Equation of state and thermal stability of Al_3BC

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Abstract

The lattice parameters of Al_3BC have been measured up to 5 GPa at ambient temperature using energy-dispersive X-ray powder diffraction with synchrotron radiation. A fit to the experimental p – V data using Birch–Murnaghan equation of state gives values of the Al_3BC bulk modulus 116(4) GPa and its first pressure derivative 9(2). In the 1.6–4.8 GPa range at temperatures above 1700 K Al_3BC undergoes incongruent melting that results in the formation of Al_3BC_3 , AlB_2 and liquid aluminum.

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1. Introduction

Aluminum-rich phases of the Al–B–C system have been the topic of several recent investigations because cermets based on aluminum boroncarbide are promising ceramic materials of high hardness and low density. In fabrication of advanced Al/B/C cermets, the basic product of a reaction between aluminum and boron carbide at relatively low temperatures is Al_3BC [1]. This phase was first described as phase X [2]. Later Meyer and Hillebrecht [3] synthesized the pure compound and defined its composition and crystal structure (Fig. 1). As no data are found in the literature on the Al_3BC high-pressure behavior, our interest has been in studying the equation of state and thermal stability of this phase up to 5 GPa using X-ray powder diffraction with synchrotron radiation.

2. Experimental

Pure Al_3BC was synthesized at 1150 K from the elements with an excess of aluminum as described in [3]. Combustion elemental analysis and electron probe microanalysis gave

a Al:B:C ratio of about 3:1:1. Secondary ion mass spectroscopy showed that the oxygen impurity content is less than 1 at%.

The high-pressure experiments up to 5 GPa were carried out using a multianvil X-ray system MAX80 at beamline F2.1, HASYLAB-DESY. The experimental set-up has been described elsewhere [4]. Energy-dispersive data were collected on a Canberra solid state Ge-detector with fixed Bragg angle $2\theta = 9.238(5)^\circ$ using a white beam collimated down to $100 \times 100 \mu\text{m}^2$ and the detector optics with 2θ acceptance angle of 0.005° , which ensures a high resolution of the observed diffraction patterns. The detector was calibrated using the K_α and K_β fluorescence lines of Cu, Rb, Mo, Ag, Ba, and Tb.

To decrease the deviatoric stress that was generated during ‘cold’ compression and, thus, attain quasi-hydrostatic pressure conditions during equation-of-state measurements, the samples were preannealed at 900 K and a given pressure for 10 min. The sample pressure was determined from the lattice constant of NaCl (pressure marker) using Decker’s equation of state [5].

The temperature of the high-pressure cell was controlled by a Eurotherm PID-regulator within ± 4 K in the 400–1900 K range. The sample temperature was measured by a Pt/Pt10%Rh thermocouple. The correction for the pressure effect on the thermocouple emf was made using the data of Getting and Kennedy [6]. Pressures at different temperatures were evaluated from the lattice parameters of highly ordered graphite-like hexagonal boron nitride using the p – V – T equation of state of hBN [4]. The pressure variations with increasing temperature were found not to exceed ± 200 MPa in the 2-mm

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Fig. 1. Crystal structure of Al_3BC is a closest packing of Al atoms with a layer sequence ABACBC. Isolated boron atoms are placed in all octahedral voids between the layers A and C while isolated carbon atoms occupy half of the trigonal voids in the layers B [3].

central part of the cell over the experimental temperature range.

In studying Al_3BC thermal stability, the samples were compressed to a given pressure at ambient temperature, and then the diffraction patterns were collected in the ‘autosequence’ mode at a linear heating at a rate of 25 K/min. Collection time was 60 s for each pattern.

3. Results and discussion

3.1. Equation of state of Al_3BC

Synchrotron radiation diffraction patterns of the Al_3BC subcell exhibit broadened reflections (101), (102), (103), (104),

Fig. 2. Lattice parameters of Al_3BC versus pressure at ambient temperature. The dashed lines represent least-squares fits to the experimental data using Eq. (1).

Fig. 3. The p – V data for Al_3BC at ambient temperature. The solid line is the best fit of the experimental data to the Birch–Murnaghan equation of state, with $B_0 = 116$ GPa and $B'_0 = 9$. The dashed line is equation of state of Al_3BC_3 [7].

(006), (105), (110), (106), and occasionally (004), (108), (202), (204), (116). Lattice parameters of the subcell at ambient pressure were calculated to be $a = 3.491 \pm 0.002$ Å and $c = 11.54 \pm 0.01$ Å, in good agreement with those reported in [3]. With increasing pressure, the diffraction lines of Al_3BC broaden and weaken considerably and above 5 GPa only the lines associated with the (102), (103), (104) and (006) reflections could be resolved.

Fig. 2 shows the lattice parameters of Al_3BC versus pressure. The one-dimensional analog of the first-order Murnaghan equation of state of the form

$$\frac{r}{r_0} = \left[1 + \left(\frac{\beta'}{\beta_0} \right) p \right]^{-1/\beta'} \quad (1)$$

was used for approximation of the non-linear relation between normalized lattice parameters and pressure. Here r is the lattice parameter (index 0 refers to ambient pressure); β_0 is the axial compression modulus¹, and β' is the pressure derivative of β_0 . The dashed lines in Fig. 2 correspond to Eq. (1) with parameters obtained from a least-squares fit to the experimental data. The ratio between axial compression moduli towards the a and c axes is 1.19 ± 0.03 , which points to the higher compressibility of Al_3BC in the c -direction. This fact can be attributed to a pronounced two dimensional character of the Al_3BC crystal structure in which layers of edge sharing Al_6B octahedra alternate with layers of trigonal bipyramidal Al_5C polyhedra linked by common corners [3].

Experimental values of the Al_3BC relative volume versus pressure are plotted in Fig. 3. A non-linear three-parameter least-squares fit to the experimental p – V data using Birch–Murnaghan equation of state gave zero-pressure value of bulk modulus $B_0 = 116 \pm 4$ GPa and its pressure derivative $dB_0/dp = 9 \pm 2$. These values point to a higher compressibility of Al_3BC as compared to Al_3BC_3 ($B_0 = 153$ GPa [7]).

¹ $(\beta_0)^{-1} = k_r = -(d \ln r / dp)_{p=0}$ is the linear compressibility.

Fig. 4. Diffraction patterns of Al_3BC taken at a linear-heating rate of 25 K/min at 1.6 GPa.

The latter is probably due to a clearly ionic character of Al_3BC_3 [8] while Al_3BC seems to be more metallic [3].

3.2. Phase stability of Al_3BC

At 1.6 GPa heating of Al_3BC up to 1680 K results in a decrease of the lines' width, which is indicative of the structural ordering of the phase at a temperature increase under pressure. Starting with 1680 K, the lines of Al_3BC_3 and AlB_2 appear in the diffraction patterns (Fig. 4). At the same time a drastic decrease in the intensity of the lines of initial Al_3BC is observed. A considerable increase of the background points to the formation of a liquid in the system, which gives grounds to conclude that a process of incongruent melting

of Al_3BC takes place:

Complete disappearance of the Al_3BC lines is observed at about 1700 K. With further temperature increase up to 1850 K, the phase composition of the system does not change because of the high thermal stability of Al_3BC_3 [7]. Diffraction patterns of the samples quenched down to ambient conditions exhibits lines of Al_3BC_3 , AlB_2 and metallic aluminum.

At 4.8 GPa, Al_3BC decomposition starts at higher temperatures (1720 ± 20 K) and also results in the formation of Al_3BC_3 , AlB_2 and liquid aluminum.

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