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# Preparation and Characterization of New Misfit Layer Selenides $SnVSe_3$ and $SnNb_2Se_5$

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New "$SnVSe_3$" and "$SnNb_2Se_5$" phases have been synthesized from the corresponding elements. The structure of these compounds may be described as a mixed sandwiched layered type where one [SnSe] slab alternates with one [$VSe_2$] slab for $SnVSe_3$ and with two [$NbSe_2$] slabs for $SnNb_2Se_5$.

Crystal structure and electrical and magnetic properties of ternary chalcogenides with misfit layer structures have attracted much attention in the last few years.[1-4] In addition, misfit layer compounds may be appropriate hosts for intercalation reactions.[1] Two types of stoichiometry and stacking sequences have been described for misfit layer sulfide compounds, namely $MM'S_3$ and $MM'_2S_5$. The former consists of a stacking sequence of C (MS, NaCl-related slab) and H ($M'S_2$, $CdI_2$-related slab) sublattices, while the ...HHC... sequence is found for 1:2:5 phases.[5] For mixed selenides, several 1:1:3 phases have been reported such as $SnNbSe_3$[6] and $BiMSe_3$ (M: Ti, V, Nb, Ta).[7] Oosawa et al.[8] preliminary reported that 1:2:5 type selenide ($BiNb_2Se_5$) is formed and all the 1:2:5 type chalcogenides behave as hosts for intercalation. In this communication, new "$SnNb_2Se_5$" and "$SnVSe_3$" phases are described.

Samples with nominal compositions "$SnVSe_3$" and "$SnNb_2Se_5$" were prepared from the elements in the desired proportions by heating the pelleted mixtures in evacuated silica ampoules. For the $SnNb_2Se_5$ sample, heating rate was 1°/min, the temperature was maintained at 300 °C for 1 day, and at 900 °C for 7 days. For $SnVSe_3$, the temperatures were 500 °C for 1 day and 800 °C for 7 days, with heating rates of 2°/min. Both compositions led to polycrystalline black powders with luster.

Powder X-ray diffraction patterns were obtained with a Siemens D500 diffractometer, equipped with graphite-monochromatized CuKα radiation. Electron diffraction patterns were obtained with a JEOL 200CX microscope. Samples were ground in an agate mortar, dispersed in acetone and placed on carbon-covered copper grids for their examination.

The X-ray diffraction pattern of $SnVSe_3$ and $SnNb_2Se_5$ showed several intense lines, which are multiple order reflections of the basal planes, and few weak lines. The observed and calculated d-spacings and relative intensities for each (00*l*) reflection are shown in Table 1. From these values,

Table 1. Powder X-ray diffraction line spacings and observed intensities

| | | | $SnVSe_3$ | | | $SnNb_2Se_5$ | | |
|---|---|---|---|---|---|---|---|---|
| *h* | *k* | *l* | $d_{obsd}$ | $d_{calcd}$ | $I/I_0$ | $d_{obsd}$ | $d_{calcd}$ | $I/I_0$ |
| 0 | 0 | 2 | $12.39_6$ | $12.10_2$ | 4 | - | - | - |
| 0 | 0 | 4 | $6.04_1$ | $6.05_1$ | 33 | $9.28_1$ | $9.26_2$ | 6 |
| 0 | 0 | 6 | $4.02_2$ | $4.03_5$ | 8 | $6.15_1$ | $6.17_5$ | 95 |
| 0 | 0 | 8 | $3.01_6$ | $3.02_6$ | 100 | $4.63_3$ | $4.63_1$ | 11 |
| 0 | 0 | 10 | $2.40_8$ | $2.42_1$ | 11 | $3.71_1$ | $3.70_5$ | 14 |
| 0 | 0 | 12 | $2.00_7$ | $2.01_7$ | 6 | $3.08_9$ | $3.08_7$ | 100 |
| 0 | 0 | 14 | $1.72_2$ | $1.72_9$ | 4 | $2.64_7$ | $2.64_6$ | 26 |
| 0 | 0 | 16 | $1.50_7$ | $1.51_3$ | 18 | $2.31_7$ | $2.31_5$ | 24 |
| 0 | 0 | 18 | - | - | - | $2.06_0$ | $2.05_8$ | 21 |
| 0 | 0 | 20 | - | - | - | $1.85_3$ | $1.85_2$ | 7 |
| 0 | 0 | 22 | - | - | - | $1.68_5$ | $1.68_4$ | 9 |
| 0 | 0 | 24 | - | - | - | $1.54_8$ | $1.54_3$ | 42 |

the calculated *c* unit cell parameter was $24.20_4$ and $37.05_1$ Å for $SnVSe_3$ and $SnNb_2Se_5$, respectively. These values are consistent with a stacking sequence as follows: for $SnVSe_3$, each repeating unit along the [001] direction is formed by two C and two H sublattice slabs following an HCHC sequence; for $SnNb_2Se_5$, two C and four H slabs form the HHCHHC unit. This pattern is characteristic of the 1:1:3 and 1:2:5 mixed chalcogenide phases already described.[1-5)]

Figure 1 shows the electron diffraction patterns of $SnVSe_3$ and $SnNb_2Se_5$

platelike particles with the incident beam parallel to [001]. The patterns shown in Fig. 1 *a* and *b* are characteristic of a superposition of an hexagonal pattern due to the $VSe_2$ and $NbSe_2$ pseudohexagonal sublattice H layers and a square pattern due to the SnSe pseudocubic C sublattice[9, 10] with a single relative orientation. This zone axis electron diffraction pattern does not allow the distinction of each structural type (HHC or HC). For $SnNb_2Se_5$, only few distorted regions showed a pattern like that shown in Fig. 1 *c*. This intricate pattern has also been found in other misfit layer chalcogenides[10] and can be interpreted in terms of two orientations of the $NbSe_2$ layers differing by 30°.

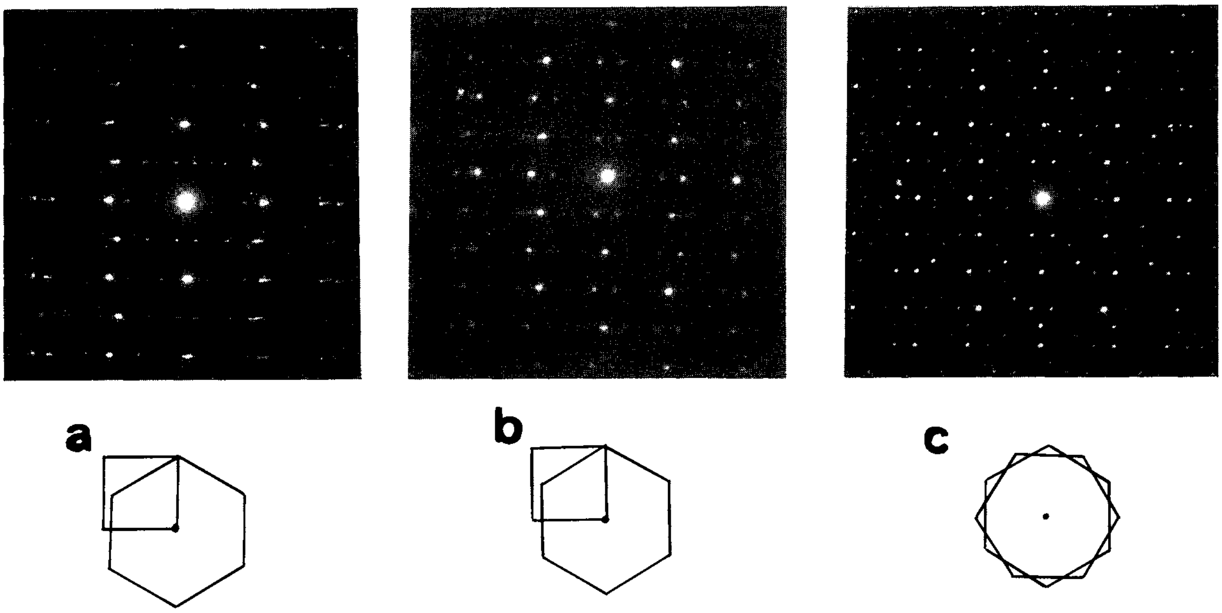

Fig. 1. Electron diffraction patterns with incident beam parallel to [001] of platelike particles of *a*) "$SnVSe_3$", *b*) "$SnNb_2Se_5$" with single orientations of H and C sublattices, *c*) "$SnNb_2Se_5$" with two orientations of H sublattice differing by 30°.

Finally, the possibility of lithium intercalation in these phases has been examined. The preliminary results were obtained by the reaction with an excess of 1.6 M *n*-butyl lithium solution in hexane under an argon atmosphere. The X-ray diffraction pattern of the lithiated powder $SnNb_2Se_5$ sample shows significant changes in the *c* parameter which increases to $37.84_0$ Å after including 0.04 Li atoms per formula unit. On the contrary, the intercalation of 0.04 Li atoms per $SnVSe_3$ unit leads to negligible changes in unit cell parameters. The fact that lithium intercalation induced little changes in the unit cell parameter was related with the compensating effects of $Li^+$ size, the electrostatic attractions between negatively-charged slabs and $Li^+$, and the repulsion between the slabs.11) The differences in the behaviour of $SnVSe_3$ and $SnNb_2Se_5$ may be related with the presence of consecutive H layers separated by a wide Van der Waals gap in the latter phase. Similar differences were found in the intercalation of lithium in $PbTiS_3$ and $PbTi_2S_5$.12) Further work related to this field is under progress.

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