論文 **Original Paper**

Perovskite-type new boride in the Sc–Ni–B system

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Abstract: A search for perovskite-type new borides in the Sc–TM–B (TM = Ti, V, Cr, Mn, Fe, Co, and Ni) system has been carried out. As a result, the chemical formula of the compound $ScNi_3B_{0.5}$ was obtained. This compound has the cubic perovskite-type structure (space group: *Pm*3*m*) with the lattice parameter $a = 0.37760(7)$ nm. $ScNi_3B_{0.5}$ exhibits metallic behavior down to 4.2 K. The magnetic susceptibility of $ScNi_3B_{0.5}$ shows Pauli paramagnetism. No superconductivity appears down to the lowest temperature by the electric and magnetic measurements. The micro-Vickers hardness and oxidation resistivity in air are also reported for $ScNi_3B_{0.5}$.

Keywords: Perovskite-type boride, Electric property, Magnetic property, Hardness, Oxidation resistivity

1. Introduction

Many studies of simple and complex perovskite-type oxides have been performed due to the interesting features as the superconductivity, the metal-insulator transition, ion conduction characteristics, dielectric properties, and ferro-elasticity [1–4]. On the other hand, there have been few studies on the non-oxide perovskite-type compound [5–8]. Systematic investigation of the synthesis and fundamental characterization of the non-oxide perovskite-type compounds is necessary.

In this study, we focus on the search for perovskite-type new ternary borides in the Sc–TM–B systems (TM = Ti, V, Cr, Mn, Fe, Co, and Ni).

2. Experimental details

2.1 Synthesis

Polycrystalline samples of Sc–TM–B system were prepared by the arc melting method using 99.9% Sc (tips), 99.9% TM elements (tips) and 99.8% B (powder) as raw materials. These were weighed in the atomic ratio Sc:TM:B = 1:3:1. The mixture of the starting materials, about 2 g for each sample, was placed on the water-cooled copper hearth in the reaction chamber. Argon was used as a protective atmosphere. A small amount of the residual oxygen in argon was eliminated by fusing a button of titanium. The starting materials were then melted for 3 min by argon arc plasma flame with dc power source at 20 V and 100 A. The samples were then turned over and melted three times under the same condition. Finally, synthesized samples were wrapped in the tantalum foil and annealed at 1573 K for 20 h under vacuum to ensure homogeneity.

2.2 Characterization

For the chemical analysis, the samples were fused using $NaHSO_4$ as a flux reagent. The obtained material was then dissolved in HCl. The chemical composition of each sample was analyzed by induction-coupled plasma atomic emission spectrometry (ICP–AES), using Zn as the internal standard. Crystal structure characterization of the samples was performed by X-ray powder diffraction (XRD). The electrical resistivity of the samples was measured by means of a dc four probe method from 0.5 K to room temperature. The magnetic susceptibility measurements were performed in a field of 5000 Oe using a commercial SQUID magnetometer (Quantum Design Inc., MPMS–5) from 5 K to room temperature. The micro-Vickers hardness of the crystals was measured at room temperature. A load of 300 g was applied for 15 s and 10 impressions were recorded for the crystals. TG and DTA were performed between room temperature and 1473 K to study the oxidation resistivity of the crystals in air. A pulverized sample of about 25 mg was heated at a rate of 10 $Kmin^{-1}$.

3. Results and discussion

The arc melted samples were silver in color and exhibited a metallic lustre. The result of the chemical analysis shows that the chemical compositions before and after synthesis are almost the same. In addition, contamination

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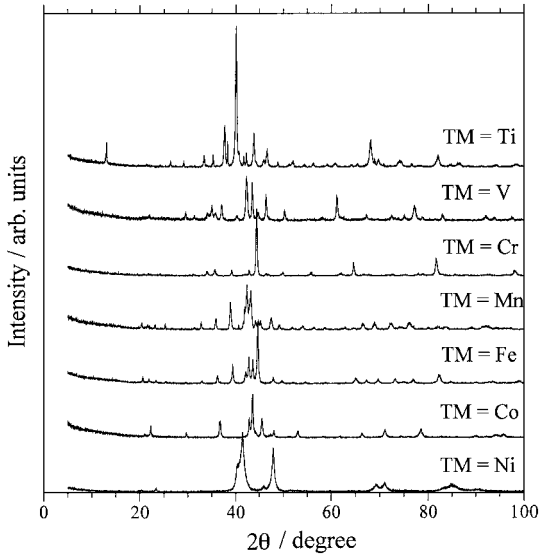

Fig. 1. Powder XRD patterns for the Sc–TM–B (TM = Ti, Cr, Mn, Fe, Co and Ni) system; nominal composition is Sc:TM:B = 1:3:1 (atomic ratio).

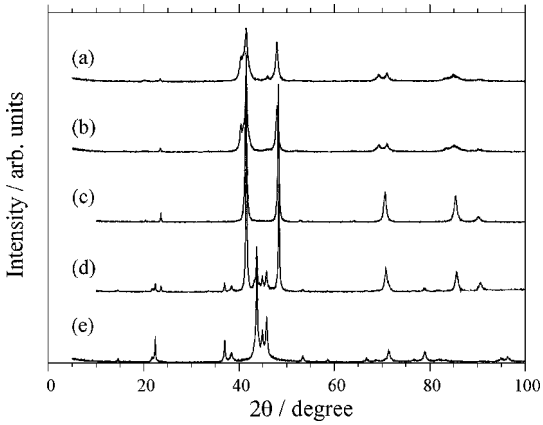

Fig. 2. Powder XRD patterns for $ScNi_3B_x$; (a) $x = 1.00$ (20 at.% B), (b) $x = 0.71$ (15 at.% B), (c) $x = 0.50$ (11.1 at.% B), (d) $x = 0.44$ (10 at.% B) and (e) $x = 0.21$ (5 at.% B).

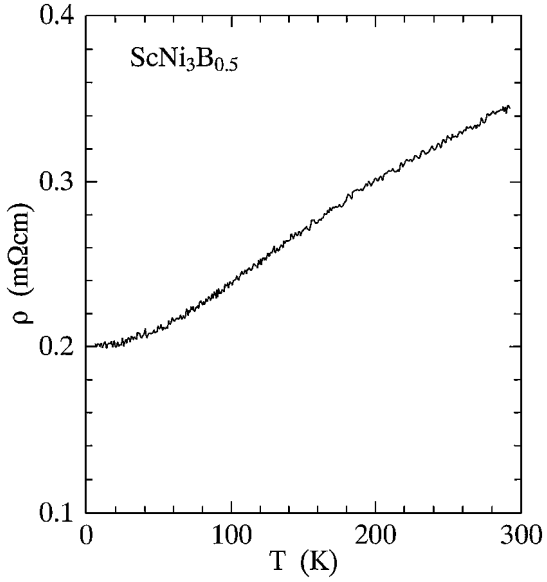

Fig. 3. Temperature dependence of the electrical resistivity for $ScNi_3B_{0.5}$.

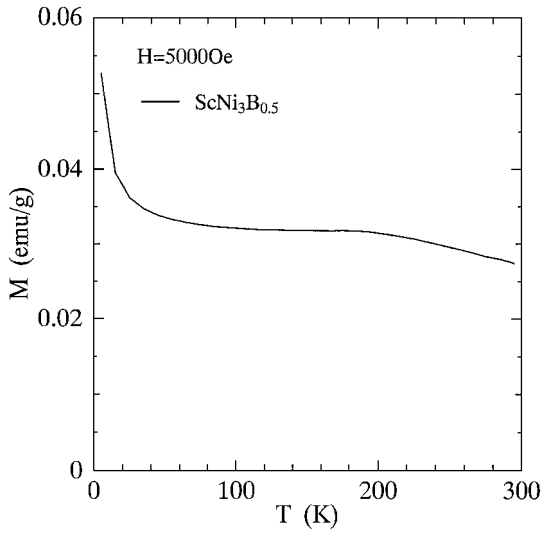

Fig. 4. Temperature dependence of the magnetization in $H = 5000$ Oe for $ScNi_3B_{0.5}$.

from the electrode (tungsten) and hearth (copper) could be disregarded in this study.

Fig. 1 shows powder XRD patterns for the Sc–TM–B (TM = Ti, V, Cr, Mn, Fe, Co and Ni) systems. As result, a new perovskite-type boride has been obtained in the system of Sc–Ni–B. Fig. 2 shows the powder XRD patterns for $ScNi_3B_x$; (a) $x = 1.00$ (20 at.% B), (b) $x = 0.71$ (15 at.% B), (c) $x = 0.50$ (11.1 at.% B), (d) $x = 0.44$ (10 at.% B), and (e) $x = 0.21$ (5 at.% B). In the case of (c), boron content $x = 0.5$, the XRD pattern corresponds to an almost single phase sample. Other samples include different phase(s). So we conclude that the chemical formula of the compound is $ScNi_3B_{0.5}$. This compound has the cubic perovskite-type structure (space group: $Pm3m$) with the lattice parameter $a = 0.37760(7)$ nm. In the structure, Sc is at the corners of the cube. Ni is at the six face-centered sites and B at the body-centered site.

Fig. 3 shows the temperature dependence of the electrical resistivity for $ScNi_3B_{0.5}$. The $ScNi_3B_{0.5}$ exhibits metallic behavior down to 4.2 K. No super-conductivity appears at the lowest temperature.

Fig. 4 shows the temperature dependence of the magnetization of $ScNi_3B_{0.5}$ in a field $H = 5000$ Oe. Magnetic susceptibility for $ScNi_3B_{0.5}$ show Pauli paramagnetic behavior. No trace of superconductivity is found down to 2 K.

One of the important mechanical properties, the hardness [9,10], is measured for $ScNi_3B_{0.5}$. The micro-Vickers hardness for the $ScNi_3B_{0.5}$ is 4.6 ± 0.1 GPa.

Fig. 5 shows TG–DTA curves for $ScNi_3B_{0.5}$. The TG

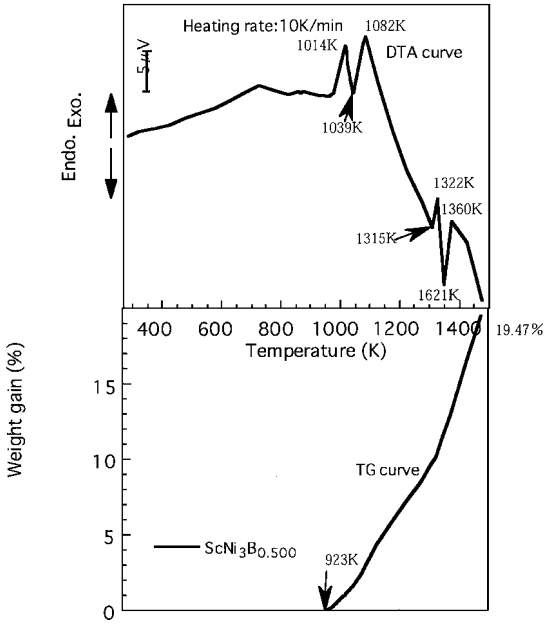

Fig. 5. TG–DTA curves for $ScNi_3B_{0.5}$.

analysis indicates that the onset temperature of the oxidation for $ScNi_3B_{0.5}$ is 923 K. Sharp exothermic peaks of the DTA curve appeared at 1014 and 1082 K. The weight gain of $ScNi_3B_{0.5}$ by heating in air up to 1473 K is 19.47%. Sc_2O_3, $ScNiO_3$, and Ni are identified as the oxidation products of $ScNi_3B_{0.5}$.

4. Conclusions

A search for perovskite-type new borides in the Sc–TM–B (TM = Ti, V, Cr, Mn, Fe, Co and Ni) system has been carried out. We can draw the following conclusions from this study [11]:

(1) A new perovskite-type boride has been discovered only for TM = Ni, the chemical formula of the compound is $ScNi_3B_{0.5}$.

(2) $ScNi_3B_{0.5}$ has cubic perovskite-type of structure (space group: $Pm3m$) with the lattice parameter a = 0.37760(7) nm.

(3) $ScNi_3B_{0.5}$ exhibits metallic behavior.

(4) The magnetic susceptibility of $ScNi_3B_{0.5}$ shows Pauli paramagnetism.

(5) The micro-Vickers hardness of $ScNi_3B_{0.5}$ is 4.6 ± 0.1 GPa.

(6) TG analysis indicates that the onset temperature of oxidation for $ScNi_3B_{0.5}$ is 923 K.

Exothermic peaks in the DTA curve are found at 1014 and 1082 K. Sc_2O_3, $ScNiO_3$, and Ni are identified as the oxidation products.

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