

Synchrotron-based, energy dispersive x-ray diffraction study of TiH₂

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Introduction

Hydrogen storage research has recently invested a great deal of efforts into investigations of metal hydrides. High-pressure studies of hydrogen storage materials are critical for identifying new equilibrium and metastable states that can be accessed, as these materials are compressed to very small volumes [1]. Although titanium hydride is not the ideal candidate for storing hydrogen, Ti hydrides can act as active species to catalyze the reversible dehydrogenation of other hydrides and carbon nanotubes [2]. In addition, the basic science interest of this project lies in investigating the structure and especially the high-pressure behavior of TiH₂ in order to identify phase transitions and possibly new quenchable phases [3]. In the present study, we report the first in situ, high-pressure synchrotron x-ray diffraction studies of titanium hydride. To the best of our knowledge, this work is the first attempt to measure the equation of state of TiH₂ using synchrotron x-ray diffraction and diamond anvil cells.

Methods and Materials

For in situ X-ray diffraction studies, the powdered sample was compressed in a Mao-Bell-type diamond anvil cell (DAC). A rhenium gasket was preindented to a thickness of 70 μm using diamonds with 420 μm diameter culets. The sample and a few grains of ruby powder to measure pressure were placed inside a 130 μm diameter hole drilled in the preindented rhenium gasket. No pressure-transmitting medium was used in this experiment. All X-ray diffraction patterns were collected at the 16-BM-D beamline at the High Pressure Collaborative Access Team, Sector 16 of the Advanced Photon Source of Argonne National Laboratory, using a white beam with energies between 5 and 75 keV. The collected diffraction patterns were analyzed with Powder Cell [4] and General Structure Analysis System [5,6].

Results

Energy-dispersive x-ray diffraction patterns of TiH₂ were collected in the diamond anvil cell between ambient pressure and 33 GPa in 11 steps. Figure 1 shows the first high pressure pattern collected at 2 GPa, the pattern collected at the highest pressure investigated, and a pattern measured after decompression to ambient conditions.

Discussion

In TiH₂ there are two tetrahedral interstitial sites per Ti and hydrogen occupies those sites. Reminiscent of most dihydrides of transition metals, TiH₂ at 25°C and ambient pressure has the fluorite-type structure with space group Fm-3m. This is an fcc lattice with $a=4.45\text{Å}$ and a unit cell volume of 88Å^3 . When the temperature is lowered to about 17°C, TiH₂ undergoes a Jahn-Teller γ - γ' phase transition. The new structure has the space group I4/mmm [1].

Upon compression to 2 GPa at ambient temperature, TiH₂ undergoes a phase transition to a lower symmetry structure,

accompanied by a tetragonal distortion of the unit cell. Subsequently, the transition was found to begin at an even lower pressure [3]

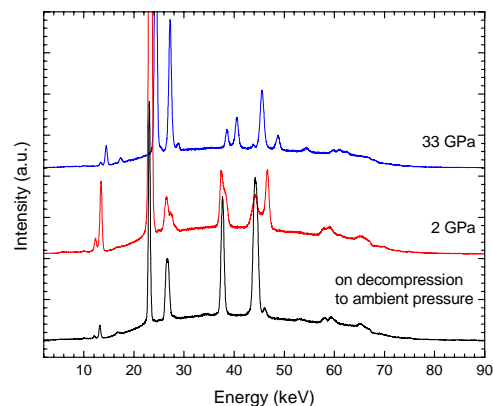


Fig. 1. High-pressure, energy-dispersive synchrotron x-ray diffraction patterns of TiH₂ collected at HPCAT, APS.

The lower symmetry structure has the space group I4/mmm with the unit cell parameters $a=3.08\text{Å}$ and $c=3.97\text{Å}$ and volume = 37.63Å^3 . A full profile Rietveld refinement was performed on all the diffraction patterns collected. A Birch-Murnaghan fit to the unit cell volume, plotted versus pressure, yielded a bulk modulus of $118\pm 6\text{ GPa}$ using a fixed pressure derivative of 6. After decompression to ambient pressure, TiH₂ reverted back to its initial cubic structure, but with a slightly smaller unit cell.

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