The $Sn_{1-x}Sb_{1+x}$, x ~ 0.5, Solid Solution: the Relationship Between α and β

Lasse Norén[a], Jeppe Christensen[b], Sven Lidin[b], Siegbert Schmid[c] and Ray L. Withers[a]

[a] Research School of Chemistry, The Australian National University, Canberra, ACT 0200, AUSTRALIA

[b] Div. Oorganisk kemi, Arrheniuslaboratoriet, Stockholms Universitet, SE-106 91 Stockholm, SWEDEN

[c] School of Chemistry, Building F11, University of Sydney, Sydney, NSW 2006, AUSTRALIA

This is part of a broader study of the binary solid solution β-SnSb, its structure and composition range. In this part we focus on the structure of the nominal "SnSb" alloy and also present data indicating that previous studies in this system have not been on equilibrated samples. The structure is related to the NaCl-type but is best described as a 3+1 D modulation on a rhombohedrally distorted primitive cubic average cell of *α-Po* type. The space group symmetry (in the hexagonal setting) is $R\bar{3}m$ (0, 0, ~1.31) (No 166.1) with $\mathbf{q}_h$ = 1.3109(9) **c*** and the parent cell parameters a_h = b_h = 4.3251(4) Å, c_h = 5.3376(6) Å.

1. Introduction

The β-$Sn_{1-x}Sb_{1+x}$, x ~ 0.5, solid solution (β-SnSb) has recently attracted interest in materials research both as a possible replacement for lead solder as well as a potential lithium storage material. The true structure, as well as the precise extent of the solid solution range, has been hotly debated ever since the compound was first reported in 1927 [1]. Its crystal structure has been reported as being of disordered, simple cubic *α-Po* type [1], of ordered *NaCl*-type [2], and as a rhombohedrally distorted variant of the *NaCl*-type [3].

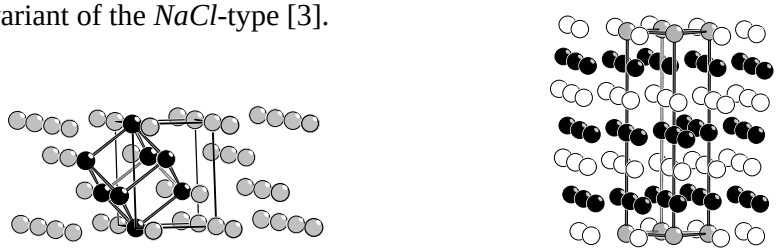

Figure 1: Disordered β-SnSb described both in terms of a primitive cubic (PC) unit cell [1] (see the black atoms) as well as a rhombohedrally distorted variant thereof in the hexagonal setting (thin lines). The ordered structure of β-SnSb is shown in (b) in the hexagonal setting [3]. The lattice points of this hexagonal cell are placed on the gray atoms above. Note that the *c*-axis of this cell is twice that of the hexagonal cell in (a).

Likewise, the reported solid solution ranges have varied considerably. An underlying problem from the structural point of view is that Sn and Sb are next to one another in the periodic table making the distinction between them difficult using conventional X-ray sources. The different composition ranges reported for this b-phase are likely due

to problems in reaching equilibrium, as diffusion in the solid state is slow. This makes it possible that metastable high temperature structures are maintained for long time periods at lower temperatures making it difficult to establish "true" phase ranges.

This study aims to address both these problems and the preliminary investigation on nominal SnSb shows that the structure is considerably more complicated than what has been reported to date.

2. Experimental

The compound was made by melting stoichiometric amounts of the pure elements together in an evacuated silica tube and heat treat the product for 1 week at 300 °C. The compound was then crushed in an agate mortar and pellets were pressed, these were annealed in evacuated Pyrex tubes at 280 °C and periodically checked with powder diffraction, the total annealing time was 3 months. The TEM investigation was carried out in a Philips EM 430 TEM on crushed grains of the samples dispersed onto holey carbon coated copper grids. X-ray pattern was taken using both $CuK_{\alpha 1}$ and synchrotron radiation.

3. Results

The smooth change of lattice parameter with composition indicate a solid solution for the range investigated but it is clear that SnSb, even after 3 month annealing, has not quite reached equilibrium. Thus it is likely that other studies in this system [1-5] have been done on non-equilibrated samples, as their annealing times have been substantially shorter.

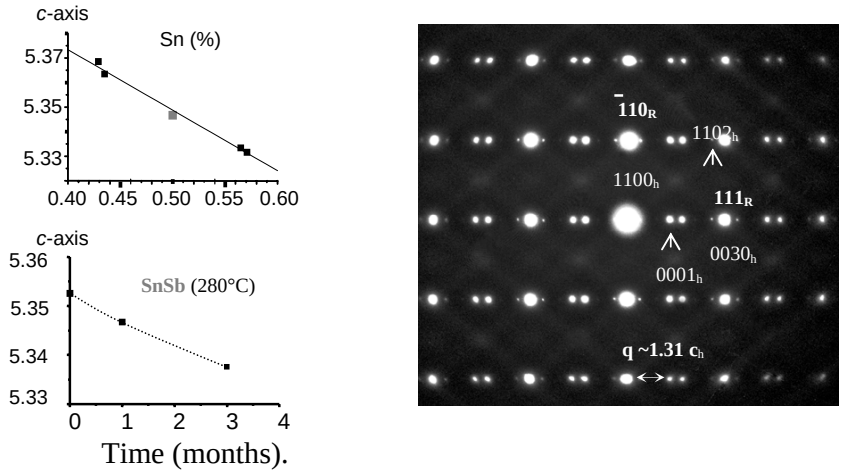

Figure 2: Lattice parameters of $Sn_{[1-x]}Sb_{[1+x]}$ solid solution on one month annealed samples (a) and the *c*-axis change vs time for SnSb (b). The EDP (c) show the incommensurate modulation along c*, indexed both on the rhombohedral parent and on a (3+1)D hexagonal cell.

As can be seen in the electron diffraction pattern (edp) the structure of SnSb is incommensurately modulated with a modulation wave-vector "**q**"~1.31 *c**. The resulting space group is $R\bar{3}m$ (0, 0, ~1.311). The parent cell parameters, as refined from synchrotron data was $a_h = b_h = 4.3251(4)$ Å, $c_h = 5.3376(6)$ Å with $\mathbf{q}_h = 1.3109(9)\ \mathbf{c}^*$. The modulation is displacive in origin and is related to the intra-layer separation distance in the structure (*c.f.* Fig. 1b and Fig. 3b). The refinement of the modulated structure agrees well with the recorded diffraction pattern (GoF 1.18, R_p

4.79, R_{wp} 6.55). The refined waves show the magnitude and directions of the displacement of the atom layers and the likely composition of the layers.

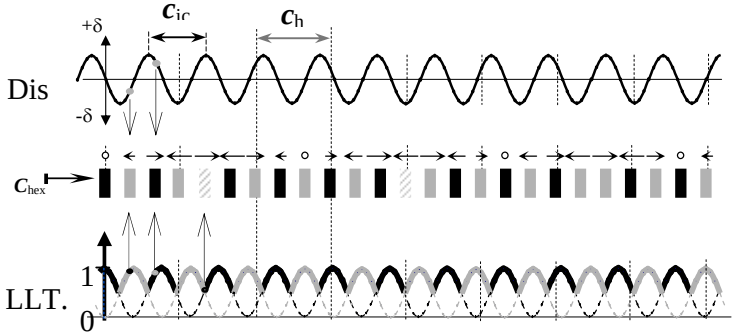

Figure 3: The displacive wave for the atom layers (a), the stacking sequence and displacement of the atom layers along c_h-axis in the structure (b) and the Likelihood of Layer Type (LLT) waves. Sb = black, Sn = gray.

If we start - in (3b) - with an Sb layer (black wave =1 in Fig. 3c) with no displacement (Fig. 3a) we see that the next layer ($^1/_3$ c_h) is Sn and that this layer is displaced in a negative direction as we move along the c_h-axis (Fig. 3a). The layer following (at $^2/_3 c_h$) is Sb (Fig 3c) and is displaced in a positive direction (3a). The layer at $c_h = {}^3/_3$ is Sn and at $^4/_3$ is a "phason wobble" with equal probability for Sb or Sb (striped in Fig. 3b). As is seen in Fig. 3b this result in that two Sn layers next to one another are displaced in opposite directions while Sn-Sb and Sb-Sb layers appear to move towards one another. The displacement shifts are the origin of the satellite reflection (as Sn and Sb scatter X-rays, of the wavelength used, almost identically)

4 Conclusions

The nominal SnSb compound in the "β-SnSb" solid solution is a modulated structure and is best described on a rhombohedrally-distorted cell of α-Po type with the modulation along the rhombohedral axis. The compound takes a long time to reach equilibrium and it is very likely that the discrepancies in regards to the solid solution ranges are due to non-equilibrated samples.

Acknowledgments

R.L.Withers and S.Schmid thank the Australian Research Council (ARC) for financial support in the form of an ARC Discovery Grant (DP0557222).

References

[1] A. Osawa, *Nature*, **124** (1927) 14.
[2] E.G. Bowen and W. Morris Jones, *Philos. Mag.* **12** (1931) 441.
[3] G. Hägg and A.G. Hybinette, *Philos. Mag. Ser. 7*, **20** (1931) 913.
[4] B. Predel and W. Schwermann, *J. Inst. Met.*, **99** (1971) 169.
[5] P.J.T.L. Oberndorff, A.A. Kodentsov, V. Vourinen, J.K. Kivilahti and F.J.J. van Loo, *Ber. Bunsen-Ges. Phys. Chem.*, **102** (1998) 1321.