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Growth conditions, electrical resistivity, microhardness and thermal properties of Nb_5Sn_2Ga single crystals synthesized from high-temperature tin solutions

Shigeru Okada[a,*], Kunio Kudou[b], Toetsu Shishido[c], Iwami Higashi[d], Hiroyuki Horiuchi[e], Tsuguo Fukuda[c]

[a]*Faculty of Engineering, Kokushikan University, 4-28-1 Setagaya, Setagaya, Tokyo 154-8515, Japan*
[b]*Faculty of Engineering, Kanagawa University, 3-27-1 Rokkakubashi, Kanagawa, Yokohama 221-8790, Japan*
[c]*Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba, Sendai 980-0812, Japan*
[d]*Department of Chemistry, Chiba Institute of Technology, Shibazono, Narashino, Chiba 275, Japan*
[e]*Earth Science Laboratory, Faculty of Education, Hirosaki University, Bunkyocho 1, Hirosaki, Aomori 036-8560, Japan*

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Abstract

Single crystals of a new ternary intermetallic compound Nb_5Sn_2Ga were prepared from high-temperature tin solutions by a self flux method using Nb and Ga metals as starting materials under a He gas. The crystal was examined by X-ray diffraction and chemical analyses. The ternary single crystals Nb_5Sn_2Ga were generally obtained in the form of prismatic shape extending in the [001] direction, and with (100) and (110) faces. The Vickers microhardness value on (001) plane and (100) or (110) planes of crystals is in the range of 8.5–10.1 GPa. The electrical resistivity determined on crystal is in the range of 253.1–276.7 $\mu\Omega$ cm. The oxidation of Nb_5Sn_2Ga crystal starts at about 562°C. The final oxidation products were NbO_2, $Nb_{12}O_{29}$, Nb_2O_5, SnO_2 and Ga_2O_3.

Keywords: Nb_5Sn_2Ga; Single crystal; Sn flux; Crystal morphology; Electrical resistivity; Vicker-microhardness; Thermal properties

Single crystals of a new superconducting ternary intermetallic compound Nb_5Sn_2Ga (space group I4/mcm) were prepared from self-component tin solutions using niobium and gallium metals as starting materials [1,2]. This is the first compound synthesized in the Nb–Sn–Ga system. It was reported that the crystal growth and crystal structure [1], the range of solid solution and the properties of superconductivity on as-grown Nb_5Sn_2Ga crystals [3]. However, there is a little information about chemical and physical properties of Nb_5Sn_2Ga crystal. The purpose of this paper is to clarify the conditions for growing relatively large crystals of Nb_5Sn_2Ga in high temperature tin solutions by a self flux. Crystallographic data, crystal size, crystal morphology, Vickers microhardness and electrical resistivity of the crystals were measured, and oxidation at high-temperature in air was studied.

Synthesis of the ternary Nb_5Sn_2Ga crystal was performed by the high-temperature solution growth method using tin as a self flux. The purities of the starting materials were as follows: Nb (99.9%), Ga (99.999%) and Sn (99.999%). The Nb and Ga were mixed together at atomic ratios of between 2:1 and 4:1 (Table 1). Tin was added to these mixtures at a ratio of 5:1, w/w. The mixture of starting materials was placed in a high-purity alumina crucible and heated under a He gas. The temperature of the furnace was raised at a rate of 400°C h^{-1} up to 1400°C and

Table 1
Typical crystal growth conditions of Nb_5Sn_2Ga

Run	Starting composition Nb:Ga (atomic ratio)[a]
1	2:1
2	3:1
3	4:1

[a] Sn was added to this mixture in the ratio 5:1 by weight.

*Corresponding author.

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held for 10 h, and then slowly cooled down at a rate of 1°C h^{-1} to 1000°C. Then the furnace was rapidly cooled down to room temperature. The crystals were separated by dissolving Sn in dilute HCl (6 M) for 2–4 days. Relatively large crystals of Nb_5Sn_2Ga were selected under stereomicroscope for chemical analysis. The crystal morphology was examined by an optical microscope and a scanning electron microscope (SEM). Some of the crystals were examined with an energy-dispersive detector (EDX). The chemical composition of the grown crystals were determined by means of the inductively coupled plasma (ICP) emission analysis. X-ray diffraction analyses were performed using a Burger precession camera with zirconium-filtered MoKα radiation and a four-circle X-ray diffractometer with graphite-monochromatized MoKα radiation.

The Vickers microhardness of the as-grown Nb_5Sn_2Ga crystal was measured in several directions on (001) plane and (100) or (110) planes, at room temperature in air. A load of 100 g was applied for 15 s at about 5 to 9 points for each crystal, and the values obtained were averaged. The electrical resistivity of the crystals was measured by means of a direct-current four-probe technique at room temperature in air. Thermogravimetiric (TG) analysis and differential thermal analysis (DTA) were performed up to 1200°C to study the oxidation of crystals in air. Specimens of 15–25 mg were heated at rate of 10°C min^{-1}.

The ternary single crystals Nb_5Sn_2Ga were generally obtained in the form of prismatic shape extending in the [001] direction, and with (001) and (110) faces. These crystals had a silver metallic luster. The maximum sizes of the crystals were about $10\times1\times1$ mm^3 (Fig. 1). The basic crystal data and chemical analyses results are presented in Table 2. The structure is ordered W_5Si_3 type [4]. The range of solid solution of the compound is very narrow. The unit cell volume varies from 579.7 to 584.5 ($\cdot10^{-3}$) nm^3 with increasing tin content in the chemical formula. According to [5] the atomic radius (12-fold coordination) is 1.53 and 1.58 Å for Ga and Sn, respectively. When the tin content is increased above its stoichiometric composition, the inter atomic distance of Nb–Ga is also increased. This is caused by the partly replacement of Ga by Sn [3]. The single crystals obtained from run 2 were closest to the stoichiometric composition. The precession photographs taken along the [001] and [110] zone-axes presented in Fig. 2, it shown that the crystal of Nb_5Sn_2Ga obtained from run 2 was grown as a single-phase structure. Therefore, the Vickers microhardness, the electrical resistivity and oxidation were measured for the sample of run 2.

Table 2
Crystal data and result of chemical analysis for Nb_5Sn_2Ga

	Run 1	Run 2	Run 3
Formula	Nb_5Sn_2Ga	Nb_5Sn_2Ga	Nb_5Sn_2Ga
Crystal system	Tetragonal	Tetragonal	Tetragonal
a (nm)	1.0584 (1)	1.0586(2)	1.0606(2)
c (nm)	0.5175(1)	0.5177(1)	0.5196(1)
$V(\cdot10^{-3}$ $nm^3)$	579.7	580.2	584.5
Space group	I4/mcm	I4/mcm	I4/mcm
Z	4	4	4
Chemical composition[a]	$Nb_5Sn_{1.95}Ga_{1.08}$	$Nb_5Sn_{1.97}Ga_{1.06}$	$Nb_5Sn_{2.12}Ga_{0.94}$
D_x (g cm^{-3})	8.84	8.83	8.77
D_m (g cm^{-3})[b]	–	8.83	–

[a] Chemical analysis was done using the ICP method.
[b] D_m was determined by means of a pycnometer using H_20 at 20°C.

The Vickers microhardness and the electrical resistivity of as-grown Nb_5Sn_2Ga were listed in Table 3. The microhardness values as measured on the (100) or (110) face of Nb_5Sn_2Ga crystals are found to be relatively lower than the values of (001) face. This anisotropic nature of microhardness seems to be related to the difference in the number of Nb atoms per unit area between the (001) plane and the (100) or (110) planes [3]. The greater number of Nb atoms on the (001) plane compared with (100) or (110) planes gave a higher value of microhardness.

The electrical resistivity of as-grown Nb_5Sn_2Ga crystals was measured at room temperature on the (100) or (110) planes. The electrical resistivity are listed in Table 3. The electrical resistivity value of the Nb_5Sn_2Ga crystals was found to be larger than the value of Nb_5Sn_2Si, Ta_5Ga_2Sn, and $Nb_5(Ge_xSn_{1-x})_2Ge$ crystals with ordered-W_5Si_3 type structure [6].

The oxidation reaction was studied by TG and DTA, as shown in Fig. 3. The TG curve show that oxidation reaction starts at 562°C for Nb_5Sn_2Ga. Weight gain of the specimen after TG determination, heated up to 1200°C in air, was measured at about 37.3 wt%. The exothermic peaks of the DTA curve were found at about 608, 796 and 925°C, respectively. The oxidation products were analyzed by a X-ray diffractometer at room temperature. The crystal was heated at 1200°C for 5 min, and the final oxidation

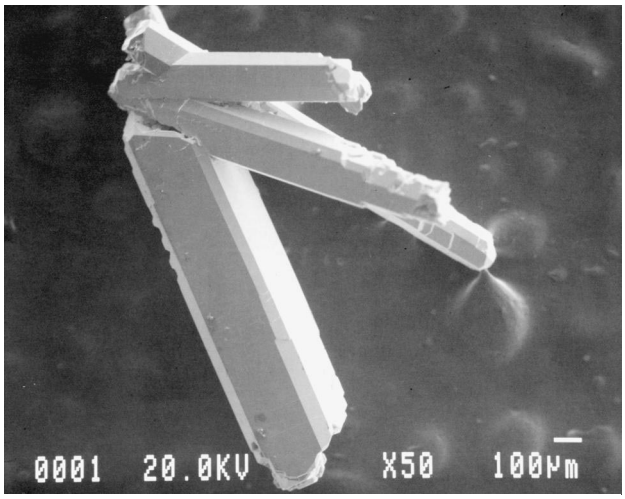

Fig. 1. SEM photograph of Nb_5Sn_2Ga (run 2) single crystals.

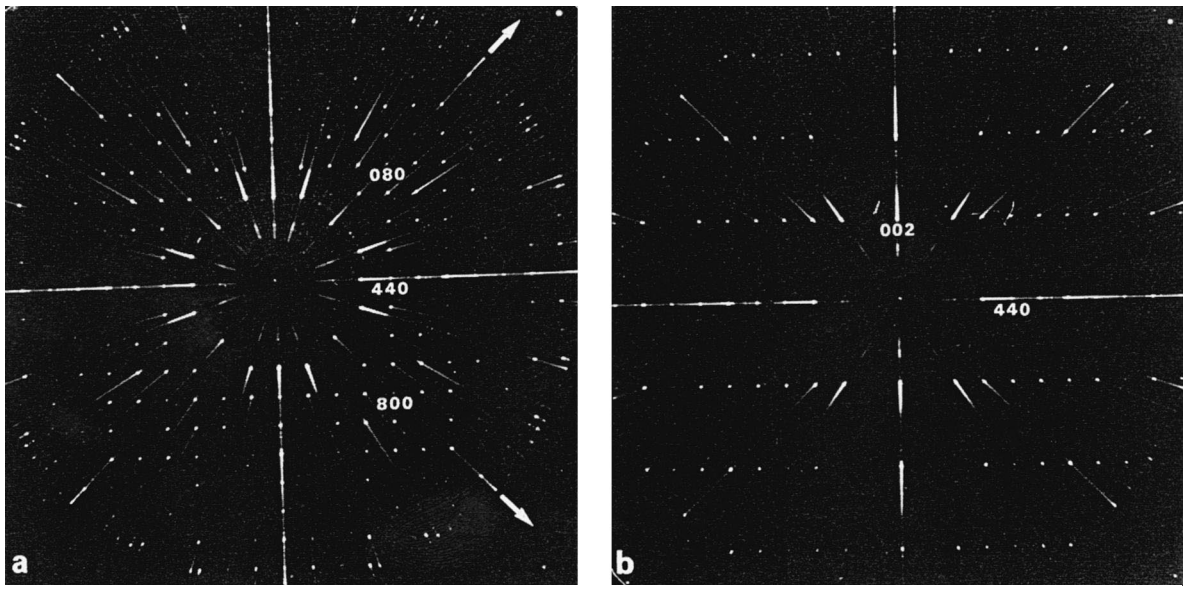

Fig. 2. X-ray precession photographs of Nb_5Sn_2Ga (run 2): (a) [001] and (b) [110] zone axes.

Table 3
Vickers microhardness and electrical resistivity of Nb_5Sn_2Ga

Compound	Indentation plane	Microhardness Hv (GPa)	Electrical resistivity ρ ($\mu\Omega$ cm)
Nb_5Sn_2Ga	(001)	10.1–9.1	–
	(100) or (110)	8.9–8.5	253.1–276.7

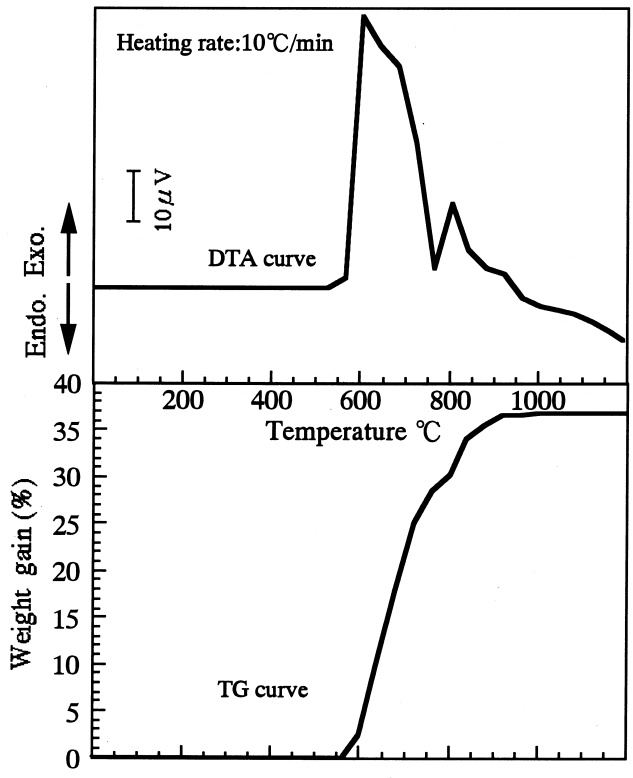

Fig. 3. Differential thermal analysis (DTA) and thermal gravimetric (TG) curves for Nb_5Sn_2Ga single crystals. Samples were heated in air at a rate of 10°C min^{-1}.

products were NbO_2 (monoclinic, -), $Nb_{12}O_{29}$ (orthorhombic, Amma), Nb_2O_5 (monoclinic, P2), SnO_2 (tetragonal, $P4_2/mnm$), and Ga_2O_3 (rhombohedral, R3c), respectively.

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