Flux growth and habit modification of CaWO_4 crystals

S K ARORA, R S GODBOLE and TOMY ABRAHAM

Department of Physics, Sardar Patel University, Vallabh Vidyanagar 388 120, India

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Abstract. The poor quality of natural scheelite necessitates growing these crystals in the laboratory. The flux growth method has been modified to obtain crystals of better quality. Various habits of the grown crystals are reported. The effect of the growth conditions like temperature, cooling rate, charge composition, etc. to yield different morphology has been investigated.

Keywords. Scheelite; flux growth; habits.

1. Introduction

Natural crystals of CaWO_4 , namely scheelite, have been rarely mined and those available are mostly euhedral and associated with fluorite in a contact metamorphic zone formed in limestone adjacent to granitic intrusions. Although in places like Korea and Czechoslovakia its occurrence is abundant, it is difficult to find large single crystals of scheelite. Natural species of this material are also practically opaque, fractured and fine-grained. Some water clear variety (Golubkova 1951) found in Central Asia has, however, been found to be badly pitted. This necessitated the need to obtain these crystals from synthetic methods.

The methods of growth and properties of CaWO_4 crystals have been published. This material has attracted the attention of crystal growers because of its unbound resourcefulness with regard to application in optical masers (Nassau 1963), lasers (Cockayne 1964), industrial radiography (Halmshaw 1971) and recording γ -rays (Klick and Schulman 1949). These crystals also show excellent fluorescent behaviour (Kroger 1948).

The possibility of a good yield of CaWO_4 crystals from fluxed melts has also been studied. Employing LiCl flux (Anikin 1958; Pakter and Roy 1971, 1973) we have attempted to modify the growth procedure of these crystals and study their habit modification.

2. Experiments and observations

2.1. *Equipment and chemicals*

The furnace shown in figure 1 consists of a cylindrical alumina muffle of inner diameter 11 cm, length 45 cm and wall thickness 1.3 cm, wound with super

Figure 1. Growth furnace. L—Lid; E—Enclosure; M—Muffle; H—Heating element; B—Brick; A—Asbestos powder; C—Crucible. and T—Thermocouple.

kanthal wire (M/s Aktebolaget Kanthal, Sweden) of gauge 15, specific resistance 145 microhm cm. A regulated power of 1.5 kW was supplied to the heating element through voltage stabilizer and a transformer to attain a temperature of 1000 °C.

The AnalaR grade reagents used for the growth experiments were: LiCl (Chemapol Praha, Czek), CaWO_4 (E Merck, AG Darmstadt), $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ (BDH) and $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ (Sarabhai Merck Chemicals). Crucibles of pure platinum of 15 ml and 100 ml capacity and wall thickness of 0.05 and 0.2 cm respectively, provided with loosely fitting lids, were used.

2.2 Flux growth

2.2a. Direct flux. The flux can be evaluated by assessing its effectiveness in growing good quality crystals. Out of several fluxes for CaWO_4 (Kukui *et al* 1967; Zeldes and Livingston 1961; van Uitert and Soden 1960) LiCl has been found to yield good crystals. The other fluxes, viz., NaCl, KCl, Na_2WO_4 , etc. produced poorer crystals containing excessive inclusions.

The growth materials were (powders of CaWO_4 and LiCl) weighed in a chemical balance of 0.25 divisions mg^{-1} sensitivity, mixed thoroughly and then packed into the platinum crucible. The crucible was covered with the lid and then loaded into the furnace, the temperature of which was slowly raised upto 870 °C to avoid violent eruptions of the crucible contents. The charge was held for about 1 hr at this temperature which was about 200° higher than that needed to keep in solution all nuclei of crystal growth. The charge was then rapidly cooled down to 750 °C. Further, slow and controlled cooling at the rate of 3° hr^{-1} was carried out until a temperature of 550 °C was reached, after which the furnace was switched off to allow it to cool down to room temperature overnight. The crystals were recovered by leaching the crucible contents with hot distilled water.

The optimum composition range was determined to provide the most favourable condition for crystal growth. At 700°C a proper flux (LiCl)-to-solute (CaWO_4) ratio was determined for maximum crystallization of the solute CaWO_4 (6.4 g) and LiCl (19.2 g) were mixed and heated in 100 ml platinum crucible upto 880°C and then cooled down to 550°C . This experiment was repeated by keeping the solute constant but gradually increasing the solvent. The results in figure 2 demonstrate a maximum crystal yield of 6.12 g for a solvent of 21.20 g. A few crystals thus grown are displayed in figure 3. The size of the crystals obtained was 3 mm to 9.5 mm across.

2.2b. *Chemically reacted flux.* Crystals were also grown by double decomposition method (Patel and Arora 1973) employing stoichiometric quantities of

Figure 2. Graphical representation of the weight of solute (CaWO_4) crystallized versus weight of solvent (LiCl).

Figure 3. Some crystals grown by flux cooling. Maximum size 1 cm across, Scale in mm.

sodium tungstate and calcium chloride to produce calcium tungstate according to the following chemical reaction;

The quantity of product NaCl is quite insufficient to dissolve the other product CaWO_4 . Its function to act as flux is to be adequately supplemented by LiCl so that the resultant NaCl along with LiCl forms a suitable solvent for CaWO_4 . The amount of LiCl to be chosen is, however, determined from the solubility data. Growth procedures were the same as described in § 2.2a.

The above reaction is not complicated by the formation of any binary or ternary compounds or solid solutions. The resulting LiCl- CaWO_4 -NaCl system on cooling, gives rise to supersaturation leading to the slow precipitation of CaWO_4 . The low viscosity and the duration of soaking shows that the solution is in equilibrium and does not distinguish between the starting mixtures [$\text{CaCl}_2 + \text{Na}_2\text{WO}_4 + \text{LiCl}$], or [$\text{CaWO}_4 + \text{NaCl} + \text{LiCl}$], as is evidenced by the fact that heating the reactants at 950°C forms a homogeneous solution. CaWO_4 is the only stable solid phase under the described growth conditions. The size of the crystals obtained by this method was 1.5 mm to 6 mm across.

2.3. Characterization

The crystals were characterized by Debye-Scherrer powder photographs employing CuK_α radiation. The unit cell dimensions were calculated, their values being $a = b = 5.21 \text{ \AA}$ and $c = 11.30 \text{ \AA}$. Their density, measured pycnometrically, was 5.993 g. ml^{-1} .

2.4. Habit investigation

Contrary to the results of Voigt and Neels (1971), we have observed remarkable changes in the growth forms. The various experiments performed and the pertinent results obtained have been illustrated in table 1.

Figure 4 represents the schematic geometry of the wide range of as-grown habits.

3. Discussion

The crystals, grown by direct flux, were mostly larger as compared to those grown by the double decomposition method. However, judging from external shape and transparency, the latter method gave good quality crystals. The flux LiCl-NaCl therefore appears to be more versatile and adequate for CaWO_4 . The improvement in crystal quality obtained using the mixed flux is perhaps due to the suppressed evaporation of LiCl, which otherwise would evaporate faster above 750°C in the absence of NaCl. The external shape of a crystal depends on factors such as lattice structure, chemical nature of growth solution, cooling rate, crystallization temperature, supersaturation, addenda, etc. These factors do not however satisfactorily explain the morphology of these crystals.

Table 1. Correlation of crystal habits with charge components and cooling rate.

Expt. number	Charge composition (g)	Growth procedure	Rate of cooling ($^{\circ}\text{C hr}^{-1}$)	Habits developed
1.	$\text{LiCl} : 21.48$ $\text{CaWO}_4 : 6.40$	Direct flux	6	A, B, C, D*, E
2.	do.	do.	20	B, C, D*, F
3.	do.	do.	30	A, C, E*
4.	$\text{LiCl} : 21.48$ $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O} : 7.33$ $\text{CaCl}_2 \cdot 2\text{H}_2\text{O} : 3.27$ (resulting $\text{CaWO}_4 : 6.4$ and $\text{NaCl} : 1.3$)	Chemically reacted flux	6	A, E, D*
5.	do.	do.	20	C*, D, E, F
6.	do.	do.	30	A*, C, D

* more prominent

Figure 4. Schematic geometry of the scheelite habits (A to F) obtained in laboratory.

The fact that external growth parameters remain the same and the change in supersaturation in growth appears to be a plausible reason for the varying morphology. The as-grown crystals are shown in figure 5 corresponding to the geometry of figure 4.

The primary habit A is often observed in experiments 1 and 4 (table 1) when the supersaturation is low. Experiments 3 and 6 also give rise to this habit. This is because of fast cooling due to which low supersaturation is rapidly attained in the end stage of growth. Habit A is probably due to low supersaturation since such crystals are invariably smaller in size. This habit modifies to B, C, D, E or F depending on growth conditions, giving rise to different growth rates along different directions as the growth proceeds. If, for example, the growth along c -direction is retarded, edge truncation occurs and the faces β (113) appear (habit B). Otherwise, the faces e (101) appear (habit C) due to decrease in growth rate along $\langle 101 \rangle$ when, however, the growth rate falls simultaneously along $\langle 100 \rangle$ and $\langle 101 \rangle$ resulting in habit D. When the growth is relatively faster along a and b directions and slower along c direction, habit E develops with the new face c (001).

The fact that these habits are observed in the same charge is probably due to development of non-uniform temperature distribution within the crucible volume. It may, however, be emphasized that the primary habit A transforms into others, such as B, C, etc., due to attainment of higher supersaturation. When the growth rate is retarded along $\langle 101 \rangle$ alone, the faces e (101) broaden and, as a result, habit F is shaped out. One is inclined to conjecture, therefore, that relatively faster cooling rate tends to enhance the growth rate in directions other than c and $\langle 101 \rangle$. Near the eutectic, the primary habit A is again observed indicating lower supersaturation in the last stage of growth.

Further, the other three sets of experiments, viz., 4, 5 and 6 have NaCl as one of the products which suppresses the evaporation of LiCl and therefore supersaturation varies resulting in a change in the crystal morphology (table 1). Typically, the presence of NaCl might not hinder the growth along c -axis which is enough to cause habit B not to grow in the set of experiments 4, 5 and 6.

It is noteworthy that the platy habits (figure 6) (Dana 1963), which show pronounced growth along a and b directions and the growth along c -directions being tremendously retarded, would not find their origin in the cooling experiments. Probably due to the high pressure in earth the growth along c may be dwarfed. It is, therefore, likely that crystals grown under pneumatolytic or hydrothermal conditions might reveal this habit.

4. Conclusions

- (i) While larger sized crystals of scheelite can be grown by using direct flux technique, superior quality crystals can be obtained by employing reacted flux technique.
- (ii) The morphology of crystals may vary as the flux is changed, say, from LiCl to LiCl-NaCl.
- (iii) The rate of cooling plays a significant role on the development of different habits.

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Figure 5. As-grown crystals corresponding to the habits of figure 4 (A to F).

Figure 6. Platy habits of natural scheelite.

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