論文 **Original Paper**

Crystal Growth, Structure and Properties of a New Ternary Intermetallic Compound Nb_5Sn_2Ga

Shigeru OKADA*1, Toetsu SHISHIDO*2, Kunio KUDOU*3, Hideo KANARI*4 and Tsuguo FUKUDA*5

Abstract: Single crystals of a new ternary intermetallic compound Nb_5Sn_2Ga were synthesized by the high-temperature Nb–Sn–Ga system solutions under a He gas. The Nb and Ga were mixed together at atomic ratios of between 1.5:1 and 6:1. Tin was added to these mixtures at a ratio of 5:1 in weight. The mixture was heated at 1400°C for 10 h, and then slowly cooled down at a rate of $1°Ch^{-1}$ to 1000°C. Then the furnace was rapidly cooled down to room temperature. Single crystals of Nb_5Sn_2Ga, having a metallic luster, were generally obtained in the form of prismatic shape extending in the [001] direction and with (100) and (110) faces. The largest crystals prepared have maximum dimensions of about 10 mm × 1 mm × 1 mm. The nominal compositions of Nb_5Sn_2Ga crystals were widely changed as Nb to Ga 2:1, 3:1 and 4:1, and the compositions of the obtained crystals were close to the Nb_5Sn_2Ga. Single crystal X-ray analysis showed that the new compound Nb_5Sn_2Ga has a tetragonal symmetry with $a=1.0586(2)$nm, $c=0.5177(1)$nm, space group $I4/mcm$, ordered W_5Si_3-type structure. The superconductivity, electric property, Vickers microhardness and oxidation resistivity on the single crystals of Nb_5Sn_2Ga were determined. The compound shows superconductivity at $T_c=1.75$ K and $\Delta T_c=140$ mK. The electrical resistivity determined on crystal is about 120×10^{-6} Ωcm at room temperature. The Vickers microhardness value on (001) plane and (100) or (110) planes of crystals is in the range of Hv=8.5–10.1 GPa. The oxidation of Nb_5Sn_2Ga crystal starts at about 562°C. The final oxidation products were NbO_2 (monoclinic), $Nb_{12}O_{29}$ (orthorhombic), Nb_2O_5 (monoclinic), SnO_2 (tetragonal) and Ga_2O_3 (rhombohedral), respectively.

Keywords: Nb_5Sn_2Ga, Single crystal, Crystal morphology, Crystal structure, Superconductivity, Vickers microhardness, Thermal properties

1. Introduction

Single crystals of a new superconducting ternary intermetallic compound Nb_5Sn_2Ga isostructural with tetragonal Nb_5Sn_2Si (space group $I4/mcm$) [1] were prepared from self-component tin solution [2, 3]. It was reported that the crystal growth and crystal structure [2], the results of X-ray photoelectron spectroscopy (XPS) (the chemical state of Nb, Sn and Ga) [4], and the superconductivity [5] and electric property [6] on as-grown Nb_5Sn_2Ga crystals. 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 solution by a self flux. X-ray diffraction for Nb_5Sn_2Ga single crystals grown from three different compositions were carried out. The crystal size, crystal morphology, crystallographic data, superconductivity, electrical resistivity and Vickers microhardness of the compounds were determined, and the oxidation reaction heated in air was studied by thermogravimetric (TG) analysis and differential thermal analysis (DTA). The oxidation products were analyzed by a X-ray diffractometer (XRD) at room temperature.

*1 工学部土木工学科　助教授　工学博士
Department of Civil Engineering, Faculty of Engineering, Associate Professor, Dr. of Engineering
*2 東北大学金属材料研究所　講師　工学博士
Institute for Materials Research, Tohoku University, Lecturer, Dr. of Engineering
*3 神奈川大学工学部機械工学科　助手　工学博士
Department of Mechanical Engineering, Faculty of Engineering, Kanagawa University, Research Associate, Dr. of Engineering
*4 工学部土木工学科　教授　工学博士
Department of Civil Engineering, Faculty of Engineering, Professor, Dr. of Engineering
*5 東北大学金属材料研究所　教授　理学博士
Institute for Materials Research, Tohoku University, Professor, Dr. of Science

Table 1. Typical growth conditions and chemical formula of Nb_5Sn_2Ga crystals.

Run No.	Composition of the starting mixture in atomic ratio Nb : Ga	Chemical formula of crystals	Crystal shape
1	1.5 : 1	—	Powder
2	2 : 1	$Nb_5Sn_{1.95}Ga_{1.08}$	Rectangular, powder
3	3 : 1	$Nb_5Sn_{1.97}Ga_{1.06}$	Rectangular, powder
4	4 : 1	$Nb_5Sn_{2.12}Ga_{0.94}$	Rectangular, powder
5	6 : 1	—	Powder

2. Experimental details

2.1 Preparation of crystals

Synthesis of the ternary Nb_5Sn_2Ga crystals was performed by the high-temperature solution growth method using tin as a self flux. The starting materials used were small pieces of 99.9% Nb, 99.999% Ga button and 99.999% Sn powder. The Nb and Ga were mixed together at atomic ratios of between 1.5:1 and 6:1 (Table 1). Tin was added to these mixtures at a ratio of 5:1 in weight. The mixture of starting materials was placed in a high purity (99.9%) dense alumina crucible. A pure helium gas flow at a rate of 200 ml min^{-1} was introduced into the furnace as a protecting atmosphere against oxidation. The temperature of the furnace was raised at a rate of 400°Ch^{-1} up to 1400°C and kept for 10 h, and then slowly cooled down at a rate of 1°Ch^{-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 to 4 days. As shown in Table 1, rectangular single crystals of Nb_5Sn_2Ga were obtained when the ratio of Nb to Ga were taken as 2:1, 3:1 and 4:1.

2.2 Chemical and X-ray diffraction analyses

Relatively large crystals of Nb_5Sn_2Ga were selected under stereomicroscope, and chemical compositions of the crystals grown were determined by means of the inductively coupled plasma (ICP) technique. 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). X-ray diffraction analyses were performed using a Burger precession camera with zirconium-filtered Mo Kα radiation and a four-circle X-ray diffractometer with graphite-monochromatized Mo Kα radiation.

2.3 Properties

2.3.1 Measurement of hardness, superconductivity, electric and oxidation resistivity

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 0.98 N was applied for 15 sec at about 5 to 9 points for each crystal, and the values obtained were averaged. The superconducting transition temperature T_c was determined by measuring the AC susceptibility. The electrical resistivity of the crystals was measured by the direct-current four-probe technique between 1.5 and 298 K. 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°Ch^{-1}.

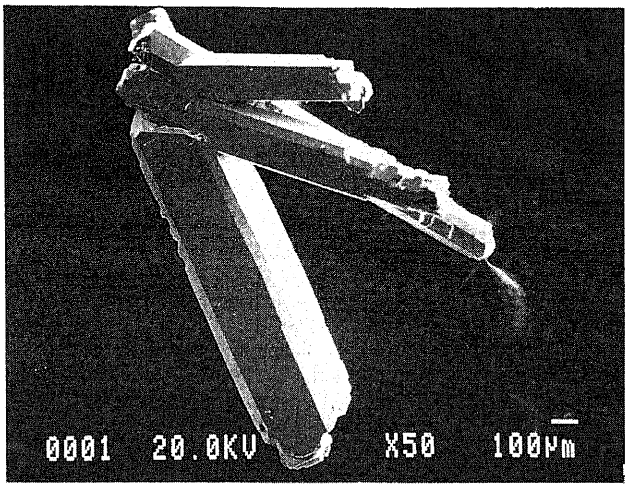

Fig. 1 A SEM photograph of Nb_5Sn_2Ga (Run No. 3) single crystals.

3. Results and discussion

3.1 Growth, morphology and structure of the single crystals

Rectangular single crystals were obtained when the ratio of Nb to Ga in the melt were taken as 2:1, 3:1 and 4:1 (Table 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 mm × 1 mm × 1 mm (Fig. 1). The range of solid solution of the compound is very narrow. The single crystals obtained from run number 3 were closest to the stoichiometric composition. Therefore, the Vickers microhardness, superconductivity, electrical resistivity and oxidation were measured for the sample of run number 3. Also, precession photographs taken along the [001] and [110] zone-axes using the crystal obtained from run 3 are shown in Fig. 2. The results of crystal structure analyses for the compounds of runs 2–4 revealed that

Table 2. Crystal data and result of chemical analysis for Nb_5Sn_2Ga.

	Run No. 2	Run No. 3	Run No. 4
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 ($\times 10^{-3}nm^3$)	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 (gcm^{-3})	8.84	8.83	8.77
D_m (gcm^{-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_2O at 20°C.

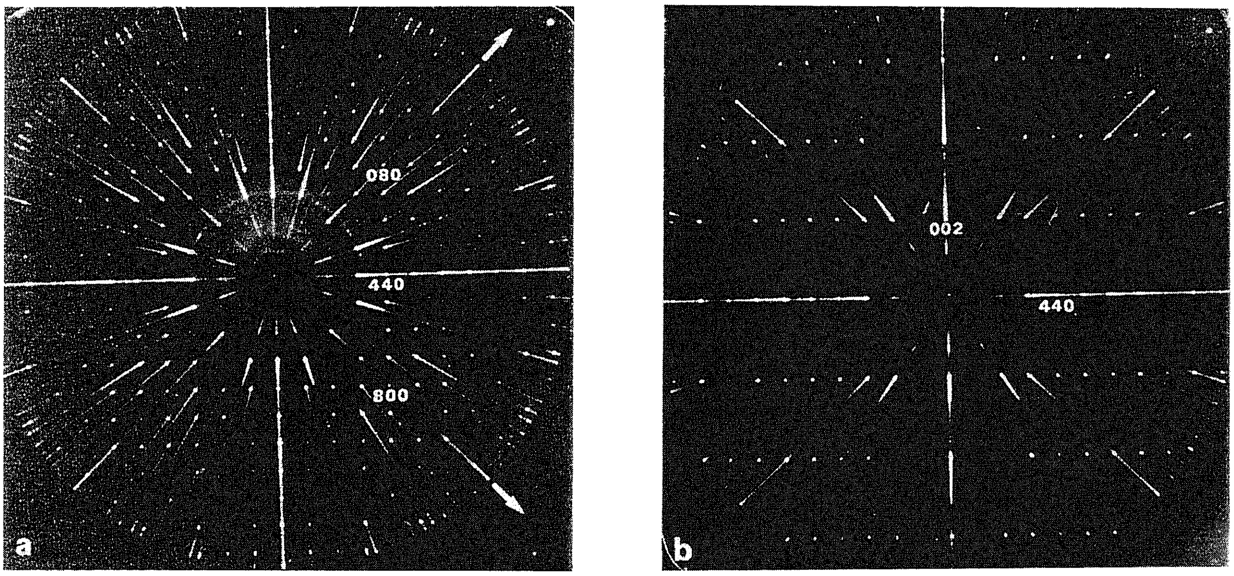

Fig. 2 X-ray precession photographs of Nb_5Sn_2Ga (Run No. 3): (a) [001] and (b) [110] zone axes.

they are all tetragonal, space group *I4/mcm*, and isostructural with Nb_5Sn_2Si [7], Ta_5SnGa_2 [8, 9] and $Nb_5(Ge_x,Sn_{1-x})_2Ge$ (x=0.25) [10] whose basic structure is W_5Si_3 type [1]. The unit cell parameters are listed in Table 2. The unit cell volume varies from 579.7 to 584.5 ($\times 10^{-3}$)nm^3 with increasing tin content in the chemical formula. According to ref. 11 the atomic radius (12-fold coordination) is 1.53 Å and 1.58 Å for Ga and for Sn, respectively. When the tin content is increased above its stoichiometric composition, the interatomic distance of Nb-Ga is also increased. This is caused by the partly replacement of Ga by Sn [5]. The arrangement of atoms in the crystal is shown in Fig. 3. The crystal structure of Nb_5Sn_2Ga is composed of two kinds of atomic polyhedra, $GaNb(1)_8$ and $Nb(2)Sn_4$. Both polyhedra form colums parallel to the *c*-axis, respectively.

Table 3. Superconductivity and electric properties of Nb_5Sn_2Ga crystals.

T_c	1.75 K (midpoint)
ΔT_c	140 mK
ρ (298 K)	120×10^{-6} Ω cm
ρ (4.2 K)	10×10^{-6} Ω cm

3.2 Superconductivity and electric property

The real part of the susceptibility as a function of the temperature is shown in Fig. 4. T_c was determined to be 1.75 K at the midpoint of the transition, and ΔT_c defined by 10 and 90% of the transition was 140 mK. The electrical resistivity of as-grown Nb_5Sn_2Ga crystals was meas-

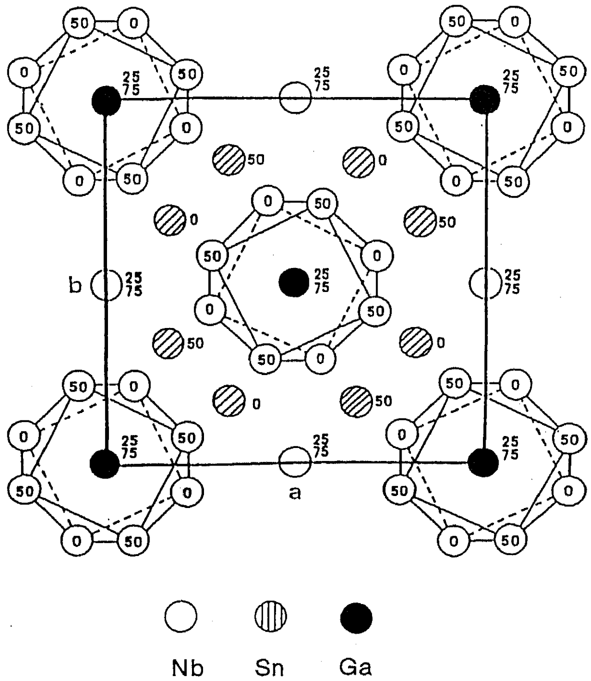

Fig. 3 A view of the crystal structure for Nb_5Sn_2Ga along the *c*-axis. Open circles are Nb, solid circles are Ga and shaded circles are Sn atoms, respectively.

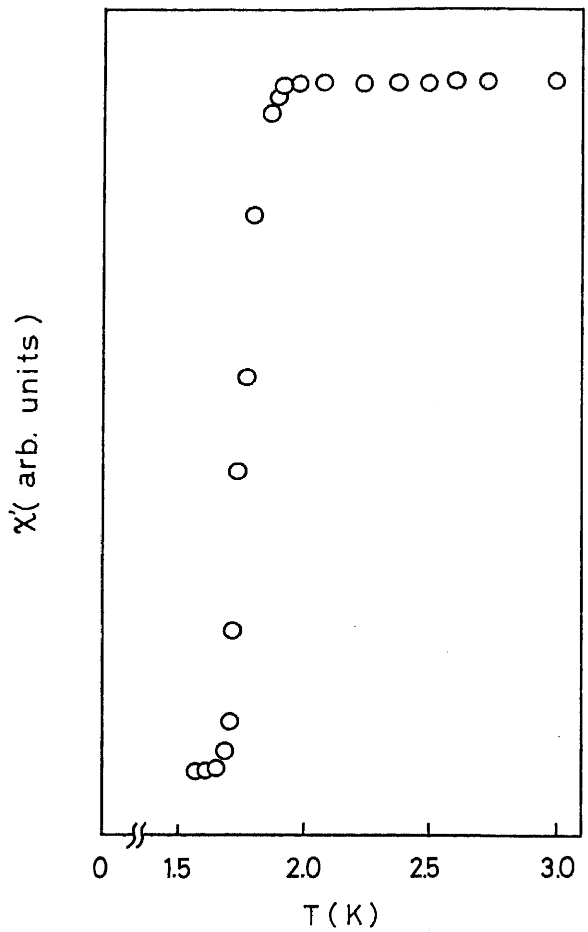

Fig. 4 Temperature dependence of the AC magnetic susceptibility of Nb_5Sn_2Ga.

Table 4. Vickers microhardness of Nb_5Sn_2Ga crystals.

Compound	Indentation plane	Microhardness Hv (GPa)
Nb_5Sn_2Ga	(001)	10.1–9.1
	(100) or (110)	8.9–8.5

ured at room temperature on the (100) or (110) planes. The superconductivity and electrical resistivity are listed in Table 3. The resistivity is about 120×10^{-6} Ωcm and is metallic. 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 [10].

3.3 Microhardness

The Vickers microhardness [12] of as-grown Nb_5Sn_2Ga were listed in Table 4. 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 [5]. The greater number of Nb atoms on the (001) plane compared with (100) or (110) planes gave a higher value of microhardness.

3.4. Oxidation reaction

The oxidation reaction was studied by TG and DTA [13, 14], as shown in Fig. 5. 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°C, 796°C and 925°C, respectively. The oxidation products were analyzed by a XRD at room temperature. Fig. 6 shows the XRD pattern after the crystal was heated at 1200°C for 5 min, and the oxidation products were NbO_2 (monoclinic, space group -), $Nb_{12}O_{29}$ (orthorhombic, space group *Amma*), Nb_2O_5 (monoclinic, space group *P*2), SnO_2 (tetragonal, space group $P4_2/mnm$), and Ga_2O_3 (rhombohedral, space group $R\bar{3}c$), respectively.

4. Conclusions

The purpose of this study is to clarify the conditions for growing relatively large crystals of Nb_5Sn_2Ga in high temperature tin solution by a self flux under a He gas. The mixture of the raw materials was raised at a rate of 400°Ch^{-1} up to 1400°C and kept for 10 h, and then slowly cooled down to room temperature. X-ray diffraction of Nb_5Sn_2Ga single crystals grown from three different com-

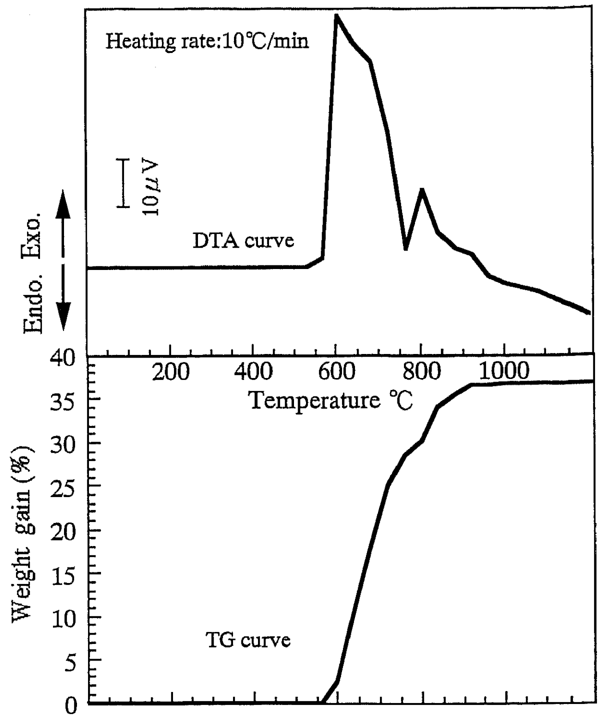

Fig. 5 Differential thermal analysis (DTA) and thermal gravimetric (TG) curves for Nb_5Sn_2Ga single crystals. Samples were heated in air at a rate of $10°Ch^{-1}$.

positions were carried out. The crystal size, crystal morphology, crystallographic data, superconductivity, electrical resistivity and Vickers microhardness of the compounds were measured, and the oxidation reaction heated in air was studied. The conclusions derived from this study are as follows:

(1) Single crystals of Nb_5Sn_2Ga were generally obtained in the form of prismatic shape extending in the [001] direction and with (100) and (110) faces.

(2) The largest crystals prepared have maximum dimensions of about 10 mm × 1 mm × 1 mm.

(3) The nominal compositions of Nb_5Sn_2Ga crystals were widely changed as Nb to Ga 2:1, 3:1 and 4:1.

(4) Nb_5Sn_2Ga has a tetragonal symmetry with $a=1.0586(2)$nm, $c=0.5177(1)$nm, space group *I*4/mcm and ordered W_5Si_3-type structure.

(5) The compound shows superconductivity at $T_c=1.75$ K and $\Delta T_c=140$ mK. The electrical resistivity is about 120×10^{-6} Ωcm.

(6) The Vickers microhardness value on (001) plane and (100) or (110) planes of crystals is in the range of Hv=8.5–10.1 GPa.

(7) The oxidation of Nb_5Sn_2Ga crystal starts at about 562°C, and the final oxidation products were NbO_2 (monoclinic, space group -), $Nb_{12}O_{29}$ (orthorhombic, space group *Amma*), Nb_2O_5 (monoclinic, space group *P*2), SnO_2 (tetragonal, space group $P4_2/mnm$), and Ga_2O_3 (rhombohedral, space group $R\bar{3}c$).

Acknowledgements

The present study was performed under the cooperative research program of the IMR, Tohoku University. The authors would like to thank Drs, M. Ogawa and K. Iizumi of Tokyo Institute of Polytechnics for helpful in the ex-

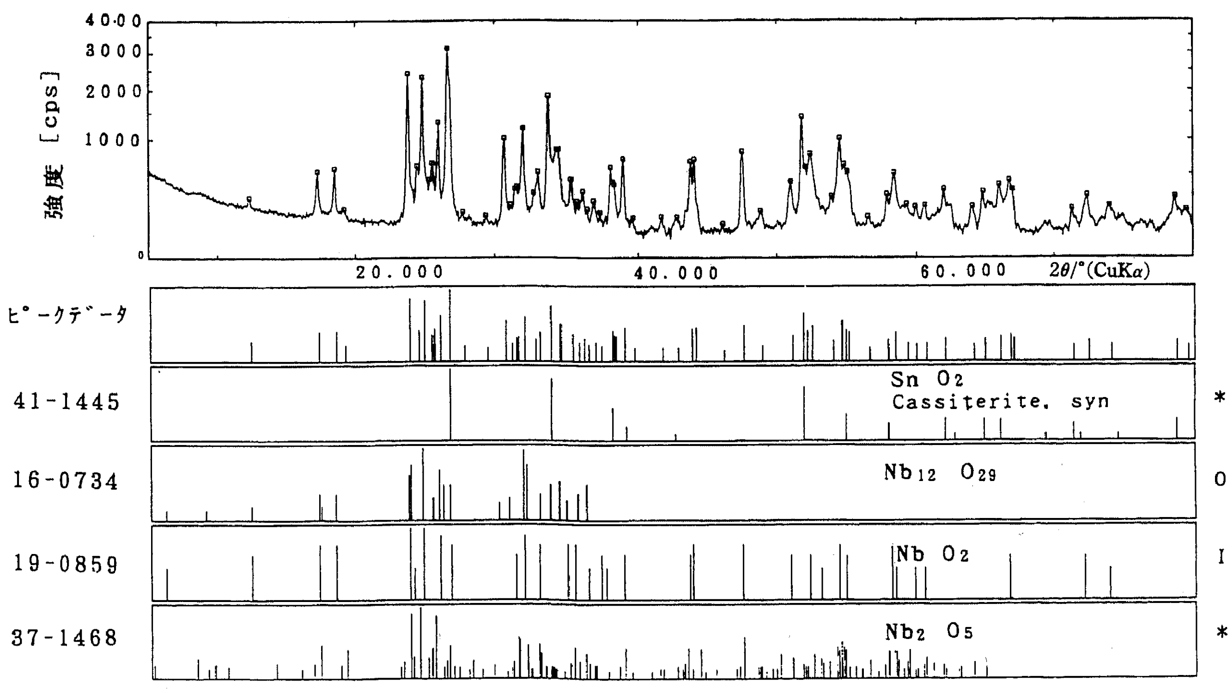

Fig. 6 XRD pattern of after the oxidation reaction. Nb_5Sn_2Ga crystal was heated at 1200°C for 5 min.

periments.

(Received September 30, 1999)

References

[1] R. Horyn and K. Lukaszewicz, Bull. Acad. Polon. Sci., Ser. Sci. Chim., 18 (1970) 59.

[2] T. Shishido, K. Ukei, N. Toyota, T. Sasaki et al., J. Cryst. Growth, 96 (1989) 1.

[3] K. Ukei, T. Shishido and T. Fukuda, Acta Cryst., C 45 (1989) 349.

[4] T. Shishido, M. Oku, S. Okada, K. Kudou, J. Ye, T. Sasaki et al., J. Alloys Compounds, 281 (1998) 196.

[5] T. Shishido, K. Ukei, N. Toyota, M. Tanaka, H. Horiuchi and T. Fukuda, J. Alloys Compounds, 202 (1993) L1.

[6] S. Okada, K. Kudou, T. Shishido, I. Higashi, H. Horiuchi and T. Fukuda, J. Alloys Compounds, 281 (1998) 160.

[7] T. Shishido, J. Ye, N. Toyota et al., Jpn. J. Appl. Phys. 28 (1989) 1519.

[8] J. Ye, H. Horiuchi, T. Shishido, K. Ukei and T. Fukuda, Act Cryst., C 46 (1990) 1193.

[9] M. Tanaka, H. Horiuchi, T. Shishido and T. Fukuda, Act Cryst., C 49 (1993) 437.

[10] T. Shishido, M. Tanaka, K. Ukei, H. Horiuchi et al., Nippon Kagaku Kaishi, 3, 262 (1994) (in Jananese).

[11] B. Aronsson, Acta Chem. Scand., 9 (1955) 1107.

[12] S. Okada, T. Shishido, K. Kudou, I. Higashi, M. Ogawa et al., J. Ceram. Soc. Japan, 107 (2) 184 (1999).

[13] S. Okada, K. Iizumi, K. Kudaka, K. Kudou et al., J. Solid State Chem., 133, 36 (1997).

[14] T. Shishido, K. Kudou, S. Okada, J. Ye et al., J. Alloys Compounds, 280 (1998) 65.