論文 **Original Paper**

Crystal Growth and Properties of $ErRh_3B_2$

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Abstract: Single crystals of ternary boride $ErRh_3B_2$ have been successfully grown from copper solution by slow cooling method. Crystals of $ErRh_3B_2$ are hexagonal rectangulars belonging to the monoclinic system isomorphous with $ErIr_3B_2$: space group $C2/m$ with the cell dimensions $a=0.5355(1)$ nm, $b=0.9282(1)$ nm, $c=0.3102(1)$ nm, and $\beta=90.89(3)^\circ$. A superlattice appears along both the a- and c- axes with the periods of $3a$ and $6c$, respectively. $ErRh_3B_2$ exhibits metallic behaviour from room temperature down to 0.5 K. The electrical resistivity for perpendicular to the c-direction is about 3 times larger than that for parallel to the c-direction. Magnetization measurements show considarable anisotropy. At $Tc=27$ K, the data indicates ferromagnetic order with the spins directed parallel to the c-axis. Micro-Vickers hardness for this layer structure compound indicates that the bonding strength of the intraplane is larger than that of the interplane.

Keywords: $ErRh_3B_2$, crystal structure, electrical resistivity, magnetization, micro-Vickers hardness

1. Introduction

The crystal chemistry of R-Rh-B(R = rare earth element) system has received considerable attention from researchers in the fields of magnetism and superconductivity[1,2]. Physical propeties of these borides 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 desireble.

In this paper we report the growth of the single crystals of $ErRh_3B_2$ by slow cooling using molten copper as a flux (solvent). Crystal structure, electrical resistivity, magnetic properties and micro-Vickers hardness are presented.

2. Experimental details

The raw materials used were small pieces of 99.9% Er, 99.9% Rh powder, 99.9% B powder. They were weighed in stoichiometric proprtion of Er : Rh : B = 1 : 3 : 2 and mixed with 99.999% Cu powder in a weight ratio 1 : 10. The mixture was placed in a dense alumina crucible, which was inserted in a vertical electric furnace. Ar gas was flowing in the furnace as a protecting atmosphere against oxidation. The mixture was heated at a rate of 400° Ch^{-1} and held at 1350° C for 10 h. The solution was cooled down to 1100° C at a rate of 5° Ch^{-1} and then furnace cooled 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 Inductive Coupled Plasma Atomic Emission Spectroscopy (ICP-AES). 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. The electrical resistivity of the crystal was measured by means of a DC four probe method from 0.5 K to room temperature. The magnetic susceptibility measurements were performed using a commercial SQUID magnetometer (Quantum Design Inc., MPMS-5) as a function of temperature. The electrical resistivity and magnetic susceptibility measurements were performed both parallel and perpendicular to the c-axis. The micro-Vickers hardness for the crystal was measured at room temperature. A load of 300 g was applied for 15 s and 10 impressions were recorded for the crystal. The obtained values were averaged and the experimental error was estimated.

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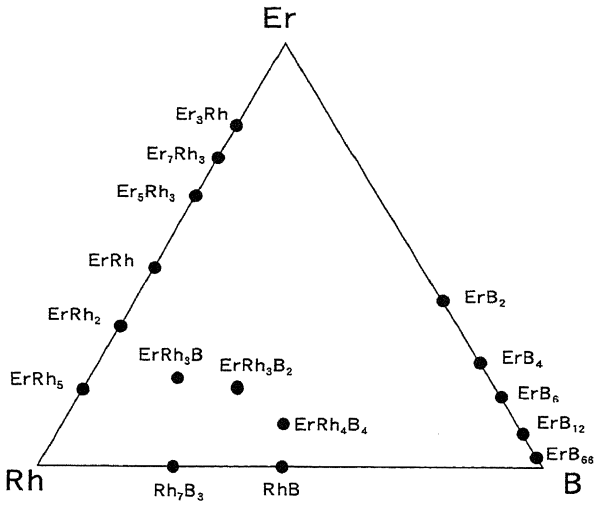

Fig. 1 Tentative phase diagram in the system of Er-Rh-B.

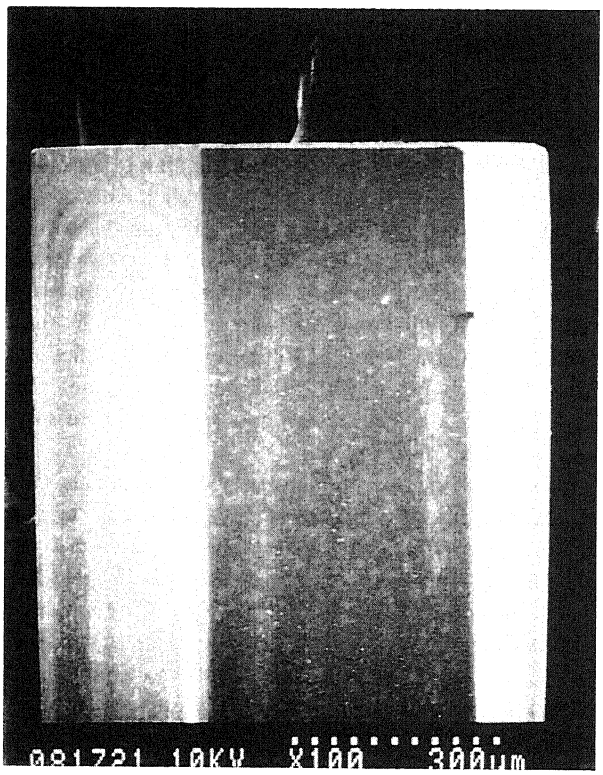

Fig. 2 Single crystal of $ErRh_3B_2$.

3. Results and discussion

$ErRh_3B_2$ exists at rhodium-rich portion in the Er-Rh-B tentative ternary phase diagram as shown in Fig. 1[3]. The single crystals of $ErRh_3B_2$ were successfully grown by the flux method using molten copper as a solvent[4]. A hexagonal prism of $ErRh_3B_2$ maximum dimensions $1 \times 1 \times 1$ mm^3 with silver metallic luster as shown in Fig. 2 were extracted. No evidence has been obtained of the presence of a Cu-containing phase in the crystal, as concluded from

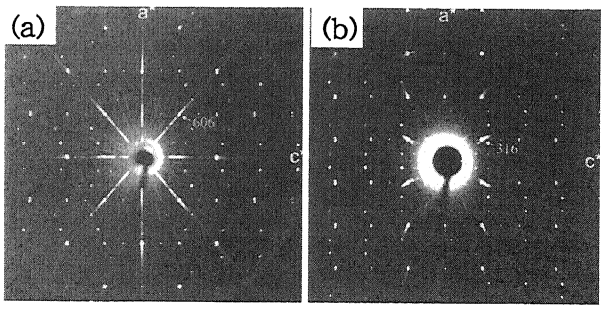

Fig. 3 Zero layer (a) and first layer (b) X-ray precession photographs of the $ErRh_3B_2$ crystal in [010] zone axis.

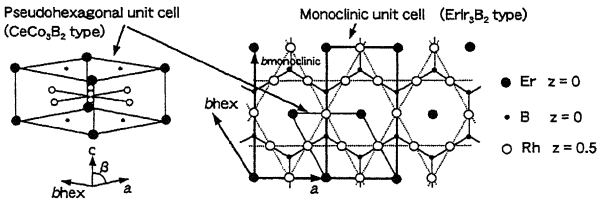

Fig. 4 Crystal structure of RT_3B_2 (R = rare earth element, T = transition metal) compounds showing the relationship between the hexagonal $CeCo_3B_2$ type structure and the monoclinic $ErIr_3B_2$ type structure.

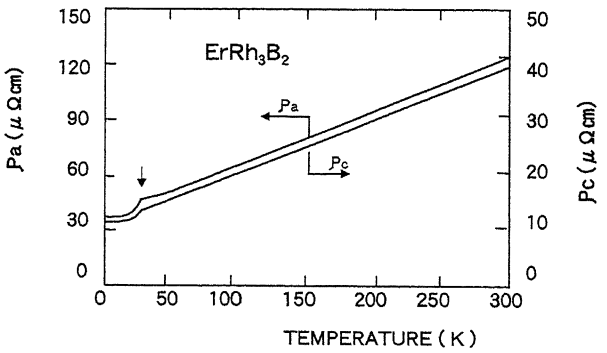

Fig. 5 Temperature dependence of the electric resistivity parallel and perpendicular to the c-axis of $ErRh_3B_2$.

chemical analysis and EPMA of as-grown and fractured surfaces. Chemical analysis for the crystals shows that the chemical composition of the compound corresponds almost to an atomic ratio Er : Rh : B = 1 : 3 : 2. The crystal structure investigation of the single crystal $ErRh_3B_2$ shows that it belongs to the monoclinic system isomorphous with an $ErIr_3B_2$ structure (space group; $C2/m$)[5], which is slightly distorted from the hexagonal $CeCo_3B_2$ type-structure within the basal plane; the lattice parameters are a = 0.5355(1) nm, b = 0.9282(1) nm, c = 0.3102(1) nm, and β = 90.89(3)°. As shown in Fig. 3, a superlattice appears along both the a and c axes with the periods of $3a$ and $6c$, respectively[6]. Figure 4 shows crystal structure of RT_3B_2 (R = rare earth element, T = transition metal) compounds showing the relationship between the

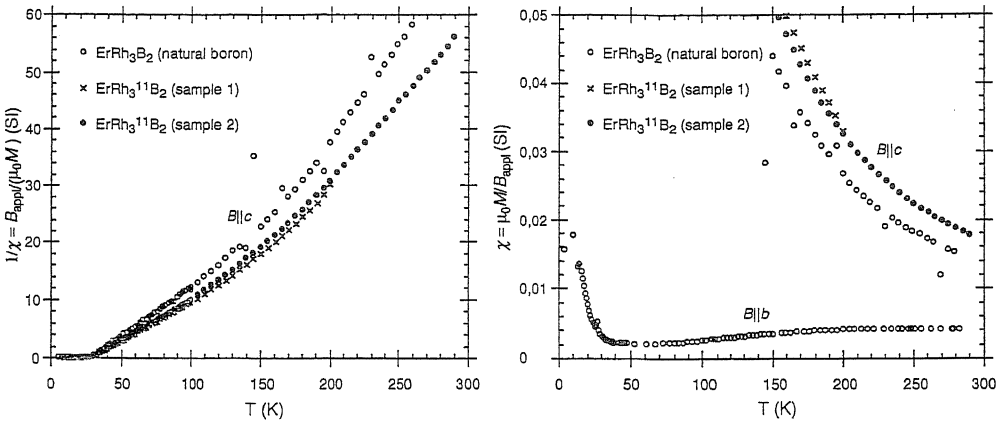

Fig. 6 Magnetic data for parallel and perpendicular to the c-axis of $ErRh_3B_2$. The inverse susceptibility $1/\chi = B_{appl}/\mu_0$ M is shown on the left and the susceptibility $\chi = \mu_0 M/B_{app}$ in low magnetic field on the right.

hexagonal $CeCo_3B_2$ type structure and the monoclinic $ErIr_3B_2$ type structure.

Fig. 5 shows the temperature dependence of the electric resistivity of $ErRh_3B_2$ crystal[7-9]. Sample measured exhibits metallic behaviour from room temperature down to 0.5 K. The data indicate some magnetic order below 27 K. No superconductivity appears at the lowest temperature. The results of the susceptibility measurements[10,11] in low magnetic field are shown in Fig. 6. The data indicate ferromagnetic order below $Tc = 27$ K but show considerable anisotropy. The c-axis susceptibility (κ_c) follows principally a Curie-Weiss behaviour. The κ_c data in the high temperature region ($T > 200$ K) give effective moments $\mu_{eff} = 9.0\ \mu_B$ in comparison with the expected value of $9.59\ \mu_B$ for the free ion Er^{3+}. The b-axis susceptibility (κ_b) is considerably smaller than κ_c and decreases with decreasing temperature until a broad minimum at 60 K is reached. Below 40 K κ_b increases rapidly with decreasing T and its curvature has an inflection point at Tc. The highly anisotropic magnetic properties of $ErRh_3B_2$ may be explained by the short Er-Er distance along the c-axis, which is actually shorter than the radius sum. This short distance would lead to some delocalization.

The value of micro-Vickers hardness for (001) and (100) planes of the $ErRh_3B_2$ crystal is 11.7 ± 0.3 GPa and 10.7 ± 0.2 GPa, respectively. This indicates that the bonding strength of the intraplane is larger than that of the interplane[8,9].

4. Conclusion

The single crystals of ternary boride $ErRh_3B_2$ were successfully grown by the flux method using molten copper as a solvent. Idiomorphic single crystals with silver metallic luster, whose shape is a hexagonal prism with maximum dimensions $1 \times 1 \times 1$ mm^3, were extracted from the solution. $ErRh_3B_2$ belongs to a monoclinic system isomorphous with $ErIr_3B_2$: space group $C2/m$, $a = 0.5355(1)$ nm, $b = 0.9282(1)$ nm, $c = 0.3102(1)$ nm, and $\beta = 90.89(3)°$. A superlattice appears along both the a- and c-axes with the periods of $3a$ and $6c$, respectively. $ErRh_3B_2$ exhibits metallic behaviour and the electrical resistivity of a-direction is about 3 times larger than that of c-direction. The results of the magnetic susceptibility measurements indicate ferromagnetic order below $Tc = 27$ K but show considerable anisotropy. The value of micro-Vickers hardness for (001) plane is larger than (100) plane; this indicates that the bonding strength of the intraplane is larger than that of the interplane.

Acknowledgments

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