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Dendritic and Twin Type Lead Sulphide Crystals Grown by Flux Method

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Abstract: Lead sulphide crystals have been grown by flux method using sodium polysulphide as flux material. Dendritic, twin type and platelet like crystals are reported. Reasons behind the growth of different geometrical shaped crystals are briefly discussed. It is established that these crystals grow by two-dimensional nucleation mechanism and by spreading and piling of growth layers.

Key words: PbS, flux method, twins, dendrite, Na_2S_x, cooling rate

Introduction

Lead sulphide is a member of II-IV family of semiconducting compounds. It possesses narrow band gap of 0.2 eV and has been extensively used for infrared detector. It is also useful in optoelectronic devices. In view of its important applications, the efforts have been taken to grow the crystals of PbS by Flux method using Sodium Polysulphide (Na_2S_x) as a flux. Na_2S_x melts have proven to be excellent solvent for preparation and growth of variety of sulphides. Patil and Wani, (2001) have reported the growth of CDS crystals using sodium polysulphide (Na_2S_x) as a flux.

The cooling rate is the most important experimental parameter in flux method. It governs the rate of mass deposition. Depending upon the rate of cooling, crystals having different geometrical shapes such as dendritic, twins and platelets were resulted. Availability of growth entities, arriving on the surface of growing crystal, depend upon bulk supersaturation, growth temperature, impurities and system hydrodynamics. Transport of solute from bulk of liquid to kinks or steps on the surface of crystal is driven by supersaturation.

Survey of literature reveals that good amount of experimental and theoretical information is advocated by a number of authors (Patil *et al*., 1998; Scheel and Elwell, 1972; Scheel, 1974; Sekerka, 1968; Kovacs *et al*., 1971; Glicksman and Singh, 1989; Morris *et al*., 1967; Jackson *et al*., 1967; Rubinstein *et al*., 1991a, b) on dendrites and (Garcia-ruiz, 1986; Short and Henry, 1973; Nistor and Tacson, 1982; Popolitov *et al*., 1982; Strakhov, 1969; Abrahams, 1975; Tomov *et al*., 2000; Berger *et al*., 1991; Han *et al*., 1992; Mansour and Scholz, 1990; Hashimoto *et al*., 1988; Machado *et al*., 1988; Zhe and Gray, 1998; Pfitzner and Lutz, 1996; Zondy, 1995; Sato *et al*., 1994; Anada *et al*., 1988; Kozlova and Dukova, 1982; Grimson *et al*., 1982; Yasuda and Sunegawa, 1982) on twin type crystals of various types of materials.

It is found that very little work has been reported on growth of dendritic and twin type of lead sulphide crystals. Emphasis has therefore been laid on the description of growth of PbS crystals in the present paper.

Materials and Methods

Crystal Growth Experiment

A.R. grade powders of lead, sulphur and sodium sulphide were mixed in appropriate proportion thoroughly and this mixture was transferred to 80 mL platinum crucible. PbS crystals were then

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Table 1: XRD data of crystalline PbS

Ob. No.	2-θ observed	d-value		I/I_o		hkl planes
		Observed	Reported	Observed	Reported	
1	25.8	3.4502	3.429	80	84	111
2	29.8	2.9956	2.969	100	100	200
3	42.8	2.110	2.099	78	57	220
4	50.8	1.7957	1.790	68	35	311
5	53.2	1.7202	1.714	37	16	222
6	62.4	1.4869	1.484	27	10	400
7	68.8	1.3634	1.362	33	10	331
8	70.8	1.3297	1.327	55	17	420
9	78.8	1.2135	1.212	42	10	422

Table 2: Lattice parameters

Lattice parameters	a (Å)	Volume of unit cell $(Å)^3$
Observed	5.9256	208.06
Reported	5.9362	209.18

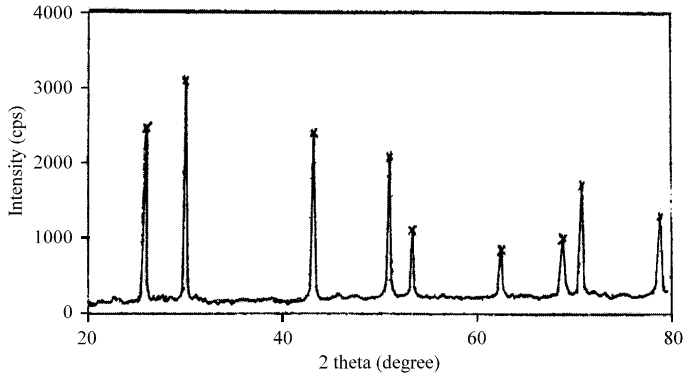

Fig. 1: XRD of PbS

grown using flux method as reported by (Patil and Wani, 2001). The cooling rate was maintained to 40°C h^{-1}. Crystals having shapes of dendrite, twin and platelet were resulted and represented photographically.

X-Ray Diffraction Analysis

Structural analysis of as grown PbS crystals was carried out. Lead and sulphur were observed in expected stoichiometric proportion.

X-Ray diffraction analysis of PbS crystals was performed with Phillip X-Ray diffractometer Model-PW 1730 using CuKα radiation with Ni Filter (λ = 1.5418 Å). Figure 1 represents the XRD and Table 1 shows corresponding XRD data. It is clear from Table 1 that the observed 'd' values of peaks are matching well with reported ASTM 'd' values of respective peaks. XRD analysis confirmed that the grown crystals are of lead sulphide.

Educated guess method was adopted to estimate the lattice parameters of unit cell and crystal system. Lattice parameters are represented in Table 2. Grown crystals have cubic structure as derived from observed data.

Results and Discussion

The grown crystals of lead sulphide were examined under optical metallurgical microscope, Carl-Zeiss Epiqnost 2HD model. The observations are described in what follows.

Crystals shown in Fig. 2 through 5 are dendritic in nature. Such crystals were observed near walls of crucible in growth solution. A dendritic crystal of feather shape is depicted in an optical photomicrograph in Fig. 2. This crystal might have fastest growth rate. Crystals shown in Fig. 3 and 4 have straight stems along c direction and branches at an acute angle with stem. Figure 5 shows a crystal without branches but goes on spreading as growth proceeds. Width might have broader at the cost of branches. It must have grown at lower growth rate and may be relatively away from walls of crucible as compared to crystals in Fig. (2-3). Crystals nearer the walls of crucible are more dendritic in nature. This may be because of conduction of heat away from the walls and from growth solution near the walls of crucible will be with faster rate as compared to the charge deep inside the crucible. Thus crystals nucleate spontaneously and start growing in initial stage of highly supersaturated atmosphere. So, branches of crystals near wall may become longer and angles become more acute as reported earlier for dendritic growth.

Rate of cooling was maintained constant throughout the growth experiment. So 'linear growth rate' would have been very high at the beginning of cooling process and the growth would be more dendritic in nature as reported by (Scheel and Elwell, 1972; Scheel, 1974).

Figure 6 through 12 represent twin type crystals which appear externally to consist of two or more crystals symmetrically united and have the form of L (Fig. 6 and 7), inverted T (Fig. 8) and cross (Fig. 9 through 12). In each twin crystal, twin plane is perpendicular to the surface in which the wings are lying. Such crystals were observed in the core of growth solution.

Horizontal wing of crystal in Fig. 6 is short as compared to vertical wing along c axis. It may be because of insufficient feed and lack of symmetrical environment. Crystal in Fig. 7 has two symmetrical wings around its twinning plane. The angle between c axis (vertical wing) and twin plane is 450 as shown schematically in Fig. 13(a).

Figure 8 shows horizontal platelet with vertical one. Horizontal wings may be considered as twins of vertical platelet with twinning plane on either sides at 450 from vertical (Fig. 13b).

Crystals in Fig. (9-11) are twins with cross form. These crystals might not have acquired their complete shape. It may be because of unsymmetrical environment and insufficient time to grow.

Figure 12 represents a better grown crystal as compared to crystals in Fig. (9-11). Wings are intersecting each other and symmetrical around twinning plane. One short wing is expected to be a twin of another short (H-H in Fig. 13c) and longer wing to be a twin of another long (A-A in Fig. 13c). Twin crystals with their respective twinning planes are shown schematically in Fig. 13(a-c).

It may be expected that the characteristic morphology of PbS twin crystals is formed at earlier stage of growth and becomes less pronounced at later stage of growth as reported by Yasuda and Sunegawa (1982) for quartz crystal.

Twining is a prominent phenomenon contributing to new components to initial individual crystal and thus, influencing the microstructure evolution. Since twining is consequence of faults in mono-layer arrangement on the crystalline surface, it is an inherent process during all stages of microstructure evolution: nucleation, coalescence, crystal growth and grain growth which are recognized as fundamental structure forming phenomenon of materials (Berna *et al*., 1995; Berna and Adamik, 1998) Twinning can be due to faults in the attachment of atoms to growth sites, the chance of such faults being greater at higher deposition rates. The presence of foreign atoms or molecules during the growth of crystallites can also lead to twinning (Hinton *et al*., 1963). A possible energetic explanation of this phenomenon is that the stress field generated by dislocations and foreign atoms may be relieved by the formation of twins (Harris, 1952).

The growth of PbS twin crystals may perhaps be due to several kinds of causes namely: rapid growth due to larger cooling rate, rapid growth favours branching of crystals in course of growth, irregularities like mechanical damage on the surface of crystals.

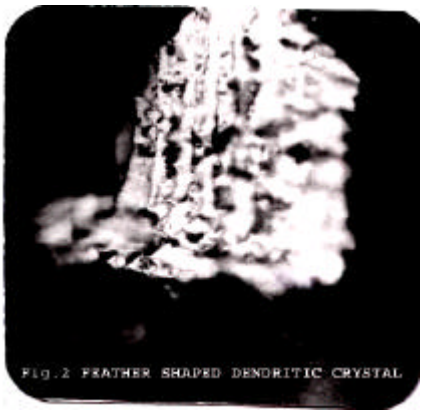

Fig. 2: Feather shaped dendritic crystal (x 500)

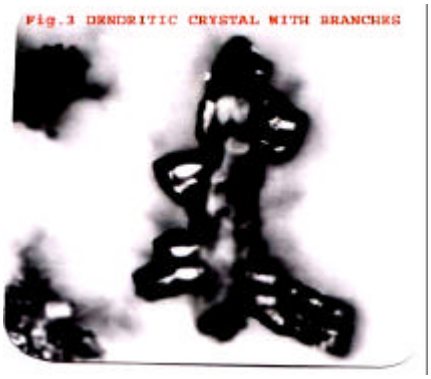

Fig. 3: Dendritic crystal with branches (x 300)

Fig. 4: Dendritic crystal with branches (x 300)

Fig. 5: Dendritic crystal without branches (x 300)

Fig. 6: Crystal without branches (x 300)

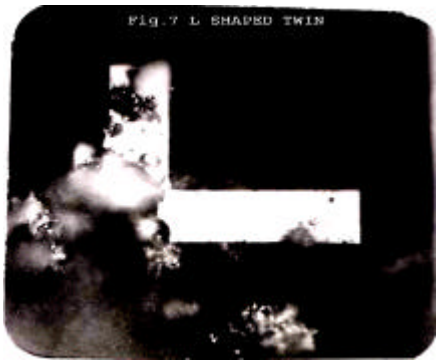

Fig. 7: L shaped twin (x 300)

Fig. 8: Inverted T shaped twin (x 300)

Fig. 9: Cross shaped twin (x 400)

Fig. 10: Cross shaped twin (x 300)

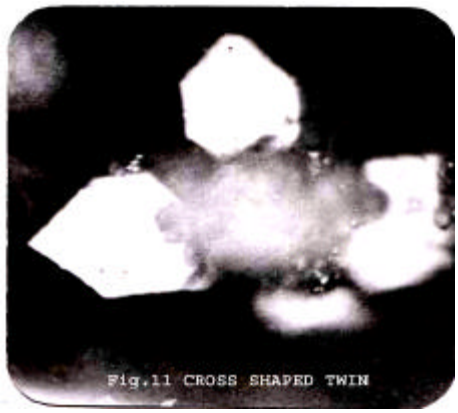

Fig. 11: Cross shaped twin (x 400)

Fig. 12: Cross shaped twin (x 300)

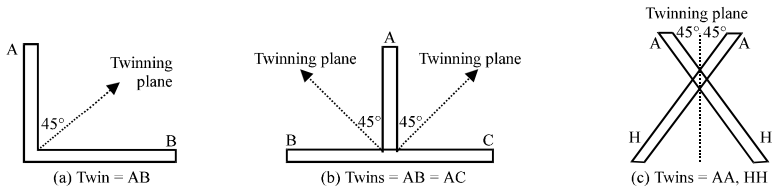

Fig. 13(a-c): Schematic representation of twin crystals with their respective twinning planes

Reported twins and dendrites were observed under the same growth conditions. So it is reasonable to expect twins to grow rapidly like dendrites. Individuals comprising a twin crystal may have different orientations of their atomic structures and related geometrically to each other as if one part was derived from other by reflection over a twinning plane common to both. Two (or more) individuals grow together with only a part of their similar edges in parallel positions. The reported twin crystals of PbS were expected to be due to a mirror image along a twin plane as these crystals are having kinked shape.

In variety of cases the change of preferred orientation into a new growth orientation with increasing thickness is ascribed to twinning. The crystallographic relations between all initial orientations observed so far and the possible crystal orientation changes that can be accomplished by 2 fold twinning.

Fig. 14: Regular shaped platelet (x 400)

Fig. 15: Platelet with saucer shaped pits (x 400)

According to (Buckley, 1951) and (Azaroff, 1960), galena (natural lead sulphide) crystals were composed of mosaic blocks each misoriented with respect to its neighbor by small angle. This misorientation may favour the growth of twins. It may be expected that in cubic crystals (PbS) of high symmetry, the crystallographic structures of the blocks will be continuous with respect to host surface and the host and the guest will not be distinguishable.

Crystals shown in Fig. 14 through 17 are the rectangular platelets. Under ideal growth conditions, PbS (cubic) crystal should be crystallized in the form of cube. But under experimental conditions it develops into rectangular parallelepiped as reported by (Dana and Ford, 1926). This observation may be extended and applied to the growth of rectangular platelets as represented in Fig. 14 through 17.

Figure 15 shows the saucer shaped pits (S-pits) on the surface of a crystal. Etching may be activated due to temperature and in undersaturation environment which forms the etch pits by pinhole dissolution mechanism. Successive etching leads to the development of shallower and more rounded etch pits. There are etch hillocks on the surface of crystal shown in Fig. 16. Under certain experimental conditions, (high undersaturation etc.), the rate of formation of reaction product, of etching process, may exceed the rate with which they diffuse into etching solution. Then reaction product may be attached to the crystal surface which may result into etch hillocks.

Figure 17 shows a crystal with growth striations on its face. There are parallel, straight and bunched layers called as striations which may be formed as result of impurity adsorption and supersaturation fluctuations taking place during the development of the face.

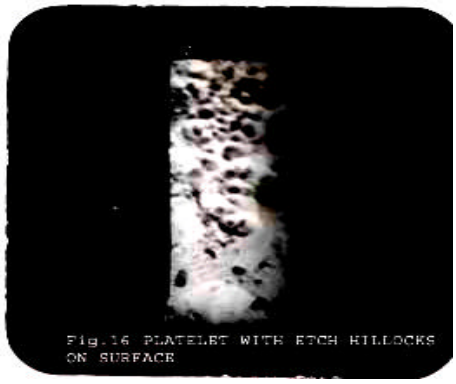

Fig. 16: Platelet with ETCH hillocks on surface (x 400)

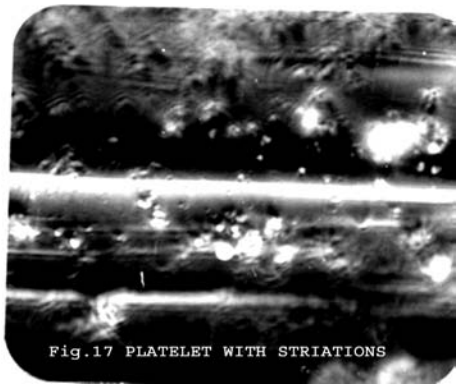

Fig. 17: Platelet with striations (x 400)

Conclusions

- Dendritic crystals grow with fast rate of deposition.
- Twins are expected to grow rapidly like dendrites.
- Growth rate of twin crystals would be relatively smaller as compared to dendritic crystals.
- Growth rate of twin crystals would be relatively larger as compared to regular shaped crystals.
- Twinning may be due to higher rate of deposition because of larger chance of generating faults at this rate.
- Growth rate of crystals is expected to be decreasing with following sequence: Dendritic crystals with feather shape → dendritic crystals with branches → dendritic crystals without branches → twin type of crystals → regular shaped crystals.

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