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300-K Equation of State and High-Pressure Phase Stability of Al_3BC_3

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The lattice parameters of Al_3BC_3 have been measured at room temperature up to 7.5 GPa using X-ray powder diffraction with synchrotron radiation. From the obtained pressure–volume relation for Al_3BC_3, the isothermal bulk modulus of $B_0 = 153 \pm 6$ GPa and its pressure derivative of $dB_0/dp = 19 \pm 4$ have been calculated by fitting a Birch–Murnaghan equation of state. Al_3BC_3 undergoes no structural transformations up to 1800 K over the 2.5 to 5.3-GPa pressure range. © 2000 Academic Press

Key Words: **Al_3BC_3; high pressure; high temperature; equation of state; phase stability; hardness.**

INTRODUCTION

In 1964 Matkovich *et al.* (1) discovered yellow platelet-shaped crystals of a new ternary phase of the Al–B–C system. The authors assigned the composition $Al_4B_{1-3}C_4$ with variable boron content to this compound. According to later investigation by Inoue *et al.* (2), the composition of the phase was determined to be $Al_8B_4C_7$.

Hillebrecht and Meyer solved the crystal structure of this phase using X-ray single crystal diffraction (3) and determined the composition to be Al_3BC_3. Interesting features of the structure are linear $[CBC]^{5-}$ anions which are isoelectronic to CO_2. $[CBC]^{5-}$ is the 16-electron system with the highest negative charge. Al_3BC_3 shows a superstructure caused by trigonal bipyramidal coordinated Al1 atoms (Fig. 1).

Al_3BC_3 is isotypic with Mg_3BN_3 (4). Since for Mg_3BN_3 the phase transition to an orthorhombic phase was found to occur at 4 GPa and 1500 K (5), the similar phase transition might be expected for Al_3BC_3.

The present work was aimed at studying room temperature equation of state of Al_3BC_3 to 7.5 GPa and its thermal phase stability to 1800 K and to 5.3 GPa using energy-dispersive powder diffraction with synchrotron radiation.

EXPERIMENTAL

Sample Preparation

Transparent, yellow leaflet crystals of Al_3BC_3 were prepared from the elements in molten aluminum according to the method described in (6). The samples were heated under argon atmosphere (molar ratio Al/B/C = 40:2:3) in graphite crucibles to 2200 K for 1 h, followed by cooling at a rate of 100 K h^{-1} to 1300 K and then at a rate of 300 K h^{-1} to room temperature. The excess aluminum was removed by diluted hydrochloric acid. The by-product, boron containing Al_4C_3, was separated under a microscope. The Al_3BC_3 single crystals were manually crushed in a boron carbide mortar.

High-Pressure High-Temperature X-ray Diffraction

The high-pressure experiments were carried out using the multianvil-type X-ray system MAX80 with anvils of cemented carbide. The diffraction measurements were performed in an energy-dispersive mode at the beam line F2.1 of HASYLAB-DESY (Hamburg). The conditions were 4.5 GeV and 140 to 70 mA of positron current.

The experimental setup has been described earlier (7). The primary polychromatic synchrotron beam was collimated to 60 μm (height) by 100 μm (width) and was perpendicular to the vertical axis of the sample chamber. The diffracted beam was collected in the vertical plane using an intrinsic Ge solid-state detector and a Canberra multichannel analyzer.

The detector was calibrated against energy using X-ray fluorescence $K\alpha$ and $K\beta$ lines from Rb, Mo, Ag, Ba, and Tb. The diffraction angle, $\theta = 4.691 \pm 0.001°$, was calculated from diffraction pattern of NaCl taken at ambient conditions.

The temperature of the high-pressure cell was controlled by an Eurotherm PID-regulator within ± 4 K. The sample

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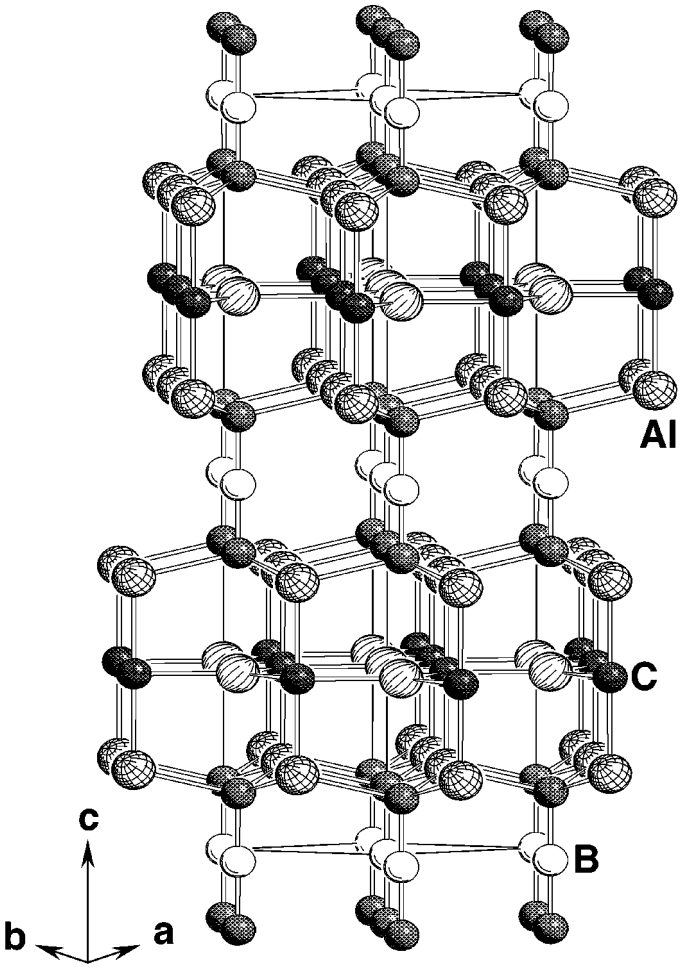

FIG. 1. Crystal structure of Al_3BC_3 (subcell).

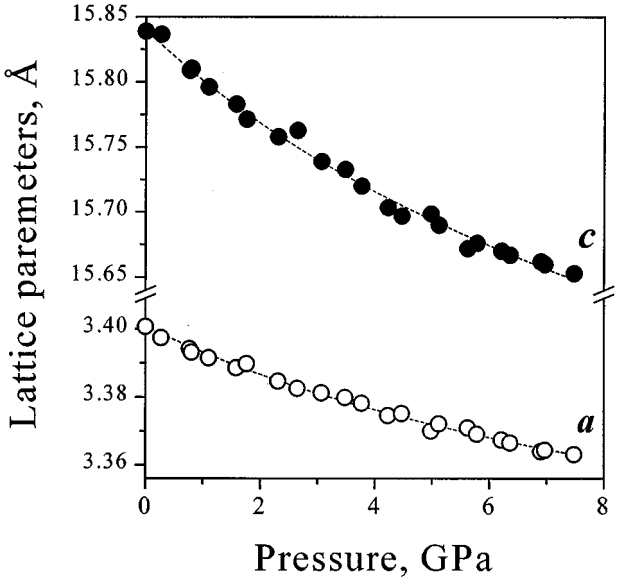

FIG. 2. Pressure dependence of the lattice parameters of Al_3BC_3.

temperature was measured by a Pt10%Rh–Pt thermocouple. The correction for the pressure effect on a thermocouple electromotive force was made using the data of Getting and Kennedy (8). In high-temperature experiments the sample was placed in a graphite ampoule as above 1340 K, Al_3BC_3 reacts with h-BN discs, other setup components, and the thermocouple.

Pressures at different temperatures were determined from the d_{002} value of hexagonal graphite-like boron nitride using its thermoelastic equation of state (9).

Hardness Measurements

The hardness was measured on a MXT70 (Matsuzava) apparatus with a Vickers indenter at loads of 25 and 50 g. Indents were measured on a NU-2E microscope (Carl Zeiss Jena) in a reflected light in the phase contrast mode at 750 × magnification. The hardness was calculated by the equation $H_V = 0.4636 \times P/a^2$, where P is load on the indenter and $2a$ is the indent diagonal.

RESULTS AND DISCUSSION

Synchrotron radiation diffraction patterns of the Al_3BC_3 subcell exhibit broadened reflections: (*100*), (*101*), (*006*), (*103*), (*104*), (*105*), (*008*), (*106*), (*107*), (*110*), and occasionally (*114*), (*109*), (*201*), (*116*), (*204*), (*118*). Lattice parameters of the subcell at ambient pressure were calculated to be $\boldsymbol{a} = 3.401 \pm 0.003$ Å and $\boldsymbol{c} = 15.84 \pm 0.02$ Å, in good agreement with those reported in (3).

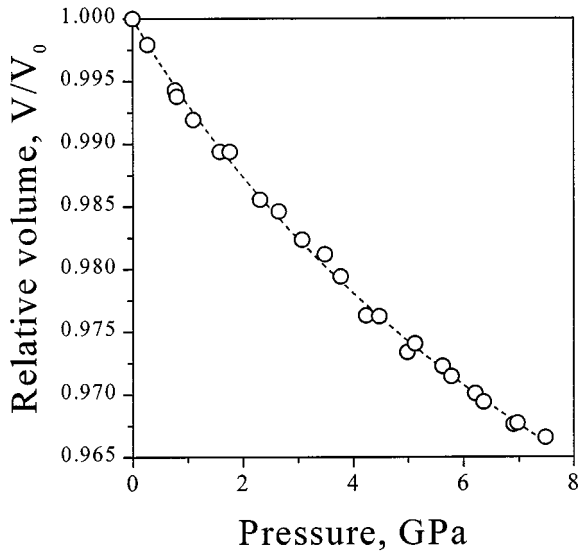

FIG. 3. Pressure–volume data for Al_3BC_3 at 300 K. Dashed line is the Birch–Murnaghan isotherm that is obtained from a least-squares fits to our measurements.

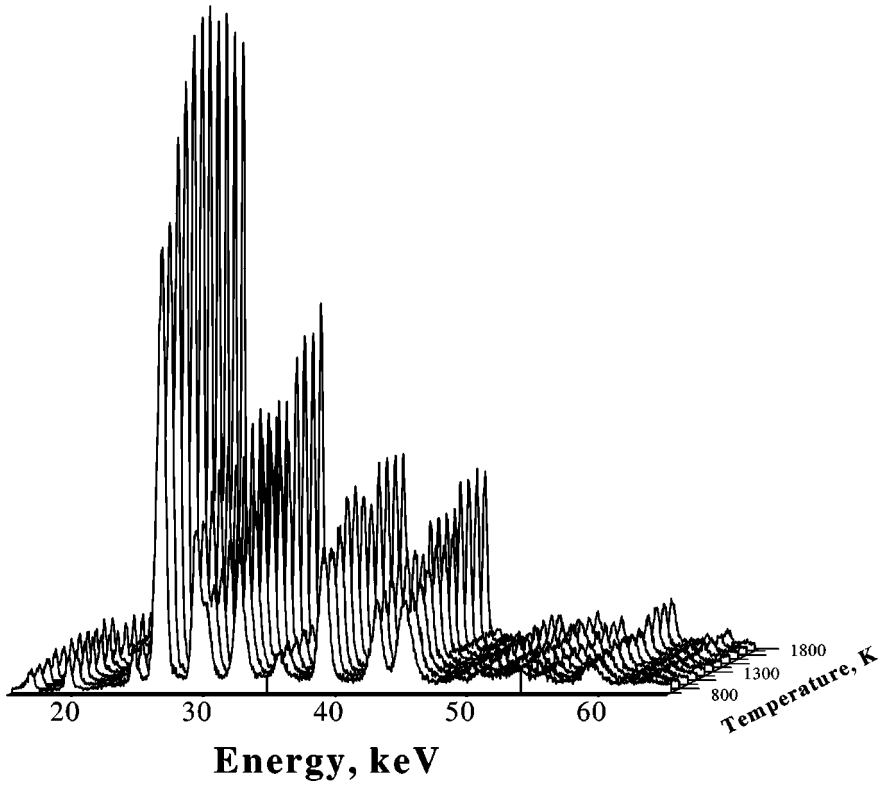

FIG. 4. Diffraction patterns of Al_3BC_3 taken during heating at 5.3 GPa.

The pressure dependencies of Al_3BC_3 lattice parameters at room temperature are plotted in Fig. 2. The ratio between linear coefficients of Al_3BC_3 compressibility toward the ***c*** and ***a*** axes is $k_c/k_a = 1.06 \pm 0.04$, which points to the absence of anisotropy of the Al_3BC_3 lattice in terms of elastic properties.

A nonlinear three-parameter least-squares fit to the experimental p-V data using the Birch–Murnaghan (third-order Eulerian finite-strain) equation of state (10) gave zero-pressure value of bulk modulus $B_0 = 153 \pm 6$ GPa and its pressure derivative $dB_0/dp = 19 \pm 4$. Experimental and calculated values of Al_3BC_3 volume are given in Fig. 3.

A relatively high value of bulk modulus of Al_3BC_3 allowed one to expect a high hardness of this phase. However, Vickers hardness of Al_3BC_3 single crystals has been found to be rather low: 20.7 GPa under a 25-g load and 18.2 GPa under a 50-g load. For comparison, hardness of $Al_3C_2B_{48}$ and α-AlB_{12} at a 200-g load are 33 and 27 GPa, respectively (11).

With the aim to study the phase stability of Al_3BC_3 at high pressures and temperatures, diffraction patterns from the sample were collected at a fixed pressure (2.5, 3.7 and 5.3 GPa) and temperatures that increased stepwise in 50 K increments. From the diffraction patterns (characteristic sequence taken at 5.3 GPa is presented in Fig. 4), it is seen that the temperature increase causes the ordering of Al_3BC_3 structure, which manifests itself in considerable decrease of the lines' width. No formation of new crystalline phase is, however, observed up to 1800 K. Thus, it was found that in spite of a structural similarity of Al_3BC_3 to Mg_3BN_3, the former undergoes no structural transformations up to 1800 K over the whole pressure range under study.

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