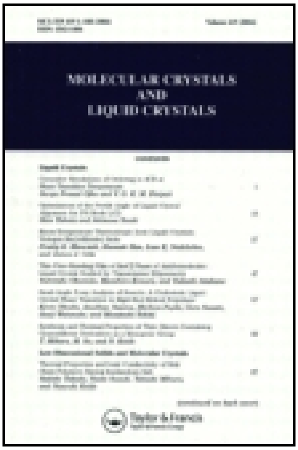

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Crystal Growth of New Compound $Sc_2B_{1.1}C_{3.2}$ with Graphite-Like Layers

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Crystal Growth of New Compound $Sc_2B_{1.1}C_{3.2}$ with Graphite-Like Layers

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An Sc based borocarbide $Sc_2B_{1.1}C_{3.2}$ with a two-dimensional graphite-like network has been synthesized by a solid state chemical reaction route. Crystals have been grown by floating-zone method at different speeds and growth direction could be assigned to be parallel to <110> axis.

Keywords: Crystal growth; Scandium boron-carbides; $Sc_2B_{1.1}C_{3.2}$; Graphite-related compound

INTRODUCTION

From examining the phase diagram of the Sc-B-C system[1], a novel compound with nominal chemical formula $Sc_2B_{1.1}C_{3.2}$ was found. The trigonal crystal structure (a=b=23.710(9)Å, c=6.703(2)Å, P3m1) is composed of alternate $-[B_{1/3}C_{2/3}]_\infty$-Sc-C-Sc-$[B_{1/3}C_{2/3}]_\infty$- layers. This compound has strong similarities to graphite intercalation (GIC) compounds with respect to its graphite-like layered structure. Up to now only three compounds have been reported with the $[BC]_\infty$ graphite-like framework that is, LiBC[2], MgB_2C_2[3] and BC_3[4]. The planar $[BC]_\infty$ layers of the first two compounds are isostructural to graphite layers and the stacking is like that of BN with a C-B-C-B sequence in adjacent layers. Although the information about the atomic structure of the BC_3 compound is limited and the BC distribution has not been unambiguously determined experimentally, this compound has been the subject of extensive research for carbon nanotube synthesis and related electronic structure investigations[5,6].

Thus the single crystal growth of new graphite-related compound becomes more interesting owing to the fact that these compounds could combine desired materials with interesting physical properties.

EXPERIMENTAL PROCEDURES

Single Crystal Growth

Polycrystalline sintered rods of $Sc_2B_{1.1}C_{3.2}$ were used as feed and seed rods. They were prepared by solid state reaction as described in ref.[11]. The crystal was grown by a floating-zone method in a xenon-lamp image furnace under continuous flow of Ar (99.999 wt%) gas. Both the feed rod and the growing crystal were synchronously driven downward at a rather low speed under counter-rotation of 35rpm.

Characterizations

After the powder was dissolved into a $HNO_3 + HCl$ (1:1) solution kept at 150°C for 16 hours, the scandium and boron contents were determined by a chelate titration and inductively coupled plasma atomic emission spectroscopy, respectively. The carbon content was determined by a volumetric combustion method using a carbon determinator (WR-12, Leco Co.). Oxygen impurity was analyzed by a standard inert gas fusion method (TC-136, Leco. Co.).

XRD pattern analysis was carried out using a standard X-ray powder diffractometer (R-2000, Rigaku Co.) with CuKα radiation. The Kα1 peak intensities were determined after rejecting Kα2 peaks, using RINT software (Rigaku Co.).

CRYSTAL STRUCTURE DISCRIPTION

The crystal structure of $Sc_2B_{1.1}C_{3.2}$ compound has been determined by a single crystal data and could be assigned to represent a new structure type of rare-earth boron carbides[7]. The final structure solution and refinement was based on a unit cell (a=b=23.710(9)Å and c=6.703(2)Å) with space group P3m1. The novel crystal structure is proposed to consist of alternate $-[BC_2]_\infty$-Sc-C-Sc-$[BC_2]_\infty$- laminar layers. In the structure of $Sc_2B_{1.1}C_{3.2}$ compound all the carbon and boron atoms in $[BC_2]_\infty$ layer form graphite-like nets with the mean C-C and B-C distance of 1.51(5) and 1.55(5), respectively. No B-B bond is found in this layer. This layer is actually not flat but exhibits significant puckering. The projection on the (110) plane (Fig. 1) indicates a regular undulation in the graphite-like layer. Interestingly, the "Sc_2C" units appear to be rather loosely accommodated between the graphite-like layers. This is reflected by the rather large mean Sc-C and Sc-B distance of 2.549(9)Å, whereas the mean Sc-Sc distance of 3.164(5)Å reflects a close metal-metal contact. The isolated C atoms in the middle layer now are accommodated in voids within this dense Sc arrangement with a mean Sc-C distance of 2.295(17)Å. If all the atomic positions are fully occupied, there should be 98 Sc, 54 B and 157 C atoms in one unit cell. This results in a composition of $Sc_2B_{1.1}C_{3.2}$. The chemical analyses of the pieces cut from different crystals confirmed this composition.

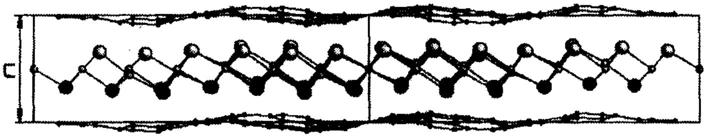

FIGURE 1 Projection of $Sc_2B_{1.1}C_{3.2}$ structure on the (110) plane.

SINGLE CRYSTAL GROWTH

Crystal growths at different lower speeds (from 2 to 6 mm/hr) have been tried in order to obtain the high quality crystal. Crystal growths at different speeds show nearly same unstable crystallization behavior and need continuous up and down adjustment of the heating power. Usually at the initial stage of crystal growth, higher temperature is necessary to melt the feed and seed rod entirely, then the growth temperature should be decreased gradually in order to keep the diameter of the molten zone homogeneous and stable. But sooner or later this stable process will be broken because of the touch of feed rod and growing crystal. It is not conclusive that this phenomenon is related with the diameter and density variance of feed rod. When increasing heating power a little to remove the touch and then gradually decreasing to the previous level it leads to another new stable growth process. Therefore such kind of circulation will be repeated until crystal growth finish. The obtained crystals were cut perpendicular to the growth direction by spark erosion and metallographically analyzed. All the grown specimens showed occurrences of sub-grains. A typical photograph of the crystal cross section is shown in Fig. 2. This specimen contains several large grains but each large grain is composed of several sub-grains.

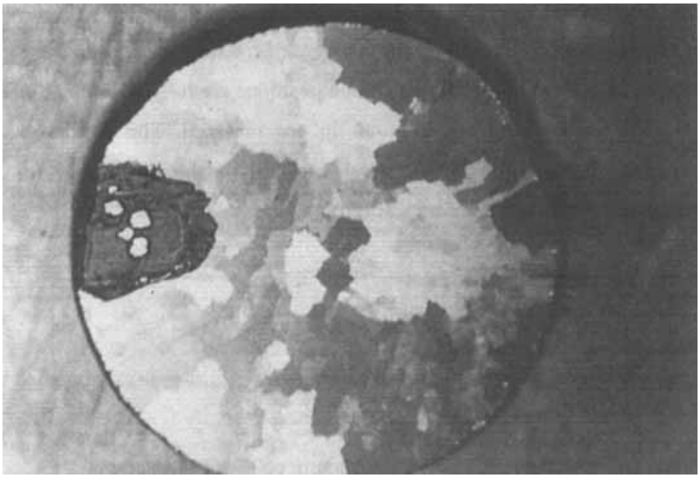

FIGURE 2 Cross section photograph of the crystal $Sc_2B_{1.1}C_{3.2}$.

The backscattering Laue technique failed to determine the crystal growth direction because of the sub-grains. The Laue patterns of the polished crystal surfaces which are perpendicular to the growth direction only show some vague and intermittent rings. For the crystal cut perpendicular to the growth direction, another two small flat surfaces parallel to the crystal growth direction were also polished. All the three polished surfaces of the crystal were set as a θ-2θ configuration for the XRD analysis, respectively. Their XRD patterns were shown in Fig.3 denoted as crystal //1, crystal //2 and crystal ⊥, respectively (// and ⊥ represent the surface parallel or perpendicular to the growth direction). The powder XRD patterns of the synthesized powder samples and powders pulverized from single crystal were also given in Fig. 3. The crushed single crystal sample shows strong trend of preferred orientation along *c*-axis. The main preferred orientation of crystal ⊥ is along <770> axis, so it can be concluded that the crystal growth direction is mainly along this direction. If this assignment is correct, the XRD pattern of the crystal // should show 00*l* reflections. But 70*l* reflections were found in the two patterns of crystal //1 and crystal //2. This can be explained that these two surfaces were polished by random directions so it was not exactly perpendicular to <001> axis. The different diffraction intensities of these two crystal // patterns also confirm this explanation.

The chemical analyses of three pieces cut from different crystals show the close composition of $Sc_2B_{1.11}C_{3.26}$, $Sc_2B_{1.09}C_{3.35}$ $Sc_2B_{1.16}C_{3.33}$ with oxygen impurity content oabout 1.00 wt%. The structure model suggests the existence of some homogeneous region between boron and carbon in the graphite-like layer. Here at least 5% more boron substitution of carbon still gives the pure phase.

CONCLUDING REMARKS

Crystals of new compound $Sc_2B_{1.1}C_{3.2}$ with graphite-like layers have been grown by the floating zone method at different speeds and growth direction could be assigned to the <110> axis. The $Sc_2B_{1.1}C_{3.2}$ compound shows deintercalation behavior for a HNO_3 + HCl (1:1) solution. The XRD pattern of the black residue consisted amorphous-like broad peak and a sharp peak being comparable to the graphite 002 peak. Thus the grown crystals would be useful for more precise deintercalation experiments.

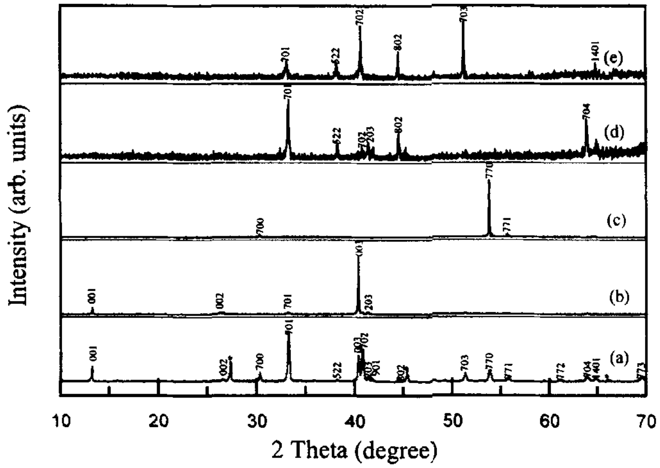

FIGURE 3 X-ray diffraction patterns for $Sc_2B_{1.1}C_{3.2}$ in (a) powder synthesized sample (*denote Ge internal standard), (b) pulverized single crystal, (c) crystal ⊥, (d) crystal //1 and (e) crystal // 2.

Acknowledgments

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References

[1] Ying Shi, A Leithe-Jasper and T. Tanaka, "New Ternary Compounds Sc_2BC_3 and $ScB_{15}C_{1.60}$ and Subsolidus Phase Relations in Sc-B-C System at 1700°C", J. Solid State Chem., submitted.

[2] M. Wörle, R. Nesper, G. Mair, M. Schwarz and H. G. V. Schnering, Z. anorg. allg. Chem. **621,** 1153 (1995).

[3] M. Wörle and R. Nesper, J. Alloys and Comp. **216,** 75 (1994).

[4] J. Kouvetakis, R. B. Kaner, M. L. Sattler and N. Bartlett, J. Chem. Soc. Chem. Commun., 1758 (1986).

[5] Z. Weng-Sieh, K. Cherrey, N. G. Chopra, X. Blasé, Y. Miyamoto, A. Rubio, M. L. Cohen, S. G. Louie, A. Zettl and R. Gronsky, Phys. Rev. B **51,** 11229 (1995).

[6] D. Tomanek. R. M. Wentzcovitch, S. G. Louie and M. L. Cohen, Phys. Rev. B **37,** 3134 (1988).

[7] Ying Shi, A. Leithe-Jasper, L. Bourgeois, Y. Bando and T. Tanaka, "$Sc_2B_{1.1}C_{3.2}$, a New Structure Type of Rare-earth Carbide with Graphite-like Layers", submit to J. Solid State Chem.