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Growth of molybdenum disulphide using iodine as transport material

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Abstract. In the present paper an attempt has been made to describe the chemical vapor transport (CVT) technique used for the growth of molybdenum disulphide (MoS_2) single crystals. Iodine (I_2) is used as transporting material for this purpose. The energy dispersive analysis by X-ray (EDAX) confirmed the stoichiometry of the as-grown crystals. The lattice parameters of these crystals were determined from the X-ray diffraction analysis. The grown crystals were examined under the optical zoom microscope for their surface microstructure study.

Keywords. Single crystals; chemical vapor transport; structural characterization.

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1. Introduction

Molybdenum disulphide (MoS_2) belongs to a class of group VI dichalcogenides having C_7 type crystal structure. It has layered crystal structures, which is formed of unit layers consisting of transition metal (Mo) atoms sandwiched by chalcogen (S) atoms [1]. The compound studied can be considered as strongly bonded two-dimensional X–Mo–X layers loosely coupled to one another by relatively weak van der Waals-type forces [2]. These compounds have attracted considerable attention, during recent years due to their semiconducting as well as lubricating properties. MoS_2 has been widely studied because of its catalytic applications [3]. The surface structure of some complex compounds of molybdenum is not clear and also the orientation of the metal sulphide particles on the support could be crucial to the catalytic properties [4–8]. A clear knowledge of the MoS_2 crystal growth is therefore needed [9,10]. MoS_2 is a layered semiconductor, which is of interest to research in the field of semiconductor physics [11,12], catalysis [13] and tribology [14]. Traditionally, MoS_2 has been considered as a good lubricant for high-vacuum application.

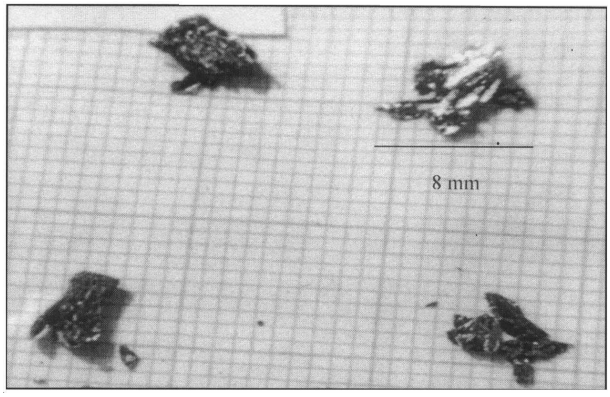


Figure 1. Photograph of MoS_2 single crystals grown by CVT method.

Now a days many developments on transmission electron microscopy (TEM) of high resolution and weak beam dark field (WBDF) allow the determination of the crystalline structure and shape of the small crystals [15,16]. Chemical vapor transport has been reported as a reliable method of growing metal dichalcogenide single crystals [17–19]. The compounds were identified experimentally by X-ray diffraction. The lattice parameters were obtained and compared with the standard calculated values. In this work, MoS_2 single crystals were grown by chemical vapor transport method using iodine as a transporting material.

2. Experimental

For the growth of MoS_2 single crystals, stoichiometric amounts of molybdenum powder (purity: 99.95%) and sulphur powder (purity: 99.95%) were taken in quartz ampoule; then evacuated (10^{-5} Torr) and sealed. The sealed ampoule was placed in a two-zone furnace at a constant reaction temperature to obtain the charge of MoS_2. Slowly heat the ampoule up to 973 K and maintain it at this temperature for 36 h for compound synthesis. After this, the furnace power was switched off and the ampoule was allowed to cool down to room temperature. The charge so prepared was rigorously shaken to ensure the proper mixing of the constituents. For crystal growth, the synthesized compound was transferred into another evacuated ($\sim 10^{-5}$ Torr) quartz ampoule with iodine (2 mg/cc of ampoule volume). The sealed ampoule was finally placed coaxially in a two-zone furnace with reaction zone at higher temperature and the growth zone at a lower temperature for a definite time period. The shining black opaque single crystals of MoS_2 were obtained by CVT technique. Complete details of the growth parameters are summarized in table 1. The large size crystals of MoS_2 are shown in figure 1.

For X-ray diffraction study, several small crystals were finely ground with the help of an agate mortar and filtered through 100-micron sieve to obtain grains of nearly equal size. The powder obtained during the growth process was prepared for the X-ray diffraction study experiment. The X-ray diffractograms were taken with Philips

Table 1. Growth parameters of MoS_2 single crystals grown using chemical (iodine) vapor transport technique.

Initial material (MoS_2)		Ampoule dimension		Temperature distribution			Physical characteristics of crystals		
Weight	Transporting agent	Length (mm)	Inner diameter (mm)	Hot zone (K)	Cold zone (K)	Growth time (h)	Plate area (mm^2)	Thickness (cm)	Color
10	I_2 (2 mg/cc)	250	22	1130	1073	336	25	0.02	Grey Black

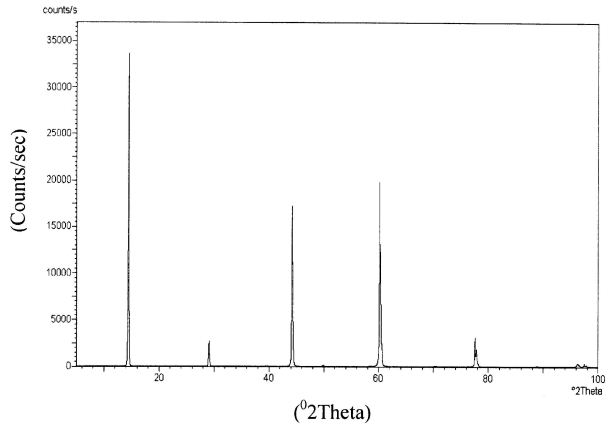
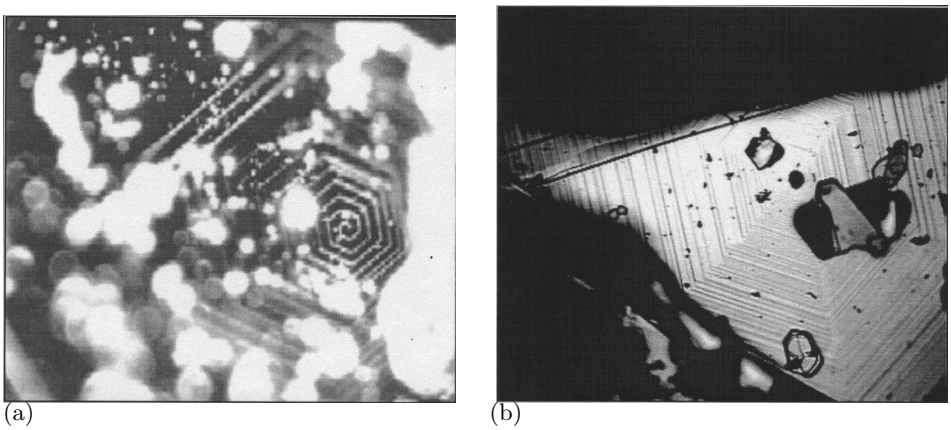


Figure 2. The X-ray diffractrogram of MoS_2 single crystals.

Table 2. X-ray diffraction data for MoS_2 single crystals.

(h k l)	d-Spacing	Peak width (2θ) (°)	Relative intensity (%)	Peak intensity (counts/s)	Particle size
0 0 3	6.133	0.36	100.0	22965.47	424.35
0 0 6	3.067	0.36	8.83	2028.09	413.66
1 0 4	2.272	0.30	0.37	85.37	546.29
0 0 9	2.045	0.36	57.42	13186.68	396.12
1 0 7	1.826	0.30	0.55	125.20	566.79
1 1 0	1.576	0.36	0.12	27.26	373.02
1 1 3	1.535	0.36	64.21	27.26	370.02
2 0 2	1.338	0.36	0.19	43.75	523.28
2 1 1	1.034	0.48	1.13	259.26	213.99

X-ray diffractometer PW 1820 employing CuK_α radiation. The X-ray diffraction pattern obtained for MoS_2 is shown in figure 2. The energy dispersive analysis by X-ray (EDAX) has been carried out for the determination of the stoichiometric proportion of Mo and S. The grown crystals were examined by Carl Zeiss made optical microscope (Model: Axiotech 100HD) for their microstructure study.



(a) (b)

Figure 3. (**a**) Microstructures of MoS_2 single crystal. (**b**) Microstructure on the surface of as-grown MoS_2 single crystals taken for $\times 400$ magnification.

3. Results and discussion

As shown in figure 2, large size single crystals of MoS_2 are grown by chemical (iodine) vapor transport technique. The X-ray diffractograms of MoS_2 grown by CVT technique were analysed. $(h\,k\,l)$ Values corresponding to prominent reflections, d-values, peak width and peak intensities are shown in table 2. The particle size for a number of reflections are also presented in table 2. The values of the lattice parameters a and c, the volume (V) and X-ray density (ρ) obtained from the analysis of the diffractogram of the crystal are presented systematically in table 3. The lattice parameters a and c obtained for MoS_2 single crystals were compared and found in agreement with values obtained by Traill [20]. The result of EDAX analysis shown in table 4 confirms that the stoichiometry of the grown crystal has been maintained.

The surface of each grown crystal was examined under an optical zoom microscope aided with computer software. The microstructure is as shown in figure 3. Figure 3a shows an isolated polygonal spiral and figure 3b shows a single spiral starting from a black dot. An electron microprobe analysis of the dark spot revealed the absence of material. This means that the dot should be a hole. From the shadows of dust particle shown at the bottom of the picture, it can be easily confirmed that the spiral seen in figure 3b is a depression.

Table 3. Results obtained from X-ray diffractogram.

Sample (MoS_2)	$a = b$ (Å)	c (Å)	Volume $(Å)^3$	X-ray density (g/cc)
Value obtained in the present work	3.11 ± 0.04	18.89 ± 0.64	158.22	5.0417
Standard value [20]	3.16	18.33	–	–

Table 4. The EDAX data for MoS_2 single crystals.

	MoS_2	
Wt (%) of elements	Mo	S
Taken	59.94	40.06
Obtained from the EDAX	62.19	37.81

4. Conclusions

The single crystals of MoS_2 have been grown successfully by chemical vapor transport technique using I_2 as a transport material. The X-ray diffraction analysis indicates that the grown crystals possess hexagonal crystal structure. The EDAX analysis confirmed the stoichiometry of the materials. The layer-type growth mechanism of the crystals was observed from the microstructure study of the grown crystals.

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