

CHAPTER 1

EXISTING INFORMATION

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1.1 INTRODUCTION

From a vast background of the various kinds of information available in literature about the Scheelite and the related oxide single crystals, the present work was picked up and thus the details of the work carried out have been compiled in the form of this thesis. It is in the fitness of things to bring out a suitable picture of the relevant existing information.

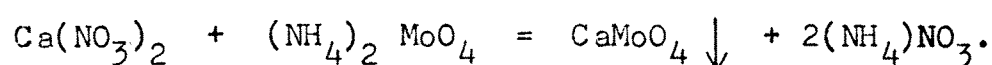
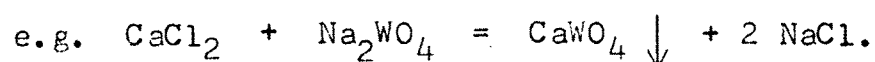
For the last a few years, Scheelite-type single crystals have found increasing importance in the fields of electronics and optics. Of all these compounds, molybdates and tungstates are known to be excellent luminescent materials. Calcium molybdate shows the highest luminescence efficiency, being reduced by inclusion of SrO, BaO, ZnO or CdO during preparation (1). These ternary compounds in pure single crystal form and with suitable dopants such as rare-earth ions and/or transition metal ions are of considerable interest in optomechanical, photoelectrical and electro-acoustical industries.

The elements of group Va and VIa of the periodic classification form oxyanions of the type $M^V O_4^{3-}$ and $M^{VI} O_4^{2-}$, where M is metal ion, vanadium, tantalum,

chromium, molybdenum or tungsten. Of these compounds, the tungstates and molybdates have probably been investigated more at length than any other system (2). However, due to slow reactions in solutions and due to inability to grow their well formed crystals, further studies to understand these crystals are hampered. The scope of this chapter is to review some aspects of the existing information on calcium molybdate, CaMoO_4 .

1.2 PREPARATION

The alkali earth metal-ion tungstates and molybdates can be prepared in laboratory by precipitation from aqueous solutions of alkali-earth nitrates or chlorides with Na_2WO_4 or $(\text{NH}_4)_2\text{MoO}_4$ aqueous solutions.



1.3 CRYSTALLIZATION

Several techniques have been applied for the growth of both pure and doped single crystals of calcium molybdate. In general, single crystals of tungstates and molybdates of the Scheelite-group can be grown from their pure melts (essentially by Czochralski's method) and from aqueous solutions under hydrothermal

conditions and also from molten solutions (3-5). Scheelite (CaWO_4) and Powellite (CaMoO_4), having the divalent cation with ionic radii, R , around 1 \AA have been satisfactorily crystallized in alkali chlorides by hydrothermal method. The grown crystals with pyramidal habit were transparent, colourless, of 1-3 mm in size and having principal crystallographic forms : $\{111\}$, $\{011\}$, $\{001\}$ (4). Crystal growers (6-10) have mostly applied Czochralski technique, wherein a crystal is rotated while being pulled from the melt, for the growth of pure and doped calcium molybdate crystals. According to Preziosi et al (6), clear uncoloured crystal of calcium molybdate was conveniently pulled at a speed of upto one inch per hour with a rotation speed of 10 to 15 rpm. However, when trivalent ions are added, the pulled crystal was coloured blue. Crystals of Powellite, CaMoO_4 , with Gd^{3+} ions were prepared using Czochralski method by Meil'man and Solov'ev (7), the melt containing 0.02 to 1 at. % Gd^{3+} , for investigation of the ESR spectrum. To study the dielectric behaviour, Brower and Fang (8) had grown single crystals of CaMoO_4 by Czochralski method and a spectrochemical analysis indicated the following impurities to be present : Al, Cr, Si, Sr 0.001 - 0.01 %; Ag, Ba, Cu, K, Li, Mg, Na, Pb < 0.001 %. Calcium molybdate with

0.1 mole % Nb^{5+} was obtained by the Czochralski method using an inductively heated furnace. Crystals pulled were typically 15 mm diameter and 5 cm long (10). High quality crystals of CaMoO_4 , 0.4 - 1.2 mm in size were obtained using the temperature-gradient zone melting technique (11), the technique was adopted since the growth can be carried out somewhat below the melting point of the crystal. Single crystals of calcium molybdate containing various paramagnetic ions, viz. Nd^{3+} , Yb^{3+} , Mn^{2+} , Gd^{3+} and Ce^{3+} have been successfully grown by Potkin (12) using (LiCl + KCl) melt by employing temperature-gradient method. LiCl + KCl melt was perhaps selected on the basis of earlier work by Anikin (5). Packter and Roy (13-15) have crystallized molybdates and tungstates of alkaline earth-metal from unstirred supersaturated solutions of LiCl melts in alumina crucibles by continuous cooling from 800°C to room temperature. Packter (16,17) also studied the precipitation of alkaline earth metal molybdate powders from their aqueous solution; crystal number, final morphology and particle sizes were determined. CaMoO_4 was also produced by mixing aqueous solutions of Na_2MoO_4 and CaCl_2 for the determination of precipitation induction periods in the range from several seconds down to about 5 ms (18). The spherulitic growth of calcium molybdate in silica gel media with pH

range 5-7 has been studied by Kurien and Ittyachen (19,20). For its crystal growth, solutions of CaCl_2 1 M to 0.25 M and $(\text{NH}_4)_2\text{MoO}_4$ 0.05 M to 0.02 M were mixed in a U-tube, spherulites of CaMoO_4 obtained were quite small in size.

1.4 PHASE DIAGRAMS

The solubility and phase diagrams of the molybdates with various salts are well known. Petrosyan et al (21), in particular, in order to determine the conditions of growth of crystals from a solution of Na_2MoO_4 melt, constructed phase diagrams of the system $\text{Na}_2\text{MoO}_4 - \text{M MoO}_4$ (M is Ca, Sr or Ba). Sodium molybdate acts as an indifferent solvent and has a fairly low melting point, which may lead to a decrease in the crystallization temperature of the individual molybdate in its melt in systems with a low eutectic melting point. To construct the phase diagrams they used differential thermal analysis (DTA), visual-polythermal analysis (VPA) and X-ray and densitometric methods.

In the case of calcium, strontium, and barium tungstates and molybdates, a suitable solvent is an eutectic mixture of the chlorides of potassium and lithium, which melts at about 360°C ; the solubilities of

the above compounds in this LiCl + KCl mixture at 500°C are about 4 wt. % for CaWO₄ and 10 wt. % for BaMoO₄. The solubilities of the other tungstates and molybdates of Ca, Sr and Ba lie between these values. No double-decomposition reactions were observed between the solute and the solvent in the range 400-600°C. This LiCl + KCl eutectic is not very corrosive at temperatures up to 600°C (12). Parker and Brower (22) studied the solubility and phase diagrams of solute CaMoO₄ using Li₂SO₄ as a solvent. In order to study the precipitation of alkaline earth metal molybdate powders Packter (16,17) used equivalent solutions of calcium, strontium and barium nitrates and sodium molybdate of initial metal salt concentrations from 0.0004 to 0.4 M at 25°C. Packter (17) also studied precipitation kinetics of barium, strontium and calcium molybdates from aqueous solution. Barium molybdate precipitates were studied from equivalent solutions of initial metal salt concentrations from 0.0004 to 0.003 M, strontium molybdate precipitates from 0.002 to 0.015 M solutions, and calcium molybdate precipitates from 0.01 to 0.06 M solutions at 25°C.

1.5 CRYSTAL STRUCTURE

Calcium molybdate belongs to an interesting

morphotropic and isostructural series of Scheelite-type crystals (divalent metal ion molybdates and tungstates) represented by the general formula ABO_4 where A is Mg, Ca, Sr, Ba, Cd, Zn, Fe, Co or Ni, and B is Mo or W. The crystal structure is characterized by the space group C_{4h}^6 or the tetragonal $I4_1/a$ (space group No. 88) (23), with four molecules ($z = 4$) in the unit cell. The site symmetry at both A and Mo is S_4 . The unit cell is body centred Bravais lattice with dimensions.

$$a = 5.22 \text{ \AA}, \quad b = 5.22 \text{ \AA} \quad \text{and} \quad c = 11.43 \text{ \AA}$$

The Scheelite structure ($CaWO_4$) and other members of the isostructural series were first analysed by Vegard (24). Figures 1.1 and 1.2 show the structure of Scheelite. This may be viewed as composed of WO_4^{--} anions ionically bonded to Ca^{++} cations. The four fold axes are alternately right handed and left handed 4_1 screw axes, passing through the centre of each of the square prisms into which the figure is divided. The metal sites are found on planes separated by $\frac{c}{4}$ and perpendicular to the $\frac{c}{4}$ -axis; the metal ions on the planes at $\frac{c}{4}$ and $\frac{3c}{4}$ are related to those on the ab and $\frac{c}{2}$ planes by glides. The nearest metal ions lie in planes separated by $\frac{c}{4}$, and the direction

joining the two ions, Ca-Ca, W-W and W-Ca makes an angle of $42^{\circ} 40'$ with the ξ -axis.

Put simply, the large A ions (e.g. Ca, Sr, Ba) are surrounded by 8 oxygens at the corners of two interpenetrating spheroids, the smaller B ions (e.g. W) show tetragonal oxygen co-ordination. Each tungsten ion in CaWO_4 is bonded covalently to four oxygens, forming a slightly distorted or squashed tetrahedron with the W-O distance of 1.78 \AA [Fig. 1.3(a)]. The diagonal plane of this tetrahedron makes an angle of about $31^{\circ} 54'$ with the a-axis Fig. 1.3(b). The calcium atoms, on the other hand, are surrounded each by eight oxygens, which form two distorted tetrahedra with Ca-O distances of 2.48 \AA and 2.44 \AA Fig. 1.4(a) and 1.4(b) respectively. The basic Scheelite structure shows zig-zag chains, -M-M-X-X-M-M- in the ξ direction with large interatomic distances $(a^2/4 + c^2/16)^{1/2}$. It also shows zig-zag chains with a different sequence such as -M-X-M-X-M-X- in a direction and smaller interatomic distances of $a/2$. Sillen and Nylander (25), while giving history of the crystallography of Scheelite-structures, carefully reviewed the evidence for oxygen positions in them. They were led to propose oxygen co-ordinates which were nearly constant fractions of the a, b and c unit cell dimensions, but with increasingly

(This figure actually pertains to CaHfO_4 , not CaWO_4)

large limits of uncertainty (Table 1.1). Then later Zalkin and Templeton (26) and Kay et al (27) reported the refinement studies for CaWO_4 using X-ray diffraction data and neutron diffraction data respectively. Structure refinement on additional Scheelites (SrWO_4 , BaWO_4 , CaMoO_4 , SrMoO_4) by neutron diffraction has been attempted by Gürmen et al (28). For the cell origin at $\bar{4}$, they have given the co-ordinates of all atom positions of the structure AXO_4 ($A = \text{Ca, Ba, Sr}$) and ($X = \text{W or Mo}$) as

$$\begin{aligned}
 & (0,0,0; 1/2,1/2,1/2) + \\
 & 4 A \text{ in } 4 b \text{ at } (0,0,1/2); (0,1/2,3/4) \\
 & 4 X \text{ in } 4 a \text{ at } (0,0,0); (0,1/2,1/4) \\
 & 15 O \text{ in } 16 f \text{ at } (X,Y,Z); (\bar{X},\bar{Y},Z); (X, 1/2 + Y, 1/4 - Z) \\
 & \quad (X,1/2 - Y, 1/4 - Z); (\bar{X},Y,\bar{Z}); (Y,\bar{X},\bar{Z}) \\
 & \quad (\bar{Y},1/2 + X, 1/4 + Z); (Y, 1/2 - X, 1/4 + Z)
 \end{aligned}$$

Figure 1.5 shows a b-axis projection of the unit-cell and the following observations can be made :

1. The tetragonal bond length, X - O, is independent of the A species for a given X.
2. The setting angle of oxygen tetrahedron in the

Table 1.1 Oxygen co-ordinates of some Scheelites

| Crystal | Oxygen co-ordinates | | |
|-------------------|---------------------|-------------|---------------|
| | X | Y | Z |
| CaWO ₄ | 0.25 ± 0.02 | 0.15 ± 0.02 | 0.075 ± 0.015 |
| BaWO ₄ | 0.25 ± 0.02 | 0.11 ± 0.02 | 0.075 ± 0.015 |
| SrWO ₄ | 0.25 ± 0.02 | 0.14 ± 0.02 | 0.075 ± 0.015 |

ab plane (angle between the XY projection of $O_0 - X_1$ and the X-axis) diminishes systematically with increasing A, changing from 32 to 27.8 for the tungstates.

3. The presence of two slightly different bond lengths connecting the A ion with its eight oxygen neighbours ($O_0 - A_1$, $O_0 - A_2$) is evident.
4. The average of the two A - O distances for each Scheelite is comparable with the empirical inter-ionic radii given by Pauling (29).

$CaMoO_4$ is essentially isostructural to Scheelite; there are, however, characteristic deviations in the details of both kinds of polyhedra, which have to do with somewhat different O - co-ordinates in the two structures.

The co-ordinates of basis atoms, inter-atomic distances in Ca polyhedra and Mo polyhedra and bond-lengths-near neighbour distances in $CaMoO_4$ cell are presented in Tables 1.2, 1.3, 1.4 and 1.5 respectively.

1.6 PROPERTIES

Some of the properties pertaining to

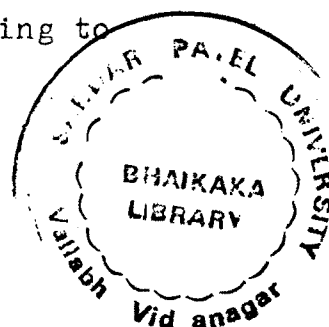


Table 1.2 Co-ordinates of the Basis Atoms in CaMoO₄,
Origin at $\bar{4}$

| Atom | $\frac{x}{a}$ | $\frac{y}{b}$ | $\frac{z}{c}$ |
|------|---------------|---------------|---------------|
| Ca | 0.0 | 0.0 | 0.0 |
| Mo | 0.0 | 0.0 | 0.500 |
| O | 0.257 | 0.145 | 0.167 |

Table 1.3 Interatomic Distances(\AA) in the Ca polyhedra of CaMoO_4

| Ca-O | ⋮ | O-O |
|-----------|---|-----------|
| 2, 45 (4) | ⋮ | 3, 19 (2) |
| 2, 48 (4) | ⋮ | 3, 75 (4) |
| | ⋮ | 2, 78 (4) |
| | ⋮ | 2, 96 (4) |
| | ⋮ | 3, 05 (4) |

Table 1.4 Interatomic distances and Valence Angles in Mo(W) Polyhedra

| Interatomic distances Å | | Valence angles | |
|-------------------------|--------------------------------|---|---|
| 1st coord sphere | 2nd coord sphere | 1st coord sphere | 2nd coord sphere |
| B-O | B-O | O-B-O | O-B-O |
| B-O ₁₋₄ | B-O ₅₋₈ | O ₁ -B-O ₂ = 114° 50' | O ₅ -B-O ₆ = 99° |
| 1.76 | 2.96(4) | | |
| | 2.94 | | |
| Ca:O ₄ | O ₃ -O ₄ | O ₃ -B-O ₄ = 107° | O ₇ -B-O ₈ = 114° 55' |
| | 2.82(2) | | |

Table 1.5 Bond lengths and near-neighbour distancesCaMoO₄

| | |
|-------------------|-------------------|
| $O_o - X_1$ | 1.757 ± 0.005 |
| $O_o - A_1$ | 2.459 |
| $O_o - A_2$ | 2.471 |
| $O_o - O_1$ | 2.964 |
| $O_o - O_2$ | 3.093 |
| $O_o - O_4$ | 2.924 |
| $O_o - O_6$ | 2.820 |
| α | $115^\circ 0'$ |
| γ | $106^\circ 46'$ |
| $X_1 - O_4$ | 2.945 |
| $A_1 - X_1$ | 3.871 |
| $A_2 - X_2$ | 3.695 |
| $(O_o - A)_{Av.}$ | 2.465 |
| $(O - A)_{oxide}$ | 2.405 |

calcium molybdate, studied by several workers, have been listed in Table 1.6.

1.7 ADDITIONAL INFORMATION

1. Alkaline earth-metal molybdates are of great technical importance, being used in various optical, acousto-optical and other physical applications (36-39).
2. There is much interest in quantum electronics of tetragonal crystals with structure of Scheelite when the dopant is a transition metal, which helps to extend the wavelength range of masers and to increase the performance (12).
3. Polycrystalline samples of calcium, cadmium, zinc and other molybdates and tungstates are used in luminescent coatings (40-42). Single crystals of some molybdates and tungstates are employed in recording γ -rays in scintillation counters (43,44).
4. Single crystals of alkaline earth compounds are finding increasing use as laser material matrices, gamma radiation detectors in

Table 1.6 Some pertinent properties of CaMoO_4

| Molecular weight | Melting point $^{\circ}\text{C}$ | Specific gravity g.ml^{-1} | Crystal habit | Colour | ΔH KCal/mole | ΔF KCal/mole | Structural data tetragonal $a = b \neq c$ | DC conductivity σ 20°C $\Omega^{-1} \text{cm}^{-1}$ |
|------------------|----------------------------------|-------------------------------------|--|----------------------------|-------------------------------------|-------------------------------------|--|--|
| 200.01 (30) | 1449 (31) | 4.38-4.53 (30) | Pyramidal (4) | Colourless (30) | -369.5 + 0.3 (from elements) | -344.0 + 0.5 (from elements) | $a=5.224$ (35) $c=11.430$ | $3 \cdot 10^{-10}$ (21) |
| | 1450 (32) | 4.22+ 0.03 (21) | Tetragonal bi-pyramidal (truncated) (13) | Clear uncoloured (6) | -39.6 + 0.1 (from oxides) (34) | -40.0 + 0.2 (from oxides) (34) | $a=5.23$ (55) $c=11.44$ | |
| | 1480 (33) | 4.35 (20) | Platelets (16) | Transparent colourless (4) | | | $a=5.226$ (56) $c=11.43$ | |
| | 1445 + 5 (21) | | | | | | $a=5.225$ $c=11.424$ (4) $c/a=2.186$ | |

ΔH is the heat of formation from the elements and from the oxides at 298.15 K.

ΔF is the free energy of formation from the elements and from the oxides at 298.15 K.

scintillation counters and other related fields (21).

5. After the early work of Kröger (42) and Botden (45) there has been a renewed interest in the molybdate and tungstate luminescence of Scheelites during recent years. Van Loo (46,47) discussed the luminescence of PbWO_4 and PbMoO_4 . Treadaway and Powell (48,49) and Grasser et al (50,51) have studied the CaWO_4 luminescence in detail. Blasse and Schipper (52) reported on the luminescence of SrWO_4 and BaWO_4 . Tyner and Drickamer (53) presented a study on the pressure and temperature dependence of the decay time and the intensity of the luminescence of several molybdates and tungstates. Groenink et al (54) observed the luminescence in calcium molybdate.
6. Several of the Scheelite structures are now of interest as possible host lattice for lanthanide ions (57).
7. Calcium molybdate has been of particular interest in Raman and Infrared spectroscopy

(58-63).

8. The frequency and angular dependence of the EPR line width of tetragonal Nd^{3+} centres in CaMoO_4 single crystals was investigated (64). A study was made on the EPR spectra of Er^{3+} centres in CaMoO_4 and SrMoO_4 at temperatures from 4.2 to 10 K (65). The influence of an external electric field on the ESR spectrum of Gd^{3+} ions in CaMoO_4 was studied by Domracheva et al (66). The EPR spectrum studies of Mn^{2+} in CaMoO_4 , CdMoO_4 , CaWO_4 and SrWO_4 has been investigated in the temperature range 4.2 - 380 K (67). The EPR spectrum studies of CaMoO_4 doped with niobium (68) and Mo^{5+} in CaMoO_4 (69) are also reported.
9. Recently, the defect chemistry of ABO_4 type compounds has been discussed in detail by Groenink with the aid of the ideas put forward by Schamlzried for the ternary compounds (70,71).

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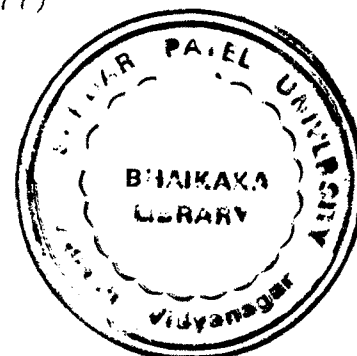
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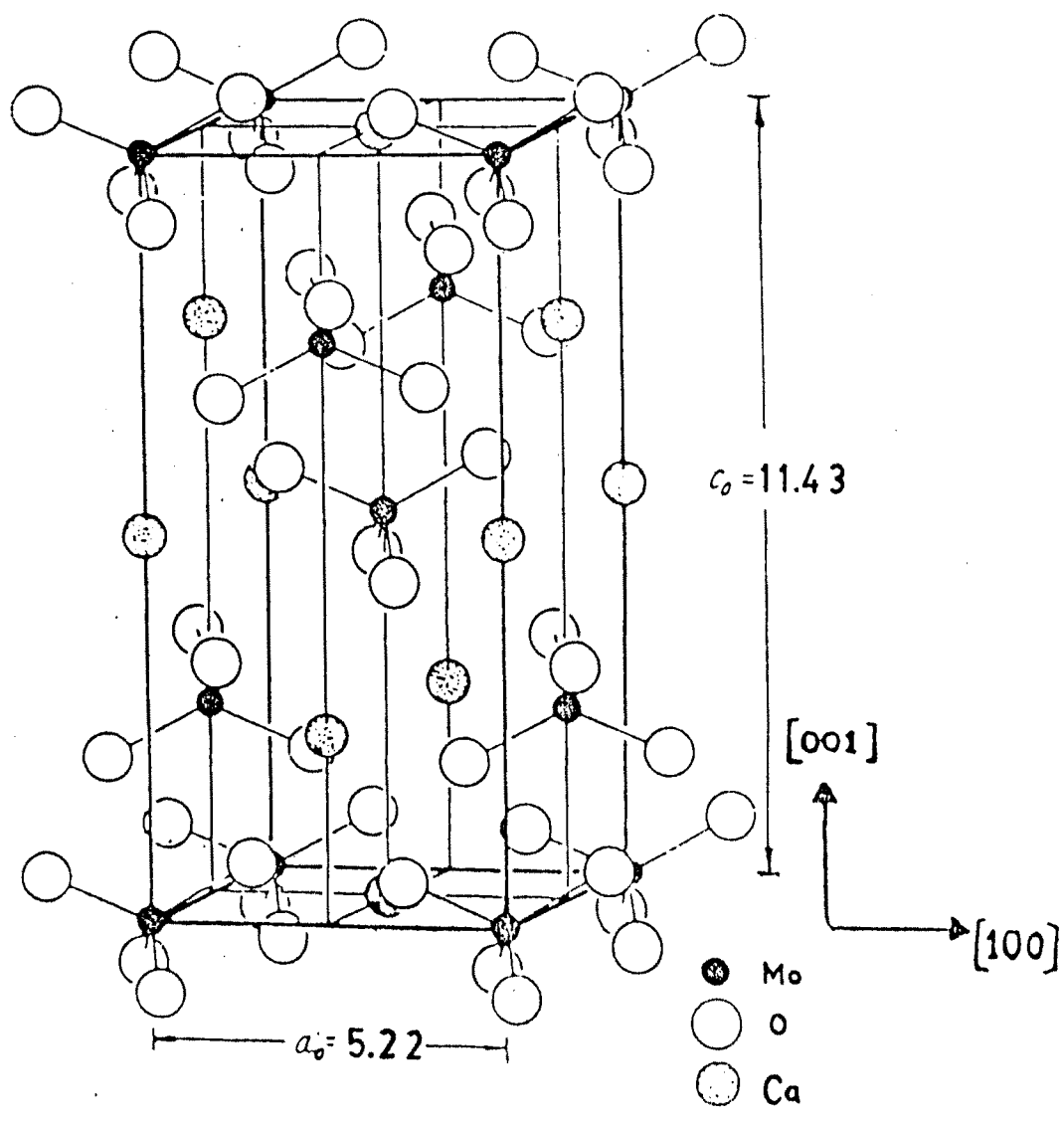


Fig. 1.1 The unit cell structure of CaMoO_4 .

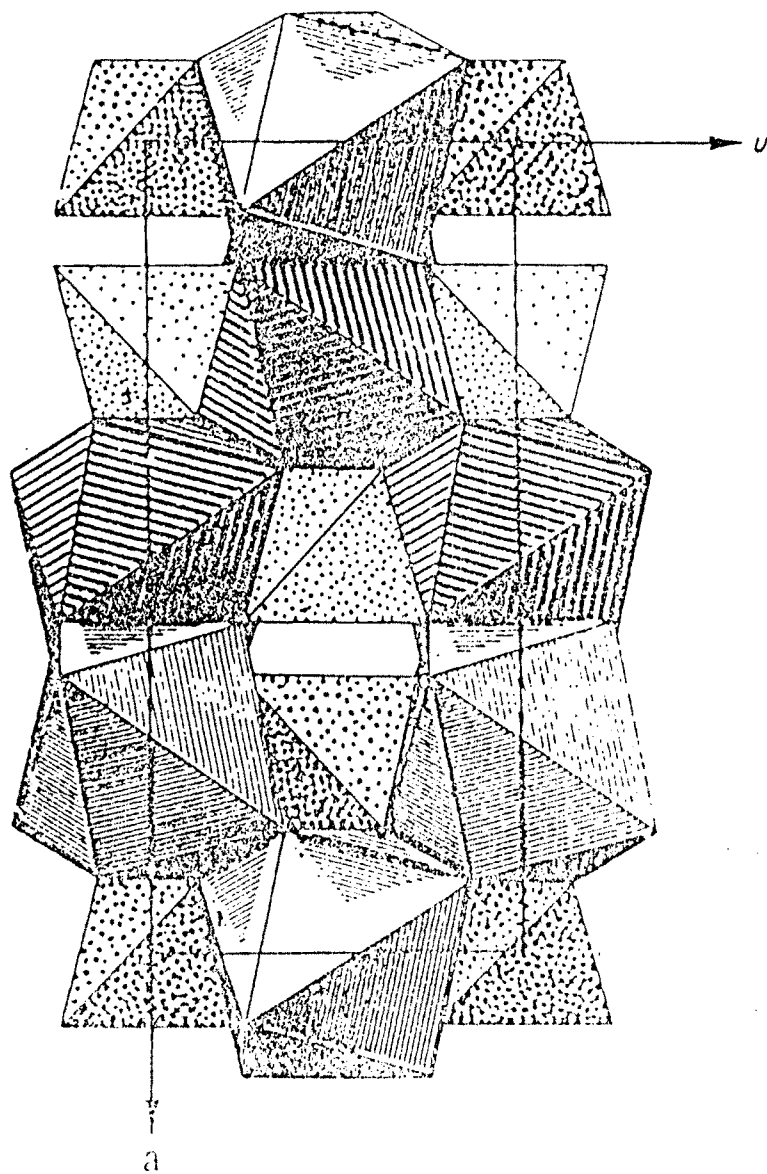
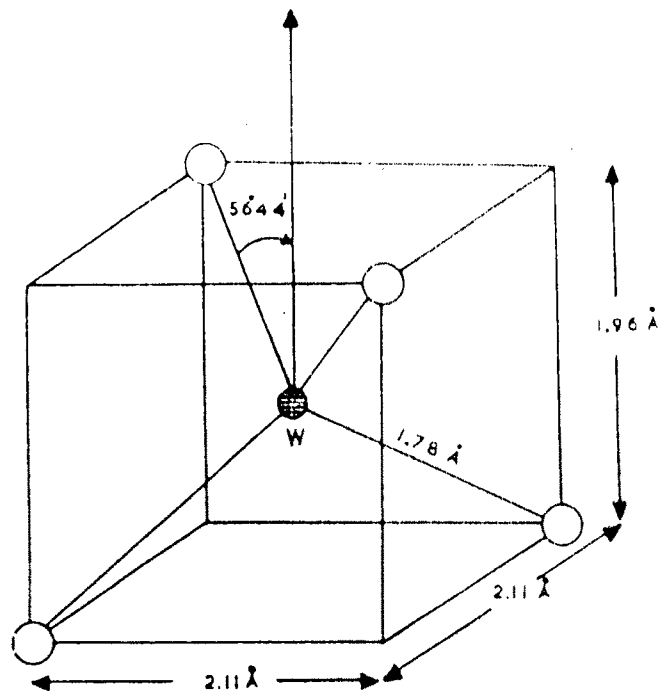
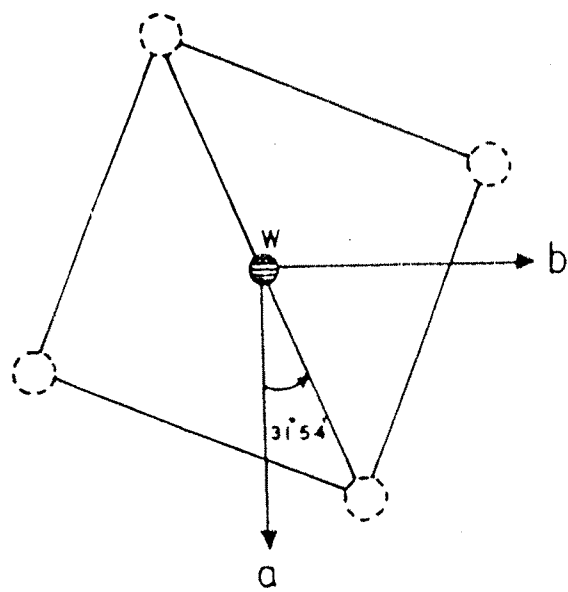


Fig. 1.2 The Scheelite structure.



(a)



(b)

Fig. 1.3(a,b) WO_4 squashed tetrahedron.

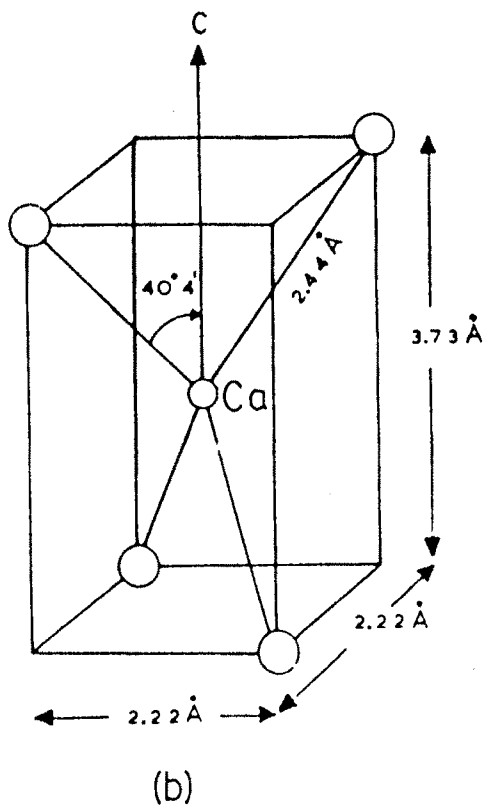
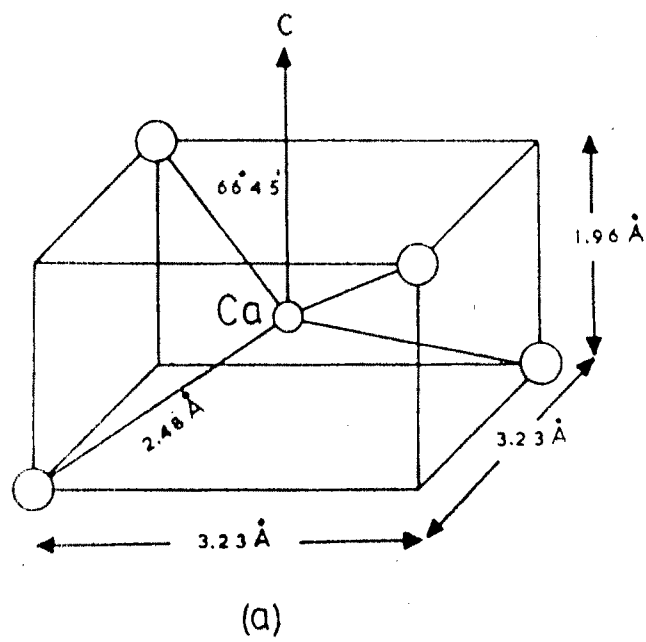


Fig. 1.4
(a,b)

'Long' and 'short' bond distorted tetrahedra about the Ca sites.

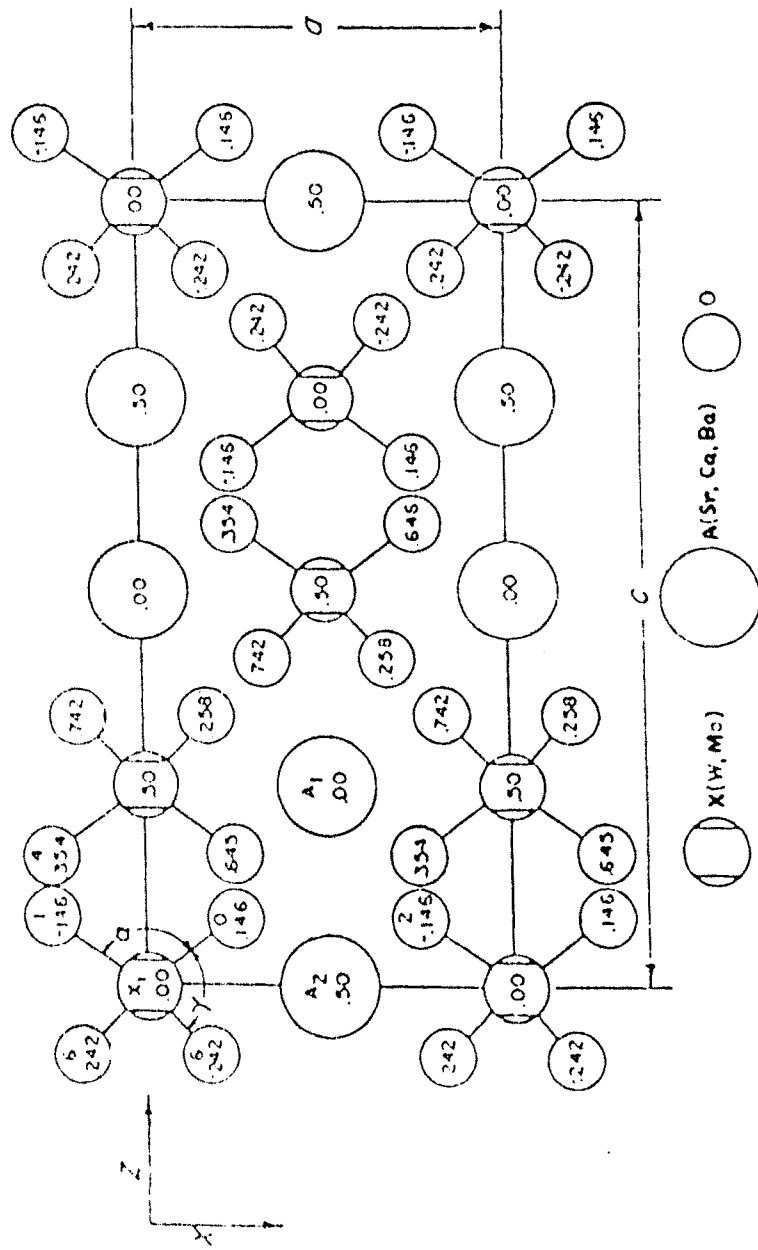


Fig. 1.5 The 'b' axis projection of the Scheelite unit cell.