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Heterogeneous ceramic system prepared from semiconducting compound InSb

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A cermet compact consisting of unreacted semiconducting InSb, semiconducting In_2O_3 , and metallic Sb has been prepared by partial oxidation of polycrystalline bulk InSb at elevated temperatures in flowing oxygen. Unusually constant electric resistivity of this heterogeneous system has been observed in the temperature range from 4.2 to 300 K. Stability of the electric resistance depends on the degree of conversion β in the oxidation reaction: $2 \text{InSb} + \frac{3}{2} \text{O}_2 = \text{In}_2\text{O}_3 + 2 \text{Sb}$. Our thermogravimetric and x-ray studies revealed an escape of Sb from the system at higher temperatures and longer reaction times. The initial polycrystalline InSb was prepared by the method of rapid quenching.

A study has been performed of the electrical resistivity and phase transformation of bulk polycrystalline InSb into a cermet system. The variation of resistivity with the degree of phase transformation exhibits rather unusual resistance behavior in a wide temperature range between the temperature of liquid helium (4.2 K) and that of the room (300 K). Polycrystalline InSb used in these experiments was prepared by rapid quenching, the transformation into the InSb/ In_2O_3 /Sb-system was performed by partial oxidation at elevated temperatures.

The semiconducting properties of InSb are well known today.¹⁻⁴ Under some circumstances (applied pressure and temperature) the system InSb may also become superconductive.⁵⁻⁷ However, to our knowledge, the conversion of the InSb system into cermet compact has not been reported yet. It is the aim of this letter to demonstrate this.

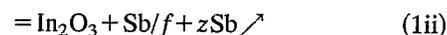
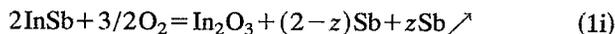
We have shown in our previous studies⁸ that the temperature dependence of magnetoresistivity $\Delta R/R_0$ as $f(T)$ for polycrystalline InSb in the temperature interval of 20–100 °C is lowered, when 1 mass % of La_2O_3 is added into this system. Such a type of material, i.e., InSb/ La_2O_3 used in our current experiments was subjected to partial oxidation at elevated temperatures. Final results, properties of a new cermet system, we compared of course also with those obtained for pure InSb.

Initial InSb/ La_2O_3 and InSb were prepared as polycrystalline materials by rapid quenching⁹ in the form of tapes up

to 50 μm thick, 3–6 mm wide and 30–40 mm in length. Because of their brittleness, manipulating them was rather difficult. Therefore, we crushed them in an achate mortar to a fine powder and pressed them into compact pellets 12 mm in diameter and 1 mm thick. These pellets then underwent annealing procedure in flowing oxygen under conditions close to those we used for preparation of superconductors.¹⁰ In the present case we used the temperature interval 200–500 °C (melting point of InSb is 525 °C), and the annealing time was 1–50 h.

Resistivity was then measured by the four-point dc method in a temperature interval of 4.2 K (boiling helium) to 300 K (room temperature). Phase transformation was examined by x-ray powder diffraction XRPD analysis and from these results, the type and degree of phase transformation was evaluated.

To demonstrate properties of obtained heterogeneous system we chose a processing temperature 400 °C and a time of oxidation annealing 1, 10, 25, and 50 h. New products of this procedure were In_2O_3 and metallic Sb, the rest were unreacted InSb, according to



where \nearrow means an escape of Sb from the system and “ f ” is the molar ratio of the reaction products $\text{In}_2\text{O}_3/(2-z)\text{Sb}$, i.e.,

TABLE I. Studied samples and their processing conditions. “ β ” is the conversion degree, i.e., mass ratio of converted to initial InSb, “ f_m ” is the relative mass change of the oxidized system (1) according to Eq. (2), “ z ” is the volatilized portion of Sb, and “ f ” is the molar ratio of the reaction products of Eq. (1), i.e., $f=1/(2-z)$.

No.	Material annealed	Annealing			β	f_m	z	f
		Temp °C	Time (h)	Medium				
1	InSb/ La_2O_3	400	1	O_2	0.359	1.036	0	0.500
2	InSb/ La_2O_3	400	10	O_2	0.741	0.989	0.450	0.645
3	InSb/ La_2O_3	400	25	O_2	0.781	0.962	0.582	0.705
4	InSb/ La_2O_3	400	50	O_2	0.836	0.881	0.947	0.950
5	InSb	400	50	O_2	0.801	0.912	0.824	0.850

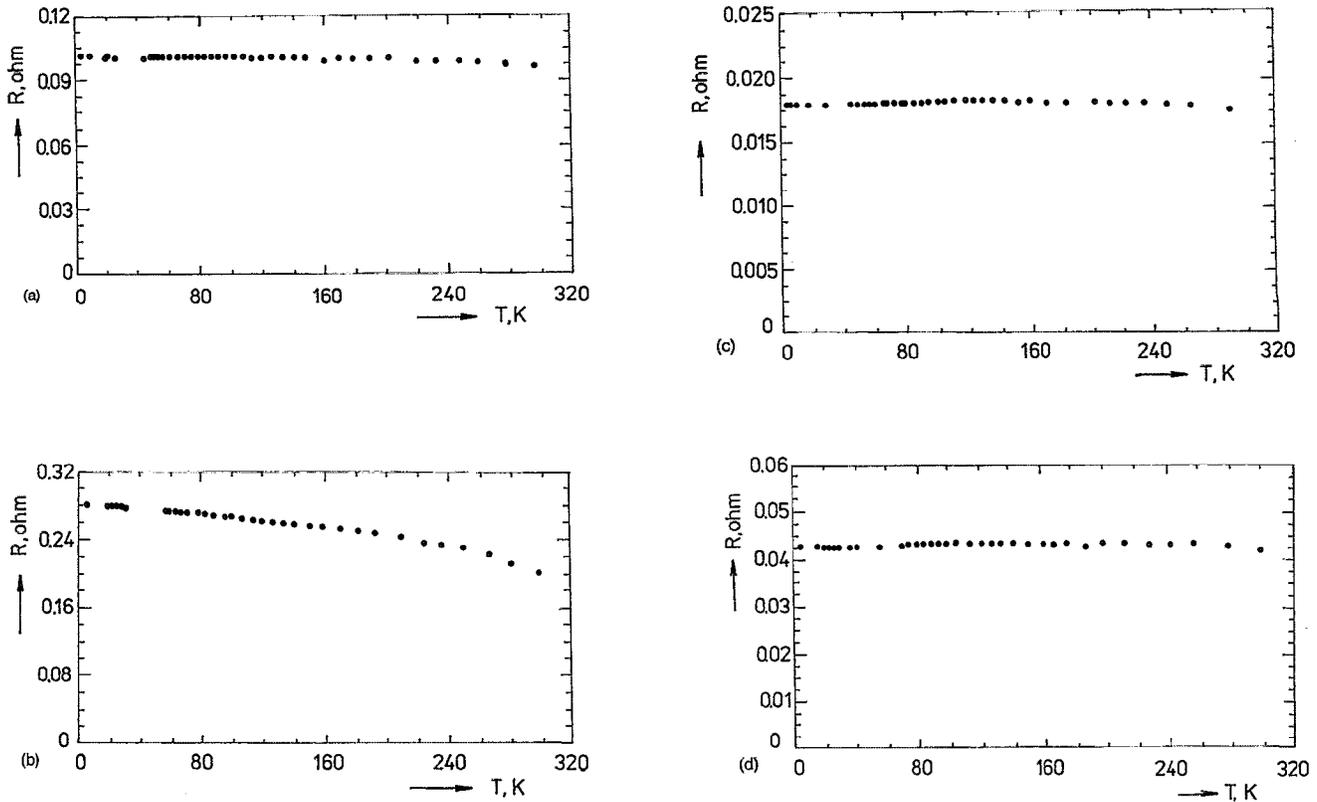


FIG. 1. Temperature dependence of resistance for samples partially oxidized at 400 °C: (a) 1, (b) 10, (c) 25, (d) 50 h.

$1/(2-z)=f$; “ z ” is the volatilized portion of Sb. Processing conditions and some properties for five samples annealed in flowing oxygen at 400 °C during 1–50 h are summarized in Table I, where conversion degree “ β ” represents mass ratio of the converted InSb/La₂O₃ (or InSb) portion to the initial unconverted one. It means that the resulting cermet compact consists of initial stoichiometric semiconducting InSb, semiconducting In₂O₃, and metallic Sb.

Temperature dependence of electrical resistance for samples 1–4 of Table I oxidized isothermally at 400 °C during 1, 10, 25, and 50 h is illustrated in Fig. 1. The investigated temperature interval was 4.2–300 K. As a result of the presence of semiconducting and metallic components, we obtained a relatively constant value of resistance in the whole, rather wide temperature interval. Low value of resistivity demonstrates the creation of ceramic cermet compact.

XRPD diffraction patterns for samples 1–4 of Table I for selected interval of angles $\theta=11^{\circ}$ – 17° are shown on Fig. 2. Changes in XRPD intensities correspond to the changes in content and mutual ratio of individual components InSb, Sb, and In₂O₃ caused by the reaction time of isothermal oxidation annealing.

The results of XRPD analysis showed that the increasing reaction time at 400 °C influenced the change of integral intensities of XRPDs of I_{InSb} and $I_{\text{In}_2\text{O}_3}$ according to the concentration changes represented by reaction (1). However, the x-ray intensity ratio $I_{\text{In}_2\text{O}_3}/I_{\text{Sb}}$ did not retain the constant value at increasing annealing time as would follow from Eq.

(1) and $x=0$, indicating that a part of antimony escaped from the system in the form of metallic Sb or oxide Sb₂O₃. Since the partial pressure of antimony vapor at 400 °C is around 10^{-6} Torr for it to volatilize, it seems to be less probable that a pure Sb would escape from the system. Nonappearance of the Sb₂O₃ diffractions in the XRPD pattern and the thermogravimetric (TG) measurements confirmed that Sb₂O₃ should pass off in vapor. Consequently, the conversion degree β could only be evaluated from integral x-ray intensities I_{InSb} and $I_{\text{In}_2\text{O}_3}$, while the molar ratio f of the reaction products of

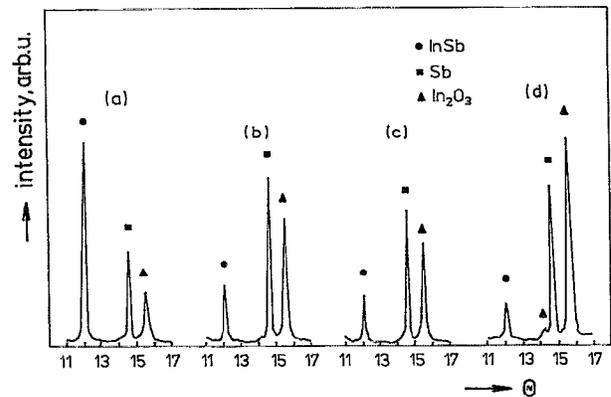


FIG. 2. X-ray diffraction patterns for selected interval of angles $\theta=11^{\circ}$ – 17° for samples of Fig. 1: (a) 1, (b) 10, (c) 25, (d) 50 h.

reaction (1), i.e., $f = \text{In}_2\text{O}_3 / (2-z)\text{Sb} = 1 / (2-z)$ is evaluable from the x-ray intensity ratio $I_{\text{In}_2\text{O}_3} / I_{\text{Sb}}$ and more precisely from the TG measurements. The relative mass change of the oxidized system (1), f_m , is given as

$$f_m = [2(1-\beta)M_{\text{InSb}} + \beta M_{\text{In}_2\text{O}_3} + (2-z)\beta M_{\text{Sb}}] / 2M_{\text{InSb}} \\ = 1 + 0.1014\beta - 0.2573\beta z, \quad (2)$$

where M_x represents the molecular weight of the constituent x (InSb, In_2O_3 , or Sb).

Table I summarizes the values β , f_m , z , and f depending on isothermal reaction time at 400 °C. The increase of the f value over the expected value $f = \text{In}_2\text{O}_3 / 2\text{Sb} = 0.5$ appears already at the reaction time 10 h. The highest possible value of f_m is 1.1014 at $\beta = 1$ (a complete conversion) and $z = 0$ (no escape of antimony from the system).

In summary, a heterogeneous cermet system InSb- In_2O_3 -Sb has been prepared from semiconducting polycrystalline InSb/ La_2O_3 (or InSb) by partial oxidation at elevated temperatures. Relatively constant electrical resistivity has been found for this type of material for interval of temperatures 4.2–300 K. The character of this dependence is given by phase composition of the obtained product, i.e., by

InSb (semiconductor), In_2O_3 (semiconductor), and Sb (metal). More detailed studies of the cermet compact prepared under various processing conditions (temperatures, time) for interval of measuring temperatures up to 150 °C as well as detailed thermogravimetric (TG), differential thermogravimetric (DTG), and differential-thermal analysis (DTA) studies are on the way now and the results will be published soon.

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