CRYSTAL GROWTH: REACTED FLUX AND GEL METHOD

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ABSTRACT

The growing of single crystals of various substances has gained these days considerable concern and attention of several crystallographers. There are quite a few puzzling problems where research would benefit by the availability of the single crystals which have neither been grown at all or atleast not in the right form or with suitable size and sufficient purity. A wide variety of crystal growth methods are in use today. The author is principally interested here to show that one can devise methods for crystal growth which can be performed in a small laboratory and without requiring exorbitant funds and equipment. The author presents in this article a detailed analysis of the chemically reacted flux method and also the gel method of crystal growth.

Key words: Crystal Growth, Reacted flux, Gel method.

1. INTRODUCTION

The existence of large, clear and apparently perfect crystals of many minerals in nature had excited the attention of earlier workers in the field of crystallography, and provided an urge to try to obtain such specimens in laboratory. Since then crystal growth studies have been a subject of considerable concern and interest to a large number of crystallographers. Consequently, a wide variety of methods, each having its own importance and potentiality, has been developed and is in use today. The primary purpose of this talk is to discuss the 'chemically reacted flux method' and the 'gel method' for the growth of large as well as perfect single crystals in laboratory. Though there are a number of other methods of crystal growth but the present talk will be confined to these two methods only. The reason, why these two particular methods have been chosen here, is to emphasize upon the fact that these methods are highly simple in nature and also inexpensive and hence can be well exploited even in small laboratories which do not have sophisticated equipment.

2. REACTED FLUX METHOD

This method consists essentially in allowing two substances to react together in the molten state to form the desired product. It is desirable that the desired product should be insoluble in water and the other reaction product be soluble in water. Thus for example, the following double decomposition reaction [1] is carried out to yield single crystals of barium tungstate.

$$BaCl_2 + Na_2WO_4 = BaWO_4 \downarrow + 2NaCl.$$

According to this chemical reaction the aqueous solutions of $BaCl_2$ and Na_2WO_4 react to form $BaWO_4$, which precipitates out, being insoluble in a solution of NaCl. Several such reactions help to separate out an insoluble product. It was thought worthwhile to apply such a double decomposition reaction in molten phase for the growth of $BaWO_4$ single crystals.

For this purpose, stoichiometric proportions of the reactants, *i.e.*, $BaCl_2$ and Na_2WO_4 were thoroughly mixed and the charge heated for three hours in a Pt. crucible at 1000° C. At this temperature the charge completely melts, and the reaction proceeds yielding $BaWO_4$ and NaCl. The charge was then cooled slowly upto about 700° C at the rate of 5° C/hr. and afterwards the furnace was switched off. The crucible contents were washed with water which dissolved soluble NaCl leaving behind insoluble crystals of $BaWO_4$. It was considered in the beginning that $BaWO_4$ might have crystallised out as a result of slow precipitation as the reaction proceeds forward. But our experiments on flux growth have suggested that, in fact, the $BaWO_4$ results as powder only which gets dissolved in NaCl at high temperature, and on cooling the necessary supersaturation is brought about in ($BaWO_4$ – NaCl) solution causing $BaWO_4$ to grow as crystals.

It is noteworthy that $BaWO_4$ is the only stable solid phase under the described growth conditions [2]. The size of the crystals was found to be a function of crucible-size and soak-time at the growth temperature. Large and more perfect crystal-yield was obtained using greater evaporation periods and larger crucibles.

Such reactions have been used in this laboratory for growing sulphates of Ba and Sr also [3, 4]. It is observed that if the heat of formation or lattice energy of resulting products of the reaction is more than those of the reactants, then the reaction would proceed in forward direction in melt

In the present case, this gives about five calories favouring the formation of $BaWO_4$ and NaCl. Some crystals of $BaWO_4$ grown by this technique are shown in Fig. 1, while the direct flux-evaporation has given us these crystals of about 11 mm across [5], (also refer Table I).

TABLE I

List of various crystals grown by chemically reacted flux method in our laboratory

Reaction employed	Crystal grown	Crystal system and habit	size in mm
$BaCl_2 + 2NaF$ [6]	$BaF_2 \cdot BaCl_2$	Tetragonal	$6 \times 2 \times 0{\cdot}1$
$BaCl_2 + Na_2SO_4$ [3]	$BaSO_4$	Orthorhombic (001), (102)	6
$SrCl_2 + Na_2SO_4$ [4]	$SrSO_4$	Orthorhombic (011), (101)	5
$BaCl_2 + Na_2WO_4$ [2]	$BaWO_4$	Tetragonal (111) bipyramidal	

This method has the following advantages:

1. We do not need separately the flux for the crystal. The necessary flux comes from the reaction itself.

2. Once the reaction is complete, slow evaporation of the solution gives quite good cystals.

3. One can choose a temperature of about 900° C only which is much lower than the melting point (1500° C) of $BaWO_4$, and hence allow the reaction to proceed more slowly, which gives more perfect crystals.

4. One can study the effect of change in stoichiometry produced by the addition of excess of either of the reactants on the growth morphology or crystal size and perfection.

3. GEL METHOD

This is yet another simple method employing double decomposition reaction. Unlike the reacted flux method, the substances in this technique are allowed to react together at ambient temperatures.

The origin of crystal growth in gels may be traced back to 1896 when the German Chemist and photographer, R. E. Liesegang, observed the periodic precipitation of slightly soluble salts. While experimenting with chemical reactions in gels, he covered a flat glass plate with a layer of gelatin impregnated with potassium chromate, and added a small drop of silver nitrate. As a result of double decomposition reaction, silver chromate precipitated in the form of concentric rings. This attracted the attention of Stong in 1962 who published an article in the Scientific American showing the possibility of crystal growth in gel media. Soon after this, Vand, Henisch and McCauley [7] of Pennsylvania Material Research Laboratory published a short note describing preliminary results of a study of growing crystals in gels; a useful paper by Henisch *et al.* giving all the details of the method appeared in 1965 in the Journal of Physics Chemistry Solids [8]. It then became apparent that the gel method could particularly be useful for growing single crystals of a class of materials which could not be readily crystallised at high temperatures.

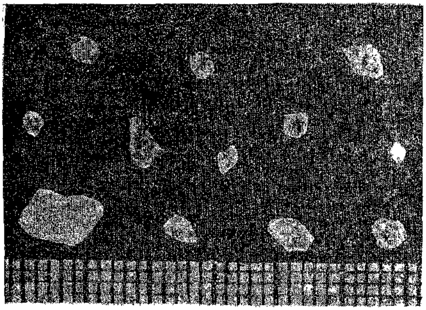

FIG. 1. A few single crystals of barium tungstate grown by the chemically reacted flux method (scale mm).

The technique involves growing single crystals by allowing reaction of two solutions of soluble salts by diffusion through a gel with subsequent nucleation, and the crystal growth continues due to gradual precipitation of the insoluble product phase of the reaction within the gel. For example, consider the reaction [1].

$$BaCl_2 + Na_2WO_4 = BaWO_4 \downarrow + 2NaCl.$$

The salt solutions on the left hand side of above equation react and result in the nucleation of $BaWO_4$ in crystal form. The other product of the reaction, *i.e.*, NaCl formed remains in solution-state within the gel, while $BaWO_4$ crystals grow in the gel, it being insoluble in the gel medium. After carrying out large number of experiments, it is observed that the silica gels are the best and most versatlie media for growing crystals more rapidly and perfectly. Most gels are isotropic except when under strain. The mechanical properties of fully developed gels can vary widely, depending on the density and the precise conditions during gelation period. For example, silica gels with a molecular silica-to-water ratio of 1 :30 or 1 :40 can easily be cut with a knife. At 1 :20 the medium is rather stiff and still denser gels have conchoidal fracture-surface similar to glass.

In our experiments we prepared gels, like others, by the addition of an acid to sodium silicate solution. Depending on whether we add acid to silicate solution or the other way, it is called acid-set gel or alkali-set-gel. The time of gel-setting varies from a few minutes to several days depending upon the concentration of sodium silicate and the quantity of the acid added. The firmness of the gels also depends on the amount of acid added and hence the pH value of solution. Sodium silicate solutions with high concentration acidity set very early and form quite stiff gels.

There are seveal ways to set-up the experimental arrangement to grow the crystals. For the reaction written earlier, the simplest method is to incorporate one reactant, say $BaCl_2$ solution in the acid-silicate mixture-gel in a single tube or beaker before gellation occurs, and to pour solution of another reactant, Na_2WO_4, over the gel after the gellation has occurred. Another simple method employs a U-tube in which the gel is first formed in the tube and salt solutions are added in the two limbs after the gel is set. These two experimental arrangements gained considerable attraction of crystal growers, chiefly due to the work of Henisch [8] on the growth of calcium tartarate single crystals in particular. Since then various modifications in the crystallization apparatus have been suggested. For example, O'Connor [9] designed his double diffusion system containing two reservoirs and a horizontal tube for growing CuCl crystals. Henisch [10] used fritted disc to obtain AgI from AfI-HI complex. Other important modifications are of Nassau [11], Arend and Huber [12]. We have designed our own single-tube and double-tube systems [13] (Fig. 2) which have the following advantages:

1. These systems provide greater lateral freedom for diffusion of ions to growth sites.

2. In the double-tube system, the water placed over the set gel can be changed and hence the unwanted reaction product, NaCl in the above case can be pipetted out that would avoid crystal contamination.

3. These systems can provide a good fecility for investigating the possibility of crystal growth on seeds in gels. The crystals grown in the tube from one gel can be seeded as such into another gel before setting by simply transferring the tube.

4. The effect on crystal growth due to change in stoichiometric proportions can be studied.

For growing $BaWO_4$ crystals using the above reaction (1, 14) acetic acid set gel was made by acidification of pure sodium silicate solution. CH_3COOH was found suitable because this acid changes the pH value very little with time, and when mineral acids were used they spoiled the crystals. Relatively translucent gels were obtained with sodium silicate solution of density 1·05 g/ml and CH_3COOH of 2N. The gel was prepared from 7·5 pH solution measured before setting. The crystallisation began in the 2nd week after pouring the feed solutions, *viz.*, $BaCl_2$ and Na_2WO_4, and was complete in about seven weeks to give a maximum size of the crystals. It is observed that the following factors affect the ultimate size and degree of perfection of the crystals grown by this method.

I. Concentration of reactants.
II. Gel-density.
III. pH-value of gel solution.
IV. Temperature.
V. Crystallization apparatus.

I. *Concentration of reactants*

The single crystals of $BaWO_4$ grown from N/10 $BaCl_2$ and N/10 Na_2WO_4 feed solutions reached a maximum size of 3·5 mm. In this case large number of nucleation centres were observed and hence the crystals grew smaller in size. While studying the effect of reactant concentration on the growth, it was observed that:

(i) Employing $BaCl_2$ and Na_2WO_4 solutions each of N/30 gave fewer crystals with slightly larger size. These crystals were more transparent also as compared to those obtained with N/10 concentrations.

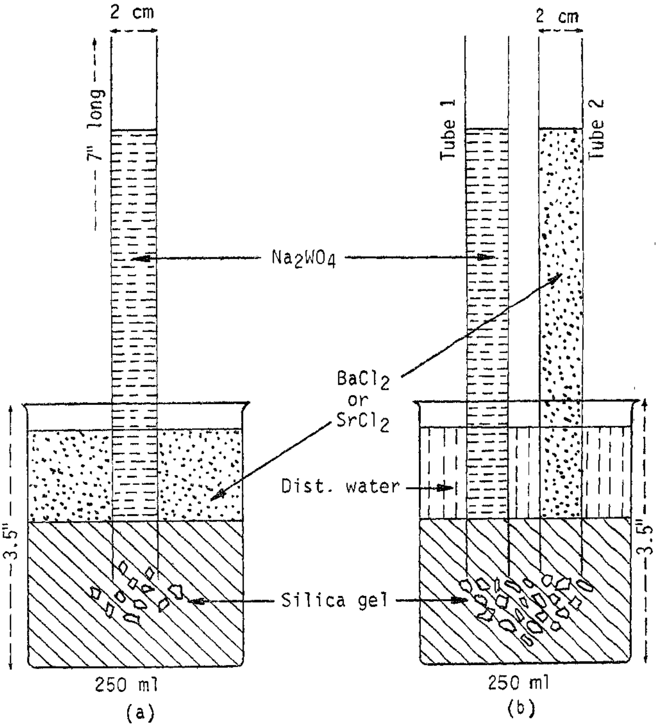

FIG. 2. Crystallisation apparatus for gel-growth: (*a*) single tube systems, (*b*) double tube system.

(2) By raising the normality of each solution from N/10 to 4N, agglomerated spherical crystals grew.

(3) Using N/2 to N/5 concentration of Na_2WO_4 and N/30 of BaCl gave transparent crystals of 5 mm size.

Thus it is concluded that, in the case of tetragonal tungstates, higher concentration of anions and lower concentration of cations yields good quality and large size crystals.

II. *Gel-density*

Denser gels always produced very poor crystals. On the other hand, gels of low density take a long time to set and hence are mechanically unstable. A specific gravity of 1·04 g/ml of gel solution appears to be the lower practical limit for growing tungstate crystals. However, Henisch has suggested 1·02 as the limit for calcium tartarate. It is of interest of note that impure gel always produced spherulites and such other flawed crystals as shown in Fig. 3 (*a*, *b*). Therefore, for growing perfect single crystals, the commercial sodium silicate solution was centrifuged carefully to remove the suspended impurities in the beginning.

FIG. 3. Some spherulites and such other flawed crystals: (*a*) $BaWO_4$, (*b*) $SrWO_4$ grown using impure gels.

III. *pH value of gelsolution*

In the case of tungstates, pH of the gel was found to be not a very significant factor to affect the growth. However, when working between 7 and 8 pH, the crystals produced were fewer in number and larger in size. Of course, different crystals require different optimum pH value for their growth to occur. For example, it is reported in literature that calcite grows at 7 pH, gold at 4·5–5, CuCl at 5·0, KI at 8, and so on.

IV. *Temperature*

It plays a vital role to affect both nucleation and size of the crystal grown in gels. So far as growth of tetragonal tungstates in our laboratory is concerned, any temperature between 20° and 38° C did not produce any noticeable change on either the size or the quality or the morphology of the crystals. But there are instances which show a marked change of temperature on growth. It was observed during the growth of $BaSO_4$ and $SrSO_4$ [13] that the crystals grown at 35° C were bounded by (011), (101) faces while at 20° C they exhibited additional (001) faces.

Henisch [8] has reported that repeatable results on the growth of calcium taratarate could be obtained between room temperature and 45° C.

V. Crystallization apparatus

It is observed that the single-tube and the double-tube experiments produced larger and more perfect crystals [1]. The crystals grew little larger when the tube of 2·0 cm diameter were used than those of smaller diameters. The nucleation sites were controlled to limited few in these systems. The mechanism of growth in gels is very simple, however, it is difficult to control nucleation centres. In fact, nucleation ı a key issue which would govern the practical utility of this technique. For $BaWO_4$, it is found that beginning with highly dilute (0·02N) solutions if we go on increasing the concentration of feed solutions at the rate of 0·25N per day by pipetting out some quantity of solutions from tubes and replacing the by equal amount of fresh solution of higher normality, we could control

TABLE II

List of various crystal grown by gel method jn our laboratory

Material grown	Remarks		Crystal size
	Gel type	Reaction employed	
PbS [15, 16]	HCl set gel	Hydrolysis of thioacetamide	1 mm
$BaSO_4$ [13]	HNO_3 set gel	$BaCl_2 + Na_2SO_4$	1-2 mm
$SrWO_4$ [13]	do.	$SrCl_2 + Na_2SO_4$	1-2 mm
$PbSO_4$ [17]	do.	$Pb(NO_3)_2 + Na_2SO_4$	3 mm
$PbCl_2$ [17]	HCl set gel	$Pb(NO_3)_2$	dendrites
$BaWO_4$ [14]	CH_3COOH set gel	$BaCl_2 + Na_2WO_4$	7·5 mm
$SrWO_4$ [14]	do.	$SrCl_2 + Na_2WO_4$	7·5 mm
$KClO_4$	do.	$KF + HClO_4$	11 mm

the nucleation sites to a countable number. Just two to three growth centres produced with this particular method are exhibited in Fig. 4 of the whole tube. This procedure produced impressively transparent crystals of 7·5 mm size [Fig. 5 (*a*, *b*)] and of a very good quality. Determination of dislocation density in them, by etching technique, came out to be only 10^1 to 10^2 per cm^2, which is a considerably low value.

FIG. 4. A tube showing controlled growth centres in gel medium.

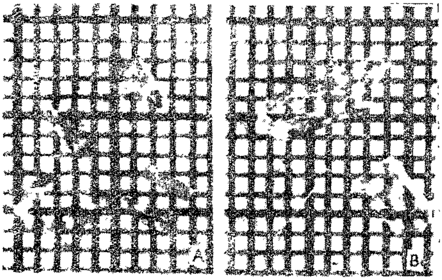

FIG. 5. A few single crystals of: (*a*) $BiWO_4$, (*b*) $SrWO_4$, grown in pure silica gels employing the apparatus of Fig. 2 (mm scale).

These double-tube and single-tube systems can be used accompanied by the above method of controlling nucleation centres for the growth of large as well as perfect single crystals. This has been verified on $KClO_4$ single crystals which have also been grown in the laboratory upto 11 mm across. The crystals grown in this laboratory using gel method are listed in Table II.

REFERENCES

[1] Arora, S. K. .. "Studies on crystal growth and defects of some tetragonal tungstates," *Ph.D. Thesis*, 1973 (Chaps. 7, 11 and 12).

[2] Patel, A. R. and Arora, S. K *Journal of Crystal Growth*, 1973, **18**, 175–178.

[3] Patel, A. R. and Jacob Koshy *Journal of Crystal Growth*, 1968, **1**, 498–499.

[4] Patel, A. R. and Bhat, H. L. *Journal of Crystal Growth*, 1971, **8**, 153–156.

[5] Patel, A. R. and Arora, S. K. *Journal of Crystal Growth*, 1974, **23**, 95–100.

[6] Patel, A. R. and Singh, R. P. *Journal of Crystal Growth*, 1969, **5**, 70–72

[7] Vand, V., Henish, H. K. and McCauley, J. W. *Acta Cryst.*, *1963*, **16**, A 137.

[8] Henish, H. K., Dennis, J. and Hanoka, J. I. *Journal of Physical Chemistry Solids*, 1965, **26**, 493–500.

[9] Armington, A. F. and O'Connor, J. J. *Mathematical Research Bulletin*, 1967, **2**, 907–911.

[10] Suri, S K , Henisch, H. K. and Faust, J. W., Jr. *Journal of Crystal Growth*, 1970, **7**, 277–281

[11] Shiever, J. W. and Nassau, K. *Mathematical Research Bulletin*, 1972, **7**, 613–614.

[12] Arend, H. and Huber, W. *Journal of Crystal Growth*, 1972, **12**, 179–180.

[13] Patel, A. R. and Bhat, H. L. *Journal of Crystal Growth*, 1972, **12**, 288–290.

[14] Patel, A. R. and Arora, S. K. *Journal of Crystal Growth*, 1973, **18**, 199–201.

[15] Sangwal, K. .. *Journal of Physical Society D* (*Applied Physics*) (In Press).

[16] Sangwal, K. and Patel, A. R. *Journal of Crystal Growth*, 1974, **23**, 282–288.

[17] Bhat, H. L. .. "Studies on growth and defect properties of barite group crystals," *Ph.D. Thesis*, 1973.