CHAPTER 6

HABIT MODIFICATIONS OF LEAD MOLYBDATE

CRYSTALS IN GEL

6.1 Introduction

The crystal habit is the general shape of a crystal and is characterized by the crystal form and the relative sizes of the crystal faces. The faces that appear on a crystal are structurally related and the closest packed planes of the structure will appear as primary faces on the crystal. Several attempts have been made to predict the habit of a crystal with respect to the possible crystal forms\(^{144}\),\(^{145}\). A crystal may be considered to have undergone a change of habit if faces of one or more forms disappear or appear or if their relative sizes change in response to a change in the growth parameters. The factors primarily responsible for habit modifications are

1. The environmental symmetry\(^{146}\)
2. Supersaturation\(^{147}\)
3. Impurities\(^{148}\)
4. Combined effect of supersaturation and impurities\(^{149}\)
5. Composition of disordered phase\(^{150}\).

The lead molybdate crystals occur in nature as Wulfenite with different habits like square tabular, extremly thin, octahedral and also in prismatic forms.
These variations in the crystal habit may be due to significant variations in the conditions under which it is crystallized. We do not know the exact conditions existed in nature, which has affected the habits of the lead molybdate crystals. It was Vesselinov (8) who made an attempt to study the relation between the structure and morphology of this crystal using PBC. Apart from this basic study between structure and morphology by Vesselinov, no other work was found in literature regarding the habit modification of this crystal. A study of habit modification of lead molybdate in synthetic growth systems is important to crystal physicists and minerologists, for it could give valuable information concerning the condition of formation of natural wulfenite. Keeping these points in mind it was thought in the present work to carry out systematic studies on the habit modifications of this crystal in gel medium. In the present chapter, attention is primarily concentrated on the role of pH of the gel solution and concentrations of the reacting solutions as habit modifiers.

6.2 Experimental arrangements

As discussed in chapter 5, double diffusion experiments were arranged using standard U-tubes of 25 mm diameter. Gel solutions were prepared using sodium silicate and were allowed to set slowly in the U-tube. The pH values of the gel were controlled by nitric acid. Solutions of special strength were prepared using lead nitrate and
**Table 4**

Top solutions: (1) 0.25 N Lead nitrate
(2) Standard Ammonium molybdate solution 'S'

<table>
<thead>
<tr>
<th>Different Regions</th>
<th>Habit obtained when pH = 4</th>
<th>Habit obtained when pH = 5</th>
<th>Habit obtained when pH = 6</th>
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<tbody>
<tr>
<td>Region I</td>
<td>Polyhedral Pyramidal crystals as in fig. (16)</td>
<td>Octahedral bipyramidal crystals as in fig. (27) (smaller size)</td>
<td>Small Polyhedral Pyramidal crystals as in fig. (16)</td>
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<tr>
<td>Region II</td>
<td>Octahedral bipyramidal crystals as in fig. (27)</td>
<td>Octahedral bipyramidal crystals as in fig. (27)</td>
<td>Polyhedral Pyramidal crystals as in fig. (16)</td>
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<tr>
<td>Region III</td>
<td>Platelet crystals as in fig. (28) (Smaller size)</td>
<td>Platelet crystals as in fig. (28) (Smaller size)</td>
<td>Octahedral bipyramidal crystals as in fig. (27)</td>
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<tr>
<td>Region IV</td>
<td>Spherulites and Aggregates as in figs. (22) (23)</td>
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<tr>
<td>Different Regions</td>
<td>pH of the Gel = 5</td>
<td>Habits obtained for top solutions at Left: 1 N Right: Std Lead nitrate soln. of Amm. Moly.</td>
<td>Habits obtained for top solutions at Left: 0.25 N Right Std. Lead nitrate soln. of Am. Molybdate</td>
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<tr>
<td>Region I</td>
<td>Polyhedral pyramidal crystals as in fig. (16)</td>
<td>Octahedral bipyramidal crystals as in fig. (27)</td>
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<tr>
<td>Region II</td>
<td>Slightly bigger polyhedral pyramidal crystals as in fig. (16)</td>
<td>Slightly bigger octahedral bipyramidal crystals as in fig. (27)</td>
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<tr>
<td>Region III</td>
<td>Octahedral bipyramidal crystals as in fig. (27)</td>
<td>Platelet crystals as in fig. (28)</td>
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<tr>
<td>Region IV</td>
<td>Spherulites and aggregates as figs. (22), (23)</td>
<td>Spherulites and aggregates as in fig. (22), (23)</td>
<td></td>
</tr>
</tbody>
</table>
ammonium molybdate for top solutions. Important experimental
details and growth parameters are summarized in Tables-4 and
5. For verifying the reproducibility of the results on
habit modifications ten groups of identical experiments were
arranged simultaneously. In all the sets of experiments
the density of gel solutions was 1.03, the length of the gel
column was 10 cms and mean temperature of growth was 27°C.
All crystals were harvested after six weeks. As discussed
previously, for explaining the observations we can divide
the whole gel column into four regions as in fig. (15),
where crystals of different habits were formed, viz, region I
near the lead nitrate solution, region II just below region I,
region III near the ammonium molybdate solution and region IV
at the centre of the gel column.

6.3 The effect of pH on habit modifications.

In crystal growth experiments using gel medium, the
structure of the gel has profound influence to start nuclea-
tion as well as for the perfection of the crystal. The gel
medium consists of sheet like structures of varying degrees
of surface roughness and porosity. The cell walls are ordi-
narily curved. According to Halberstadt et al (151) the cell
walls seen in dense gels have pores from less than 0.1µ to
0.5µ and in low density gels it is less than 0.1 to 4µ. The pH value during gelling has profound influence on gel
structure. As the pH increases the gel structure changes
from a box like network to a structure consisting of loosely
bound platelets and cellular structure becomes less distinct.
The quality of the crystals grown in these gels will change when pH values change. Experimental evidences give full support to this aspect \(^{(130),(104)}\). The pH value not only determines the quality of the crystal, but also changes the habit of the growing crystal. As for example in the growth of strontium tartrate tetrahydrate single crystals in Silica gel, Patel et al \(^{(138)}\) have studied the role of pH on the morphology of the crystal. In aqueous solution growth also, pH value plays an important role in the habit modification of crystals.

For the study of habit modification of lead molybdate crystals, due to changes in pH values, a series of trial runs were arranged with U-tubes for different pH values and concentrations of the top reacting solutions. Out of these three pH values and one pair of concentration value of the reacting top solutions were found suitable to study habit modification. The optimized concentrations of the top solutions are standard solution S of the ammonium molybdate and 0.25 N lead nitrate solution. The optimized pH values are 4, 5 and 6. In all these experiments, as mentioned before, four specific regions were there, where crystals of different habits were formed. The details are shown in table-4. When the pH was 4 polyhedral pyramidal crystals as shown in fig. (16) were formed in region I. In region II octahedral bipyramidal crystals as in fig. 27 were formed and in region III platelet crystals as in fig. 28 were formed. When the pH
was changed to 5 for the same concentration of the top solutions octahedral bipyramidal crystals were formed in both regions I and II. The polyhedral pyramidal shaped crystals were not formed now in region I, but the number of platelets increased in region III. When the pH was changed to 6 the polyhedral pyramidal crystals reappeared in region I and octahedral bipyramidal crystals were replaced by polyhedral pyramidal crystal in region II and octahedral bipyramidal crystals were formed in region III. The platelets have now disappeared. In all these experiments spherulites and aggregate crystals as shown in figs. (22) and (23) were always formed in region IV. Although, occasionally these aggregates and spherulites were found in other regions, they were mostly concentrated in the central region IV of the gel column. It was interesting to note that among the bipyramidal crystals there were crystals having flat faces on the top of the pyramid and also among the platelet crystals there were platelets with and without truncations at the corners.

6.4 Effect of concentration of the reacting solutions on habit modifications.

The change in the pH of the gel produces significant changes in cellular structure such as cell size, wall thickness, pore size etc. when reacting solutions are entering the cells of the gel medium through the pores, each cell can be considered as a growth vessel similar to that of an aqueous solution growth container. In solution growth slow
mixing, low concentrations of the reacting solution etc., are some of the suppressing factors of nucleation. In the case of gel medium, the suppressive action comes from the dimensions of the cellular structure, pore size distribution which are mainly depending on pH. For a given cellular structure and pore size distribution on account of a particular pH, the flow of the reacting solution inside the 'growth vessel' will be regulated. The concentrations of the reacting solution existing inside the growth vessel depend on the concentrations of the solutions taken on the top of the gel. The role of concentrations as a habit modifier has been studied by many people (147) and (154) the recent one in the gel method by Patel et al (138) is significant.

Although Vesselinov (137) tried to grow lead molybdate crystals by solution growth method, for two different concentrations of the reactants, no attempt has been made to study the habit modification of this crystal. In this work, to study the effect of concentrations on habit modification, after a series of trial experiments, we have optimized one pH value and two pairs of concentrations of the reacting solutions, for effective habit modifications. Keeping the pH of the gel at 5 and the standard solution of ammonium molybdate as such, the concentration of the lead nitrate solution was changed from 1 N to 0.25 N. The details of the habits obtained are summarized in table 5. When the concentration of lead nitrate was 1 N, polyhedral
pyramidal crystals were formed in region I (fig. 16). In region II octahedral bipyramidal crystals as in fig. (27) were formed. When the concentration of lead nitrate was 0.25 N, polyhedral pyramidal crystals were replaced by octahedral bipyramidal crystals in region I and II and the octahedral bipyramidal crystals were replaced by platelet crystals (fig. 28) in region III. In both the cases aggregates and spherulites were formed always in region IV as in fig. (22) and fig. (23).

6.5 Discussion

The formation of crystal in different regions have been discussed in chapter 5. In the beginning the diffusion process is relatively rapid at the centre of the gel column (region IV). This initial condition will produce complicated oscillating movement which may gradually subside. The aggregates and spherulites are considered as the product of this rapid process. After this initial stage diffusion will be stabilized. At this stable condition perfect crystals will start to nucleate in other regions. The various habits produced are due to the arrival of the respective concentrations of lead and molybdate ions manifested by the pH of the gel medium. In a separate diffusion experiment it was noticed that lead nitrate solution diffuses more rapidly than that of ammonium molybdate solution through the gel medium. In regions I and II the percentage of positive lead ions is
much higher than that of the negative molybdate ions for a particular concentration of the top solutions. Similarly in region III the percentage of negative molybdate ions is more than that of the positive lead ions. The crystals of different habits found in the respective regions are formed due to the different percentage of the lead and molybdate ions in the growth region manifested by the pH of the gel, and different concentration profile may exist in the growth region which will yield new habits for the growing crystal. For a given concentration, the change in pH of the gel, simply changes the concentration profile in the 'growth vessel' because of the change in the cellular structure and hence the characteristics habit modification in the different regions. The walls of the growth vessel and pore size regulate the inflow of the lead and molybdate ions inside the 'growth vessel'. The above discussion on the habit change of lead molybdate crystals grown in the regions I to III reveals important statements on the diffusion velocity of lead and molybdate ions. At high lead concentrations (region I) the equilibrium form may be altered due to the adsorption or supersaturation effects, while in region II and III the solutions diluted with respect to lead ions leads to crystal exhibiting the most stable \{001\} faces.

One should be cautious about the interpretation of the results of diffusion studies, since authors like Kirov
(loc. cit) feels that diffusion methods of growing crystals are generally inadequate and crystals are grown under indefinite conditions. The author was fully aware of the limitations of the diffusion methods and carefully incorporated the new concepts of Kirov, on the diffusion mechanisms for explaining the observed habit modification of PbMoO$_4$ crystals. However, one of the objections that can be raised is, whether by changing the concentration and pH, is it possible in similar growth systems to produce habit modifications in other crystals? Also why in other gel methods such different regions are not observed? Answer lies in the fact that no growth method is universal in all respects. The conditions of each crystallization process depend on the nature of the reacting solutions and also on the nature of the crystal being grown.
Fig. 27 & 28 Octahedral bipyramidal and platelet crystals of Pb₄SeO₄ formed due to the changes in pH and concentration (X 75)

Fig. 29 Twinning on (001) face (X 75)

Figs 30, 31 & 32 - Twined crystals (X 75)