PART 1
CHAPTER - 1

EXISTING INFORMATION ABOUT LEAD MOLYBDATE CRYSTALS

General Introduction

The basic principle of all methods of single crystal growth is to control the change of state. Melting, sublimation, solution and vapour reaction are the mechanisms commonly used for effecting the state of change. These states of change of substance are done with temperature variation and sometimes pressure as control element. The best controlled growth of crystals is by reaction in gel media. This method is becoming more popular nowadays among the crystal growers. Both synthetic and natural crystals are useful for research in many applied branches of science. The greater part of the minerals that form the crust of the earth have been formed by solidification from fused rock material. Many natural crystals are crystallized from solution also. But the conditions of their formation are often different from those that
can be duplicated in the laboratory. Some minerals may be formed from vapour phase like those formed in connection with volcanic eruption.

The mystery of exact conditions of growth mechanism of crystals and the environments which prevailed while they were in the process of growth, can be inferred to some extent from the study of their finished faces after the cessation of growth. After the end of the growth, the crystals are likely to be subjected to dissolution in nature and from the study of such etched faces, the conditions which prevailed to produce such figures can be understood. The internal imperfections and disorders such as dislocations, stacking faults, twinning, grain boundaries etc., alter the appearance of the face to a great extent. The surface topography is an important tool to study the dynamical characteristics of the crystal. The surface microtopographs of crystals of the same material grown under different conditions are different. The growth conditions responsible for these differences between natural and synthetic crystals of the same compound are the duration of growth and the environmental media.

In this laboratory exhaustive and systematic microtopographical studies have been carried out on both natural and synthetically grown lead molybdate crystals. This thesis contains a detailed account of the studies made on the growth of this crystal by gel method and its superiority over other samples of different origin by
surface microtopographic observations.

The present chapter is devoted to a brief introduction of the existing information on lead molybdate crystals.

1.2 Introduction

Because of its rarity and variety of uses in science and industries, lead molybdate is one of the highly priced minerals among the crystals. It has low acoustic and optic losses and can be grown without much optical damages. For these reasons lead molybdate has captivated a unique place in the instrumentation field such as acousto-optic devices\(^1\)\(^2\). Because of its high figure of merit for acousto-optic applications, it is suitable for the construction of two stage horizontal and vertical acoustically driven light deflector\(^3\). This crystal has also been widely investigated as a host crystal for laser applications\(^4\).

1.3 Occurrence

Natural lead molybdate crystal is known as Wulfenite. It is named after the Austrian mineralogist Franz Xaver Wulfen (1728-1805). This mineral is of secondary origin found in lead and zinc deposits in the oxidation zones. It is usually associated with vanadinite, mimetesite, cerussite, limonite and calcite. Wulfenite is the next most common molybdenum mineral after molybdenite. Of the many known localities, the following places are well known for its occurrence. In Germany, it is found at Berggiesshubel; Saxony; Schapbachthal and Baden; in Austria at Annaberg; Beliberg; Rudnik; Mies and Carinthia; in North Africa at
Oudida; Jabel Mahser; Morocco and also at Tebessa in Algeria; in Australia in the Broken Hill district and in New South Wales. In the United States Wulfenite is found abundantly at numerous localities in the western and south western parts of the country such as Red cloud and Humburg mines, Trigo mountains, Santacruz county etc.

1.4 Structure and Symmetry

Wulfenite is examined as an example of the scheelite type of structure. It belongs to the tetragonal class. The structure was first determined by Vegard\(^5\). The unit cell constants are \(a_0 = 5.401\), \(c_0 = 12.079\), \(a_0 : c_0 = 1:2.236\). The cell content is \(\text{Pb}_4(\text{MoO}_4)_4\).

Later in 1938 Quodling and Cohen\(^6\) by X-ray studies proved that the mineral is isostructural with stolzite and wulfenite with intermediate cell dimensions which gives \(a_0 = 5.43 \text{ km}, c_0 = 12.08\) and space group as \(I4_1/a\).

Leciejewicz\(^7\) studied the X-ray diffraction of wulfenite in detail and his structural data on this crystal is of much importance. According to him, for Wulfenite the space group is \(\text{C}_4^6 \cdot I4_1/a\), \(a_0 = 5.432 \text{ Å}, c_0 = 12.107 \text{ Å}\) and \(Z = 4\).

Fig. (1) describes the Wulfenite structure by Leciejewicz, where projection of atoms on (001) plane is shown. In this structure each metal atom (Pb or Mo) is surrounded by four of the other kind at a distance of 3.84 Å, four of the other kind and four of the same kind at a distance of 4.10 Å, four of the same kind at 5.43 Å, and four of the
other kind at 6.05 Å. Because of the complicated structure and mixed character of the interatomic interactions no attempt was made by Leciejewicz to evaluate the bonds between the structural units.

Vesselinov\(^{(8)}\) applied PBC method to evaluate the wulfenite structure. Although his studies are confined to the relation between the structure of Wulfenite as an example of Scheelite type structure and the morphology of its crystals, they give a new approach to study the complicated structure and mixed character of the interatomic interactions of the crystal like lead molybdate.

The following PBC have been analysed;

- **Straight chains** \([-110], [021] \text{ and } [001]\),
- **Zigzag chains** \([-100], [111], [131], [331], [011]\) and their symmetrical equivalents. It was established that these chains alone effect the morphology of the crystal.

The chains were also distinguished according to the distances between the neighbouring metal atoms bound with oxygen. Chains within which this distance is shortest ie. 3.84 Å, only determine a single F - form \(\{001\}\). The F - forms \(\{011\}, \{112\}, \{013\}, \text{ and } \{010\}\) were added for chains which have a distance of 4.10 Å. If all chains derived were taken into account, \(\{121\}\) and \(\{110\}\) also become F - forms.

According to Bach.Jb\(^{(9)}\) and Russel\(^{(10)}\), Wulfenite has a pyramidal (4) Symmetry indicated by the morphology, though not always clearly shown. Traube.Jb\(^{(11)}\) suggested dipyramidal (4/m) symmetry by the symmetry of the etch pits
obtained. This is further confirmed by Leciejewicz(7) by X-ray diffraction studies. From the morphological consideration and etch studies Hurlbut(12) suggested that true symmetry as pyramedal (4). The true symmetry of these crystals has long been controversial, the question being whether the symmetry is dipyramidal (4/m) or pyramidal (4).

1.5 Habits(13)

Wulfenite crystals are commonly square tabular, sometimes extremely thin or with a flat vicinal pyramid replacing \{001\}, less frequently octahedral in habit and in prismatic and cuboidal. It is also observed in the form of granular massive, coarse to fine granular. The commonest forms of these crystals are e \{001\}, n \{111\} a \{100\}, u \{02\} and e \{101\}. These are shown in figures (2), (3), (4), (5), (6) and (7). There is no horizontal plane of symmetry and therefore wulfenite is hemimorphic in the distribution of the faces. The hemimorphism of wulfenite has been discussed by Weber(14).

1.6 Chemical Properties(15)

Lead molybdate consists of 39.3% molybdenum trioxide and 60.7% Lead Oxide. W (tungsten) substitute in the material with W : Mo = 1:1, indicating at least a partial series towards the isostructural compound stolzite (PbWO₄). But W is lacking in most reported analyses. Ca substitutes for Pb in the ratio Ca : Pb = 1:1.7 indicating the change over to another isostructural compound Powellite Ca(Mo,W)O₄. In synthetic crystals W, Cr, and S substitute for Mo.
On evaporation in HCl, the crystal will be decomposed with the separation of lead chloride and molybdic oxide. It is also decomposed by HNO₃ with separation of molybdic oxide. The crystal is soluble in concentrated sulphuric acid and alkalies.

1.7 Physical Properties

Lead molybdate crystals are generally found with colours which may vary from wax to orange yellow. It is also available in yellowish gray, grayish white, siskin-green, olive green and reddish brown. It has very smooth cleavage along (111) and less distinct cleavages along (001) and (113) faces\(^\text{13}\). Distinct cleavage face along (011) is also reported\(^\text{15}\). The fracture sometimes varies from subconchoidal to uneven. The hardness of the crystal lies between 2.75 to 3 on Moh's scale and its specific gravity between 6.5 and 7.0. Recently it was found that PbMoO₄ has a high figure of merit useful for acousto-optic devices\(^\text{3}\). The melting point reported is 1065°C\(^\text{16}\). The dielectric constants parallel to the a and c axis of PbMoO₄ are 34.0 and 40.6 respectively\(^\text{17}\).

1.8 Optical Properties

PbMoO₄ crystal is uniaxial negative sometimes anomalously biaxial and not optically active. The refractive indices for different wavelengths are different for natural\(^\text{18}\) and synthetic crystals\(^\text{19}\) and are shown in tables 1 and 2. These deviations can be attributed to either impurity levels
**Table 1**

Refractive indices for different wavelengths in natural PbMoO$_4$ Crystals

<table>
<thead>
<tr>
<th>Wave length (µm)</th>
<th>$n_o$</th>
<th>$n_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6867</td>
<td>2.3620</td>
<td>2.2558</td>
</tr>
<tr>
<td>0.6563</td>
<td>2.3724</td>
<td>2.2635</td>
</tr>
<tr>
<td>0.5893</td>
<td>2.4053</td>
<td>2.2826</td>
</tr>
<tr>
<td>0.5270</td>
<td>2.4542</td>
<td>2.3131</td>
</tr>
<tr>
<td>0.5175</td>
<td>2.4611</td>
<td>2.3162</td>
</tr>
</tbody>
</table>
Table - X

Refractive indices for different wavelength

in synthetic PbMoO$_4^{(19)}$ Crystals

<table>
<thead>
<tr>
<th>Wave length (μm)</th>
<th>$n_o$</th>
<th>$n_e$</th>
<th>Wave length (μm)</th>
<th>$n_o$</th>
<th>$n_e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.4046</td>
<td>2.7191</td>
<td>2.4429</td>
<td>1.500</td>
<td>2.2808</td>
<td>2.1871</td>
</tr>
<tr>
<td>0.4800</td>
<td>2.5136</td>
<td>2.3409</td>
<td>2.000</td>
<td>2.2679</td>
<td>2.1769</td>
</tr>
<tr>
<td>0.5086</td>
<td>2.4754</td>
<td>2.3185</td>
<td>2.500</td>
<td>2.2577</td>
<td>2.1686</td>
</tr>
<tr>
<td>0.5460</td>
<td>2.4388</td>
<td>2.2959</td>
<td>3.000</td>
<td>2.2474</td>
<td>2.1603</td>
</tr>
<tr>
<td>0.5770</td>
<td>2.4160</td>
<td>2.2814</td>
<td>3.250</td>
<td>2.2418</td>
<td>2.1556</td>
</tr>
<tr>
<td>0.6438</td>
<td>2.3808</td>
<td>2.2581</td>
<td>3.500</td>
<td>2.2360</td>
<td>2.1507</td>
</tr>
<tr>
<td>1.0140</td>
<td>2.3072</td>
<td>2.2066</td>
<td>3.750</td>
<td>2.2297</td>
<td>2.1455</td>
</tr>
</tbody>
</table>
or stochiometric variations. The optical transmission of this crystal in the visible region can be improved by oxygen annealing\textsuperscript{(19)}. The infrared transmission characteristics of synthetic PbMoO\textsubscript{4} show three basic absorption peaks at 4.05, 4.28, and 4.48 $\mu$m. There is a small window at 7.7 $\mu$m and zero transmission at 40 $\mu$m for almost all samples. Loiacono et al\textsuperscript{(19)} observed unusual optical properties. The colourless crystals, when exposed to natural sunlight, turn blackish. The optical behaviour of this type could be due to silver ion impurities.