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Chemical state and properties of the Nb_5Sn_2Ga grown by the self-component flux method using tin as a solvent

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Abstract

Single crystals of a new compound Nb_5Sn_2Ga were obtained by the flux method using molten tin as a solvent. The crystal structure represents a tetragonal symmetry, space group $D_{4h}^{18}I4/mcm$, ordered W_5Si_3-type structure. Lattice parameters are $a=1.0586(2)$ nm and $c=0.5177(1)$ nm. According to XPS study, the peaks of Nb, Sn and Ga 3dXP spectra negatively shift when the three elements of Nb, Sn and Ga form the compound of Nb_5Sn_2Ga. The compound shows superconductivity at $T_c=1.75$ K and $\Delta T_c=140$ mK. The residual resistivity ratio, RRR$=\rho$ (293 K)/ρ (4.2 K), is 12. The Micro-Vickers hardness (MVH) value for the (100) or (110) face is 8.9–8.5 GPa, and for the (001) face is 10.1–9.1 GPa. Oxidation of the Nb_5Sn_2Ga starts at 562°C. Weight gain of the compound heated up to 1200°C in air is 37.3%. Final oxidation product contains NbO_2, Nb_2O_5, $Nb_{12}O_{29}$, SnO_2 and Ga_2O_3.

Keywords: Nb_5Sn_2Ga; XPS; Superconductivity; TG-DTA; Microhardness

1. Introduction

Binary intermetallic compounds of Nb_4Ga_5, Nb_5Ga_4, Nb_5Ga_3 and Nb_3Ga exist in the Nb–Ga system. On the other hand, compounds of Nb_3Sn, Nb_6Sn_5 and $NbSn_2$ exist in the Nb–Sn system [1–9]. Among them, Nb_3Ga and Nb_3Sn having the A-15 type structure are particularly interesting because of the excellent superconducting properties [10–14]. For the Ga–Sn system, a eutectic composition of 8.5 at.% Sn is known and no intermetallic compounds exist [15–18]. It is interesting to extend the new compound research to the ternary system of Nb–Sn–Ga.

In a previous paper we reported the existence of a new ternary intermetallic compound Nb_5Sn_2Ga [19]; this is the first compound belonging to the ternary Nb–Sn–Ga system (Fig. 1). The present paper reports the results of XPS analysis, superconductivity, electric property, microhard-

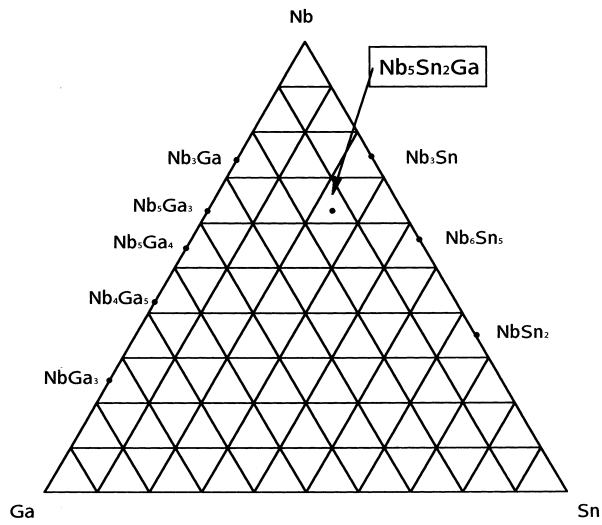

Fig. 1. Ternary phase diagram in the system of Nb–Sn–Ga. The position of the new compound Nb_5Sn_2Ga indicated by an arrow.

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ness and oxidation resistivity on the single crystals of Nb_5Sn_2Ga.

2. Experimental

2.1. Sample preparation

The raw materials used were small pieces of 99.9% Nb, 99.999% Sn powder and 99.999% Ga button. Niobium and gallium were weighed in the atomic ratios of 1.5:1, 2:1, 3:1, 4:1 and 6:1. Tin was added to these mixtures at a weight ratio of 5:1. The mixture of these three elements was put into a high purity (99.9%) dense alumina crucible. Then the crucible was inserted in a vertical electric furnace. The height of the melt was about 30 mm and the temperature at the bottom was 30°C higher than that at the top. A pure He-gas flow at a rate of 200 ml min^{-1} was introduced into the furnace as a protecting atmosphere against oxidation. Then the mixture of the starting materials was heated at a rate of 400°C h^{-1} up to 1400°C, and kept at 1400°C for 10 h, and then slowly cooled down at a rate of 1°C h^{-1}. After the temperature reached 1000°C, the furnace was rapidly cooled down to room temperature. The grown crystals were separated by dissolving Sn in dilute hydrochloric acid.

2.2. Characterization

The surface of the crystals were analyzed by scanning electron microscope (SEM). Chemical analyses were carried out using the inductively coupled plasma (ICP) technique. X-ray analyses were performed using a Burger precision camera with zirconium-filtered Mo Kα radiation and a four-circle X-ray diffractometer with graphite-monochromatized Mo Kα radiation. The superconducting transition temperature T_c was determined by measuring the AC susceptibility. The electrical resistivity was measured by the four-point method between 1.5 and 298 K. An X-ray photoelectron spectroscopic (XPS) study was performed for a fractured single crystalline surface to determine the chemical state of Nb, Sn and Ga in the compound. The spectra were taken with a spectrometer, which had a monochromatic A1 Kα source with spot size 300×450 μm^2. Thermogravimetric (TG) analysis and differential thermal analysis (DTA) were performed between room temperature and 1200°C to study the oxidation resistivity of crystals in air.

A pulverized sample of about 25 mg was heated at a rate of 10°C min^{-1}. The oxidation products were analyzed by powder X-ray diffractometry. The Micro-Vickers hardness (MVH) of the as-grown single crystals was measured at room temperature. A load of 100 g was applied for 15 s and more than seven impressions were recorded for individual faces of crystal. The obtained values were averaged and the experimental error was estimated.

Table 1
The relationship between the starting composition and the chemical formula of the rectangular crystals

Run No.	Starting composition Nb:Ga (atomic ratio)	Appearance	Chemical formula of crystals
1	1.5:1	Powder	–
2	2:1	Rectangular, powder	$Nb_5Sn_{1.95}Ga_{1.08}$
3	3:1	Rectangular, powder	$Nb_5Sn_{1.97}Ga_{1.06}$
4	4:1	Rectangular, powder	$Nb_5Sn_{2.12}Ga_{0.94}$
5	6:1	Powder	–

Sn was added to this mixture in the ratio of 5:1 in weight.

3. Results and discussion

3.1. Morphology and structure of the single crystals

As shown in Table 1, 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. The maximum dimensions of crystals are 10×1×1 mm^3. When the starting materials had a ratio of Nb to Ga 1.5:1 or 6:1, only powder-like crystals were obtained. Here, we focus our attention on the rectangular single crystals. The results of the chemical analyses for the rectangular crystals indicate that the chemical formula of the compound is near equal Nb_5Sn_2Ga (Table 1). The nominal compositions were widely changed as Nb to Ga 2:1, 3:1 and 4:1, but the compositions of the obtained crystals were close to the Nb_5Sn_2Ga. So the solid solution range of the compound is very narrow, and the compound is suggested to be the Daltonide-type one. The single crystals obtained from Nb:Ga=3:1 (Run No. 3, Table 1), are nearest to the stoichiometric composition as $Nb_5Sn_{1.97}Ga_{1.06}$. In Fig. 2 a SEM image of a rectangular single crystals obtained from Nb:Ga=3:1 is shown. So we used the crystals obtained from Run No. 3 to determine the

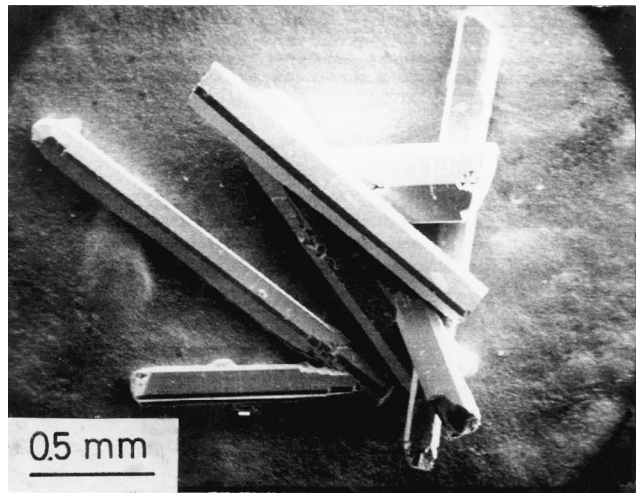

Fig. 2. A SEM photograph of Nb_5Sn_2Ga crystals grown by the flux method using tin as a self-component flux (Run No. 3).

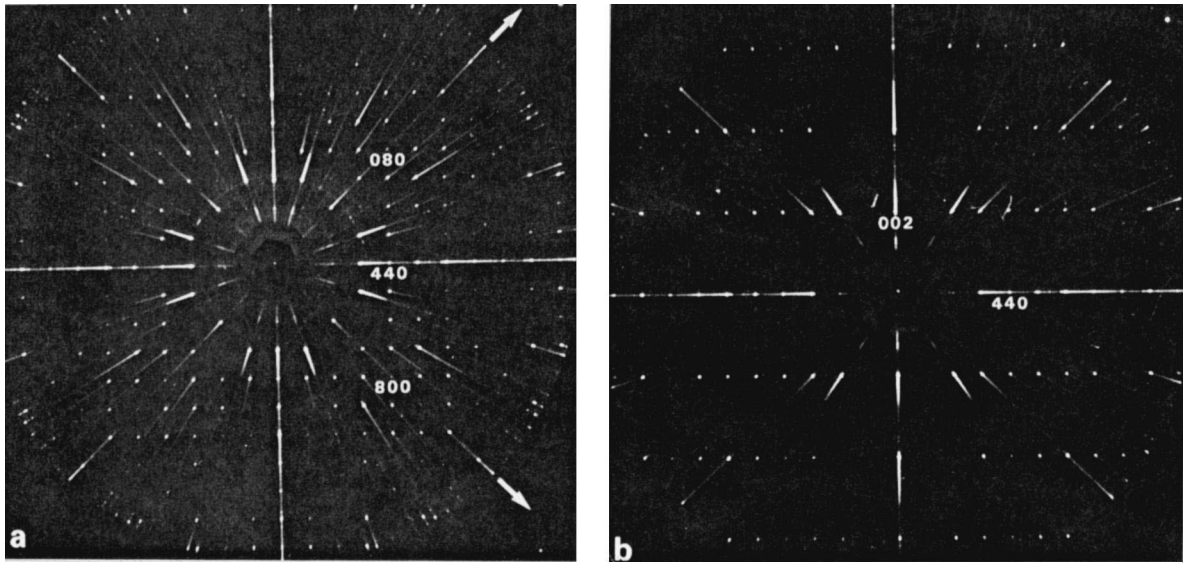

Fig. 3. X-ray precession photographs of Nb_5Sn_2Ga: (a) [001] and (b) [110] incidence.

properties of the new compound. Precession photographs for the [001] and [110] zone-axes are shown in Fig. 3; they clearly indicate tetragonal symmetry. Four circle X-ray analysis of a single crystal reveals that the Nb_5Sn_2Ga crystal is tetragonal with the space group $D_{4h}^{18}I4/mcm$ and isostructural with Nb_5Sn_2Si [20], Ta_5SnGa_2 [21,22] and $Nb_5(Ge_x, Sn_{1-x})_2Ge$, $x=0.25$ [23,24] whose basic structure is the W_5Si_3 [25] type. The lattice parameters of the tetragonal unit cell are $a=1.0586(2)$ nm and $c=0.5177(1)$ nm, respectively. The arrangement of the atoms in the crystal is shown in Fig. 4. Elongation direction of the crystals (shown in Fig. 2) is [001] and well developed facets are (100) and (110). The most important point in the self-component flux method is to eliminate a contamination from the flux material. In this study, Sn acted as a self-component flux and a new compound Nb_5Sn_2Ga has been successfully obtained from excess Sn.

3.2. X-ray photoelectron spectroscopy

XPS was performed to study the chemical states of Nb, Sn and Ga. In Fig. 5 it is shown that the binding energies of $Nb3d_{5/2}$ for the compound and elemental Nb are 202.7 and 202.9 eV, respectively. Although the negative chemical shift from element to the compound is small, a more characteristic difference is observed in their FWHM of $3d_{5/2}$. The FWHMs of the compound and elemental Nb are 1.0 and 1.5 eV, respectively. The narrowing of Nb3d shows that the electron densities on the Nb atoms in the compound is lower than that for elemental Nb. As shown in Fig. 6, the $Sn3d_{5/2}$ peak shifts from 485.0 to 484.5 eV due to formation of the compound. The change of FWHM of Sn3d is not observed. The plasmon loss peaks are observed 498 and 508 eV in the spectrum of elemental Sn, but the corresponding peaks are not observed in the spectrum of the compound. In Fig. 7 it is revealed that the binding energies of Ga3d for the compound and elemental Ga are 18.7 and 18.0 eV, respectively. As a result, all of the Nb, Sn and Ga3d XPS peaks negatively shift when the three elements of Nb, Sn and Ga form the compound of Nb_5Sn_2Ga.

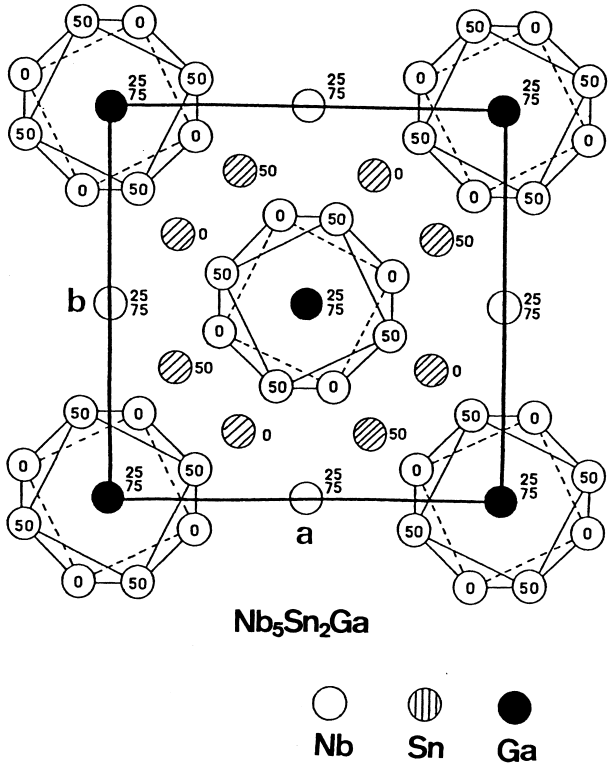

Fig. 4. Arrangement of atoms in the Nb_5Sn_2Ga crystal projected along the *c*-axis. Open circles are Nb, solid circles are Ga and shaded circles are Sn atoms, respectively.

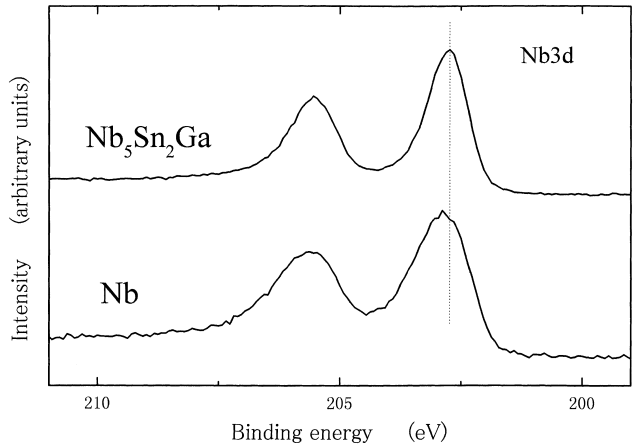

Fig. 5. XP spectra for Nb_5Sn_2Ga and Nb.

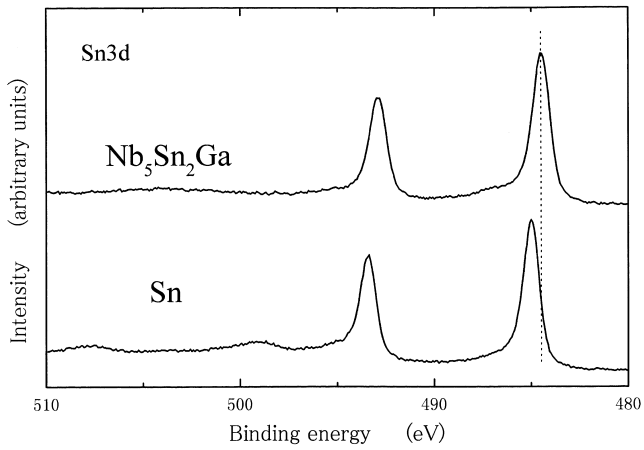

Fig. 6. XP spectra for Nb_5Sn_2Ga and Sn.

3.3. Superconductivity and electric property

In Fig. 8 the real part of the susceptibility as a function of the temperature is shown. 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 resistivity at room temperature is about 120 μΩ cm and is metallic. The residual resistivity ratio RRR=ρ (293 K)/ρ (4.2 K) is 12. These values suggest that the quality of crystals is high in electric properties. The superconductivity and electric properties of the Nb_5Sn_2Ga are summarized in Table 2.

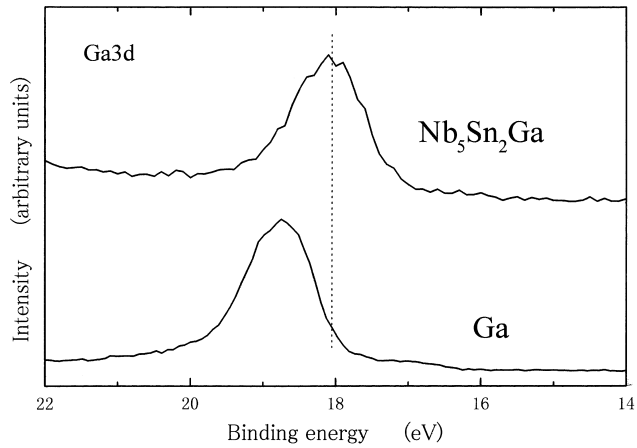

Fig. 7. XP spectra for Nb_5Sn_2Ga and Ga.

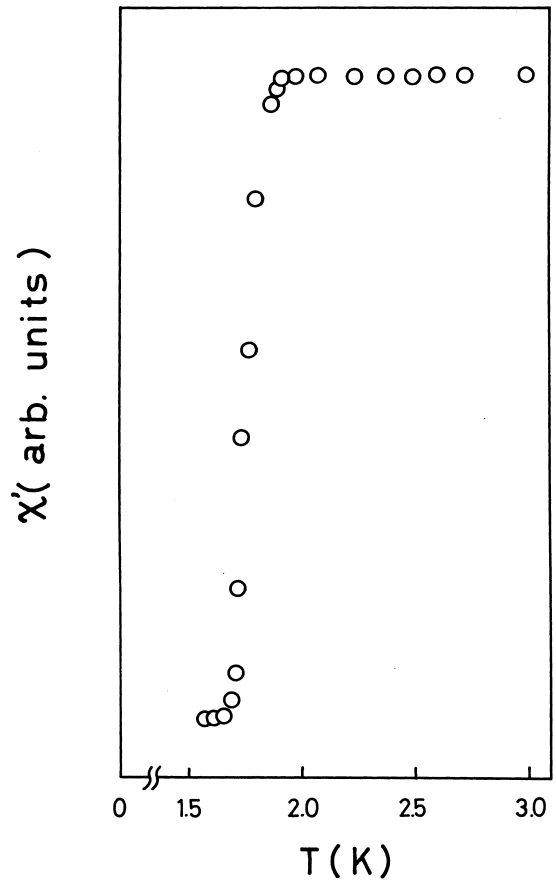

Fig. 8. Temperature dependence of the AC magnetic susceptibility of Nb_5Sn_2Ga.

3.4. Hardness [26]

The values of MVH for Nb_5Sn_2Ga are listed in Table 3. It can be seen that the value of the MVH of 8.9–8.5 GPa for the (100) or (110) face is relatively lower than the value of 10.1–9.1 GPa for the (001) face. Hardness of the compound seems to be related to its crystal structure. As shown in Fig. 4, this compound takes layer structure along the *c*-direction with the tetragonal symmetry. As a result,

Table 2
Superconductivity and electric properties of Nb_5Sn_2Ga

T_c	1.75 K (midpoint)
ΔT_c	140 mK
ρ (298 K)	120 μΩ cm
ρ (4.2 K)	10 μΩ cm
RRR=ρ (298 K)/ρ (4.2 K)	=12

Table 3
Micro-Vickers hardness of Nb_5Sn_2Ga

Compound	Indentation plane	Micro-Vickers hardness MVH (GPa)
Nb_5Sn_2Ga	(001)	10.1–9.1
	(100) or (110)	8.9–8.5

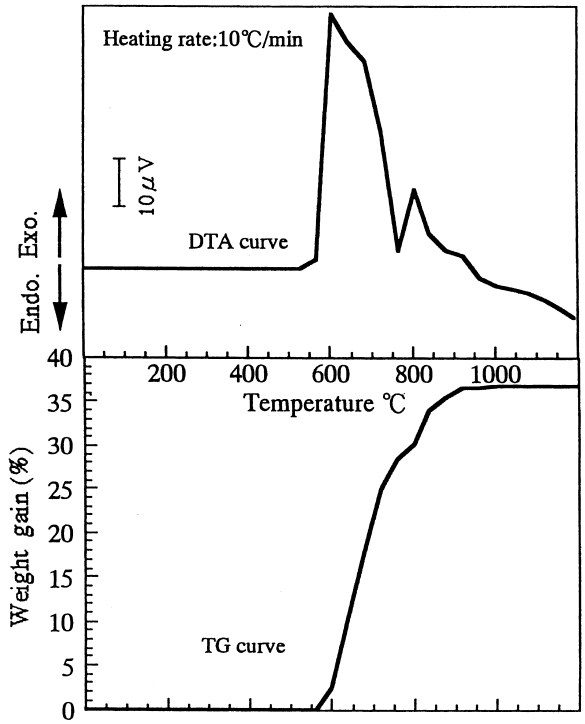

Fig. 9. TG-DTA curves for Nb_5Sn_2Ga.

the hardness of the intraplane is larger than that of the interplane.

3.5. TG-DTA [26]

TG-DTA curve is shown in Fig. 9. The TG curve represents that oxidation of the Nb_5Sn_2Ga starts at 562°C. Weight gain of the specimen heated up to 1200°C in air is 37.3%. According to the DTA curve, the exothermic peaks caused by oxidation were found at 608, 796 and 925°C, respectively. After oxidation measurement heating from room temperature to 1200°C, final product is consisted from NbO_2, Nb_2O_5, $Nb_{12}O_{29}$, SnO_2 and Ga_2O_3. Phenomenal temperature and weight gain from TG-DTA measurement for Nb_5Sn_2Ga are summarized in Table 4.

Table 4
Phenomenal temperature and weight gain from TG-DTA measurement for Nb_5Sn_2Ga

Sample	Oxidation onset (°C)	Exothermal maximum (°C)	Weight gain (%)
Nb_5Sn_2Ga (Run No.3)	562	608, 796, 925	37.3

4. Conclusion

Rectangular single crystals of maximum dimensions $10\times1\times1$ mm^3 of the new compound Nb_5Sn_2Ga were successfully obtained by the self-component flux method using excess tin as a flux. The crystal structure shows a tetragonal symmetry, space group $D_{4h}^{18}I4/mcm$, ordered W_5Si_3-type structure. Lattice parameters are $a=1.0586(2)$ nm and $c=0.5177(1)$ nm. Elongation direction of the crystals is [001] and well developed facets are (100) and (110). According to XPS study, the 3dXP spectra peaks of Nb, Sn and Ga negatively shift when the three elements form the compound of Nb_5Sn_2Ga. Superconducting transition temperature T_c of the compound is 1.75 K and the transition width, ΔT_c is 140 mK. The residual resistivity ratio RRR$=\rho$ (293 K)/ρ (4.2 K) is 12. The Micro-Vickers hardness MVH value on the (100) or (110) face is 8.7 ± 0.2 GPa, and on the (001) face is 9.6 ± 0.5 GPa. Oxidation of the Nb_5Sn_2Ga starts at 562°C. Weight gain of the compound heated up to 1200°C in air was 37.3%. Final oxidation product is consisted from NbO_2, Nb_2O_5, $Nb_{12}O_{29}$, SnO_2 and Ga_2O_3.

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