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# Synthesis and characterization of the intermetallic compound NiSbS

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**Abstract** The results recently obtained by our group to get new thermoelectric materials belonging to the M–Pn–Ch ternary systems (M=Co, Fe, Ni; Pn=P, As, Sb, Ch=S, Se, Te) are here reported. We have considered the Ni–Sb–S ternary system, and some homogeneous samples of composition near to 1:1:1 were prepared employing a new and simple synthetic route, starting from pure elements. Scanning electronic microscopy, electron-probe microanalysis and X-ray powder diffraction were used to investigate the microstructure. The NiSbS lattice parameters were determined and the crystal structure was refined by Rietveld method. The crystal cell of NiSbS belongs to the P213 space group with $a = 0.5931$ nm. The thermal stability of the ternary compounds Ni–Sb–S was investigated by DSC technique. Electrical resistivity and thermoelectric power measurements at room temperature and at 77 K were performed on platelets obtained by cleavage of the bulk.

**Keywords** Thermoelectrics · Intermetallic · Sulphides · Antimonide · Seebeck coefficient · Phase stability

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## Introduction

The M–Pn–Ch ternary systems (M=Co, Fe, Ni; Pn=P, As, Sb, Ch=S, Se, Te) are studied both for their interesting structural properties and for their applications as new materials with thermoelectric performance, thanks to the behaviour as semiconductor of some of them [1–5].

In a previous study, the Co–Sb system was studied for its possibility of doping at the Antimony site by chalcogenide elements, in particular by Sulphur, in order to increase the carrier concentration [5]. The introduction of S at the Sb site resulted in the formation of the compound CoSbS, that shows to be the most stable in the Co–Sb–S ternary system. For the compound CoSbS, room temperature (298 K) thermoelectric power ($S$) resulted to be around 200 $\mu V\ K^{-1}$ and resistivity was $5 \times 10^{-4}\ \Omega$ cm; the power factor resulted to be $0.8 \times 10^{-2}\ W\ K^{-2}\ m^{-1}$and the thermal conductivity, calculated using the Wiedemann–Franz law, would be 1.5 $W\ K^{-1}\ m^{-1}$: using these data the values typical of skutterudites figure of merit $ZT = 1.6$ was obtained [5].

Following the previous investigation on CoSbS, the intermetallic compound NiSbS was considered and its structural, microstructural and thermodynamic characterization, together with the thermoelectric properties are reported in this article.

Complete isothermal section at 298 K was first reported by Guertler et al. [6] and also complete isothermal sections were given by Williams et al. [7] at 623 and 773 K for the Ni–Sb–S ternary system. In the ternary phase diagram, only one stable ternary phase was observed and its structure determined [8–10]. Lange and Schlegel [10] reported a partial liquidus projection for the NiS–Ni–Sb–$Sb_2S_3$ concentration range, together with a reaction scheme for the invariant equilibria present in this region.

In Fig. 1, we represent the elemental cell of NiSbS (left) and the crystal of the Ullmannite mineral (right).

The Ullmannite is a natural mineral ternary compound of nominal composition NiSbS, the main impurities being Fe, Co, As and Bi. This structure belongs to the pyrite family, probably resulting from the substitution of $S_2$ groups in the Pyrite structure by SbS group in the Ullmannite structure. This replacement leads to a sizeable shifting of Ni atom along the body diagonal direction of the cube structure: in this arrangement Ni results surrounded by three Sb atoms and three S atoms [1, 11–17].

The natural Ullmannite changes its composition depending on the different deposit ore: NiS can dissolve <1 (mass%) PbS, but PbS dissolve up to 3(mass%) of NiSb [11].

The results on phase equilibria of the components of the NiS–Sb section were given by Allazov et al. [4] together with thermodynamic data on the NiSbS compound, its melting point, type of formation reaction and composition range of the phase.

Recently, the thermodynamic properties and the phase equilibria in the (Ni, Cu, Zn)–(As, Sb, Bi)–S systems were reviewed by Tesfaye et al. [11].

The Seebeck coefficient ($S$) and electrical resistivity ($\rho$) of a single polycrystalline natural specimen of NiSbS (Ullmannite) were measured by Johnston et al. [3] as a function of temperature, in particular $S \sim -9$ μV °C$^{-1}$ and $\rho \sim 9.6 \times 10^{-4}$ Ω cm at room temperature.

## Experimental

Nickel powders and sulphur powders (99.99 mass% nominal purity, Alfa Aesar, Karlsruhe, Germany) and antimony rod (99.99 mass% nominal purity, Carlo Erba, Milan, Italy) used as starting materials. Antimony was ground in an agate mortar and mixed in the stoichiometric amounts with the powders of the other two elements; the powders were then twice pressed ($p = 15$ MPa) to obtain a pellet. The ternary NiSbS compound was prepared heating in muffle furnace the pellet in a silica tube under partial pressure of Ar at 550 °C for 24 h, then at 780 °C for 10 h, annealed at 500 °C for 24 h, and then slowly cooled to room temperature. The sample was then ground again and the obtained powder pressed at $p = 15$ MPa, the powder was put in a small silica tube under partial pressure of Ar and melted again to obtain a cylindrical pellet suitable for thermoelectric measurement. The microstructure of the alloy was first investigated by light optical microscopy (LOM). Compositional and microstructural analysis were performed by scanning electron microscopy (SEM) and electron-probe microanalysis (EPMA) based on energy dispersive X-ray spectroscopy (EPMA–EDS). The surface of the specimens was polished and the microstructure investigated; the compositional contrast between the different phases was observed by means of a back scattered electrons (BSE) or secondary electrons (SE) detector. For quantitative EPMA, the samples were analysed at 20 kV acceleration voltage using cobalt as a calibration standard of the beam current, gain and resolution of the spectrometer. The structural properties were investigated by X-ray powder diffraction (XRD) collecting diffractograms by means of a Philips PW1830 diffractometer (Cu $K_\alpha$ radiation) in the range $10° \leq 2\theta \leq 90°$ and refining data by Rietveld method using the DBWS-9807 program.

Samples found in an equilibrium state, after synthesis and thermal treatments, were subjected to differential scanning calorimeter (DCS) analysis. A heat-flux calorimeter was employed (DCS 111 apparatus from Setaram), designed as a Calvet calorimeter, containing reference and working cells surrounded by two differentially connected thermal flux meters (thermopile with 120 pairs of thermocouples each). All thermocouples are of type S (Pt/Pt-10 mass% Rh). The furnace can be operated from ambient temperature up to 800 °C.

The thermoelectric power was measured by means of a home-made instrument. A heater applied on a base of a parallelepiped sample (12 × 5.0 × 6.2 mm) produces a thermal flow through the sample. Heat is then discharged on a thermal mass held at constant temperature by a

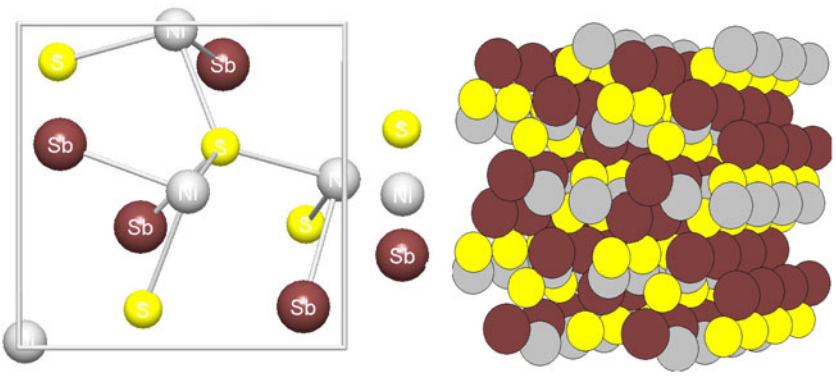


**Fig. 1** The elemental cell of NiSbS (*left*) and the crystal of the Ullmannite mineral (*right*)

thermostat at a temperature ranging between 15 and 115 °C. Two thermocouples are welded onto the surface of the rod, measuring the temperature difference, as well as the Seebeck voltage of the material. The thermoelectric power is then calculated.

## Structural and microstructural characterization

The diffraction patterns confirm the presence of the NiSbS compound, no secondary phases were detected. Lattice parameter of the NiSbS was determined employing WinplotR, Powdercell and Latcom crystal software [18, 19], as a = 0.59341 nm, in good agreement with the data reported by [2, 12] and slightly different to those reported for the Ullmannite [1, 14]. The results obtained from the power XRD, refined by the Rietveld method are reported in Fig. 2.

Morphological analysis, performed using a light optical microscope, reveals the presence of big cubic crystals, silver-grey coloured, with metallic shine. According to the data reported in literature [13–15] the compound has cleavage planes (001), as can be observed in Fig. 3.

Tests of microhardness performed on two cleavage plane of NiSbS sample show values ranging from 610 to 710 kg $mm^{-2}$ that are slightly higher in respect to Ullmannite microhardness [20].

The SEM analysis confirmed that the samples are single-phase. A typical SEM–SE microphotograph of the examined NiSbS compound is reported in Fig. 4, for which a composition of 32.4 at.% Ni, 32.9 at.% S and 34.7 at.% Sb was determined by EPMA, in good agreement with Allazov [4].

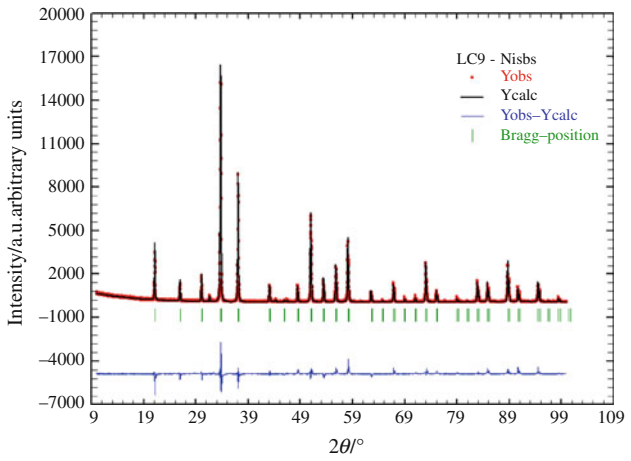


**Fig. 2** Rietveld refinement plot for NiSbS from X-ray diffraction data

**Fig. 3** Photo of pure sample of NiSbS. The cleavage *planes* are easily visible

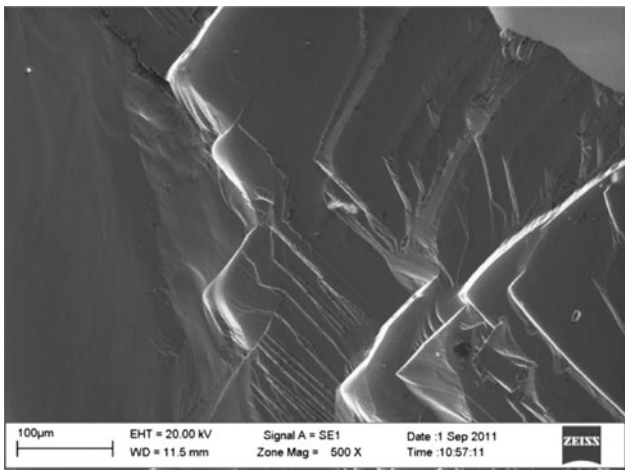


**Fig. 4** SEM–SE micrograph of the ternary compound

## Electrical and magnetic measurements

Johnston et al. [3] performed electrical measurements on a natural polycrystalline sample of Ullmannite: Seebeck coefficient and electrical resistivity were measured in a range of temperature between 77 and 400 K. The given results show a linear increasing of electrical resistivity with temperature and a Seebeck coefficient value of −9 μV $K^{-1}$ at room temperature: these results suggest that the compound has metallic behaviour, in agreement with Hulliger [21].

Electrical resistivity measurements were also performed in this work on a synthetic pure sample of NiSbS at room temperature and at 77 K. Four silver wires were spot welded onto a cleavage surface of a plate (9.0 × 15.0 mm) having thickness of 0.45 mm. It is noteworthy that the voltage measurements joints were spot welded onto the 001 surface: this can explain the different value found by [3]. Moreover, although the resistivity behaviour is metallic,

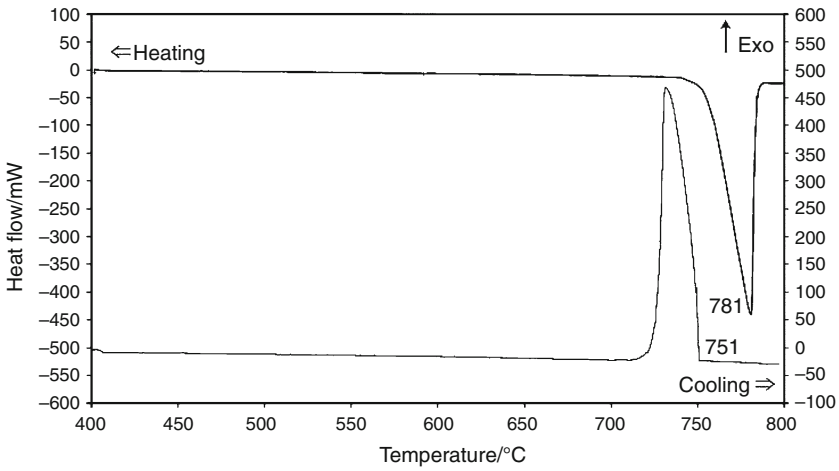


**Fig. 5** DSC heating and cooling traces for the $Ni_{33.3}Sb_{33.3}S_{33.3}$ from 400 to 800 °C at heating and cooling rate of 5 °C/min

the slope $d\rho/dT$ is higher than the slope calculated for the plot obtained by Johnston [3]. The electrical resistivity at 77 and 300 K was found to be 27 and 110 μΩ cm, respectively.

The Seebeck coefficient value, calculated at room temperature, was 50 μV $K^{-1}$.

Magnetic susceptibility was checked: $\chi_g$ is positive and its value is smaller than 0.7 emu $g^{-1}$.

## Thermal measurements

The temperature of transformation was determined by using a heat-flux calorimeter with a sensitivity limit of detection of 5–15 mV. The DSC samples were prepared by sealing 300–400 mg of the alloys under Ar in quartz vials and during the experiment the cells were maintained in a purified argon flow.

DSC analysis was carried out in continuous mode, with heating and cooling rate of 5 °C $min^{-1}$. The calibration of the apparatus was performed by measuring the melting temperature of metallic In, Sn, Pb and Zn (99.999 mass% purity) in the same conditions adopted for the experimental runs. Temperature was measured with an accuracy of ± 0.5 °C.

On heating, the onset temperature of the thermal effect was selected as the temperature of the occurring transformation and the peak temperature of the last thermal event as the liquidus temperature [22].

Figure 5 shows, as an example, a typical DSC curve obtained on heating and cooling for a sample $Ni_{33.3}Sb_{33.3}S_{33.3}$ (SEM analysis). Only a thermal effect at 781 °C was detected, which corresponds to the melting temperature of NiSbS; this alloy is one-phase sample, as observed by microscopic analysis. The experimentally determined liquidus temperature is in a fair agreement with the value of 760 °C reported by [4].

The results obtained for another sample characterized by SEM analysis having a $Ni_{34}Sb_{32.5}S_{33.5}$ atomic composition and a uniform distribution of the phases (NiSbS and a ternary eutectic mixture), showed three effects on heating at 540, 718 and 775 °C respectively. The first effect corresponds to the L → NiS + NiSb + NiSbS ternary eutectic reaction, for which the EDS analysis gave an average eutectic composition of $Ni_{48}Sb_{12}S_{40}$. The invariant temperature determined in this work is in fairly agreement with the 565 °C value reported by Allazov and Gulieva [10], considering that their measurements were carried out at 9 °C/min, using a DTA apparatus. The second effect at 718 °C corresponds to the intersection with the solid solubility limit of the NiSbS phase and the effect at 777 °C to the liquidus temperature.

## Conclusions

In the search for thermoelectric materials, the NiSbS compound was synthesised by a simple direct method. Thermal stability was investigated by DSC technique and the results were discussed and compared with the literature data. Electrical resistivity and thermoelectric power measurements were carried out at room temperature and at 77 K. As a result, the S values for this interesting phase is too low for thermoelectric applications. The differences found in the values of the electrical properties in respect to those of Ullmanite reported in literature are presumably due to the presence of large amount of impurities in the natural samples.

As a consequence of the large compositional stability of the Ulmanite that shows possibility of extensive substitutions, work is in progress to explore the field of existence of quaternary compounds $NiSb_{1-x}As_xS$ to evaluate a possible improvement of the thermoelectric properties due to the partial substitution of As for Sb.

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