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Growth of Single Crystals in the Systems with *R*–Rh–B and *R*–Rh–B–C (*R* = Rare Earth Element) from Molten Copper Flux

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A slow cooling method using molten copper as a flux was applied for crystal growth in the systems *R*–Rh–B and *R*–Rh–B–C (*R* = rare earth element). *Ternary borides*: Single crystals of RRh_3B_2 (*R* = Gd, Dy, Er, Tm, Yb, and Lu), RRh_4B_4 (*R* = Sm, Dy, Er, and Tm), and RRh_3B (*R* = Sm, Gd, Er, and Tm) were successfully obtained. Crystals of $ErRh_3B_2$ are hexagonal rectangulars belonging to the monoclinic system $a = 0.5355(1)$ nm, $b = 0.9282(1)$ nm, $c = 0.3102(1)$ nm, and $\beta = 90.89(3)^\circ$. A super lattice appears along both the *a* and the *c* axes with the periods of 3*a* and 6*c*, respectively. Single crystals of $ErRh_4B_4$ were obtained as rectangulars with a primitive tetragonal structure: $a = 0.5292(4)$ nm and $c = 0.7379(3)$ nm. Single crystals of $ErRh_3B$ were extracted as cubes. $ErRh_3B$ is cubic with $a = 0.41466(1)$ nm. $PrRh_{4.8}B_2$ crystallized as hexagonal plates. This new compound is orthorhombic: $a = 0.9697(4)$ nm, $b = 0.5577(2)$ nm, and $c = 2.564(3)$ nm. *Quaternary borocarbides*: Single crystals of the new tetragonal compounds of RRh_2B_2C have been obtained for *R* = Er and Gd as thin plates. Lattice parameters of e.g., $ErRh_2B_2C$, are $a = 0.36848(2)$ nm and $c = 1.05520(3)$ nm. © 1997 Academic Press

1. INTRODUCTION

The crystal chemistry of *R*–Rh–B and *R*–Rh–B–C (*R* = rare earth element) systems has received considerable attention from researchers in the fields of magnetism and superconductivity (1–6). Physical properties of these borides and borocarbides have been measured by using polycrystalline samples. In some cases, physical properties were observed by the presence of impurity phases in the polycrystalline samples. Thus growth and investigation of single crystals of each compound are highly desirable. However, single crystal growth of these multicomponent borides and borocarbides is difficult because their structure seems to be unstable at high temperature in spite of their high melting points.

In this paper we report the growth of the single crystals by slow cooling using molten copper as a flux (solvent). Crystal structure and some properties of the single crystals obtained are also presented.

2. EXPERIMENTAL

The raw materials used were small pieces of 99.9% *R*, 99.9% Rh powder, 99.9% B powder, and 99.999% C powder. They were weighed in stoichiometric proportions to give the desired product and mixed with 99.999% Cu powder in a weight ratio between 1:8 and 1:10. The mixture was placed in a dense alumina crucible,which was inserted in a vertical electric furnace. Purified He gas was flowing in the furnace as a protecting atmosphere against oxidation. Figure 1 shows the schematic arrangement of the growth apparatus. The mixture was heated at a rate of 400°C hr^{-1} and held at 1350–1400°C for 10 hr. The solution was cooled down to 1080°C at a rate of 1–5°C hr^{-1} and then furnace cooled back to room temperature. The crystals were separated by dissolving Cu in dilute nitric acid.

The morphology and the impurity of the crystals were investigated by optical microscopy, scanning electron microscope (SEM), and electron probe micro-analysis (EPMA). Chemical composition was analyzed by EPMA and inductive coupled plasma atomic emission spectrometry (ICP-AES) after fusion of the samples with NH_4HSO_4. Crystal structure determination was carried out using an X ray powder diffractometer, a precession camera, and a four-circle X ray diffractometer with graphite monochromatized Mo$K\alpha$ radiation.

3. RESULTS AND DISCUSSION

3.1. Ternary Borides R–Rh–B

Three compounds RRh_3B, RRh_3B_2, and RRh_4B_4 were essentially extracted from the solution. Crystal structure and physical properties concerning these three compounds are as follows. $ErRh_3B_2$ is obtained as hexagonal prisms of silvery metallic luster with maximum dimensions of

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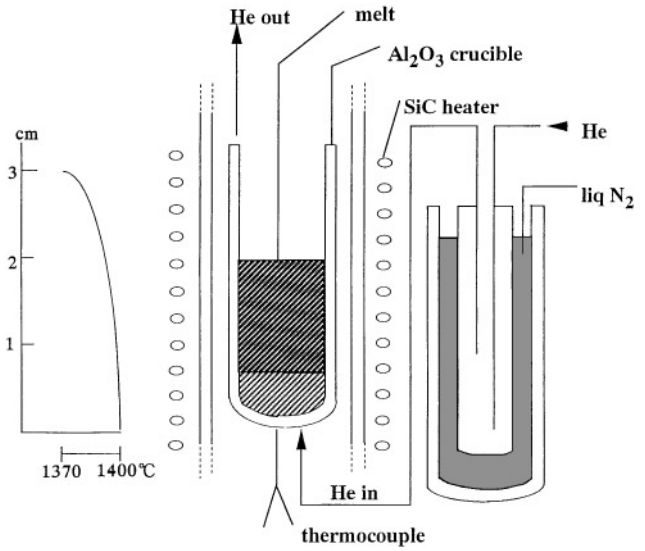

FIG. 1. Schematic arrangement of the crystal growth apparatus.

TABLE 1
Crystallographic Data of the Single Crystals {Er, Pr}–Rh–B and $ErRh_2B_2C$

Chemical formula	$PrRh_{4.8}B_2$[a]	$ErRh_3B_2$	$ErRh_4B_4$	$ErRh_3B$	$ErRh_2B_2C$
Crystal system	Orthorhombic	Monoclinic	Tetragonal	Cubic	Tetragonal
Structure type	Modified-$CeCo_3B_2$	$ErIr_3B_2$	$CeCo_4B_4$	Inverse-perovskite	$ThCr_2Si_2$
Space group	Fmmm	C2/m	$P4_2/nmc$	Pm3m	I4/mmm
Unit cell parameter					
a (nm)	0.9697(4)	0.5355(1)	0.5292(4)	0.41466(1)	0.36848(2)
b (nm)	0.5577(2)	0.9282(1)			
c (nm)	2.564(3)	0.3102(1)	0.7379(3)		1.05520(3)
β (°C)		90.89(3)			
Formula units per unit cell	12	2	2	1	2

[a] Formula unit determined by the structure analysis.

$1 \times 1 \times 3\,mm^3$ (Fig. 2). Chemical analysis shows that the atomic ratio of the compound corresponds to Er:Rh:B = 1:3:2. No Cu-containing phase has been obtained by chemical analysis and EPMA. $ErRh_3B_2$ belongs to the monoclinic system isomorphous with the $ErIr_3B_2$ structure, a distortion derivative of the hexagonal $CeCo_3B_2$-type (see Table 1). For a projection of the structure of $ErRh_3B_2$ along the *c*-direction see Fig. 2. Precession photographs reveal a super lattice along both the *a* and the *c*-axes with the periods of 3*a* and 6*c*, respectively. The details of the super structure are being investigated (7). According to a X ray

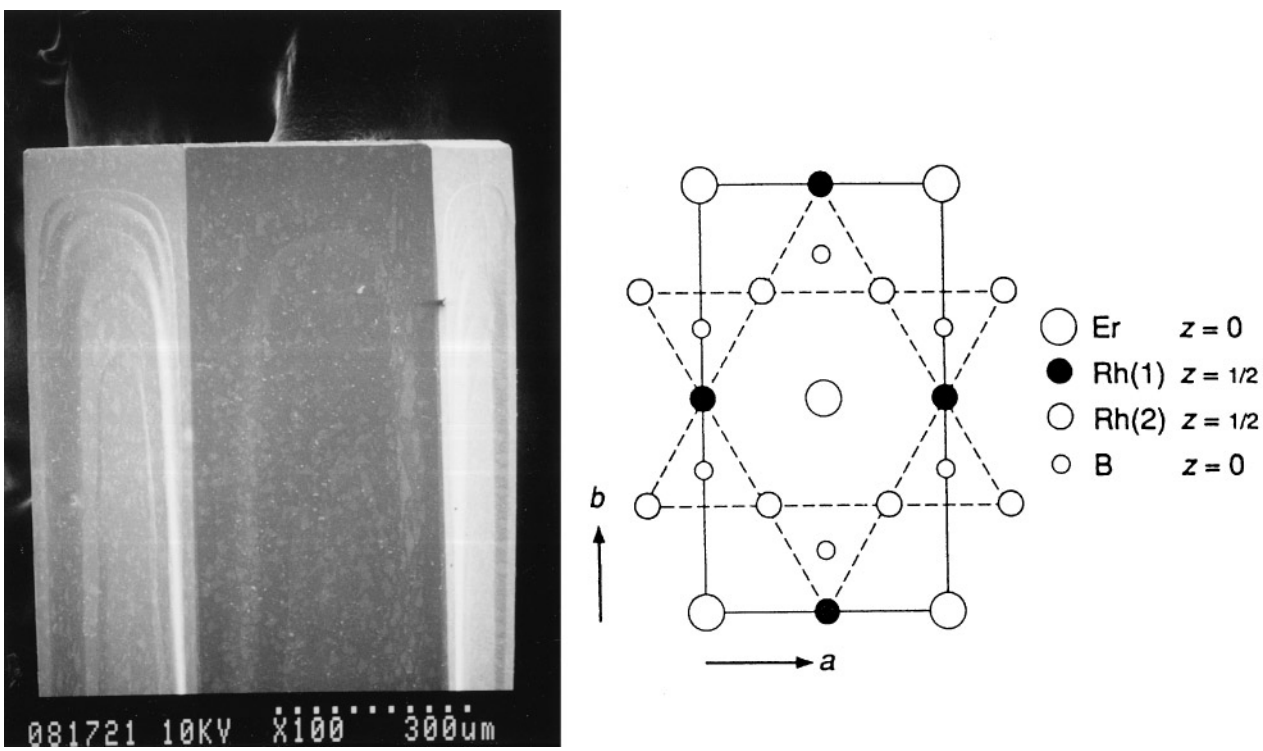

FIG. 2. Scanning electron micrograph of a hexagonal rectangular $ErRh_3B_2$ and projection of the structure of $ErRh_3B_2$ along the *c*-direction.

photoelectron spectroscopic (XPS) study, significant evidence of weak metal–boron bonding was obtained (8). This indicates that boron is an electron donor in this compound. $ErRh_3B_2$ shows a strong magnetic anisotropy and orders ferromagnetically at 27 K with its easy axis along the *c*-direction. Electrical resistivity along the *c*-direction shows a monotonic decrease with decreasing temperature. The resistivity at room temperature is about 50 $\mu\Omega\cdot$cm, and the residual resistivity ratio (RRR) = $\rho(270\text{ K})/\rho(10\text{ K})$ is about 4.

At $T_c = 27$ K, a small hump of the resistivity indicates the ferromagnetic transition. At present, single crystals of RRh_3B_2 were obtained for R = Gd, Dy, Er, Tm, Yb, and Lu using this growth method. Other single crystals of RRh_4B_4 were obtained for R = Sm, Dy, Er, and Tm as rectangular (Fig. 3). $ErRh_4B_4$ has primitive tetragonal structure (see

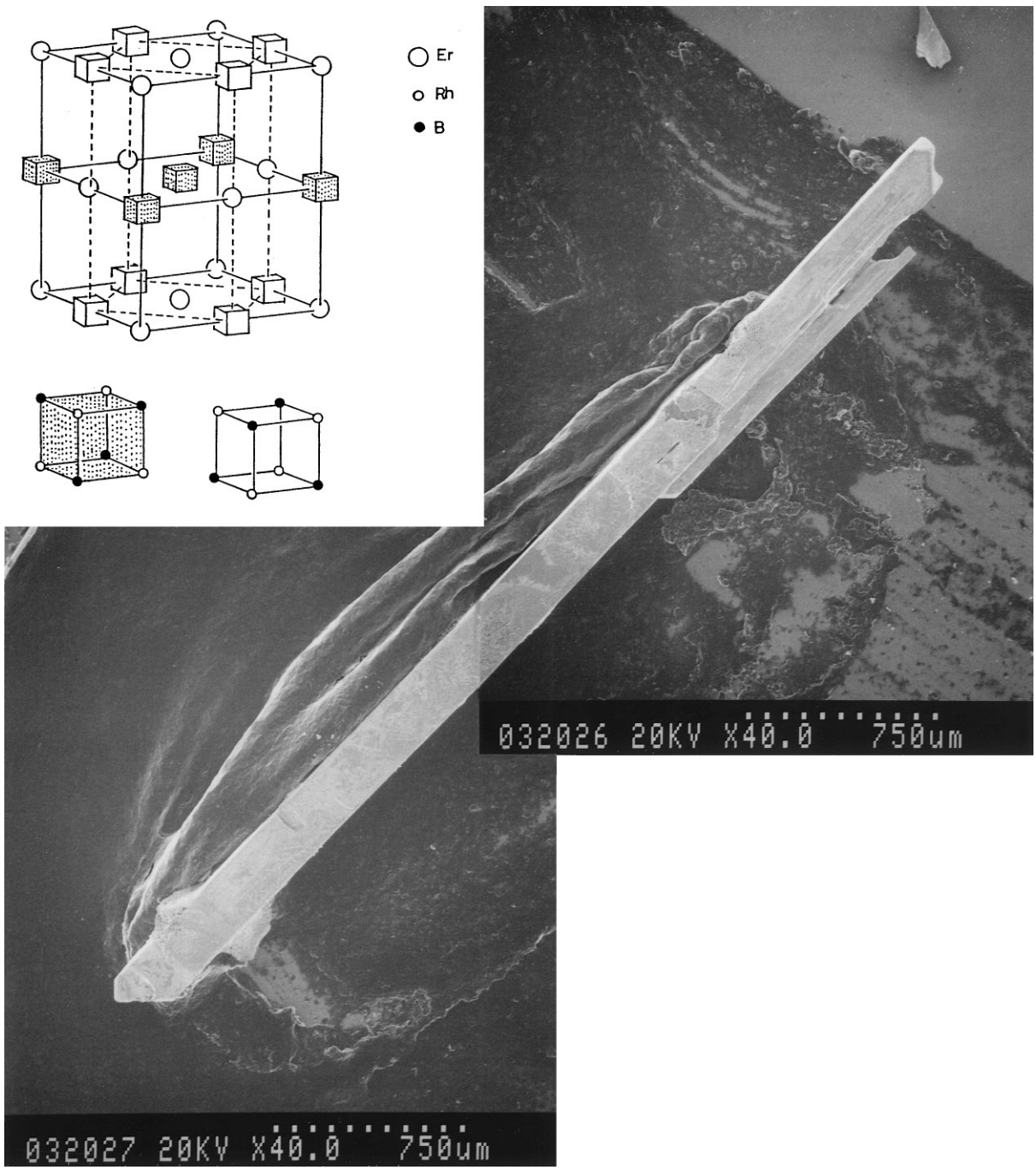

FIG. 3. Scanning electron micrograph of a rectangular $ErRh_4B_4$ and its crystal structure (9).

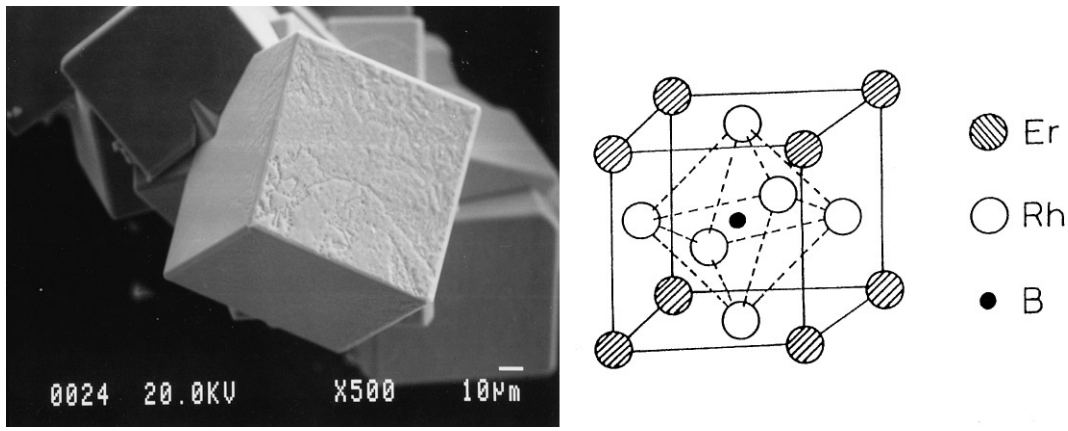

FIG. 4. Scanning electron micrograph of a cube-like $ErRh_3B$ and its crystal structure.

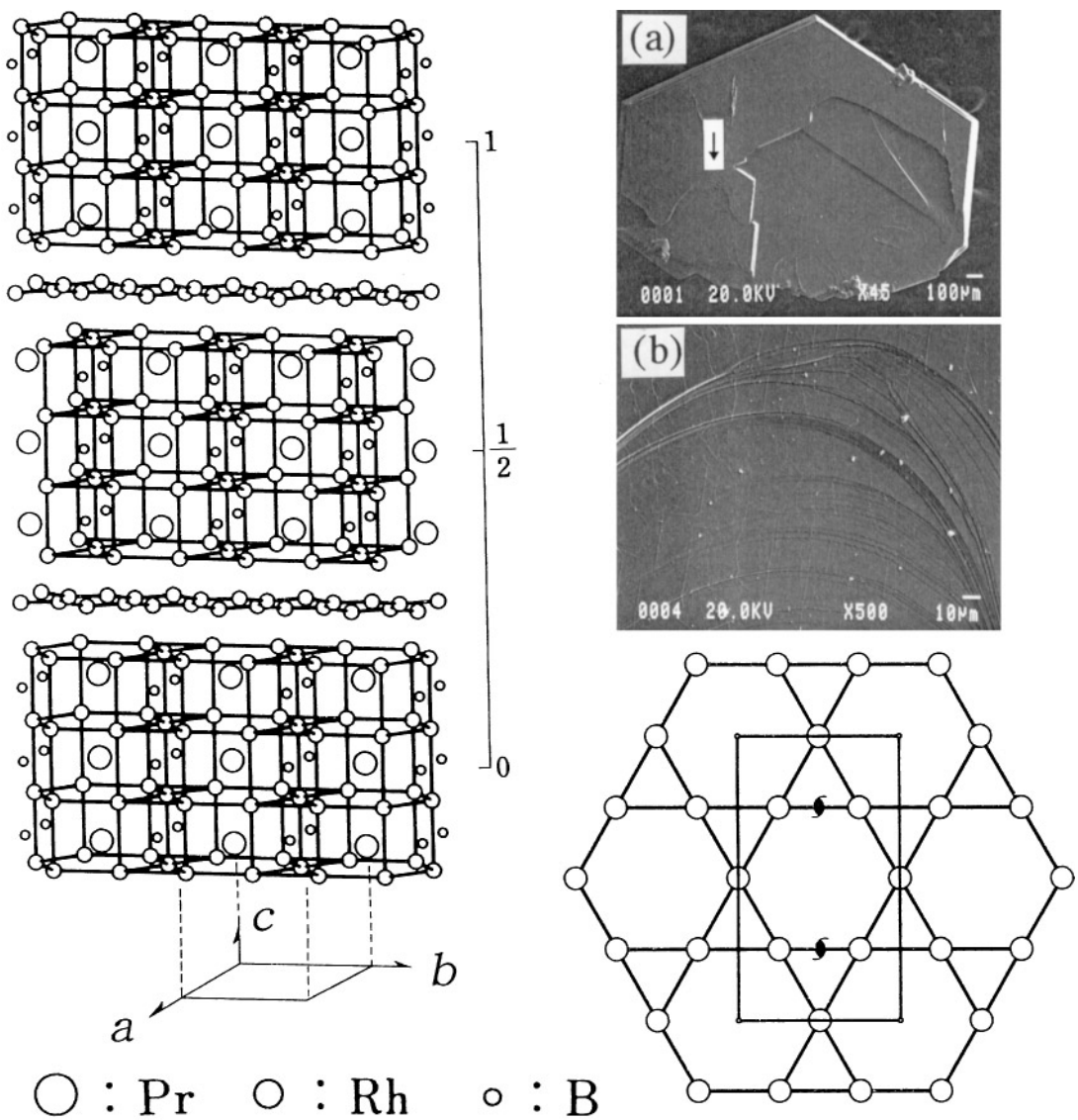

FIG. 5. (a) Scanning electron micrographs of a hexagonal plate of $PrRh_{4.8}B_2$. (b) An enlargement of the corresponding region indicated by an arrow in (a) revealing the terrace growth. Crystal structure of $PrRh_{3.8}B_2$ also presented.

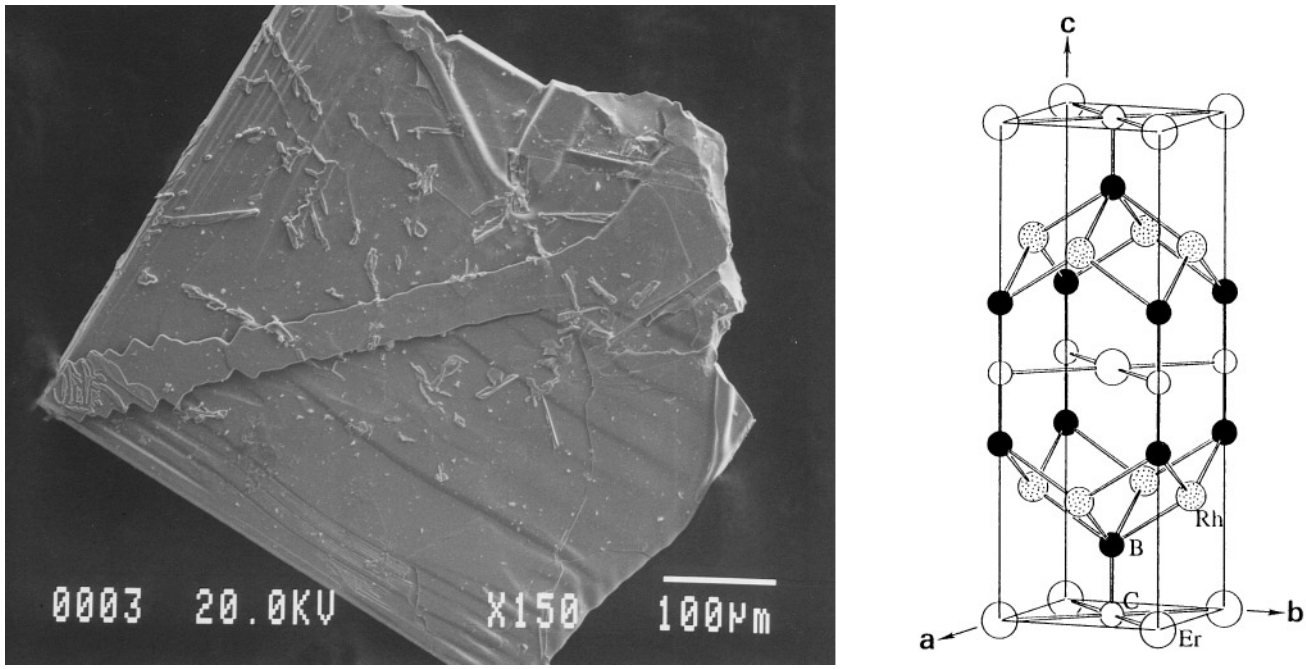

FIG. 6. Scanning electron micrograph of a square plate of $ErRh_2B_2C$ and its crystal structure.

Table 1) shown in Fig. 3 (9). Microhardness on the (100) and (110) planes of $ErRh_4B_4$ crystals is in the range of 10.9–11.3 GPa (10). The oxidation of $ErRh_4B_4$ crystals begins at 690°C (10). A superconducting transition is found at 8.55 K with the transition width $\Delta T_{c1} = 30$ mK. The reentrant transition temperature T_{c2} is 0.84 K on cooling and 0.90 K on heating. The residual resistivity ratio RRR = R (300 K)/R ($\sim T_{c1}$) is 7.8. Crystals of $ErRh_3B$ are extracted as cubes (Fig. 4). It has cubic structure with $a =$ 0.41466 (1) nm. Crystal structure of the $ErRh_3B$ is shown in Fig. 4. This compound exhibits normal paramagnetic behavior. At present, single crystals of RRh_3B were obtained for $R =$ Sm, Gd, Er, and Yb.

A new compound only obtained for $PrRh_{4.8}B_2$ (Fig. 5a) is extracted in the form of hexagonal plates. Figure 5b is an enlargement of the region indicated by an arrow in Fig. 5a; a terrace which originated from growth steps is observed in this region. This type of surface morphology of flux-grown crystals has been observed not only for $PrRh_{4.8}B_2$ but also for $ErRh_3B_2$. The crystal structure of orthorhombic $PrRh_{4.8}B_2$ (see Table 1) is shown in Fig. 5 (6). An antiferromagnetic phase transition is observed at 7 K. The magnetic easy axis lies in the *a–b* plane.

3.2. *Quaternary Borocarbides R–Rh–B–C*

Single crystals of RRh_2B_2C were obtained for $R =$ Gd (11) and Er. Figure 6 shows the single crystals of $ErRh_2B_2C$ with black metallic luster; the maximum size is obtained of about $1.0 \times 1.0 \times 0.02$ mm^3. As shown in Table 1 and Fig. 6, this compound belongs to a tetragonal system and seems to be a derivative of the $ThCr_2Si_2$ type. The electrical resistivity parallel to the *a–b* plane decreases monotonically with decreasing temperature, but no superconductivity is observed down to 1.5 K.

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