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Controlled Synthesis and Structural Tuning of Re-Doped Tin Selenide Single Crystals via Direct Vapour Transport Technique

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Abstract: Layered IV–VI semiconductors such as SnS, SnSe, GeS, and GeSe are known for their orthorhombic crystal structures composed of biplanar atomic layers aligned perpendicular to the *c*-axis. In the present study, single crystals of Re-doped tin selenide, SnSeRex (x = 0, 0.1, 0.2, 0.3, 0.4), were successfully grown using the Direct Vapour Transport (DVT) method in a custom-designed two-zone horizontal furnace. Energy Dispersive X-ray Analysis (EDAX) was employed to verify the elemental composition and ensure stoichiometric incorporation of rhenium. Structural characteristics of the synthesized crystals were thoroughly investigated using X-ray Diffraction (XRD). All samples maintained an orthorhombic crystal symmetry, indicating structural stability across the doping range. The effects of increasing Re concentration on lattice parameters and crystallinity are discussed, offering insight into the tunability of SnSe-based materials through controlled doping.

Keywords: Semiconductor, Tin Selenide, XRD, EDAX, Single Crystals

Introduction

In recent years, advancements in science and technology have been significantly propelled by the availability of high-quality materials. Among binary IV–VI semiconductor compounds, layered materials such as tin sulfide (SnS), tin selenide (SnSe), germanium sulfide (GeS), and germanium selenide (GeSe) crystallize in a distorted rock salt structure, belonging to the orthorhombic space group. These materials, often referred to as lamellar semiconductors, have garnered considerable attention due to their unique structural and electronic properties, making them suitable for diverse applications including optoelectronics [7], holographic recording systems [8], electronic switching devices [9–10], and infrared detection and emission technologies.

Among them, SnSe stands out as a promising semiconductor with a band gap of approximately 1 eV, positioning it as a potential candidate for efficient solar cell applications [11–12]. Although extensive research has been carried out on the synthesis and characterization of pure SnSe single crystals, studies involving transition metal-doped SnSe, particularly with rhenium substitution, remain limited. Motivated by this gap in the literature, the present work focuses on the synthesis and structural analysis of Re-doped SnSe crystals (SnSeRex, x = 0, 0.1, 0.2, 0.3, 0.4) using the Direct Vapour Transport (DVT) method with a two-zone horizontal furnace. The experimental results and their implications are discussed in detail in this paper

Experimental Techniques

In present investigations, crystal growth of SnSeRe family was done by direct vapour transport technique using dual zone horizontal furnace. The furnace was constructed by University Science and Instrumentation Centre (USIC), Sardar Patel University by using a special sillimanite threaded tube closed at one end, 450 mm in length, 70 mm outer diameter, 56 mm inner diameter with threaded pitch of 3 mm, imported from koppers Fabriken Feuerfester, Germany. The furnace was controlled by a microcontroller with thermal profile programming facility. High quality quartz ampoules were used for crystal growth which having dimensions of 24 cm length, 2.4 cm outer diameter and 2.2 cm inner diameter. Firstly boiled water was used to wash the ampoule after then with hot mixture of concentrated HNO_3 and H_2So_4 taken in equal proportion, followed by washing of ampoule with distilled water. Then ampoule was filled with concentrated HF and heated until whole HF evaporated, so that the inner surface of the ampoule become rough which enhances the nucleation process during the growth. At the end this ampoule was washed by double distilled water at least 8 to 10 times. A cleaned ampoule was kept in oven for nearly 24 hour to make it moisture free.

Highly pure powder of Sn (99.99%), Se (99.99%) and Re (99.99%) were taken in a stoichiometric proportion in the ampoule for the compound preparation. It was evacuated to a 10^{-5}Torr and then sealed. The sufficient care was taken for vigorous shaking so as to distribute the mixture along the length uniformly. The ampoule was set in a horizontal furnace. Its temperature was slowly raised till it reaches to 1073 K. It was maintained at this temperature for a period of 3 day for charge preparation. The ampoule was then slowly cooled and brought to room temperature. The resulting free flowing shiny homogeneous polycrystalline powder was achieved. This charged ampoule was placed in a dual zone horizontal furnace. For different member of the series the temperatures of hot zone and cold zone of the ampoule were kept as shown in Table 1. Finally resulting crystals were collected from the ampoule. The appropriate growth conditions for all samples are reported in Table 1.

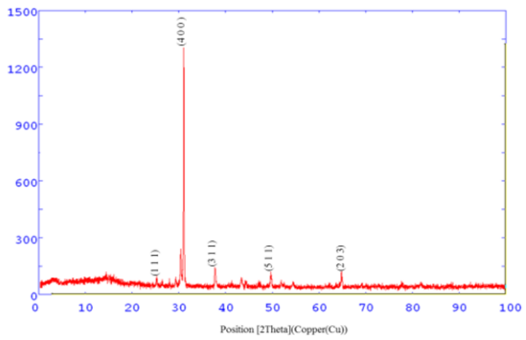
Fixed Parameters (common to all samples):

- Ampoule Dimensions: 23 cm (length) × 2.2 cm (inner diameter)
- Vacuum Level: 10^{-5} torr
- Growth Duration: 7 days
- Heating Rate: 30 °C/hour
- Cooling Rate: 20 °C/hour

Table 1: Appropriate growth conditions for all samples are reported in Table 1.

Parameter	**x = 0**	**x = 0.1**	**x = 0.2**	**x = 0.3**	**x = 0.4**
Source Zone Temperature (°C)	620	610	600	590	580
Growth Zone Temperature (°C)	600	590	580	570	560
Average Crystal Dimensions (cm)	0.9 × 0.6	0.7 × 0.5	0.9 × 0.5	0.6 ×0.4	0.9×0.5

In present case, the grown crystals have been characterized for their structural propertied using EDAX and XRD techniques. The chemical proportions of elements in grown crystals are obtained from the Energy Dispersive Analysis of X-rays (EDAX) which has been done at kalabhavan, M. S. University, Baroda. The energy dispersive analysis using X- rays (EDAX) experiment has been carried out on each grown sample for the determination of the stoichiometric proportion of Sn, Se and Re. The X–ray diffractograms were obtained for each sample with Philips X-ray diffractometer PW 1820 employing CuK$_\alpha$ radiation. The powder obtained during the growth process for each sample was prepared for the X-ray diffraction study experiment. The lattice parameters, hkl reflections and d spacing of the grown crystals were determined by comparison with JCPDS data as well as by using power X software. The X-ray diffraction patterns obtained for SnSeRex (x = 0, 0.1, 0.2, 0.3, 0.4) are shown in Fig. 1 (a), (b), (c), (d) and (e) respectively.



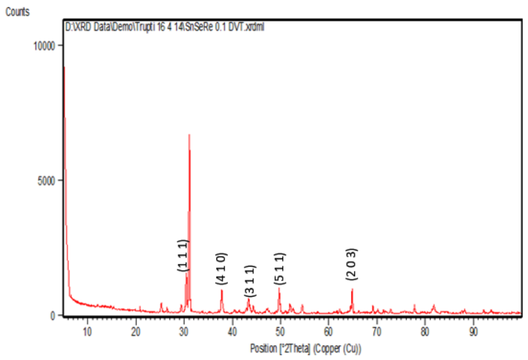


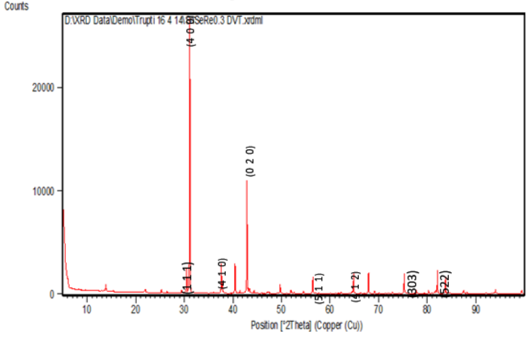
Fig. 1(a): X-ray Diffractogram of SnSe

SnSeRe$_{0.1}$ (DVT) crystal

crystal

Fig. 1(b): X-ray Diffractogram of

(DVT)



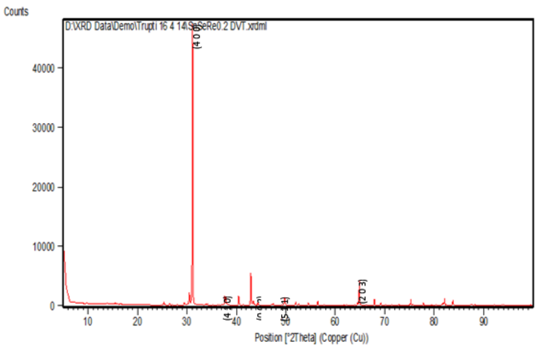


Fig. 1(c): X-ray Diffractogram of SnSeRe$_{0.2}$

SnSeRe$_{0.3}$ (DVT) crystal

Fig. 1(d): X-ray Diffractogram of

(DVT) crystal

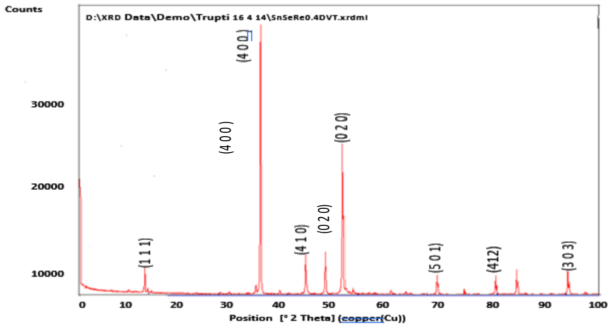


Fig. 1(e): X-ray Diffractogram of $SnSeRe_{0.4}$ (DVT) crystal

Results and Discussions

The single crystals of SnSeRex (x = 0, 0.1, 0.2, 0.3, 0.4) were grown using DVT technique. The weight of elements taken for growth is nearly equal to the weight of elements from EDAX analysis is shown in Table 2. It confirms that the stoichiometry of the each grown crystal has been maintained.

Table 2: Comparison of Elemental Composition — Taken vs. EDAX Results for SnSeRex (x = 0–0.4) Crystals

Sample	**Taken Wt (%)**			**EDAX Wt (%)**		
	Sn	**Se**	**Re**	**Sn**	**Se**	**Re**
SnSe	60.05	39.95	–	56.57	43.43	–
SnSeRe0.1	54.88	36.50	8.06	60.16	37.81	2.03
SnSeRe0.2	50.53	33.61	15.85	52.39	34.31	13.30
SnSeRe0.3	46.41	31.22	22.37	41.96	30.93	23.20
SnSeRe0.4	43.51	29.13	27.35	38.85	31.11	30.10

The X-ray diffractograms of the SnSeRex (x = 0, 0.1, 0.2, 0.3, 0.4) single crystals grown via the Direct Vapour Transport (DVT) technique were systematically analyzed. As observed in Figure 1, the diffraction patterns of the doped samples exhibit a strong similarity to that of the binary SnSe compound, indicating that rhenium doping does not significantly disrupt the crystal structure. The presence of sharp and well-defined diffraction peaks confirms the high crystallinity of the grown crystals. All samples could be indexed on the basis of an orthorhombic unit cell, affirming phase consistency across the doping range.

Table 3: Results Obtained from X- ray Diffractogram

Sample	**a (Å)**	**b (Å)**	**c (Å)**	**Unit Cell Density (g/cm³)**
SnSe	11.420	4.190	4.460	2.24
SnSeRe0.1	11.480	4.156	4.431	2.47
SnSeRe0.2	11.476	4.140	4.452	2.68
SnSeRe0.3	11.476	4.148	4.454	2.89
SnSeRe0.4	11.452	4.139	4.458	3.11

The values of the lattice parameters, unit cell volume, and unit cell density for the SnSeRex (x = 0–0.4) crystals are summarized in Table 3. The data reveal that with increasing stoichiometric substitution of rhenium (Re), the unit cell density increases. This trend is attributed to the incorporation of the heavier Re atoms into the SnSe lattice, thereby increasing the total mass per unit cell despite minor changes in volume.

The lattice parameters a, b, and c obtained for pure SnSe are in close agreement with those reported in earlier studies [13–14], confirming the successful growth and structural integrity of the crystals synthesized via the DVT method.

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