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Preparation and some properties of ScB_2 single crystals

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Abstract

ScB_2 single crystals were grown by inductive floating zone melting. The ScB_2 structure was refined on single crystal and powder data, the latter obtained from parts of single crystals which were prepared by controlled crushing. The ScB_2 structure corresponds to the AlB_2 structure type, sp. gr. $P6/mmm$, No. 191 ($R_1 = 0.0191$, $wR_2 = 0.0474$), lattice parameters are equal to $a = 0.314820(3)$ nm, $c = 0.351483(5)$ nm, $c/a = 1.117$, X-ray density is 3.670 g/cm^3. The measured hydrostatic density is 3.666 g/cm^3 which correspond to the $Sc_{0.99}B_2$ composition. The ScB_2 Young modulus value is equal to 480 GPa and the Debye characteristic temperature is 1020 K.

Keywords: Scandium diboride; Single crystal growth; Crystal structure; Young modulus; Debye temperature

1. Introduction

Due to its position in the Periodical System of Elements close to the rare earth and the *d*-electron elements, scandium exhibits a boride chemistry similar to that of the transition elements and the rare earth elements, i.e., MB_2 with AlB_2 structure and MB_{12} with a distorted UB_{12} structure (Fig. 1).

While ScB_{12} was obtained earlier in the form of single crystals [2,3] and its crystal structure was described based on single crystal data [3], the preparation of ScB_2 in the form of single crystal and its structure description based on single crystal data will be presented here for the first time.

According to X-ray powder investigations, ScB_2 is hexagonal, AlB_2 type (space group $P6/mmm$—D^1_{6h}, No. 191), $a = 0.3148$, $c = 0.3516$ nm, $c/a = 1.116$ [4–6]. The atomic positions are: Sc in 1(*a*) (0,0,0) and B in 2(*d*) $(\frac{1}{3},\frac{2}{3},\frac{1}{2})$ and $(\frac{2}{3},\frac{1}{3},\frac{1}{2})$. The only interplanar spacings and intensities of the powder diagram are listed in [4].

Physical properties of this boride were studied earlier on the hot-pressed samples. ScB_2 has a high melting temperature of (2523 ± 50) K, at room temperature its microhardness is 17.8 GPa, specific resistivity—(7–15) μΩ cm, thermal electromotive force −7.7 μV/K, thermal expansion coefficient in the temperature range 300–1100 K is equal to $(7.6 \pm 0.5) \times 10^{-6}\,K^{-1}$ (along the *a*-axis), $(6.8 \pm 0.5) \times 10^{-6}\,K^{-1}$ (along the *c*-axis) [7].

These properties of ScB_2 are close to those of CrB_2 melting point, microhardness, thermal expansion coefficient, while its density is about 35% less than the CrB_2 one. It should be specifically emphasized that ScB_2 is now considered as promising light refractory material and a substitute of CrB_2.

Taking into account the lack of information on the experimental ScB_2 single crystal structure and on fundamental properties determined on pure and perfect single crystal samples, we developed the technology of the ScB_2 single crystal growth by inductive zone melting, determination of its crystal structure by X-ray single crystal method, and investigation of its physical properties using the single crystal samples.

2. Experimental

Scandium diboride in the powder polycrystalline form was obtained by borothermal reduction of scandium oxide

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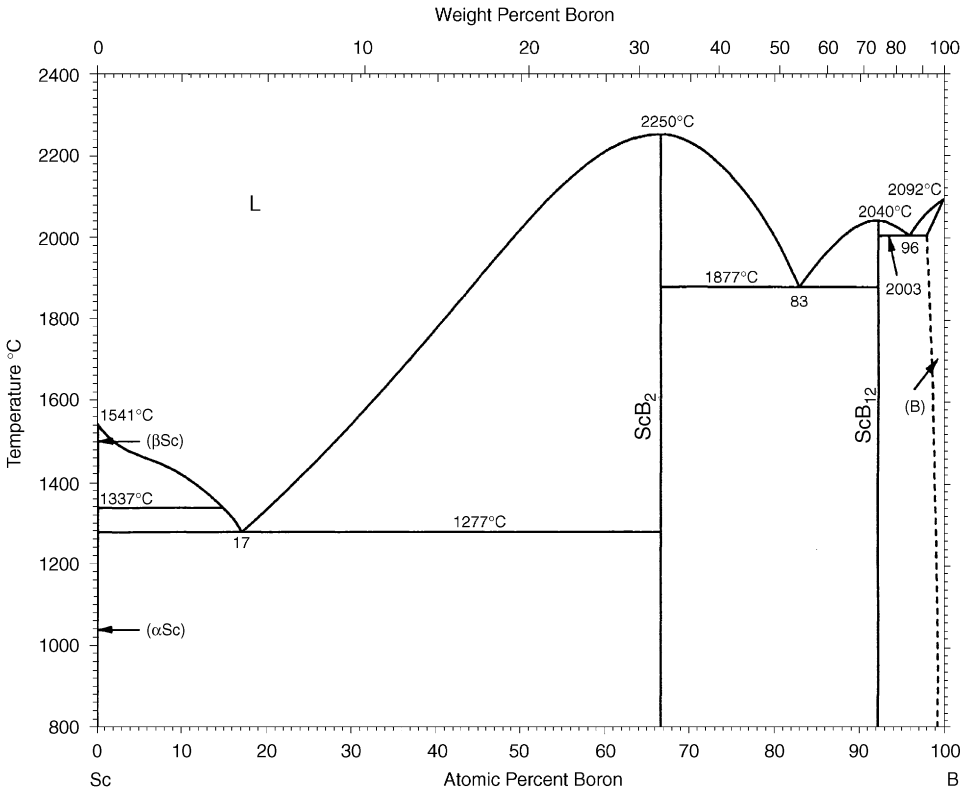

Fig. 1. Phase diagram Sc-B [1].

in vacuum according to the reaction:

$$Sc_2O_3 + 7B = 2ScB_2 + 3BO \uparrow .$$

High-purity scandium oxide (99.95% pure) and amorphous boron (99.9% pure) were used as starting materials. The process of reduction was carried out in a vacuum furnace under conditions of continuous removal of formed gaseous components; zirconium diboride crucible was used to avoid contamination by the crucible material. The obtained powder was shaped into rods using slip casting. These rods were subsequently sintered at 1700 °C under vacuum and used for ScB_2 single crystal growth.

The ScB_2 crystal growth by inductive floating zone melting method was carried out in the specialized "Crystal-1 1 1" equipment at a pressure of 1 MPa of high pure argon for suppressing of component evaporation. The first ScB_2 single crystal was grown from melt enriched by metal (some excess of metal scandium was introduced into the initial moment to the melting zone) in order to form a stable melting zone, to decrease the melt temperature and to prevent the appearance of the second phase—ScB_{12} that is more boron rich. All other single crystals were grown with seeds from the previously grown ScB_2 single crystals. The optimal growth rate was 0.2 mm/min.

Volatile impurities present in the starting boron were partially removed during synthesis and further during zone melting. The total content of impurities in the studied samples was not more than 10^{-3} mass% according to optical spectral analysis.

The obtained single crystals were about 5 mm in diameter and 50 mm in length. A typical ScB_2 crystal obtained by this method is shown in Fig. 2.

The primary analysis of crystal perfection of the obtained melted ingots was performed with the X-ray Laue pattern on HZG-4 diffractometer.

Phase analysis of the polycrystalline synthesized powder sample was carried out with the "Siemens D500" diffractometer (Cu $K\alpha$ radiation, curved graphite monochromator at the diffracted beam, angle range of $20^\circ \leqslant 2\theta \leqslant 161.5^\circ$, the scanning step is 0.02°, dwell time of 10 s per point).

For the precision determination of the ScB_2 lattice parameters the powder patterns from the ScB_2 synthesized powder and crushed single crystal with internal standard (silicon powder, $a = 0.5431083$ nm) in the range of the $60^\circ \leqslant 2\theta \leqslant 161.5^\circ$ angles with the step 0.01° were measured. Calculations of powder X-ray patterns were carried out by the Rietveld method with FullProf&WinPLOTR program package [8,9].

For ScB_2 crystal structure refinement the single crystal X-ray diffraction study was performed. The integrated intensities of Bragg reflections were collected with Oxford Diffraction "Xcalibur3" automated single crystal diffractometer ("Sapphire3" CCD-detector) using graphite-monochromated Mo$K\alpha$ radiation ($\lambda = 0.071073$ nm) at room temperature. The structure was solved and refined by the full matrix least-square method using SHELX-86 and SHELX-97 program packages [10,11]. Structure factors F_{obs} were obtained after averaging of equivalent Bragg

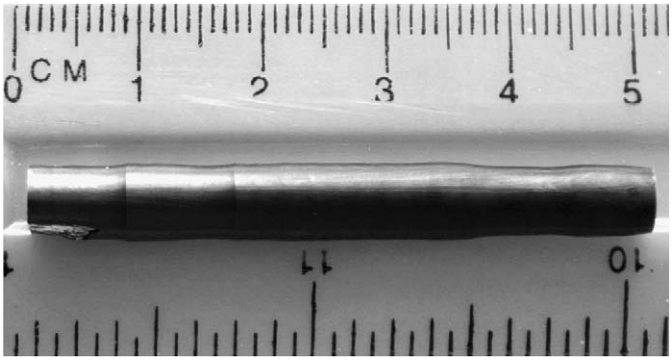

Fig. 2. View of obtained ScB_2 single crystal.

Table 1
Crystal data for ScB_2

Empirical formula	ScB_2
Formula weight	66.58
Crystal system	Hexagonal
Space group	*P6/mmm* (No. 191)
Unit cell dimensions (nm)	$a = 0.314820(3)$
	$c = 0.351483(5)$
Z	1
Cell volume (nm^3)	0.030169
Calculated density (g/cm^3)	3.670
Absorption coefficient	
(Mo $K\alpha$ 0.071073 nm)	$5.215\,mm^{-1}$
$F(000)$	31
Crystal size	$0.05 \times 0.07 \times 0.2\,mm^3$
θ range for data collection	$10^\circ \leqslant 2\theta \leqslant 55^\circ$
Empirical T_{min}/T_{max}	0.420/0.805
Index ranges	$-3 \leqslant h \leqslant 3,\ -3 \leqslant k \leqslant 3,\ -4 \leqslant l \leqslant 4$
Reflections collected	305
Number of unique reflections	27
R_{int}	0.072
Refinement method	Full-matrix least-squares on F^2
Number of free parameters	5
R_1	0.0191
wR_2	0.0474
Largest diff. peak and hole	0.169–0.236

intensities, which were corrected for Lorentz, polarization and absorption effects. Empirical absorption correction was made using the MULTISCAN program incorporated in WinGX package [12]. Lattice parameters were determined from powder data. Details of the crystallographic data and data collection parameters are given in Table 1. The Ball&Stick program [13,14] was used for structure drawing.

3. Results and discussion

An X-ray Laue pattern of the transversal cross-section of one of the grown ScB_2 single crystals is shown in Fig. 3. It can be seen that the grown sample is a single crystal with disorientation of blocks no more than 0.5° (the precision of the method) and deviation from the ⟨001⟩ axis of no more than 15°.

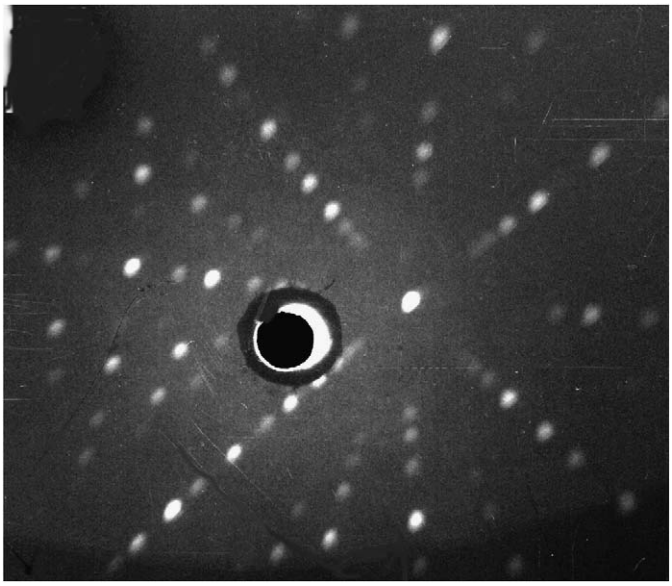

Fig. 3. The X-ray Laue pattern of ScB_2 single crystal.

The results of an atomic structure refinement according to the data of the single crystal X-ray analysis are presented in Table 2 (atomic co-ordinates and isotropic thermal parameters) and Table 3 (anisotropic thermal parameters). ScB_2 crystal structure belongs to AlB_2 type, sp. gr. *P6/mmm*, *R*-factors are $R_1 = 0.0191$, $wR_2 = 0.0474$. Sc atom occupies the special position (*a*) at the origin and boron atom occupies the special position (*d*) at $[\frac{1}{3}, \frac{2}{3}, \frac{1}{2}]$ (Fig. 4). Corresponding interatomic distances in the structure are as follows: Sc–B 0.25283(3) nm, B–B 0.18176(2) nm, Sc–Sc 0.314820(3) nm. The minimal distance in the structure is B–B one, which determines the rigidity of this structure.

The calculation of powder X-ray patterns by the Rietveld method were performed for precise lattice parameter determination. These calculations show that the lattice parameters for the polycrystalline synthesized powder and crushed single crystal are slightly different ($a = 0.314842(2)$ nm, $c = 0.350970(3)$ nm, $c/a = 1.115$ and $a = 0.314820(3)$ nm, $c = 0.351483(5)$ nm, $c/a = 1.117$, respectively). These results are in good agreement with published data ($a = 0.3148$ nm, $c = 0.3516$ nm [5]). The slight increase of c/a as well as the increase of c and the simultaneous reducing of a may be caused by some deformation of crystal lattice due to introduction of defects into the lattice during solidification. It may be related both with ScB_2 constitutional diagram features (for example deviation of composition from stoichiometry on the border solid–liquid) and different evaporation rate of individual components during ScB_2 single crystal growth.

Besides ScB_2 crystal structure refinement the obtained single crystals were used for determination of some basic physical properties such as real density, Young modulus, and Debye characteristic temperature.

The measured hydrostatic density of the ScB_2 single crystal is equal to $3.666\,g/cm^3$, the X-ray density is $3.670\,g/cm^3$

Table 2
Co-ordinates, thermal parameters and atomic arrangement for ScB_2 structure (sp. gr. *P6/mmm*)

Atom	Position	*x/a*	*y/b*	*z/c*	U_{iso}(Å^2)	Atomic arrangement
Sc	*a*	0	0	0	0.0016(3)	6Sc 12B
B	*d*	1/3	2/3	1/2	0.0034(9)	6Sc 3B

Table 3
Anisotropic thermal parameters (*u*, Å^2) for ScB_2

Atom	u_{11}	u_{22}	u_{33}	u_{12}	u_{13}	u_{23}
Sc	0.0016(4)	0.0016(4)	0.0015(5)	0.0008(2)	0	0
B	0.035(12)	0.035(12)	0.033(17)	0.0018(6)	0	0

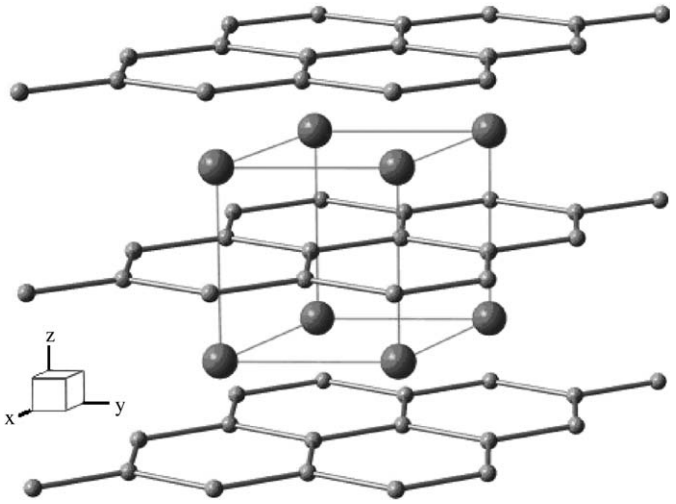

Fig. 4. The ScB_2 crystal structure.

for the polycrystalline powder and 3.665 g/cm^3 for the single crystal, which corresponds to the published density values [7]. The observed deviations are attributed to a possible deficiency of Sc in the single crystalline samples. Based on the hydrostatic density measurements the formula composition may be evaluated as $Sc_{0.99}B_2$ or $ScB_{1.96}$.

The own frequency of longitudinal oscillation of the ScB_2 single crystal rod was determined by the ultrasonic method and the Young's modulus value was calculated as 480 GPa.

With Koester's formula improved by Frantsevich [15] the ScB_2 Debye characteristic temperature was evaluated as 1020 K. This value is different from the earlier obtained low-temperature calorimetry Debye temperature 693 K [7]. Such situation was characteristic for RE borides [16] as the existence of two sublattices—metal and boron—was not taken into account. The sublattice combination results in complex phonon spectra of borides and the Debye temperature is determined by the rigid boron sublattice first of all. The consent with the MgB_2 Debye temperature equal to 930 K [17] confirmed this conclusion as both compounds have the same crystal structure and the close lattice parameters [18].

4. Conclusion

In the present paper the possibility of ScB_2 single crystal growth has been shown. These crystals and powder samples were used for refinement of the ScB_2 crystal structure and evaluation of its fundamental characteristics. ScB_2 crystallizes in AlB_2 structure type, sp. gr. *P6/mmm*, No. 191 ($R_1 = 0.0191$, w$R_2 = 0.0474$), lattice parameters are follow: $a = 0.314820(3)$ nm, $c = 0.351483(5)$ nm, $c/a = 1.117$. Comparison of the calculated X-ray (3.670 g/cm^3) and measured hydrostatic (3.666 g/cm^3) densities indicates some deficiency of the grown ScB_2 single crystals. The measured density corresponds to the $Sc_{0.99}B_2$ or $ScB_{1.96}$ composition. From ultrasound measurements the ScB_2 Young modulus is evaluated as 480 GPa and Debye characteristic temperature as 1020 K.

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