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# GROWTH CONDITIONS AND STRUCTURAL CHARACTERIZATION OF MOLYBDENUM SULPHOSELENIDE SINGLE CRYSTALS: ($MoS_xSe_{2-x}$, $0 \leq x \leq 2$)

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ABSTRACT

Single crystals of layer compounds with composition $MoS_xSe_{2-x}$, where x varies within the range 0 to 2, have been grown by the direct vapour transport technique to the maximum size of 15 mm x 10 mm x 0.3 mm. The series forms a complete range of isomorphous solid solutions, showing good agreement with Vegard's law. The composition of the above crystals was examined by ESCA (Electron Spectroscopy for Chemical Analysis). Crystal lattice parameters have been determined for the series with an X-ray diffractometer.

## Introduction

In the family of layer compounds, the transition-metal dichalcogenides have gained a considerable importance because of their various applications. The direct-vapour-transport technique has been found to be a suitable tool by several workers (1-4) for growing single crystals of layered compounds. It appears from the literature that so far no attempt has been made to grow molybdenum sulphoselenide single crystals in the solid-solution series $MoS_xSe_{2-x}$ ($0 \leq x \leq 2$) by any technique. In this paper, we report the growth of single crystals of $MoS_xSe_{2-x}$ and X-ray characterization and the ESCA (Electron Spectroscopy for Chemical Analysis) of as-grown crystals. The mixed crystals are found to be isomorphous over the complete range of compositions. According to Beal (5), the study of a mixed system, say $MoS_{x-2}Se_{2(1-x)}$, could provide much useful information about two- and three-dimensional excitations, inter-layer effects and the dependence of transition oscillator strength on covalency.

## Experimental

High quality quartz ampoules were etched vacuum backed; and 99.999% pure molybdenum, spectroscopically standardised, 99.999% pure sulphur powder, and 99.999% pure selenium powders in stoichiometric proportion were placed in an

ampoule 25 mm in diameter and 250 mm long. The total charge of 9.14 gm was used in each experiment. Then the ampoule was evacuated and sealed at a pressure of $10^{-5}$ torr at a constriction 3 mm in diameter. The ampoule was vibrated to ensure the proper mixing of powders. The mixture was distributed along the length of the ampoule, which was placed in a two-zone furnace, providing a linear gradient; the temperature of the ends of the ampoule were controlled to within + 1°C by Eurotherm controllers. The temperature of the furnace was increased in steps to 40°C per hour; the slow heating was necessary to avoid any possibility of explosion due to the strongly exothermic reaction between the elements. After 72 hours, the furnace was switched off and the ampoule was allowed to cool. At this stage the compound was in the form of free-flowing, shining polycrystalline material. The ampoule with this charge was again kept in the furnace for crystal growth. The growth conditions listed in Table I were established after several systematic experimental trials.

TABLE I

Growth Parameter Used to Produce Single Crystals of $MoS_xSe_{2-x}$.

| Nominal composition x | Reaction temperature °C | Growth temperature °C | Growth time hours |
|---|---|---|---|
| 0.0 | 800 | 1040 | 168 |
| 0.5 | 800 | 1050 | 192 |
| 1.0 | 800 | 1060 | 192 |
| 1.5 | 800 | 1080 | 216 |
| 2.0 | 800 | 1120 | 216 |

## Results and Discussion

All the crystals obtained were plate-like with c-axis normal to the plane of the plates, and all of them grew over the distributed charge inside the ampoule. Figure 1 shows the typical crystal sizes for differing compositions. The details of the growth products are given in Table II.

TABLE II

Description of growth product.

| Nominal composition x | Crystal size mm x mm x mm | Appearance |
|---|---|---|
| 0 ($MoSe_2$) | 15 x 10 x 0.3 | Grey opaque |
| 0.5 | 13 x 10 x 0.2 | Black opaque |
| 1.0 | 12 x 9 x 0.3 | Black opaque |
| 1.5 | 10 x 10 x 0.2 | Black opaque |
| 2 ($MoS_2$) | 15 x 5 x 0.07 | Black opaque |

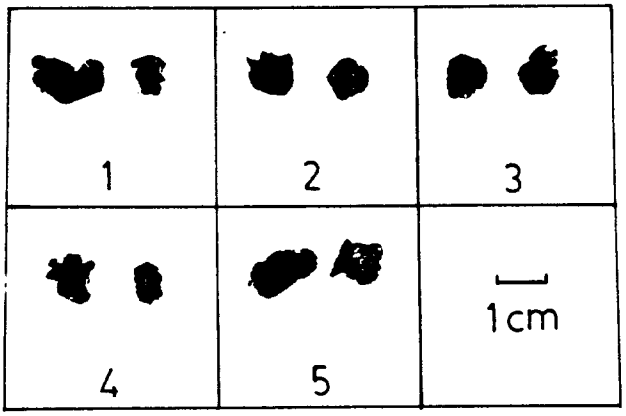


FIG. 1

Typical crystals of differing composition in the series $MoS_xSe_{2-x}$, showing crystallite size:
(1) $MoSe_2$
(2) $MoS_{0.5}Se_{1.5}$
(3) MoS Se
(4) $MoS_{1.5}Se_{0.5}$
(5) $MoS_2$

STRUCTURE:

Characterization

The system investigated in this work, namely $MoS_xSe_{2-x}$ ($0 \leq x \leq 2$), is simple because both end members $MoSe_2$ and $MoS_2$ have the same $MoS_2$ structure ($C_7$ type). The basic coordination unit for the molybdenum in these layered structures is trigonal prismatic. A S-Mo-S sandwich layer is composed of alternately occupied, face-shared prisms, the Mo and S atoms forming close-packed layers. No strong bond exists between the layers, only long-range Van der Waal's forces hold atomic sandwiches together. The stacking sequence is AbABaB, where S stacking is represented by capital letters, with the space group $D^4_{6h}$ ($P6_3/mmc$).

Composition

The compositions of the $MoS_xSe_{2-x}$ crystals were studied with electron microscopy for chemical analysis (ESCA). Figure 2 shows the ESCA traces for the energy 0 to 1000 eV. The compositions determined from ESCA are given in Table III.

Lattice-parameter determination

X-ray diffractometer traces were used to determine the unit-cell dimensions depicted in Figs. 3(a) and 3(b); the values of the 'a' and 'c' parameters in Table IV. The compositional dependence of the lattice parameters and X-ray density are plotted in Fig. 4. The 'a' parameter varies linearly with composition, according to equation(1).

$$a(x) = (3.281 - 0.06315\ x)\ A^\circ \qquad (1)$$

where x defines the solid solution $MoS_xSe_{2-x}$. Variation of the 'c' parameter is also linear and is given in equation(2):

$$c(x) = (12.918 - 0.310\ x)\ A^\circ \qquad (2)$$

TABLE III

Weight percentage of layer compounds in the series $MoS_xSe_{2-x}$ obtained by ESCA.

| Nominal composition | Observed w % | | | Calculated w % | | |
|---|---|---|---|---|---|---|
| | Mo | S | Se | Mo | S | Se |
| 0.0 ($MoSe_2$) | 35.339 | - | 64.661 | 37.77 | - | 62.23 |
| 0.5 | 41.639 | 6.957 | 51.404 | 39.946 | 7.632 | 52.422 |
| 1.0 | 49.059 | 16.472 | 34.469 | 46.357 | 15.491 | 38.152 |
| 1.5 | 52.306 | 26.169 | 21.525 | 51.259 | 26.186 | 22.555 |
| 2.0 ($MoS_2$) | 57.487 | 42.513 | - | 59.94 | 40.06 | - |

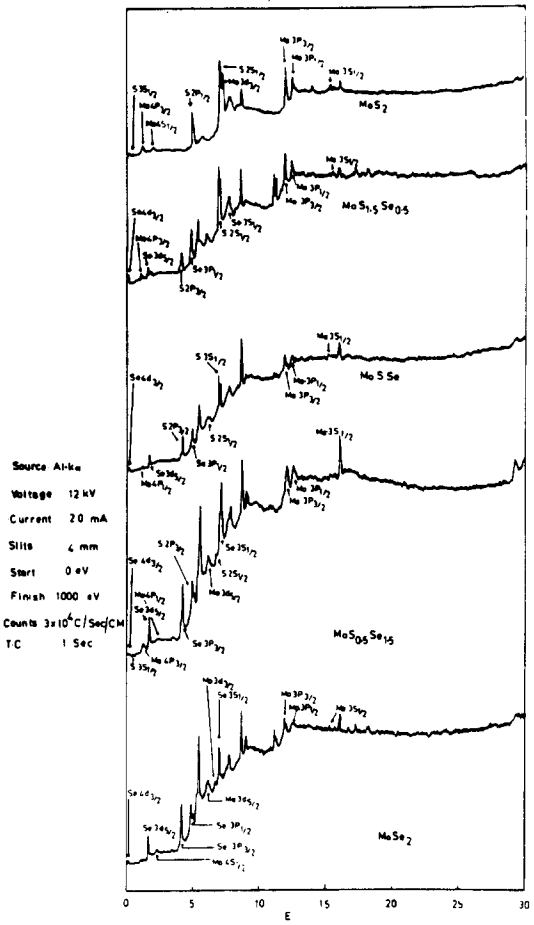


FIG. 2

ESCA traces for the energy 0 to 1000 eV for the compositions in the series $MoS_xSe_{2-x}$.

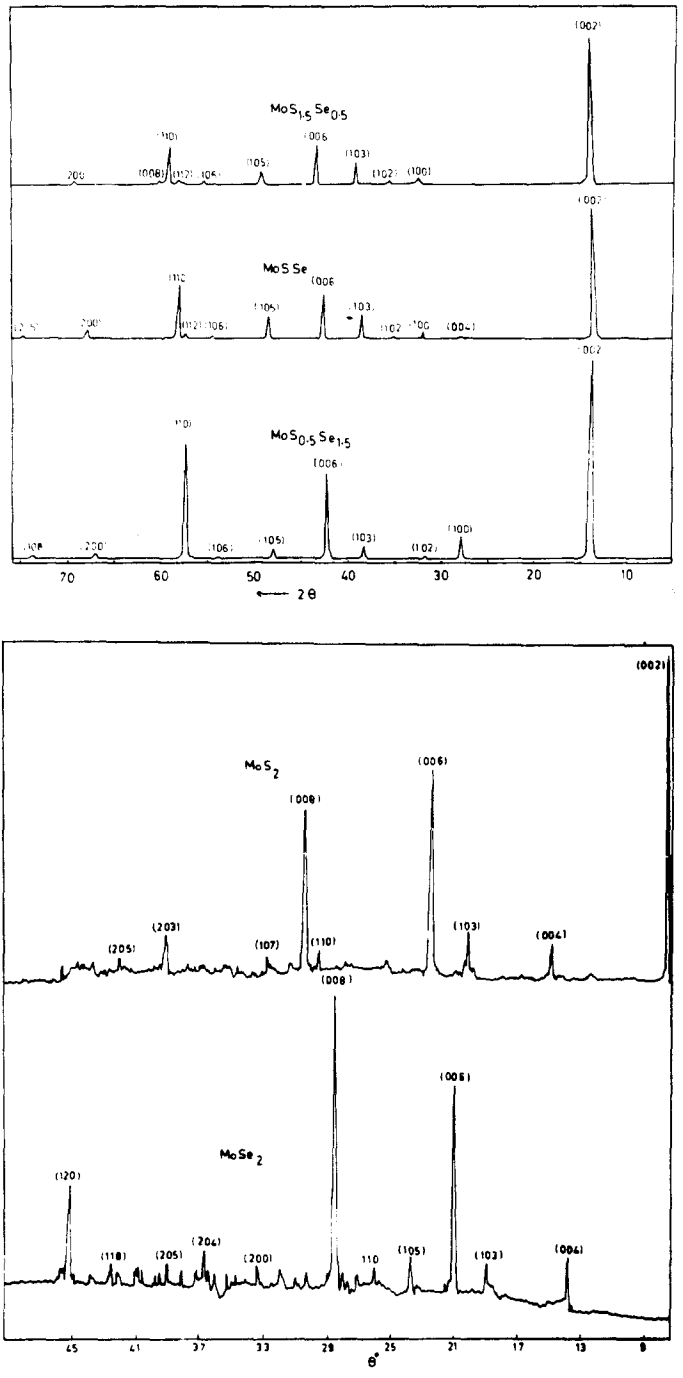


FIG. 3

(a) The X-ray diffractometer traces for $MoS_{0.5}Se_{1.5}$, MoS Se and $MoS_{1.5}Se_{0.5}$
(b) The X-ray diffractometer traces for $MoS_2$ and $MoSe_2$.

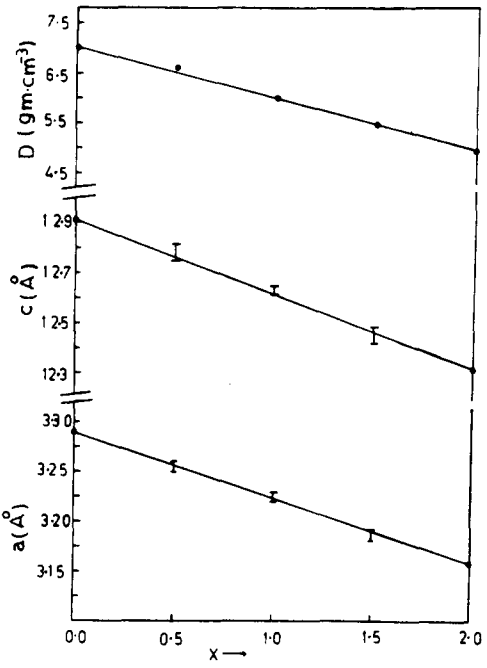


FIG. 4

Variation of 'a' and 'c' parameters and 'D' density with compositions in the series $MoS_xSe_{2-x}$.

TABLE IV

Lattice Parameters for Layered Compounds in the Series $MoS_xSe_{2-x}$ Hexagonal System Space Group $D^4_{6h}$.

| Nominal composition x | 'a' (A°) | 'c' (A°) |
|---|---|---|
| 0.0 | 3.283 | 12.918 |
| 0.5 | 3.254 ± 0.05 | 12.785 ± 0.03 |
| 1.0 | 3.224 ± 0.01 | 12.640 ± 0.003 |
| 1.5 | 3.179 ± 0.002 | 12.463 ± 0.003 |
| 2.0 | 3.166 | 12.305 |

Densities have been calculated from unit-cell dimensions for all compositions. Values of the density, absorption coefficient and c/a ratio are listed in Table V. The density follows a linear variation of the form:

$$D(x) = (7.000 - 1.012\ x)\ \text{gm cm}^{-3} \qquad (3)$$

The series of layer compounds forms a complete range of isomorphous solid solutions.

TABLE V

c/a Ratio, Calculated Densities and Absorption Coefficients for the Series $MoS_xSe_{2-x}$.

| Nominal composition x | c/a | Calculated density gm $cm^{-3}$ | Absorption coefficient $cm^{-1}$ |
|---|---|---|---|
| 0.0 | 3.934 | 7.000 | 822.85 |
| 0.5 | 3.929 | 6.529 | 752.96 |
| 1.0 | 3.920 | 6.039 | 726.96 |
| 1.5 | 3.919 | 5.583 | 691.08 |
| 2.0 | 3.8866 | 4.973 | 656.32 |

MICROSTRUCTURE:

A study of the microstructures on the as-grown faces reveals the presence of different types of spirals. A typical spiral, shown in Fig. 5, is of hexagonal shape originating from a single screw dislocation. The spirals shown in Fig. 6 are spirals of circular shape starting from a common point.

## Conclusions

1. Single crystals of $MoS_xSe_{2-x}$ have been grown by the direct vapour transport technique; they are observed to be free from contamination by any transporting agent.
2. The crystals are strain-free because they grow vertically in the form of thin platelets directly above the charge.
3. The lattice parameters vary linearly with x.

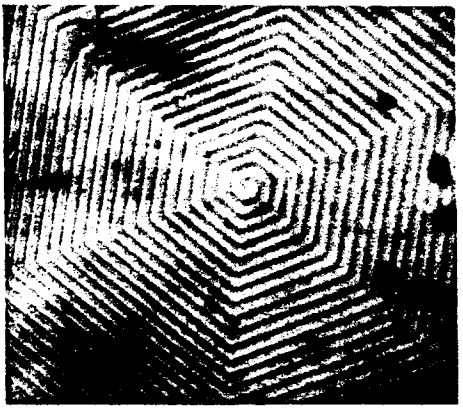

FIG. 5

Spirals of hexagonal shape originating from a single screw dislocation.

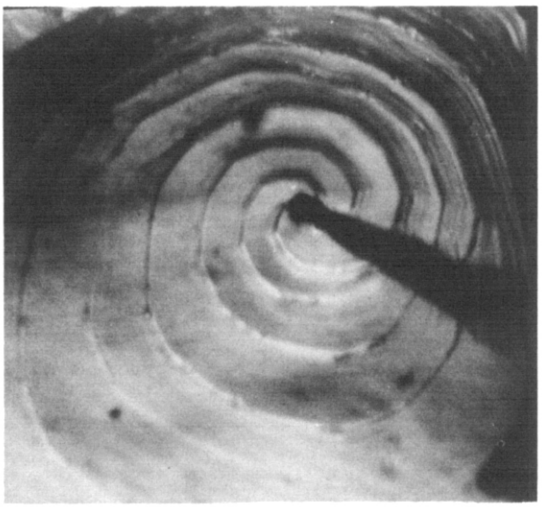

FIG. 6

Spirals of circular shape originating from a common point.

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