Abstract The crystallographic structure and electronic properties of Hf\textsuperscript{10}B\textsubscript{2} were studied as a function of pressure by combining X-ray diffraction measurements with full potential linearized augmented plane wave (LAPW) calculations. No phase transition was observed up to a pressure of 30.8 GPa, with a total volume contraction of $V/V_0 = 0.85$ and a bulk modulus value of $B_0 = 232 \pm 13$ GPa. The calculated $V_{zz}$ value at the hafnium site is linearly increasing as a function of the pressure induced volume reduction, while the $V_{zz}$ value at the boron site stays almost zero. The major contribution to the $V_{zz}$ value at the hafnium site comes from a p-p contribution next to the probe nucleus, with a relatively large d-d contribution of about 25%. This unusual large d-d contribution arises from the hafnium p-d electrons coupling.

Keywords Hafnium diboride · High pressure · TDPAC · LAPW

1 Introduction

Hafnium diboride (HfB\textsubscript{2}) is a compound with various important chemical and nuclear characteristics making it a strong candidate for application in the nuclear industry. HfB\textsubscript{2} could be an attractive material for reactors applications, due to the high neutron absorption cross-section of \textsuperscript{10}B (3840b), the high melting point ($T_m = 3380^\circ$C), low fabrication cost and low corrosion mechanisms. Transition metal borides, in general, have high melting point, high hardness and high electric
conductivity [1, 2]. They are also expected to be useful for a variety of applications such as cutting tools, reinforcement of ceramics and metals and coating materials. The diborides are members of a broad class of materials known as the boron-rich solids [3], which consist of extended networks of covalently bonded boron atoms stabilized through donation of electrons from the metal atoms. Most of the M–B₂ compounds have the AlB₂ structure in which layers of close-packed metal atoms alternate with planes of boron atoms with a graphite-like geometric structure.

In this work, the electronic properties of HfB₂ were evaluated as a function of applied pressure using combined X-ray powder diffraction technique and full potential linearized augmented plane wave (LAPW) calculations [4]. The results obtained in this study provide a better understanding and a full picture of the electronic properties of this compound as a function of V/V₀.

2 Experimental details

A stoichiometric sample of Hf^{10}B₂ was prepared by arc-melting of high purity hafnium (99.5%) drilled lumps wrapping a ^{10}B (99.95%) powder under argon atmosphere for three times. The sample was then annealed in an evacuated quartz tube under argon atmosphere at 850°C for 4 days. ^{10}B was used instead of natural boron as part of a complementary work on radiation damage of Hf^{10}B₂ and Hf^{11}B₂ conducted by us [5]. The microstructure of the sample was examined by scanning electron microscopy (SEM) and analyzed by energy dispersive spectroscopy (EDS) to determine its chemical composition. The ambient pressure X-ray diffraction of the sample was carried out using Cu-Kα₁ radiation (40 kV and 20 mA) with nickel filter and graphite monochromator, using a measured angle range of 2θ = 10–150°. The data was analyzed by the X’Pert Plus (Philips) Rietveld analysis software packages. The high-pressure energy dispersive X-ray diffraction studies were taken at the X17-C beam-line of the National Synchrotron Light Source (NSLS) at BNL [6]. The energy dispersive data was collected with a high purity germanium detector at a fixed Bragg angle (2θ ≈ 12°). The high-pressure X-ray powder diffraction measurements were taken at discrete pressure steps in the range of 0–30.8 GPa. The data was collected by the EDS technique, using the white beam of the superconducting wiggler magnet at the X17-C beam-line. Typical data collection time was about 10 min. In the lower range of the high-pressure range, angle dispersive measurements where carried out in transmission configuration using the image plate technique. The data was analyzed using a commercial Rietveld analysis software packages [7–9]. The pressure (up to 30.8 GPa) was applied via a Merrill–Bassett type diamond anvil cell (DAC), “Tel-Aviv”-type [10]. TDPAC measurements were carried out at room temperature using the ^{181}Ta 133–482 keV γ₁–γ₂ cascade (1/2⁺ → 5/2⁺ → 7/2⁺) with an intermediate state half-life of 10.8 ns. This cascade is obtained via the decay of the 18 μs 615 keV state in the ^{181}Ta probe, populated in the β decay of ^{181}Hf → ^{181}Ta [11]. The 18 μs delay before the excited level under observation is reached, gives sufficient time for electronic reorganization according to the valence change from hafnium to tantalum. For the zero pressure measurements a ~45 μCi 25 mg Hf^{10}B₂ sample sealed in a quartz tube was used. The TDPAC measurements under high pressure were done using ~0.1 mg sample activated for ~20 h in a neutron flux of about 2 × 10^{13} n/cm² s.