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Synthesis, boron-nonstoichiometry and hardness of perovskite-type rare earth rhodium borides RRh_3B_x (R = La, Gd, Lu and Sc)

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Abstract

Rare earth ternary borides, RRh_3B_x (R = La, Gd, Lu and Sc) have been synthesized by arc melting method. Borides RRh_3B_x (R = La, Gd, Lu and Sc) have perovskite-type cubic structure: space group *Pm*3*m*; *Z* = 1. The lattice parameters *a* of the stoichiometric RRh_3B for R = La, Gd, Lu and Sc are 0.4251(1), 0.4183(1), 0.4126(1) and 0.4080(1) nm, respectively. $LaRh_3B_x$ does not have boron-nonstoichiometry as $x = 0$. In $GdRh_3B_x$ and $LuRh_3B_x$, boron- nonstoichiometry ranges between $0.55 \leqq x \leqq 1$ and $0.30 \leqq x \leqq 1$, respectively. The boron-nonstoichiometry range is the widest, $0 \leqq x \leqq 1$, for R = Sc. Boron-nonstoichiometry increases with decreasing atomic radius of R. The microhardness of the stoichiometric RRh_3B for R = La, Gd, Lu and Sc is 4.2 ± 0.1, 6.8 ± 0.1, 7.7 ± 0.5 and 9.9 ± 0.1 GPa, respectively. As a result, microhardness increases with decreasing atomic size of R in RRh_3B; R is positioned at the eight corners of the cube in the perovskite-type structure. Thus, hardness is strongly dependent on R element. The hardness changes almost linearly with boron concentration *x* for R = Gd and Lu in RRh_3B_x, while no linear dependency is found for R = Sc. Ab initio calculations have been performed to obtain the equilibrium lattice constants and the bulk moduli. The calculated lattice constants are in excellent agreement with experimental results.

Keywords: RRh_3B_x (R = La, Gd, Lu and Sc); Perovskite-type phase; Microhardness; Boron-nonstoichiometry

1. Introduction

A large number of perovskite-type oxides have been studied because of their interesting features, including superconducting transitions, insulating–metallic transitions, ion conduction characteristics, dielectric properties and ferroelasticity [1–5]. Studies on non-oxide perovskite-type compounds such as the ternary borides RRh_3B (R = rare earth) [6–8], on the other hand, have been comparatively rare. Systematic investigation of the synthesis and properties of non-oxide perovskite-type compounds is necessary.

The aim of the present study is to synthesize perovskite-type rare earth rhodium borides RRh_3B_x and to find the nonstoichiometry range of boron and to investigate the dependency of hardness on rare earth atoms and boron-nonstoichiometry. In this study, La, Gd, Lu and Sc are selected as R elements, where La, Gd, Lu are the first, middle and

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the last elements of the lanthanides. Sc is located in the fourth row and the third column in the periodic table. The atomic sizes with coordination number 12 for La, Gd, Lu and Sc are 0.188, 0.179, 0.172 and 0.164 nm, respectively. Thus, the atomic radius decreases in the order of La, Gd, Lu and Sc.

2. Experimental details

The samples were prepared by the arc-melting method using small pieces of 99.9% R, 99.9% Rh powder and 99.8% B powder as raw materials. They were weighed at objective atomic ratios. Mixtures of the starting materials, about 2 g of each, were melted for 3 min in an argon arc plasma flame using a dc power source at 20 V and 100 A. The samples were turned over and were remelted three times under the same conditions. The synthesized samples were wrapped in tantalum foil and annealed at 1573 K for 20 h in vacuo to ensure homogeneity and accurate comparison of results.

For the chemical analysis, the samples were fused using $NaHSO_4$ powder as a flux reagent, and then the resulting material was dissolved in HCl. The chemical composition of each solution was analyzed by induction-coupled plasma atomic emission spectrometry (ICP-AES) using Zn as the internal standard. The crystal structures and lattice parameters of the phases were examined by the X-ray diffraction (XRD) method using Cu Kα as a radiation source. The microhardness of the samples was measured at room temperature using a square-base diamond pyramid as an indentor. A load of 300 g was applied for 15 s and 10 impressions were recorded for each sample. The obtained values were averaged and the experimental error was estimated.

3. Results and discussion

All the synthesized samples have a silvery metallic luster. Based on the results of chemical analyses, the chemical compositions of the obtained samples correspond almost to the atomic ratio of the starting compositions. In addition, no evidence of pollution of the electrodes (W) and the hearth (Cu) by the arc melting method is noted.

The crystal structure analysis reveals that all RRh_3B_x have perovskite-type cubic structure: space group $Pm3m$; $Z = 1$. As shown in Fig. 1, R is positioned at the eight corners of the cube, Rh occupy face-centered positions and B is at the center of the cube. Fig. 2 shows the X-ray diffraction patterns for stoichiometric RRh_3B (R = La, Gd, Lu and Sc). With decreasing size of the rare earth atoms, XRD peaks are shifted to the higher angle side. The lattice parameters of RRh_3B are listed in Table 1; the values of a for La, Gd, Lu and Sc are 0.4251(1), 0.4183(1), 0.4126(1) and 0.4080(1) nm, respectively. The value of lattice parameter a decreases with decreasing atomic size of R in RRh_3B.

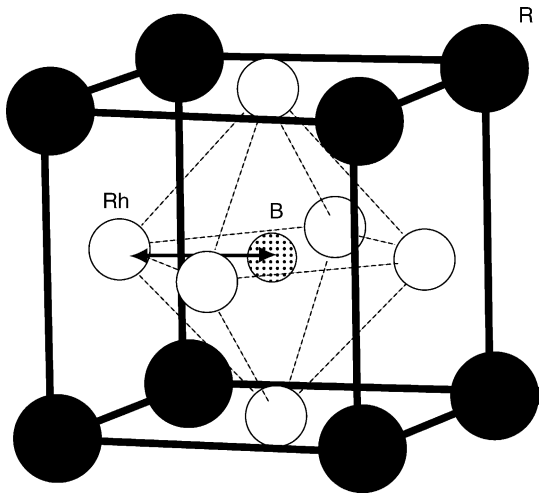

Fig. 1. Arrangement of atoms in the perovskite-type RRh_3B (R = La, Gd, Lu and Sc). The large black, large open and small gray circles represent R, Rh and B atoms, respectively. An arrow indicates the atomic distance between Rh and B in the octahedral framework of Rh_6B.

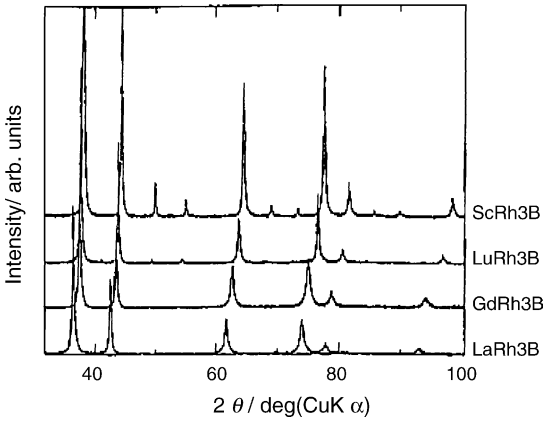

Fig. 2. Powder XRD patterns for RRh_3B (R = La, Gd, Lu and Sc).

By varying values of x, the boron-nonstoichiometry and the resulting change in the lattice parameter were studied. For $LaRh_3B_x$, the perovskite-type compound does not have boron-nonstoichiometry, which indicates that $x = 1$. Meanwhile, the B-deficient compounds can be obtained for R = Gd, Lu and Sc. In $GdRh_3B_x$ and $LuRh_3B_x$, boron-nonstoichiometry ranges between $0.55 \leqq x \leqq 1$ and $0.3 \leqq x \leqq 1$, respectively. A second phase appears $x < 0.55$ and $x = 0.33$, respectively. $ScRh_3B_x$ has a wide boron-

Table 1
Lattice parameter a, atomic distance between Rh and B, and microhardness of the RRh_3B (R = La, Gd, Lu and Sc)

RRh_3B R	Lattice parameter, a (nm)	Atomic distance between Rh and B (nm)	Hardness (GPa)
La	0.4251(1)	0.2126	4.2 ± 0.1
Gd	0.4183(1)	0.2092	6.8 ± 0.1
Lu	0.4126(1)	0.2063	7.7 ± 0.5
Sc	0.4080(1)	0.2040	9.9 ± 0.1

Table 2
Boron-nonstoichiometry in the RRh_3B_x (R = La, Gd, Lu and Sc)

RRh_3B_x R	Boron-nonstoichiometry range of x	Atomic radius of R (nm)	Electronegativity of R
La	$x = 1$	0.188	1.1
Gd	$0.55 \leqq x \leqq 1$	0.180	~1.15
Lu	$0.3 \leqq x \leqq 1$	0.174	1.2
Sc	$0 \leqq x \leqq 1$	0.164	1.3

nonstoichiometry as $0 \leqq x \leqq$ l. The aforementioned results are listed in Table 2. As shown in Table 2, boron exhibits no nonstoichiometry in the case of R = La. La has the largest atomic radius among all the R. The boron-nonstoichiometry range is the widest for R = Sc which has the smallest atomic radius among them. The present authors are strongly interested in one of the important mechanical functions of borides [9,10]. Fig. 3 shows the relationship between boron concentration x and the hardness of RRh_3B_x. The hardness changes almost linearly between $0.55 \leqq x \leqq 1$ for R = Gd. Relationship between boron concentration x and hardness is complex for R = Lu and Sc. As listed in Table 1, the values of the microhardness for stoichiometric RRh_3B are in the range of 4–10 GPa; the values of the microhardness for La, Gd, Lu and Sc being 4.2 ± 0.1, 6.8 ± 0.1, 7.7 ± 0.5 and 9.9 ± 0.1 GPa, respectively. Fig. 4 shows the microhardness of stoichiometric RRh_3B (R = La, Gd, Lu and Sc) as a function of lattice parameter *a.* The microhardness of RRh_3B is strongly dependent on lattice parameter a of the compound. Hardness increases with decreasing lattice parameter *a.* When lattice parameter a decreases, as shown in Fig. 1, the distance between R atoms is shortened. In addition, the distance between Rh and B atoms in the octahedral framework of Rh_6B is also shortened. The microhardness became larger with the contraction of the volume of the Rh_6B octahedron. As a result, microhardness increases with decreasing atomic

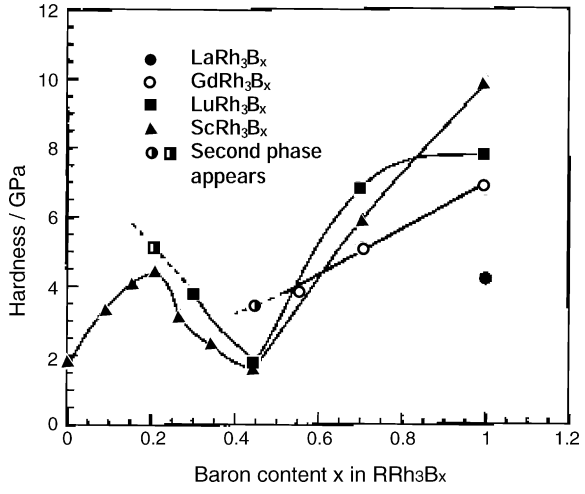

Fig. 3. Microhardness for RRh_3B_x (R = La, Gd, Lu and Sc) as a function of boron concentration x in the compound.

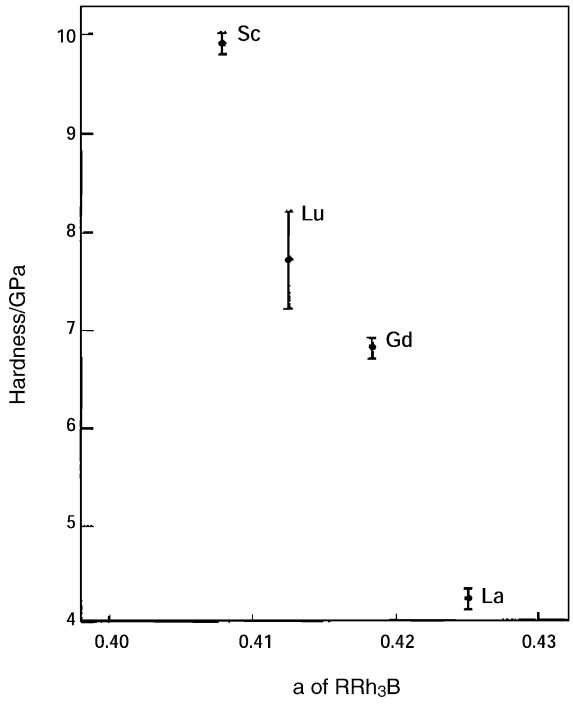

Fig. 4. Microhardness of RRh_3B (R = La, Gd, Lu and Sc) as a function of lattice parameter (nm) a.

size of R in RRh_3B. In the case of R = Sc, Sc has the smallest atomic radius among in the elements tested and it is the hardest. The electronegativity of R elements [11] selected in this study is also listed in Table 2 for reference.

Hardness is known as a material parameter which indicates resistance to elastic/plastic deformation. To describe the origin of hardness at atomistic scale theoretically, first principles calculations were performed to estimate the bulk modulus, B, from the volume dependence of the total energy.

In the present stage of our study, we consider RRh_3B perovskite-type cubic structures with R = La and Sc. We use the ab initio projected augmented wave (PAW) method [12,13] implemental in the Vienna Ab initio Simulation Program (VASP) [14–16]. Minimization of the free energy over the degrees of freedom of the electron densities and atomic positions was performed using the conjugated-gradient iterative minimization technique [17]. The cutoff energy for the plane wave expansion is taken to be 257.2 eV, which was large enough to obtain good convergence. For the Brillouin zone (BZ) integrations, $8 \times 8 \times 8$ k points were used. The exchange–correlation energy has been calculated within the generalized gradient approximation [18]. The total energy, u, is calculated as a function of the lattice constant. The variation in the total energy as a function of the lattice constant is shown in Fig. 5 for $ScRh_3B$. From the curve shown in Fig. 5, one can estimate the equilibrium lattice constant a_0 and the bulk modulus, B, which is defined as:

$$B = -\frac{V\mathrm{d}p}{\mathrm{d}V} = \frac{V\mathrm{d}^2u}{\mathrm{d}V^2}$$

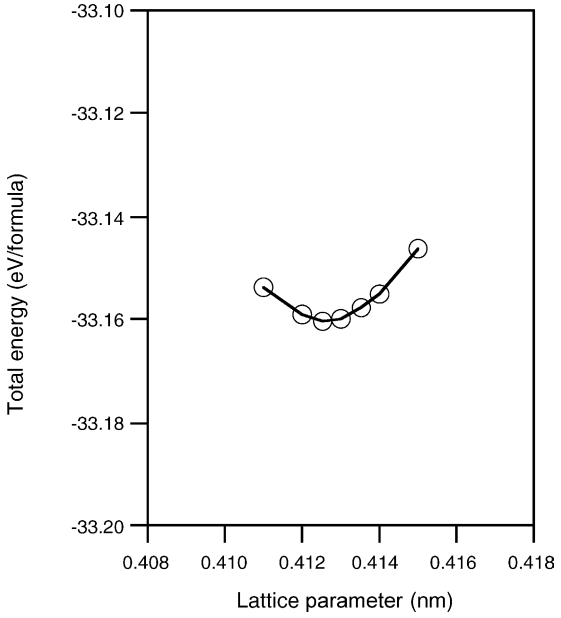

Fig. 5. The calculated total energy per formula unit as a function of the lattice parameter (nm) a for $ScRh_3B$.

Table 3
Calculated lattice constant (a_0) and the bulk modulus (B)

	a_0 (nm)	B (GPa)
$LaRh_3B$	0.429	166
$ScRh_3B$	0.413	201

where V is the volume of the unit cell and p is the pressure. Table 3 shows the obtained equilibrium lattice constant, a_0, and B for both $ScRh_3B$ and $LaRh_3B$. The lattice constant is in excellent agreement with the experimental results. The difference of the equilibrium lattice constant between the calculated result and the experimental value is only around 1%. From Table 3, it is observed that a decrease in the lattice constant leads to an enhancement in the bulk modulus. As it is discussed in Ref. [19], the electronic structures of the compounds obtained by full potential linearized augmented plane wave (FLAPW) method show that the covalency between boron and rhodium atoms. It may be concluded that more the covalent character in the bond between boron and rhodium atoms is, harder the mechanical property the compounds have.

4. Conclusion

Perovskite-type rare earth rhodium borides RRh_3B (R = La, Gd, Lu and Sc) were successfully synthesized by arc melting method. The nonstoichiometry range of boron was investigated. Then the dependency of hardness on rare earth atoms and boron-nonstoichiometry were obtained. RRh_3B belongs to perovskite-type cubic system: space group $Pm3m$; $Z = 1$. The lattice parameters a of RRh_3B for R = La, Gd, Lu and Sc are 0.4251(1), 0.4183(1), 0.4126(1) and 0.4080(1) nm, respectively. The value of lattice parameter a decreases with decreasing atomic size of R element. $LaRh_3B_x$ does not have boron-nonstoichiometry as $x = 1$. In the case of $GdRh_3B_x$ and $LuRh_3B_x$, boron-nonstoichiometry ranges between $0.55 \leqq x \leqq 1$ and $0.3 \leqq x \leqq 1$, respectively. $ScRh_3B_x$ exists in a full range of $0 \leqq x \leqq 1$. The values of the microhardness of RRh_3B for R = La, Gd, Lu and Sc are 4.2 ± 0.1, 6.8 ± 0.1, 7.7 ± 0.5 and 9.9 ± 0.1 GPa, respectively. R is positioned at the eight corners of the cube in the perovskite-type structure. Thus, microhardness increases with decreasing atomic size of R in RRh_3B. The hardness almost lineary changes with boron concentration x for R = Gd. Relationship between boron concentration x and hardness is complex for R = Lu and Sc. Ab initio calculations show excellent agreement with experimental lattice constant. A decrease in the lattice constant tends to increase the bulk modulus.

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