Equation of state and thermal stability of Al$_3$BC

Vladimir L. Solozhenko $^{a,*}$, Elena G. Solozhenko $^b$, Christian Lathe $^c$

$^a$ LPMTM-CNRS, Institut Galilée, Université Paris Nord, 99, av. J.B. Clément, F-93430 Villetaneuse, France
$^b$ Institute for Superhard Materials of the National Academy of Sciences of Ukraine, Kiev 04074, Ukraine
$^c$ Hamburger Synchrotronstrahlungs labor (HASYLAB-DESY), D-22607 Hamburg, Germany

Received 19 September 2005; received in revised form 12 January 2006; accepted 12 January 2006 by B. Jusserand

Available online 31 January 2006

Abstract

The lattice parameters of Al$_3$BC 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$_3$BC 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$_3$BC undergoes incongruent melting that results in the formation of Al$_3$BC$_3$, AlB$_2$ and liquid aluminum.

© 2006 Elsevier Ltd. All rights reserved.

PACS: 61.10.Eq; 64; 64.30.+t

Keywords: A. Aluminum boroncarbide; C. XRD; E. High pressure

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$_3$BC [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$_3$BC 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$_3$BC 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 100×100 µm$^2$ and the detector optics with $2\theta$ acceptance angle of 0.005$^\circ$, which ensures a high resolution of the observed diffraction patterns. The detector was calibrated using the $K_a$ and $K_b$ 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 highly ordered graphite-like hexagonal boron nitride using the $p$–$V$–$T$ equation of state [4]. The pressure variations with increasing temperature were found not to exceed ±200 MPa in the 2-mm

---

* Corresponding author. Tel.: +33 1 49 40 34 89; fax: +33 1 49 40 39 38. E-mail address: vls@lpmtm.univ-paris13.fr (V.L. Solozhenko).

0038-1098/$ - see front matter © 2006 Elsevier Ltd. All rights reserved. doi:10.1016/j.ssc.2006.01.015
In studying Al$_3$BC 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$_3$BC

Synchrotron radiation diffraction patterns of the Al$_3$BC subcell exhibit broadened reflections (101), (102), (103), (104), (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$_3$BC 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$_3$BC versus pressure. The one-dimensional analog of the first-order Murnaghan equation of state of the form

$$\frac{r}{r_0} = \left[1 + \left(\frac{\beta'}{\beta_0}\right)p\right]^{-\frac{1}{\beta'}}$$  \hspace{1cm} (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); $\beta_0$ is the axial compression modulus$^1$, and $\beta'$ is the pressure derivative of $\beta_0$. 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 $1.19 \pm 0.03$, which points to the higher compressibility of Al$_3$BC in the $c$-direction. This fact can be attributed to a pronounced two dimensional character of the Al$_3$BC crystal structure in which layers of edge sharing Al$_6$B octahedra alternate with layers of trigonal bipyramidal Al$_5$C polyhedra linked by common corners [3].

Experimental values of the Al$_3$BC 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$_3$BC as compared to Al$_3$BC$_3$ ($B_0 = 153$ GPa [7]).

$^1 (\beta_0)^{-1} = k = -(d \ln (\rho)/d \rho)_{\rho=0}$ is the linear compressibility.
The latter is probably due to a clearly ionic character of Al$_3$BC$_3$ [8] while Al$_3$BC seems to be more metallic [3].

3.2. Phase stability of Al$_3$BC

At 1.6 GPa heating of Al$_3$BC 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$_3$BC$_3$ 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$_3$BC 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$_3$BC takes place:

$$3\text{Al}_3\text{BC} = \text{Al}_3\text{BC}_3 + \text{AlB}_2 + 5\text{Al}$$

(2)

Complete disappearance of the Al$_3$BC 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$_3$BC$_3$ [7]. Diffraction patterns of the samples quenched down to ambient conditions exhibit lines of Al$_3$BC$_3$, AlB$_2$ and metallic aluminum.

At 4.8 GPa, Al$_3$BC decomposition starts at higher temperatures (1720±20 K) and also results in the formation of Al$_3$BC$_3$, AlB$_2$ and liquid aluminum.

Acknowledgements

The authors thank Dr F.D. Meyer for supplying us with the Al$_3$BC specimen and Prof. H. Hillebrecht for fruitful discussions. High-pressure experiments at HASYLAB-DESY were supported by the GFZ-Potsdam under the MAX80 program.

References