CHAPTER - 14

COMPARATIVE STUDIES OF LEAD MOLYBDATE CRYSTALS GROWS UNDER DIFFERENT CONDITIONS

14.1 Introduction

The differences observed in the surface microtopography of crystals are due to the environmental conditions, like duration of growth and media from which they grow. We have seen lead molybdate crystals grown in gel medium by the double diffusion of the reacting solutions during a growth period of six weeks. The perfection and morphology of the crystal, to a large extent depend upon the pH and concentration profile and diffusion rate of the surrounding medium of the growing crystal. In the pulling method of this crystal, the charge material is contained in a crucible which can be heated to above the melting point of the charge. A pull rod containing a seed crystal at its lower end, is positioned above the crucible. The seed crystal is dipped into the melt whose temperature is adjusted and the rod is pulled out slowly with a rotation. The rate of pulling, crucible contamination are some of the factors affecting the perfection of the crystal and habit faces are not generally found on these crystals.
The environmental conditions of synthetic crystals are always better known than those for the natural crystals. Natural lead molybdate crystals (Wulfenite) are secondary origin and are found among the lead and zinc deposits in the oxidation zone. It is speculated that these crystals were formed after the oxidation reactions between the molybdatum bearing waters and the lead ores like lead carbonate. We do not know the actual process of crystallization in nature, leading to the formation of crystals of different morphology and perfection. These differences in the environmental conditions may produce different surface microtopographs and in this chapter a comparative studies have been attempted to bring out the relative superiorities of the crystals of the various origins. The investigation is essentially based on (1) morphology and surface features (2) dislocation density and (3) dissolution trends of the etchants.

14.2 Morphology

The crystals grown in gel medium were impressively transparent and regularly faceted, while those grown by pulling method were semi-transparent. The habit faces of the gel grown samples were very smooth and highly polished. For natural crystals many of the habit faces were missing and were not smooth and polished. They exhibited structural inhomogeneities like inclusions, cavities, over growth and terraced features. The (001) faces of
very few thin platelet crystals were shining and only these samples were having the so-called 'vicinal faces' with striation as in the case of gel grown crystals. Fig. (80) is the 'vicinal faces' observed on the (001) faces of the natural crystal and fig. (106) show the same features observed on the gel grown platelet crystals. The colour of the natural crystals varied from orange, yellow, grey, brown and their combinations. Laboratory grown crystals were generally grey in colour and semi-transparent. The different morphology of the crystals grown by gel method are shown in figs. (16) (17) (18) (19) (20) (21) and that of the samples commonly found in nature are shown in figs. (2) (3) (4) (5) (6) (7). In nature, crystals commonly assume square tabular (001) habit, sometimes with flat 'vicinal faces'. Octahedral habits are also seen. Prismatic forms are rarely seen. Our laboratory grown crystals fall mainly in two groups. One tabular and the other octahedral. Prismatic forms were completely absent. Another important feature of the gel grown samples was the simultaneous occurrence of many thin platelet crystals with square and truncated corners, which is a rare thing found in nature. But when the vertical projection perpendicular to (001) faces of the platelets were superimposed, we get the tetragonal prism cross section of the natural crystals (fig. 107). Also the vertical projection of the gel grown samples
shown in fig. (18) is same as that of the projection of the habit shown in fig. (6) of the natural crystal. The traces of the pyramidal and square and truncated platelet forms can be seen in fig. (82). Leaving the perfection of the natural crystal, the similarities in morphology and surface features of the gel grown and natural crystals suggest that lead molybdate crystals have the same growth mechanism both in gel medium and in nature.

14.3 Dislocation density

The (001) faces of the various samples were examined by etch methods to find the density of dislocations. The density of pits was more on the (001) faces of the natural crystals than on the same faces of the synthetic crystals. On successive etching the pits due to surface defects disappeared gradually and the dislocation pits were retained. The mean density of dislocation pits for natural samples was $10^7 \text{cm}^{-2}$, for samples grown by pulling method it was $10^5 \text{cm}^{-2}$ and finally that of the gel grown samples was $10^2 \text{cm}^{-2}$. A similar trend of the dislocation density was also observed on the (111) cleavage faces of the synthetic and natural crystals. Instances of number of grain boundaries were common features on samples grown by pulling method and on natural crystals, whereas they were totally absent on gel grown samples. From these observations on dislocation densities and grain boundaries, we are inclined to conjecture that synthetic crystals,
preferably gel grown samples are superior in quality to those found in nature.

14.4 Dissolution trend of the etchants

The three etchants namely 1:4 HNO\textsubscript{3}:H\textsubscript{2}O, 1 N NaOH, and 5:3:3 HNO\textsubscript{3}:HF:CH\textsubscript{3}COOH were found suitable to study etch patterns on all samples of lead molybdate crystals. But their rate of attack on similar faces of the various samples were different. As for example for (001) face they were of the order of 8.21, 3.93 and 2.87 microns/min respectively, for gel grown, pulling and natural crystals using nitric acid. High rate of etching for the gel grown crystals suggests that impurities and structural defects are less in gel grown samples. The low rates of etching in other samples are due to the fact that impurities and structural defects may retard the rate of etching. The dendritic etch patterns (fig. 98), etch grooves (fig. 99), and grain boundaries (fig. 104) gave additional indication for the presence of structural defects in these samples.

14.5 Important conclusion

From the present studies on growth and surface microtopography of synthetic and natural lead molybdate crystals, following important conclusions can be drawn.

(a) perfect lead molybdate crystals can be grown in gel medium with the reported growth parameters. This is the first time that the crystals having habits, similar to natural lead molybdate have been grown in the laboratory.
(b) By controlling the experimental parameters, the possibility of changing the habit of lead molybdate crystals in gel medium has been revealed.
(c) A possible growth mechanism is postulated on the basis of morphology and surface microtopography of the gel grown crystals.
(d) The three etchants reported were found suitable for the dissolution studies of both synthetic and natural samples.
(e) It is pointed out that etchants using nitric acid and sodium hydroxide are effective for rotation of etch pits on the important surfaces of the crystal.
(f) On the basis of comparative studies of the morphology, surface features, dislocation density, grain boundaries and dissolution trends of the etchants, superiority in quality of the gel grown crystals is stressed.
(g) Among the etching experiments for dislocation studies of the various samples, notable contribution comes from the evidences given for the presence of edge and screw dislocations on (111) cleavage faces of the synthetic samples grown by pulling method.