressure

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ABSTRACT

The compressibility, phase stability, and vibrational properties of coffinite (USiO$_4$) were studied by in situ X-ray diffraction and infrared (IR) measurements at high pressures. An irreversible phase transition from the zircon-type to scheelite-type structure was found to occur at 14–17 GPa. Accompanying the structural transition, partial amorphization was also evident in the XRD analysis. The predicted transition pressure calculated by density functional theory is in good agreement with the experimental results. IR spectra also suggest that water is incorporated into the coffinite structure, and a pressure-induced electron transfer ($U^{4+} \rightarrow U^{3+}$) may also occur.

Keywords: Coffinite, high pressure, phase transition, XRD, IR

INTRODUCTION

An understanding of the distribution of the radiogenic elements, such as uranium (U) and thorium (Th) in the Earth’s interior is important for understanding the Earth’s age and thermal history. As an important host mineral for U and Th, zircon (ZrSiO$_4$), is extensively used in U/Pb radiometric age-dating (e.g., Houser et al. 1995; Gibson et al. 1995). Zircon has also been proposed for the immobilization and disposal of actinides that are generated by the advanced nuclear fuel cycles (Ewing et al. 1994, 1995; Weber et al. 1994, 1997). The structural chemistry and phase stability of zircon under dynamic or hydrostatic compression has been previously studied (e.g., Burns et al. 1999; Kusaba et al. 1985; Reid and Ringwood 1969; Ono et al. 2004). A phase transition from zircon to a quenchable scheelite-type structure, reidite, occurs at room temperature and a pressure of 20–30 GPa (e.g., Burns et al. 1999; Kusaba et al. 1985; Reid and Ringwood 1969; Ono et al. 2004). The critical transition pressure is greatly affected by temperature, impurities, and radiation damage (Burns et al. 1999; Kusaba et al. 1985; Reid and Ringwood 1969; Ono et al. 2004; Knittle et al. 1993; van Westrenen et al. 2004, 2005; Lang et al. 2008). Coffinite, USiO$_4$, forms as an alteration product of uraninite (UO$_2$) under reducing conditions in the presence of silica-rich solutions (Langmuir 1878) and is isostructural with zircon (Fuchs and Gebert 1958). Coffinite occurs in nature as microscopic intergrowths with other minerals like uraninite and may contain substantial amounts of lanthanide elements. Coffinite and thorite (ThSiO$_4$) are the only actinide minerals that have the zircon structure ($I4_1$/amd; $Z = 4$) (Taylor and Ewing 1978), consisting of chains parallel to the c axis formed of alternating, edge-sharing SiO$_4$ tetrahedra and UO$_8$ (or ThO$_8$) triangular dodecahedra. The stability of the zircon structure type depends strongly on the size of the large cation. Th$^{4+}$ in thorite and U$^{4+}$ in coffinite are much larger than Zr$^{4+}$ in zircon. Previous experiments have revealed that thorite transforms to huttonite with monoclinic symmetry at high temperature (Taylor and Ewing 1978) and the huttonite structure is believed to be the high-pressure phase (Finch and Hanchar 2003). No experimental results have been reported for coffinite until now, because coffinite is very difficult to synthesize (Hoekstra and Fuchs 1956). In this paper, we report the structural behavior of synthetic coffinite at high pressure and room temperature as determined by in situ XRD and IR measurements and interpreted by first-principle calculations.

EXPERIMENTAL METHODS

The synthetic coffinite (USiO$_4$) was prepared from UCl$_3$ solution and Na$_2$SiO$_3$ salt using a hydrothermal method, which was reacted in an autoclave at 250 °C and 40 atm (Pointeau et al., submitted). XRD measurements indicated a zircon-type structure for the synthesized powder. TEM observation confirmed that the coffinite is well crystallized, consisting of grains 30–50 nm in size. Both XRD and TEM measurements revealed that there are small amounts of UO$_3$ (5–10 wt%, depending on preparation conditions) with very fine particle sizes (~5 nm) mixed with the synthetic coffinite samples. The room-temperature, high-pressure experiments were performed with a symmetric diamond anvil cell (DAC). The culet of the anvils is 400 μm in diameter. Hardened steel foil with a thickness of 250 μm was indented to ~40 μm, and a 100 μm hole drilled in the center of the gasket served as sample chamber. For the XRD measurements, several runs were performed with methanol/ethanol/water (16/3/1) mixture as the pressure medium, or without a pressure medium. The in situ XRD patterns and infrared spectra were collected at the X17C and beamlines of the National Synchrotron Light Source, or without a pressure medium. The in situ XRD patterns and infrared spectra were collected at the X17C and beamlines of the National Synchrotron Light Source, respectively. A monochromatic X-ray beam with energy of 30.5 keV was used for XRD measurements. The diffraction patterns were integrated from the collected images with program FIT2D (Hammersley 1998). The lattice parameters of the zircon-type phase were derived from the refinement of the patterns using the Rietveld method with the program FullProf (Rodriguez-Carvajal 1993). The lattice parameters of the high-pressure phase were derived by a Rietveld-like full-pattern fitting or indexed from the individual diffraction peaks using the program UnitCell (Holland and Redfern 1997). Pressures in all the experiments were measured by ruby fluorescence (Mao et al. 1986). IR data were collected in two separate runs with a KBr pressure medium for mid-IR (MIR) measurements and Cu pressure...