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STRUCTURAL STUDY OF DVT GROWN $Mo_xW_{1-X}Se_2$ (x =0, 0.25, 1) SINGLE CRYSTALS

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ABSTRACT

Transition metal dichalcogenides (TMDCs) MX_2 (M=Mo,W; X= S or Se) are semiconducting compounds exhibiting layered structure. The single crystals of $Mo_xW_{1-x}Se_2$ (x=0, 0.25, 1) belonging to this family have been grown by direct vapour transport (DVT) technique. The chemical composition, basic structure and morphology of the as-grown crystals have been studied by energy dispersive analysis of X-rays (EDAX), X-ray Diffraction (XRD) and optical microscopy. EDAX study indicates that the compounds are nearly stoichiometric. The optical microscopy and XRD results show that the crystals grow predominantly as 2H-hexagonal polytypes. However, $MoSe_2$ and $Mo_{0.25}W_{0.75}Se_2$ seem to contain a little proportion of 3R- rhombohedralpolytypes.

Key words: *Semiconductors, direct vapour transport technique, X-ray technique, microstructure.*

INTRODUCTION

Transition metal dichalcogenides (TMDCs) possess very interesting semiconducting characteristics [1]. Most TMDCs form hexagonal layered structures. The Lamellar structure, consisting of M atoms sandwiched between two sheets of X atoms whereby weak Van-der Waals forces act between the layers is commonly believed to be responsible for their excellent self-lubricating properties. The layered structure of these dichalcogenides facilitates easy cleavage along the basal planes and allows intercalation by foreign chemical species in the Van-der Waals gapwhich alters the material and imparts new properties [2]. The diselenides of Mo, W and mixed system of these two compounds are diamagnetic, indirect semiconductors belongs to this family. It has been reported that these compounds have excellent optical absorption in the solar spectral region and exhibit suitable properties for various optoelectronic devices such as photovoltaic solar cells, solid lubricants etc. [3-4]. They exhibit marked anisotropy in most of their physical properties. The high optical absorption, layered arrangement between cations, high resistance against photo corrosion, inherently stable nature against the electrolytic environment and the optically matching magnitude of band gap makes $Mo_xW_{1-x}Se_2$ prominent materials in photoelectrochemical conversion [5-6]. This shows that the efficient performance of these devices always depend on the good quality layered single crystals grown at optimum growth conditions. Hence, in this paper we aim to present the structural and microstructural studies along with the growth parameters of one of the important materials of TMDC family, $Mo_xW_{1-x}Se_2$ (X=0,0.25,1).

EXPERIMENTAL

Single crystals of $Mo_xW_{1-x}Se_2$ (x = 0, 0.25, 1) were grown by direct vapour transport (DVT) technique using a two zone horizontal furnace [7]. Prior to the crystal growth, quartz tube containing stoichiometric proportion of elements, molybdenum (99.95% pure), tungsten (99.99% pure) and selenium (99.9 % pure), was evacuated at vacuum of 10^{-5} Torr. The total charge taken in each case was 8 gm. The details of the growth parameters are tabulated in Table 1.

Table 1 Growth Parameters of $Mo_xW_{1-x}Se_2$ (x = 0, 0.25, 1) Single Crystals

Crystals	Temperature Distribution		Rate of Heating (°C/hr.)	Rate of Cooling (°C/hr.)	Time (hr.)	Crystal Size (mm^2)
	Source Zone(°C)	Growth Zone (°C)				
$MoSe_2$	1080	1060	50	50	188	4-6
WSe_2	1080	1060	50	50	188	9-11
$Mo_{0.25}W_{0.75}Se_2$	1080	1060	50	50	188	3-4

The grown crystals were compositionally characterized by Energy Dispersive Analysis of X-rays (EDAX) using ESEM (Phillips, Model: XL 30). The physical structure was determined from X-ray Diffraction (XRD) plots (-2) recorded with a Philips (X'pert) X-ray diffractometer (using CuK radiation) from 10° to 100°.

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The microstructural investigations of the as-grown surfaces of the crystals were done by Axiotech 100 reflected light microscope (Carl Zeiss Jena, Germany).

RESULTS AND DISCUSSION

Shiny, gray colored, opaque and irregular shaped platelets of $Mo_xW_{1-x}Se_2$ have been grown by DVT technique. The average crystal dimensions were 3-10 mm^2 in cross sectional area and few micrometers in thickness. The chemical, structural and physical characterizations of such crystals have been carried out using EDAX, XRD and optical microscopy.

Energy Dispersive Analysis of X-Rays

Table 2 presents thestoichiometric proportions of the constituent elements, Mo, W and Se taken for the growth of $MoSe_2$, WSe_2 and $M_{0.25}W_{0.75}Se_2$ single crystals along with their derived chemical formula. It is observed that the crystals had proportionate elemental composition and were nearly stoichiometric.This analysis shows that there is a slight deficiency of selenium in $MoSe_2$ and slight excess of selenium in WSe_2 and mixed system. These may affect the defect structure rather than the stoichiometry of the compounds. The existence of such defect structure of Mo and Se in $MoSe_2$ has been reported by Hofmann [8].

Table 2 Stoichiometric data and chemical formulas derived from Energy Dispersive Analysis of X-Rays for $Mo_xW_{1-x}Se_2$ (x = 0, 0.25, 1) single crystals

Compounds and Elements		Wt (%) of the Elements in Source Used	Wt (%) of the Elements in Grown Crystals as Obtained from EDAX	Chemical Formula of Given Crystals
$MoSe_2$	Mo	37.89	38.60	$Mo_{1.02}Se_{1.98}$
	Se	62.10	61.40	
WSe_2	W	53.79	52.87	$W_{0.98}Se_{2.02}$
	Se	46.20	47.13	
$M_{0.25}W_{0.75}Se_2$	Mo	7.50	7.45	$Mo_{0.24}W_{0.73}Se_{2.03}$
	W	43.11	41.88	
	Se	49.38	50.66	

X-Ray Diffraction

Figure 1 depicts the X-ray diffractogram recorded for $Mo_xW_{1-x}Se_2$ (x = 0, 0.25, 1) single crystals. It is observed that all the diffraction peaks indexed for each compound matches well with the standard data files. For $MoSe_2$, the diffraction lines are in agreement with the JCPDS: 29-0914 (hexagonal $MoSe_2$)and JCPDS: 20-0757 (rhombohedral 3R phase of $MoSe_2$). Similarly, the XRD peaks appeared for WSe_2 single crystals corroborate that the grown crystals belong to hexagonal system with 2H polytype (JCPDS:38-1388). Few lines appeared in this diffractogram are due to the formation of WO_3 and SeO_2 (JCPDF: 24-0747, 46-1096 and 22-1314) in addition to the unreacted elements present with the grown crystals.The diffractogram of mixed system, $Mo_{0.25}W_{0.75}Se_2$, have also been analyzed with the help of standard data files (JCPDS: 29-0914, 20-0757 and 38-1388). It is found that in this case also along with predominant 2H-$Mo_{0.25}W_{0.75}Se_2$, minute amount of 3R-polytype of $MoSe_2$ may be present. This contention is based on the fact that two diffraction peaks at 2=24.17˚, 45.93˚ are observed to match with 3R phase of $MoSe_2$. However, the intensity of such 3R polytype diffraction peaks for $MoSe_2$ and mixed system is significantly less than those given in JCPDS cards. Therefore, presently grown crystals possess predominantly 2H-hexagonal structure and a little proportion of 3R polytype in $MoSe_2$ and mixed system. It may be pointed out that the diffraction peaks of very low intensity are the unreacted traces of Mo, W, Se and their oxides besides Al and these may be considered as a part of the background.

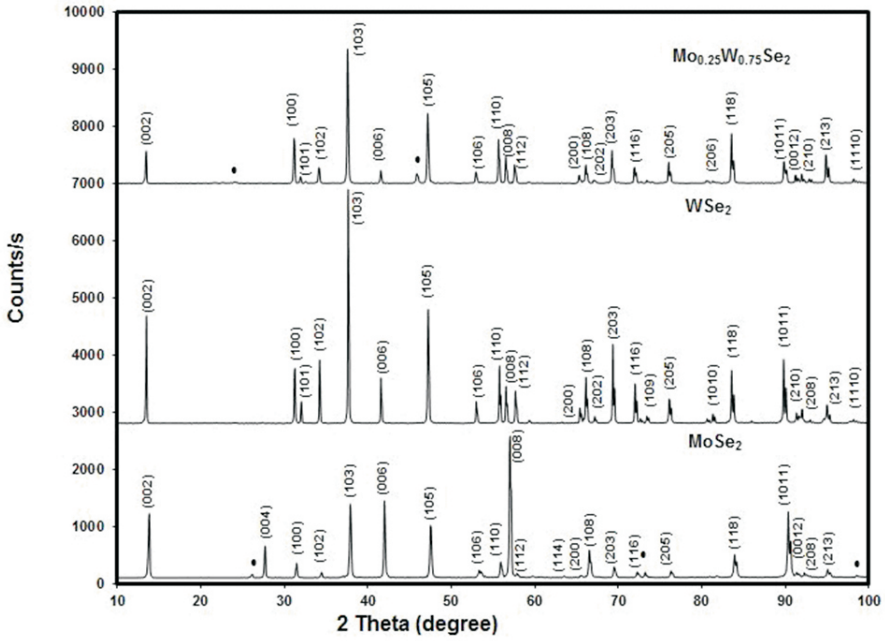

Fig. 1: X-Ray diffractogram of as–grown $Mo_xW_{1-x}Se_2$ (x = 0, 0.25, 1) single crystals, 3R phase

The lattice parameters thus, computed are a=3.285Å, c=12.920Å ($MoSe_2$), a=3.286Å, c= 13.090Å (WSe_2) and a=3.277Å, c=13.070Å (**$Mo_{0.25}W_{0.75}Se_2$**).These values of lattice parameters confirm the presence of 2H-polytype which is in close resemblance with the reported literature [9-10].

Optical Micrograph

The optical micrographs of $Mo_xW_{1-x}Se_2$ (x = 0, 0.25, 1) crystals is shown in Figure 2. The hexagonal spiral growing on the as-grown face of $MoSe_2$ crystals is originating from a point and gives a clear view of the left handed (clockwise) growth on the surface (Fig 2a). This microstructure showing the presence of crystallographically oriented spirals suggests the growth of the crystals via screw dislocation mechanism. In general, presence of screw dislocations in grown crystal shows characteristic property of growth from gaseous phase [11]. Moreover, some triangular features are noticeable on the same surface (inset of Fig.2 (a)). This probably indicates the co-existence of 2H and 3R polytypes in the same crystal. Since the positions at which this triangular features seen are only few, the grown crystals of $MoSe_2$ are primarily of 2H polytype with traces of 3R polytype. This inference seems to be in good agreement with our earlier observations of presence of 3R phase in XRD of $MoSe_2$ crystals. However, the triangular features can also belong to initiation of growth stages on the surface under observation. This fact can further be possibly verified from the a-axis oscillation photograph [12]. Fig. 2 (b) shows the optical micrograph of WSe_2 crystal. It is clear that the initiation of layers originates as a triangle and each vertex truncates on further growth of the crystal face. This ultimately results in hexagonal spirals as seen in the Figure. Also, some guest microcrystals are visible on the host surface. In case of $Mo_{0.25}W_{0.75}Se_2$ single crystal, triangular features have been observed on the as-grown face with a polygonal spiral as shown in the inset of Fig.2 (c).

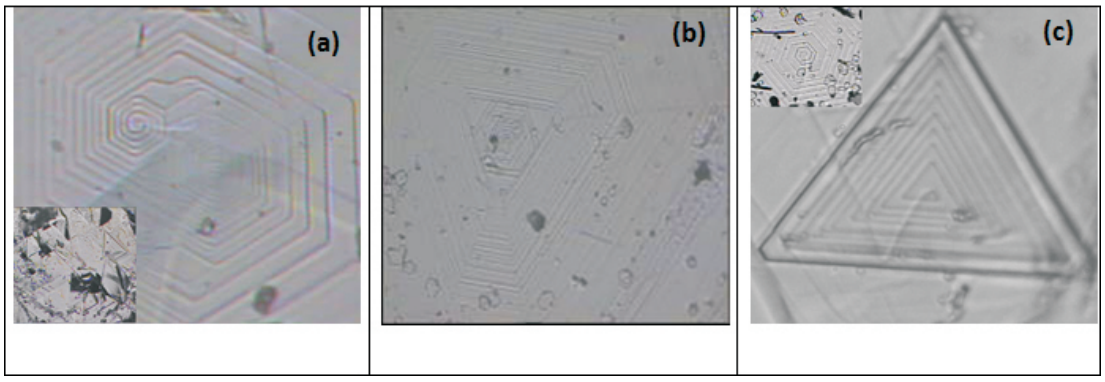

Fig. 2: Optical microphotographs for as-grown faces of (a) $MoSe_2$ crystal: a spiral and triangular features (inset); (b) WSe_2 crystal; (c) $Mo_{0.25}W_{0.75}Se_2$ crystal: Triangular feature with a polygonal spiral (inset)

CONCLUSIONS

$Mo_xW_{1-x}Se_2$ (x=0,0.25,1) crystals grown by direct vapour transport technique predominantly possess 2H-hexagonal structure. Both $MoSe_2$ and $Mo_{0.25}W_{0.75}Se_2$crystals contain a little proportion of 3R polytype. The optical micrograph shows the presence of screw dislocation on the surface of the as-grown crystals indicating the growth proceeds via screw dislocation mechanism. The presence of 2H and 3R polytypes seen in the optical micrographs confirm the results of XRD.

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