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New Investigation on the SnS-Bi₂S₃ System

¹K. Adouby, ²M.L. Elidrissi Moubtassim and ³C. Perez Vicente,
⁴J.C. Jumas and ⁵A.A. Touré

¹Laboratoire de Procédés Industriels, de Synthèse et de l'Environnement, Institut National Polytechnique Félix Houphouët-Boigny, B.P. 1313 Yamoussoukro Côte d'Ivoire

²Département des Sciences de la Matière, Faculté Polydisciplinaire de Safi,
Université Cadi Ayyad, BP 4162, Safi, Morocco

³Laboratorio de Química Inorganica, Facultad de Ciencias, Universidad de Cordoba,
Avenida San Alberto MagnoE-14004 Cordoba, Spain

⁴Laboratoire des Agrégats Moléculaires et des Matériaux Inorganiques, UMR 5072,
Université Montpellier II, Place Eugène Bataillon, 34095 Montpellier Cedex 5, France

⁵Laboratoire de Chimie des Matériaux Inorganique, UFR-SSMT, Université de Cocody
22 BP 582 Abidjan 22, Côte d'Ivoire

Abstract: The SnS-Bi₂S₃ phase diagram (a pseudo binary section of the Bi-Sn-S ternary system) has been constructed by using the X-ray powder diffraction and the thermal analyses (DTA and DSC). This diagram shows a non-stoichiometric phase over a not well-defined composition domain, with a peritectic reaction at 548°C and two narrower solid solution domains. It is established from the lattice parameter variation that the solid solution range based on the orthorhombic SnS extends till 8 mol% Bi₂S₃. The electronic local order around tin atoms has been characterized by means of ¹¹⁹Sn Mössbauer spectroscopy. The hyperfine parameters (isomer shift and quadrupole splitting) are typical of tin at the oxidation state II.

Key words: Bi and Sn chalcogenides, phase equilibrium diagram, ¹¹⁹Sn Mössbauer spectroscopy, solid solutions

INTRODUCTION

The A^{IV}X-B^VX₃ (A^{IV} = Sn, Ge, Pb; B^V = Bi, Sb; X = Te, Se, S) systems are of great interest because of the semi conducting properties of the binaries and their intermediate compounds (Imamov *et al.*, 1970; Gospodinov *et al.*, 1971; Kurbanov *et al.*, 1986; Casula *et al.*, 1991; Christakudi *et al.*, 1995, 1996; Adouby *et al.*, 2000; Karpinskii *et al.*, 2001; Konstantinov *et al.*, 2001). The Bi₂X₃ (X = Te, Se) phases and their alloys are presently of interest as thermoelectric materials. Many works on SnX-Bi₂X₃ systems (X = Te, Se) were reported. However, for X = S few investigations were fulfilled. The only study of the equilibrium diagram of the SnS-Bi₂S₃ system was reported by Gospodinov *et al.* (1971) by means of X-ray diffraction, microstructural and differential thermal analyses. According to Gospodinov *et al.* (1971) any ternary phase was formed, only two primary solid solutions were revealed in this system. The melting temperatures of the initial sulphides are 879 and 760°C for SnS and Bi₂S₃, respectively. The

orthorhombic β-SnS (high-temperature form, TII-type structure) to α-SnS modification occurs around 590°C and decreases to 560°C for 10 mol% Bi₂S₃. The solid solution domain based on Bi₂S₃ is transformed to a peritectic reaction at 600°C. It extends to 53 mol% SnS at high temperature and decreases to 20 mol.% SnS at 400°C. Kurbanova *et al.* (1986) have reported the existence of SnBi₂S₄ in the SnS-Bi₂S₃ section.

This study concerning the reaction between the bismuth and tin sulphides is of a fundamental interest as a contribution to the SnS-Bi₂S₃ section knowledge owing the few available results. On the other hand, our aim is to achieve a comparison of this system with SnTe-Bi₂Te₃ and SnSe-Bi₂Se₃ (Casula *et al.*, 1991; Adouby *et al.*, 2000, unpublished). In this optic, we have reported previously a detailed study of the phase diagrams of SnX-Bi₂X₃ (where X = Te, Se) (Adouby *et al.*, 1998, 2000). Concerning the SnTe-Bi₂Te₃ system, we have confirmed the existence of SnBi₂Te₄ and two solid solutions based on the binary phases (Kurbanov *et al.*, 1986). Concerning the SnSe-Bi₂Se₃ system, three new phases have been

Corresponding Author: K. Adouby, Laboratoire de Procédés Industriels, de Synthèse et de l'Environnement, Institut National Polytechnique Félix Houphouët-Boigny, B.P. 1313 Yamoussoukro Côte d'Ivoire
Tel: 00 (225) 30646692 Fax: 00 (225) 30640406

reported: $\text{Sn}_4\text{Bi}_2\text{Se}_7$, $\text{Sn}_2\text{Bi}_2\text{Se}_3$ and SnBi_4Se_7 and two narrow ranges of solid solutions characterized for SnSe and Bi_2Se_3 rich-domains respectively. The detailed structures of SnBi_2Te_4 , $\text{Sn}_4\text{Bi}_2\text{Se}_7$ and SnBi_4Se_7 have been also reported previously (Adouby *et al.*, 1998, 2000, unpublished; Perez Vicente *et al.*, 1999).

In this study we report the phase diagram of SnS- Bi_2S_3 system obtained by means of thermal analyses (DTA and DSC) and X-ray powder diffraction. A characterization of the local environment of tin atoms in $\text{Sn}_{1-x}\text{Bi}_{2x}\text{S}_{1+2x}$ phases is discussed in the light of ^{119}Sn Mössbauer data.

MATERIALS AND METHODS

The tin and bismuth sulphides were prepared by solid state reaction between pure elements

Bi_2S_3 : Five mixtures of 8.1298 g (0.039 mol) of Bi and 1.8710 g (0.058 mol) of S were transferred into silica tubes and flame-sealed under vacuum ($\sim 10^{-5}$ torr). The tubes were heated to 825°C in 72 h, held at 825°C for 3 days and then cooled to 30°C in 1 day. The product was pulverized, controlled by X-ray diffraction and thermal analysis and used for further reactions.

SnS: Five mixtures of 7.9054 g (0.0666 mol) of Bi and 2.1360 g (0.0666 mol) of S were transferred into silica tubes and flame-sealed under vacuum. The tubes were heated to 800°C in 26 h, kept at this temperature during 4 days, cooled to 550°C in 5 h, maintained at this temperature for 4 days and then cooled to the room temperature at a rate of 30 deg h^{-1} . The product was ground and controlled by X-ray diffraction DTA and ^{119}Sn Mössbauer spectroscopy before its use for further reactions.

The cell parameters of SnS and Bi_2S_3 are reported in Table 1. The Mössbauer spectra and their related data, recorded at room temperature and -193°C, for SnS are shown in Fig. 1.

$\text{Sn}_{1-x}\text{Bi}_{2x}\text{S}_{1+2x}$ [$(\text{SnS})_{1-x}(\text{Bi}_2\text{S}_3)_x$] samples were prepared in the $0 \leq x \leq 1$ range from the binary phases SnS and Bi_2S_3 . The appropriate stoichiometric ratios were mixed and placed inside a silica tube and flame-sealed under vacuum ($\sim 10^{-5}$ torr). Two different procedures have been followed to synthesize the samples of SnS- Bi_2S_3 section.

Table 1: Lattice parameters of orthorhombic SnS (Pnma) and Bi_2S_3 (Pbnm)

Parameters	SnS	Bi_2S_3
a(Å)	4.33 (2)	11.15 (1)
b(Å)	11.19 (2)	11.30 (1)
c(Å)	3.99 (5)	3.98 (1)
v(Å ³)	193.20 (5)	501.62 (2)

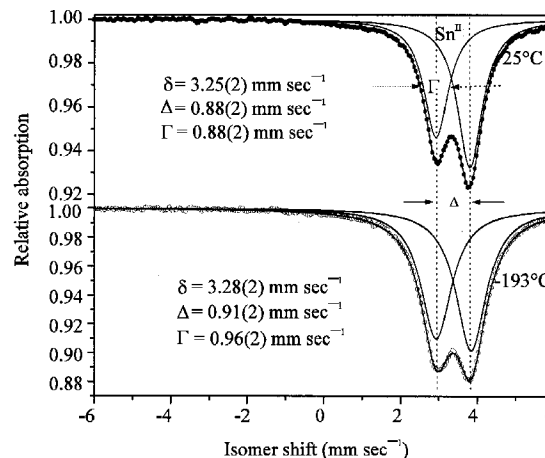


Fig. 1: Mössbauer spectra of SnS at two different temperatures. Experimental data (circles) and the fitted lines (full line)

The first series were heated to 900°C over a period of 2 days. This temperature was maintained for 24 h, the samples were then cooled to 550°C in 7 h, maintained at this temperature for 2 months and then quenched in an icy-water bath. The second series of three samples ($x = 0.72$; 0.75 ; 0.8) were prepared in order to verify the solid solution domain previously reported (Gospodinov *et al.*, 1971). The samples have been heated (30°C h^{-1}) at 700°C, maintained at this temperature during 12 days, cooled (50°C h^{-1}) to 630°C, annealed for 20 days and finally quenched in an icy-water bath.

The final products were crushed to reduce the particle size and characterized by X-ray diffraction, thermal analysis and ^{119}Sn Mössbauer spectroscopy.

The phases identification was carried out by X-ray diffraction patterns recorded alternatively on a PHYLIPS and SIEMENS D5000 diffractometers, using the Cu-K α radiation ($\lambda = 1.54051\text{Å}$) at room temperature over the angle domain $5^\circ \leq \theta \leq 40^\circ$. The patterns were refined by means of the computing program RAYON (Fraisie, 1995).

The thermal analyses (DTA and DSC) were carried out with DTA92 and DSC121 SETARAM apparatus, from the room temperature to 900 and 800°C, respectively at a 5°C min^{-1} rate. Samples were placed in evacuated quartz ampoules and the measurements were carried out under argon to avoid any oxidation phenomena. The curves were refined by the SETARAM computing programs TGTA92 and DSC121.

^{119}Sn Mössbauer spectra were recorded at 80 K in the constant-acceleration mode on an ELSCINT-AME40 spectrometer. The γ -ray source was $^{119\text{m}}\text{Sn}$ in BaSnO_3 matrix. The velocity scale was calibrated with the magnetic

sextet spectrum of a high purity iron foil absorber using a $^{57}\text{Co}(\text{Rh})$ source. The spectra were fitted to Lorentzian profiles by a least-squares method (Kündig, 1969; Ruebenbauer and Birchall, 1979) and the goodness of the fits controlled by the classical χ^2 and misfit tests (Gruverman and Seidel, 1970). All the isomer shifts reported here are given with respect to the centre of a BaSnO_3 spectrum obtained with the same source at room temperature. The equilibrium phase diagram was constructed in the light of the collected data.

RESULTS AND DISCUSSION

Phases identification: First series (annealed at 550°C): X-ray diffraction patterns of alloys containing less than 10% mol. Bi_2S_3 ($x = 0.1$) present only the characteristic Bragg reflection of SnS indicating the existence of a solid solution domain based on $\alpha\text{-SnS}$ ($\langle\text{SnS}\rangle$ low-temperature form). Samples containing 15-90% mol Bi_2S_3 ($0.15 \leq x \leq 0.9$) exhibit the diffraction peaks of both SnS and Bi_2S_3 . The further compositions exhibit the Bragg reflections of Bi_2S_3 lying with a solid solution based on this compound ($\langle\text{Bi}_2\text{S}_3\rangle = \epsilon$). The X-ray data of these first series confirm the presence of two weak solid solution ranges based on both $\alpha\text{-SnS}$ ($\langle\text{SnS}\rangle$ low-temperature form) and Bi_2S_3 ($\langle\text{Bi}_2\text{S}_3\rangle$). Obtained diagram is shown in Fig. 2.

On the SnS side, the variation of the cell parameters with the composition is in agreement with the Vegard's law (Fig. 3). The lattice a decreases linearly with x till

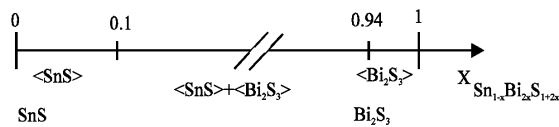


Fig. 2: Phases identification in first series

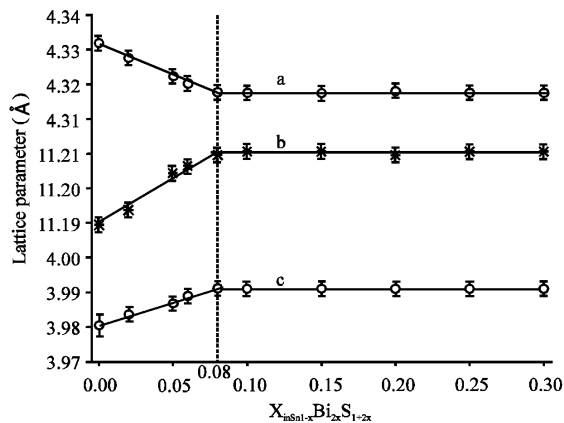


Fig. 3: Plots of the lattice parameters variation of the SnS-based solid solution

$x = 0.08$ then it stays invariant. Concerning b and c parameters, their evolution follows the Vegard's law in the same region. They increase between 0 and 0.08 and become invariant for $x > 0.08$. So, $x = 0.08$ is taken as the limit of the $\alpha\text{-SnS}$ -based solid solution under the used experimental conditions.

Second series (annealed at 630°C): This temperature favours the formation of an intermediate phase as shown in Fig. 4. The annealing of the samples at 630°C has been used to stabilize the new phase. In order to trap the ternary phase, a fast cooling from 630°C to 0°C has been used. At $x = 0.72$ and $x = 0.75$ the diffraction diagrams show new peaks (Fig. 4) meaning the existence of a new intermediate tin-bismuth-sulphur phase. As x increases, the orthorhombic SnS phase vanishes on account of the new phase. At $x = 0.75$ the new phase is obtained as a pure compound. This x value corresponds to the stoichiometric $\text{SnBi}_6\text{S}_{10}$. Finally, for higher x values additional peaks appear, corresponding to the Bi_2S_3 solid solution.

Phase equilibrium diagram: The phase equilibrium diagram has been drawing from X-ray diffraction, Mössbauer spectroscopy and thermal analyses data, carried out by recording the heating curves of all alloys. This diagram is shown in Fig. 5. It is characterized by the occurrence of two narrow solid solutions (α , β and ϵ), five invariants and one new intermediate compound within the homogeneity region. The corresponding formula of the stoichiometric composition is: $\text{SnBi}_6\text{S}_{10}$.

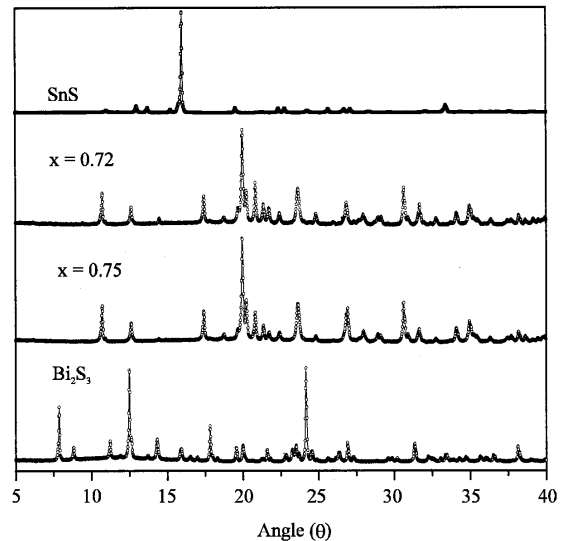
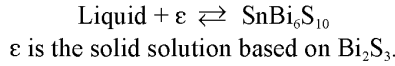
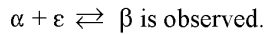


Fig. 4: Comparison of XRD patterns of $\text{Sn}_{1-x}\text{Bi}_{2x}\text{S}_{1+2x}$ obtained by second series with the pristine binaries SnS and Bi_2S_3

The X-ray diffraction patterns and thermal measurements of quenched alloys at 630°C exhibit the formation of SnBi₆S₁₀ (γ-corresponding to 75 mol% Bi₂S₃), with a weak region of homogeneity, stable from 600 to 648°C. It is formed by a peritectic reaction at 648°C:

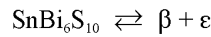


The phase transition from α to β-SnS was observed at 592±5°C and occurs at 590°C in the solid solution domain <SnS>. At this temperature the peritectoid decomposition of α-SnS:

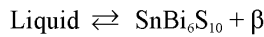


α and β are the solid solutions based on the Low-Temperature (LT) and the High Temperature (HT) forms of SnS, respectively.

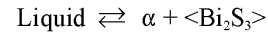
At 600°C the phase SnBi₆S₁₀ undergoes the following eutectoid decomposition:



The eutectic reaction occurs at 630°C for 33 mol% Bi₂S₃:



In the region between α-SnS and <Bi₂S₃>, we observe an invariant at 560°C (dotted line). At this temperature occurs the eutectic reaction when the used experimental conditions are not those of the formation of SnBi₆S₁₀.



In all cases, the diagram (Fig. 5) proposed in this work is quite different from the Gospodinov's one (1971). It shows the existence of one bismuth-rich intermediate phase, never reported before. The wide region based on Bi₂S₃, reported in earlier investigation, has not been confirmed and the phase SnBi₂S₄ (50 mol% Bi₂S₃) pointed, was not confirmed too (Kurbanov *et al.*, 1986). However, we note that the phase SnBi₆S₁₀ is the limit of the wide solid solution region based on Bi₂S₃ reported by Gospodinov *et al.* (1971).

The above results show that the annealing temperature is a determining-factor for the formation of the new intermediate phase obtained in the SnS-Bi₂S₃ system.

¹¹⁹Sn Mössbauer: ¹¹⁹Sn Mössbauer spectroscopy is a very efficient tool for probing the local environment of tin atoms in tin containing compounds. In this study, we focus our interest on the main hyperfine parameters: Isomer shift (δ), Quadrupole splitting (Δ) and Linewidth (Γ) variation with x. ¹¹⁹Sn Mössbauer measurements on

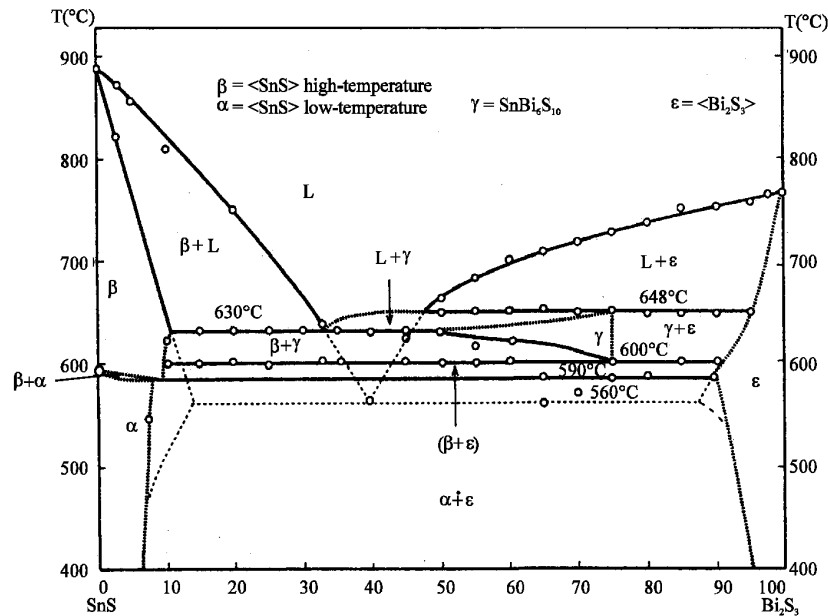


Fig. 5: Phase diagram of the SnS-Bi₂S₃ system: (α) solid solution based on LT form SnS, (β) solid solution based on HT form SnS, (L) liquid, (γ) <SnBi₆S₁₀>, (ε) solid solution based on Bi₂S₃

SnS, recorded at different temperatures (Fig. 1), have an isomer shift of 3.3 mm sec^{-1} and a quadrupole splitting ($\Delta \neq 0$) both characteristic of Sn^{II} in a distorted octahedral environment. This is in agreement with previously reported structure of SnS (orthorhombic, space group Pnma) Both Sn and S atoms are placed in 4c site ($x, y, 1/4$), where $x = 0.1198$ and $y = 0.1194$ for Sn atoms and $x = 0.4793$ and $y = 0.8508$ for S atoms. The tin atoms are octahedrally coordinated with systematic variations of bond lengths (Fig. 6) (Wiedemeier and Schnering, 1978; Wiedemeier and Csillag, 1979). The tin atom forms with its six first neighbours sulphur two types of bonds, three short bonds and three relatively long bonds. This difference of the bonds creates a distortion of the site of each atom. In this structure the stereochemical activity of the two electrons 5s or nondependent pair of tin is very marked. The structure of made up SnS thus highlights bonds Sn-S in covalent matter marked in the case of the three short bonds and an important stereochemical activity of the nondependent electronic pair of tin. The orthorhombic-SnS can be considered as a distortion of the SnTe structure (NaCl type) at room temperature. The decreasing of the asymmetry of the two peaks as the temperature decreases (Fig. 1) lies with the classical Goldanskii-Karyagin effect (Williams *et al.*, 1995).

Figure 7 shows the γ -absorption spectra of alloys of the first series and that of SnS. As can be seen, all the spectra are clearly doublets. Their asymmetric shape is

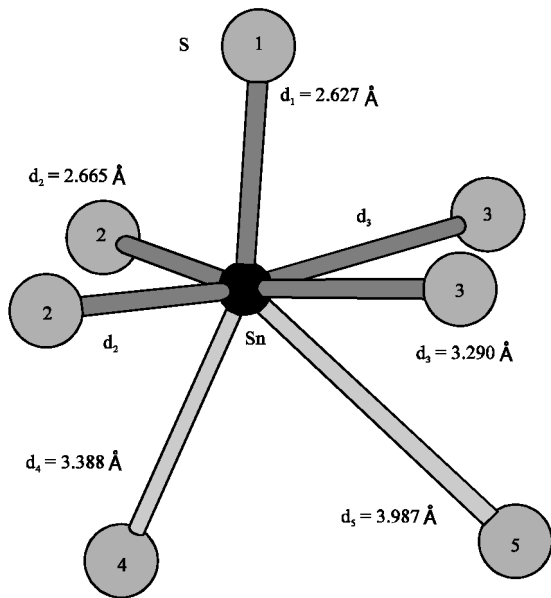


Fig. 6: Sulphur environment around a Sn atom in SnS with the different types of important interatomic distances. The tin atom is surrounded by highly distorted octahedral of S atoms

due to the Goldanskii-Karyagin effect. Table 2 summarizes the related values of the isomer shift (δ), the line width (Γ), the quadrupole splitting (Δ) -and their standard deviations ($\Delta\delta$, $\Delta\Gamma$ and $\Delta\Delta$). All the values of the isomer shift are characteristic of divalent tin compounds (Fano and Ortalli, 1974) and suggest similar environments of tin atoms in $\text{Sn}_{1-x}\text{Bi}_{2x}\text{S}_{1+2x}$ and SnS. The observed values of Γ ($0.95\text{-}1.13 \text{ mm sec}^{-1}$) are in good agreement with the existence of a unique crystallographic site for tin atoms in this series. The values of the quadrupole splitting Δ ($0.91\text{-}0.98 \text{ mm sec}^{-1}$) confirm the strong distortion of the environment of the tin atoms.

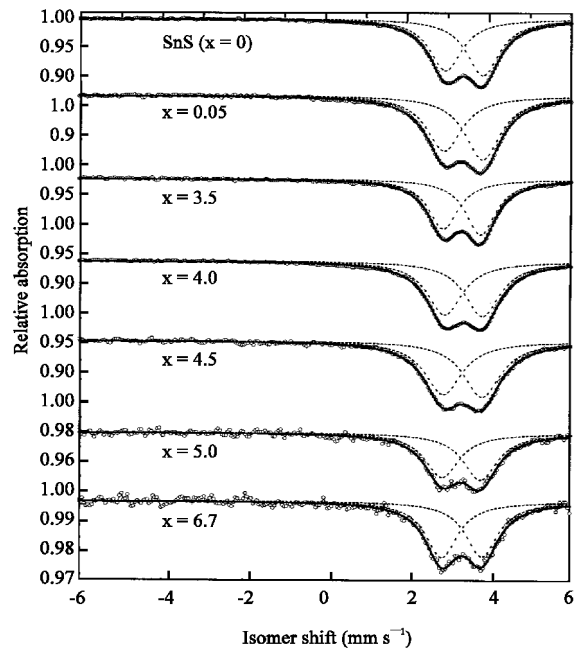


Fig. 7: Mössbauer spectra of $\text{Sn}_{1-x}\text{Bi}_{2x}\text{S}_{1+2x}$ recorded at 80 K for the samples of the first series Experimental spectra (full line) the fitted lines (dotted line)

Table 2: Isomer shift (δ), quadrupole splitting (Δ) and full width at half maximum (Γ) obtained from the fitting of the Mössbauer spectra of Fig. 7

x	δ	$\Delta\delta$	Δ	$\Delta\Delta$	Γ	$\Delta\Gamma$
in Sn_{1-x}	(mm sec^{-1})	(mm sec^{-1})	(mm sec^{-1})	(mm sec^{-1})	(mm sec^{-1})	(mm sec^{-1})
$\text{Bi}_{2x}\text{S}_{1+2x}$						
0.00	3.30	0.02	0.91	0.02	0.96	0.03
0.05	3.28	0.04	0.94	0.04	1.04	0.01
0.06	3.30	0.06	0.92	0.06	1.09	0.03
0.08	3.32	0.07	0.92	0.07	1.13	0.01
0.35	3.26	0.02	0.91	0.02	0.90	0.04
0.40	3.30	0.02	0.92	0.02	1.04	0.04
0.45	3.29	0.02	0.94	0.02	1.10	0.04
0.50	3.26	0.01	0.93	0.01	1.01	0.02
0.67	3.28	0.01	0.98	0.01	0.95	0.02

CONCLUSION

The SnS-Bi₂S₃ system was refined and its characteristics have been brought out. The phase equilibrium diagram has been obtained by means of X-ray powder diffraction, thermal analyses and ¹¹⁹Sn Mössbauer spectroscopy. A new phase and two solid solution domains were identified. The role of the annealing temperature has been pointed as the main factor of the stability of the obtained intermediate new phase in this system. Thus, the alloys annealed at 630°C show the existence of the phase (SnBi₆S₁₀), while at 550°C, any intermediate compound has been obtained. Our results are quite different of those previously reported (Gospodinov *et al.*, 1971; Kurbanov *et al.*, 1986). However, the boundaries of the new phase domain are not yet well known but their annealing-temperature dependence is clear. The solid solution based on Bi₂S₃ and the structure of SnBi₆S₁₀, are still to clarify.

This work contributes to a new description of the SnX-Bi₂X₃ (X = Te, Se, S) systems. It underlines the structural role of the chalcogen element, the nature of the one-phase domains in these systems and the existence of primary solid solution or intermediate phases. Thus, when tellurium (Adouby *et al.*, 2000) favours the formation of wide solid solution domains with a substitution-type character with SnTe and intercalation-type character with the layered Bi₂Te₃, the selenium does not allow the existence of such domains and leads to the formation of several phases: Sn₄Bi₂Se₇, Sn₂Bi₂Se₂ and SnBi₄Se₇ (Adouby *et al.*, 1998, unpublished; Perez Vicente *et al.*, 1999). Finally, sulphur has an intermediate behaviour as shown by the formation of a non-stoichiometric phase over a not well-defined composition domain.

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