Crystal growth in gel media

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Abstract. An attempt has been made in this review to cover the existing information on the growth of single crystals in gels. Preparation of various types of gels, in which crystals can be grown, has been briefly described. The growth of single crystals from gels is reviewed using the following classifications : (i) Crystal growth by reaction. (ii) Crystallization by complex dilution method. (iii) Crystal growth by reduction of solubility. A compact list of some important crystals grown in gels is given. Growth mechanism and nucleation problems are discussed. Morphologies of various gel-grown crystals are described. Researches on gel-grown single crystals are also briefly described.

1. Introduction

While crystal growth from aqueous, organic and salt solutions has been studied for a number of years, it is only since 1965 that a systematic research work on crystal growth in gels has been undertaken. In recent years considerable attention has been drawn towards such work and the number of research centres engaged in such investigations has increased. Modern technology badly needs perfect single crystals having various valuable properties such as those of semiconductors, luminophores, piezoelectrics, dielectrics and so on. Single crystals are expected to be of high perfection of crystalline structure, i. e. no more than a small number of defects such as deformation of growth forms, dislocations, etc.

In the first place such criteria are satisfied when single crystals are grown under the most favourable conditions. In this respect high melting point and water insoluble substances are the most difficult to grow because at the melting temperature they react with silica or other container materials and are insoluble in water. The same is true for substances that decompose on melting, especially those

including volatile components. When gels are used the requirements for the crystallization process are less rigid, and growth from gels at room temperature (20 to 40° C) leads to better single crystals.

The growth of single crystals in gels has received considerable importance since Liesegang (1896) first observed the periodic precipitation of slightly soluble salts in gelatin. These "Liesegang rings" inspired many other chemists and also mineralogists to study other reactions in various colloids. Among the early workers were Hatschek (1911), Holmes (1917), Fells and Firth (1926), Fisher and Simons (1926), Morse and Donnay (1931) etc. Interest in the method was revived by Stong (1962) and soon thereafter, Vand *et al* (1963) described the full potential of growing single crystals in gels. Later, Henisch *et al* (1965) published detailed procedures for growing a variety of single crystals in gels.

The gel method has the following advantages over other crystal growth methods and hence it is fully explored.

(i)	It is well-known that crystals grown at room temperature (20 to 40° C) will have lower concentrations of non-equilibrium defects than those grown at elevated temperatures.

(ii)	Crystals can be observed practically in all stages of growth.

(iii)	All crystals are delicately held in the position of their formation, thus limiting effects due to impact on the bottom or sides of the container.

(iv)	All nuclei are spatially separated, minimizing precipitation.

(v)	The procedure can be conveniently used for mass production of crystals.

(vi)	Crystals with different morphologies and sizes can be obtained by changing the growth conditions.

(vii)	The method is extremely simple and inexpensive.

2. Preparation of various type of gels

Gels can be prepared using a wide variety of techniques and materials. Preparation, advantages and disadvantages of various types of gels, used for crystal growth are given in table 1.

3. Crystal growth

The enormous flow of information related to crystal growth in gels has been divided into the following three basic parts, each of which has special advantages which are described in what follows. (i) Crystal growth by reaction; (ii) Crystallization by complex dilution method; and (iii) Crystal growth by reduction of solubility.

Table 1. Gel media used for crystal growth.

Gel Preparation	Advantages	Disadvantages	References
1. *Silica*: Mix aqueous solutions of sodium silicate or sodium metasilicate (sp. gr. 1·03-1·06) and acid (1 to 4N of mineral or organic).	1. Better crystallinity of product in gel (sp. gr. 1·03)	1. SiO_2 inclusion (in some crystals).	Henisch *et al* (1965)
2. *Gelatin*: Dissolve 5 to 6 gm. of gelatin powder in water by stirring at a constant temperature of 50°C for one hour and cool to room temperature. In order to strengthen the gel addition of 0·1 to 1·0 ml of formaldehyde is necessary.	1. Great stability over large pH range (3 to 10·5) 2. Lack of interfering ions 3. High optical clarity.	1. Attacked by molds. 2. Supports more nucleation sites.	Banks *et al* (1973)
3. *Agar* - Dissolve 1 to 5 gm. of agar powder in water, boil it and cool to room temperature.	1. Easy workup.	1. Transparency of gel decreases as the concentration of agar increases 2. Inclusion of the gel.	Brezina and Havrankova (1971).
4. *Clay (or Bentonite)*: Powdered clay slowly sifted rapidly stirred water in a blender until about 9% clay had been added. Gel sets immediately.	1. The morphology of crystals grown is similar to those in many natural occurrences. This knowledge would aid in solving geologic problems.	1. Crystals generally contain abundant steps kinks and pits. 2. Incorporation of clay particles.	Cody (1976)
5. *Polyacralamide*: Dissolve 3·99 wt. % of acrylamide and 0·02 wt. % of the cross-linking agent in water, bubble with nitrogen, degas by lowering the pressure.	1. It is more rigid and transparent for more than six months in wide range of pH from 0.2 to 13.	1. Preparation of gel is more difficult compared to other gels.	Brezina and Havrankova. (1976)

3.1 Crystal growth by reaction

Most of the work on crystal growth in gels has been done by the reaction method. It has a special advantage of growing single crystals which are insoluble

(or slightly soluble) in water and which decompose before reaching their melting point. The requirements to grow single crystals by this method are (i) the reactants employed here must be soluble in the solvent (usually water) and the product crystal must be relatively less soluble, (ii) the gel must remain stable in the presence of the reacting solutions and must not react with these solutions or with the product formed, and (iii) some solubility of the product crystal is required in order to grow crystals of any size (Armington and O' Connor 1967).

In this method two soluble reactants are allowed to diffuse through a gel where they react and form an insoluble or relatively less soluble crystalline product. This may be done by the test tube technique, as shown in figure 1, in which one of the reactants is incorporated inside the gel and the other reactant is diffused into it or by the U-tube technique (figure 2) or its modifications in which the two reactants are allowed to react by diffusion into an essentially inactive gel.

There are various crystallization apparatus used to grow single crystals by this method. The disadvantages of these crystallization apparatus include the depletion of one of the reactants which is inside the gel (Henisch *et al* 1965), the incorporation of reaction waste products by the growing crystals (Henisch *et al* 1965; Arend and Huber 1972; Patel and Venkateswara Rao 1977), supporting, handling and cleaning of the apparatus (Brezina and Havrankova 1976; Arend and Huber 1972; Patel and Bhat 1973; Blank 1973; Konak *et al* 1977; Martin and Haendler 1978) and preparation of gel inside the horizontal tube open at both the ends (Brezina and Havrankova 1976; Konak *et al* 1977; Martin and Haendler 1978). The improved design of modified gel-technique (figure 3) used by Patel and Venkateswara Rao (1980) eliminates all the inconveniences of the previous gel growth techniques and also permits the growth of mixed or doped crystals by multiple diffusion. A few single crystals of ferroelectric lead monohydrogen phosphate (PbHPO₄) grown by this method are displayed in figure 4.
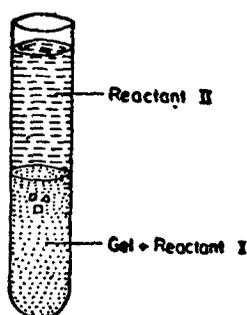
Figure 1. Schematic diagram of test tube apparatus for crystal growth by reaction method.
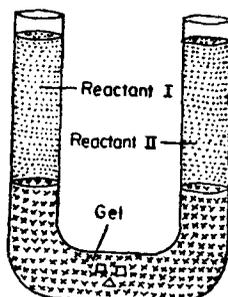
Figure 2. Schematic diagram of U-tube apparatus for crystal growth by reaction method.
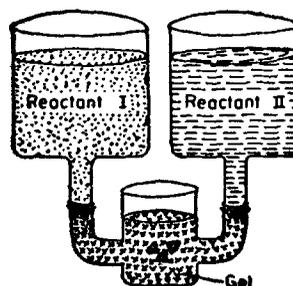
Figure 3. Schematic diagram of an improved design for crystal growth by reaction method (after Patel and Venkateswara Rao 1980).

Table 2. Some crystals grown by reaction

Crystals	Reactants	Max. size (mm)	References
1	2	3	4
Anthranilates			
P ($C_7H_6NO_2$)	$PQ + NaC_7H_6NO_2$	2×0.5	Martin and Haendler
(P = Cd, La, Y)	(Q = $(NO_3)_2$, SO_4		(1978)
Co ($C_7H_6NO_2$)$_3$	$CoQ + NaC_7H_6NO_2$	0.5	—do—
Zn ($C_7H_6NO_2$)$_3$	$ZnQ + NaC_7H_6NO_2$)	2×2	—do—
Arsenates			
$PbHAsO_4$	$PbX + YAsO_4$	$6 \times 3 \times 1$	Kock and Happ (1980)
	(X = $(NO_3)_2$, $(C_2H_3O_2)_2$		Brezina *et al* (1975)
	and Y = H, NaH)		
Carbonates			
$BaCO_3$	$BaCl_2 + XCO_3$	1.5	Cho *et al* (1977)
	(X = Na_2, K_2)		
$CaCO_3$	$CaX + YCO_3$		Barta and Zemlicka
	(X = Cl, $(C_2H_3O_2)_2$ and		(1971)
	Y = Na_2, $(NH_4)_2$ NaH		
	and $(NH_4)_2H$)		
$PbCO_3$	$Pb (NO_3)_2 + (NH_4)_2 CO_3$	20	Mohanan Pillai and Ittyachen (1978)
$SrCO_3$	$SrCl_2 + Na_2CO_3$	1×0.1	McCauley and Roy (1974)
Chlorides			
$PbCl_2$	$PbH_4C_4O_6 + HCl$	50	Abdulkhadar and Ittyachen (1980)
Fluorides			
CaF_2	$CaCl_2 + NaF$	1	Leckebusch and Recker (1972)
$AMnF_3$	$MnCl_2 + AF$	$2 \times 2 \times 2$	Leckebusch (1974)
(A = K, Rb, NH_4, Tl and Cs)			
Halides of Rb, Cs and Sn			
$CsSnA_3$	$CsA + SnA^{*}_4$	$3 \times 3 \times 3$	Suib and Weller
(A = Cl, Br, I)			(1980)
Cs_2SnA_6	$CsA + SnA^{*}_6$	$3 \times 3 \times 3$	—do—
(A = Cl, Br, I)			
$PSnX_6$	$PX + SnX^{**}$	$3 \times 3 \times 3$	—do—
(P = Cs_2, Pb_2, and X = Cl, Br)			

*$Cl_4 Br_2$, I_2 and **$Cl_4 Br_2$

Table 2 (*Contd.*)

1	2	3	4
RbSnA₃ (A = Cl, Br, I)	RbA + SnA*₃	3 × 3 × 3	Suib and Weller (1980)
RSn₂ I₄ (R = Cs, Rb)	RI + SnI₂	3 × 3 × 3	—do—
Hexachlorides			
CsPdCl₆	H₂PdCl₆ + 2 CsCl	5	Brouwer *et al* (1974)
Cs₂PtCl₆	H₂PtCl₆ + 2 CsCl	4	—do—
Cs₂IrCl₆	H₃IrCl₆ + 2 CsCl	2	—do—
K₂PdCl₆	H₂PdCl₆+2 KCl	6	—do—
Rb₂PdCl₆	H₂PdCl₆+2 RbCl	7	—do—
Rb₂PtCl₆	H₂PtCl₆ +2 RbCl	15	—do—
Rb₂IrCl₆	H₂IrCl₆ +2 RbCl	3	—do—
Iodates			
Ag₂H₃IO₆	AgNO₃ + H₅IO₆	250mm*	Arend and Huber (1972)
Cu (IO₃)₂	CuSO₄ + HIO₃	4	Nassau *et al* (1973)
CuHgI₄	(CuCl + HCl) + (HgI₂ + KI)	—	Chivian (1976)
Co₃ (IO₃). 4H₂O	CoSO₄ + HIO₃	1	Shiever and Nassau (1972)
CsI₃	CsCl + HIO₃	—	Armington and O'Connor (1971
KI₃	KCl + HIO₃	—	—do—
3La (IO₃)₃HIO₃7H₂O	La(NO₃) + HIO₃	—	Bernstein *et al* (1976)
(Mn(IO₃)₂)	MnSO₄ + HIO₃	1	Shiever and 'Nassau (1972)
Ni (IO₃)₂	NiSO₄ + HIO₃	1	—do—
RbI₃	RbCl + HIO₃	—	Armington and O'Connor (1971)
Ba(IO₃)₂	BaCl₂ + NaIO₃	1.5 × 1 × 1	Joshi and Trivedi (1980)
Ca(IO₃)₂	CaCl₂ + NaIO₃	20 × 4 × 3	—do—
Sr(IO₃)₂	SrCl₂ + NaIO₃	8 × 5 ×4	—do—
Iodides			
CuI	CuSO₄ + KI	5 × 5 × 1	Nakada *et al* (1976)
PbI₂	PbX + YI (X = (C₂H₃O₂)₂, (NO₃)₂ and Y = K, Na, H)	30 × 25 ×2	Patel and Venkateswara Rao (1980)
TlI	TlNO₃ + NaI	0.2 × 0.2	Shiojiri *et al* (1978)
SnI₂	SnCl₂ + KI	15 × 1 × 1	Thomas Abraham (1979)
SnI₄	SnCl₂ + KI	3 × 2 × 2	Thomas Abraham (1979) Desai and Rai (1980)

*Cl₄Br₂, I₂ and **Cl₄Br₂

Table 2 (*Contd.*)

1	2	3	4
Molybdates :			
$BaMoO_4$	$BaCl_2 + Na_2MoO_4$	$4 \times 1.2 \times 0.9$	Kurien and Ittyachen (1980)
$PbMoO_4$	$Pb(NO_3)_2 + (NH_4)_2MoO_4$	2	Sreedharan Pillai and Ittyachen (1980)
Oxalates :			
CdC_2O_4	$CdCl_2 + H_2C_2O_4$	7.5	Khan *et al* (1976)
$CuC_2O_4.H_2O$	$CuSO_4.5H_2O + H_2C_2O_4$	1.5	—do—
$CoC_2O_4.2H_2O$	$CoCl_2,6H_2O + H_2 C_2O_4$	2.0	—do—
$MnC_2O_4.2H_2O$	$MnCl_2.4H_2O + H_2C_2O_4$	1.0	—do—
$NaHC_2O_4.H_2O$	$Na^+ + H_2C_2O_4$	15.00	—do—
Perchlorates			
$KClO_4$	$KX + YClO_4$ $(X = Cl, Br, I, OH, F$ and $Y = H, Na)$	$20 \times 10 \times 6$	Patel and Venkateswara Rao (1978b), (1981b)
$CsClO_4$	$CsCl + HClO_4$	—	Shripathi *et al* (1980)
$RbClO_4$	$RbCl + HClO_4$	—	—do—
Phosphates			
Ag_3PO_4	$AgNO_3 + Na_2HPO_4$	1.5	Mennicke and Dittmar (1974)
$Ba_2(PO_4)_2$	$Ba(NO_3)_2 + (NH_4)_2HPO_4$	0.1	Banks *et al* (1973)
$BaHPO_4$	—do—	0.4	—do—
$BaNH_4PO_4.8H_2O$	EDTA* ⎫ in gel + NH_3 $Ba(NO_3)_2$ ⎬ aqueous $KH_2(PO_4)$ ⎭ solution	2	—do—
$CaHPO_4.2H_2O$	$CaX + YPO_4$ $X = Cl_2. (C_2H_3O_2)_2$ and $Y = H_3, NaH_2, (NH_4)_2H$	10	—do—
$MgNH_4PO_4\ 6H_2O$	$MgSO_4 + H_3PO_4 + NH_3$	7.5	—do—
$PbHPO_4$	$Pb(NO_3)_2 + H_3PO_4$	$8 \times 5 \times 1.5$	Konak *et al* (1977)
$Pb_4(NO_3)_2 (PO_4)_2$ $2H_2O$	$Pb (NO_3)_2 + H_3PO_4$	1×0.5	Brezina and Havrankova (1976)
$Sr_3(PO_4)_2$	$Sr(NO_2)_2 + (NH_4)_2HPO_4$	0.1	Banks *et al* (1973)
$SrHPO_4$	—do— —do—	0.05	—do—
$SrNH_4PO_4.8H_2O$	EDTA ⎫ in gel + NH_3 $Sr(NO_3)_2$ ⎬ aqueous K_2HPO_4 ⎭ solution	0.3	—do—
Selenates			
Ag_2SeO_4	$AgNO_3 + H_2SeO_4$	$50 \times 3 \times 2$	Boncheva-Mladenova and Dishovsky (1979a)
$Bi_2 (SeO_4)_3$	$Bi (NO_3)_3 + H_2SeO_4$	$3 \times 2 \times 1$	Boncheva-Mladenova and Dishovsky (1979b)

*Ethylene diamine tetraacetic acid

Table 2. (*Contd.*)

| 1	2	3	4
Selenides			
CdSe	Cd EDTA + $H_2NCSeNH_2$	100 μm	Blanks and Brenner (1971)
CuSe	Cu EDTA + $H_2NCSeNH_3$	50 μm	—do—
PbSe	Pb EDTA + $H_2NCSeNH_2$	3 μm	—do—
ZnSe	Zn EDTA + $H_2NCSeNH_2$	50 μm	—do—
Sulphates			
$BaSO_4$	$BaCl_2$ + XSO_4 (X = Cu,H_2, Na_2)	2	Broower *et al* (1974)
$CaSO_4$	$CaCl_2$ + XSO_4 (H = H_2, Na_2, NH_4)	2.5	Rosmalen *et al* (1976)
$La(SO_4)_3,K_2SO_4$ $2H_2O$	$La(SO_4)_3$ + KNO_3	2	Bloor (1970)
$Pr_2(SO_4)_3$ $K_2SO_4.$ $2H_2O$	$Pr_2'SO_4)_3$ + K_2SO_4	4	—do—
$SrSO_4$	$SrCl_2$ + Na_2SO_4	2	Patel and Bhat (1973)
Sulphides			
CdS	Cd EDTA + CH_3CSNH_2	0.4	Blank and Brenner (1971)
PbS	$Pb(C_2H_3O_2)_2$ + CH_3CSNH_2	2 × 2 × 2	Blank (1974)
ZnS	$ZnCl_2$ + CH_3CSNH_2	4	Patel and George (1977)
Tartrates			
$PbC_4H_4O_6$	Pb $(NO_3)_2$ + $H_2C_4H_4O_6$	—	Abdulkadhar and Ittyachen (1977)
$SrC_4H_4O_6$	$SrCl_2$ + $H_2C_4H_4O_6$	50 × 20 × 10	Patel and Arora (1976)
$Sr_{1-x}Ca_xC_4H_4O_6$	NCl_2 + $H_2C_4H_4O_6$ (N ≏ Sr_{1-x} Ca_x)	10 × 6	Patel and Arora (1977)
Thiocynates			
CdHgSCN	$Hg(NO_3)_2$ + $Cd(NO_3)_2$ + NaSCN	4	Blank (1973)
ZnHgSCN	$Hg(NO_3)_2$ + $Zn(NO_3)_2$ + NaSCN	0.5	—do—
Tungstates			
XWO_4 (X = Ba, Sr)	XCl_2 + Na_2WO_4	7 × 4 × 2	Patel and Arora (1973)
$CaWO_4$	$CaCl_2$ + Na_2WO_4	1 × 1	McCauley and Roy (1974)
Zeolites			
Sodium A Zeolite	(100 gm $Na_2SiO_3.9H_2O$ + 100 mlN($CH_2CH_2OH)_3$ +(80gm $NaAlO_2$ + 100ml N $(CH_2CH_2OH)_3$")	40 μm x 40 μm	Charmell (1971)
Sodium X zeolite	(100gm $Na_2SiO_3.9H_2O$ + 100ml N (CH_3CH_2OH) + (40gm $NaAlO_2$ + 100ml N $(CH_2CH_2OH)_3$)	60 μm	—do—
VSZ zeolite	$Na_2SiO_3.9H_2O$ + $NaAlO_2$	20 μm	Joshi and Bhoskar (1979)
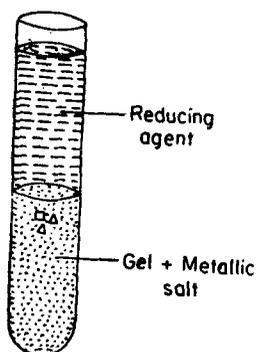
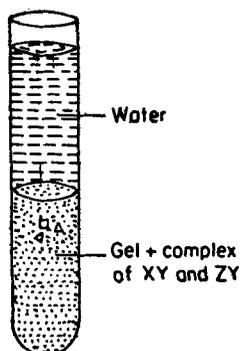Figure 5. Schematic diagram for growing metallic crystals in gels.

Figure 7. Schematic diagram for crystal growth by complex dilution method.
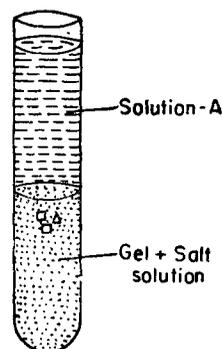
Figure 9. Schematic diagram for growing crystals by reduction of solubility (the material to be crystallized must be insoluble in solution A).

It is also possible to grow metallic crystals by this method. The first report on the growth of metallic crystals by this method has been made by Hatschek and Simon (1912). They grew gold crystals by adding 8% oxalic acid solution over the gel containing gold chloride solution. The schematic diagram, for growing metallic crystals, is shown in figure 5. Kratochvil *et al* (1968) grew gold single crystals of triangular and hexagonal habits (figure 6). Lead, copper and cuprous oxide crystals have also been grown by this method. Table 2 gives a list of some of the crystals grown by the reaction method.

3.2 *Crystallization by complex dilution method*

Crystal growth by complex dilution method was first reported by O'Connor *et al* (1968). The general feature of this method is the existence of some soluble material which itself increases the solubility of the material of interest in a nonlinear fashion with concentration of the soluble material by complex formation in solution or by formation of a soluble double salt. In the crystal growth operation, the concentration of the combined solution is reduced by diffusion into the gel. Because the solubility of the material is a nonlinear function of the concentration of soluble material, it may reappear. The procedure for growing crystals by this method is schematically shown in figure 7.

In the case of HgS, the aqueous solubilities of α-HgS and β-HgS are known to be enhanced by the presence of Na_2S. Similarly, the solubilities of silver and cuprous halides are known to increase enormously in concentrated alkali halide, alkaline earth halide solutions and their respective mineral acids. Using this method, mercuric sulphide, cuprous and silver halides, and selenium (Blank *et al* 1968a) have been grown. Figure 8 shows a few single crystals of laser quality cuprous

iodide grown by complex dilution method. The list of crystals grown by this method is given in a book by Henisch (1970).

### 3.3 *Crystal growth by reduction of solubility*

This method is particularly suitable for growing single crystals of highly water soluble substances. Gloker and Soest (1969) first reported the growth of ammonium dihydrogen phosphate (ADP) single crystals by this method. The substance to be grown is dissolved in water and incorporated with the gel-forming solution. After setting of gel, a solution which reduces the solubility of the substance is added over the set gel (figure 9) to induce crystallization. For example, potassium dihydrogen phosphates (KDP) crystals have been grown by adding ethyl alcohol over the gel containing a saturated solution of KDP (Brezina and Havrankova 1971). The formation of the crystals is due to the reduction of solubility of KDP in the liquid phase by the diffusing alcohol. A few ferroelectric crystals of triglycine sulphate (TGS) growing in test tube are shown in figure 10. The list of crystals grown by this method is given in table 3.

Table 3. Crystals grown by reduction of solubility of solute.

Crystals	Solutions		Max. size (mm)	References
	In gel	Above gel		
Cs_2PdCl_4	Cs_2PdCl_4	CH_3COCH_3	5	Marchee and Rosmalen (1977)
$Cs_2PtCl_4.H_2O$	$Cs_2PtCl_4 H_2O$	CH_3COCH_3	8	—do—
KH_2PO_4	KH_2PO_4	CH_3CH_2OH	$40 \times 8 \times 7$	Joshi and Antony (1980)
K_2PtCl_4	K_2PtCl_4	CH_3CH_2OH	18	Marchee and Rosmalen (1977)
Nacl	NaCl	CH_3CH_2OH or HCL	$4 \times 4 \times 4$	Thomas Abraham (1979)
$NH_4H_2PO_4$	$NH_4H_2PO_4$	NH_4Cl	25×2	Glocker and Soest (1969)
Rb_2PdCl_4	Rb_2PdCl_4	CH_3COCH_3	4	Marchee and Rosmalen (1977)
Rb_2PtCl_4	Rb_2PtCl_4	CH_3COCH_3	10×1	—do—

4. Growth mechanism

Even though crystals can be grown in a variety of gels, the general observation is that silica gels are the best to grow good quality single crystals. A gel can be regarded as a loosely interlinked polymer. The gelling process itself takes an amount of time which can vary widely from minutes to many days, depending on the nature of the material, its temperature and history. Since gelling
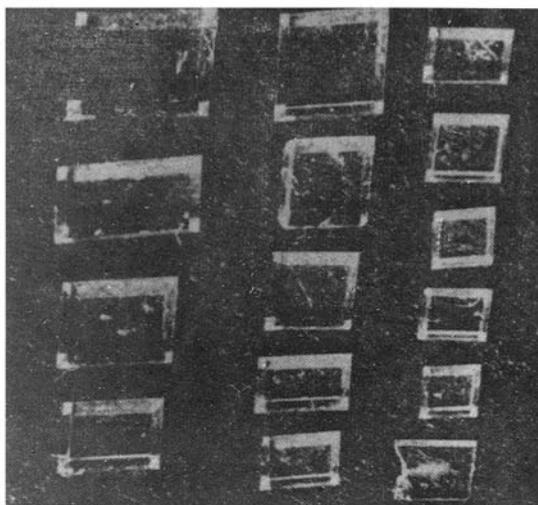
(4)
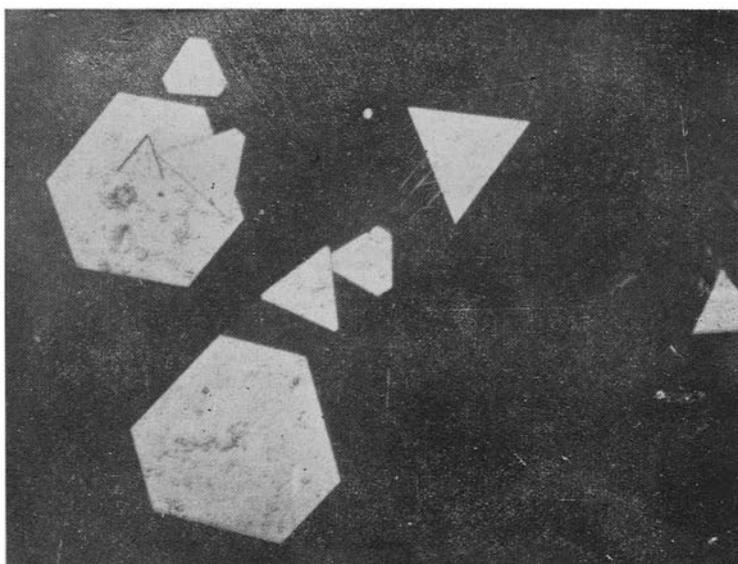
(6)
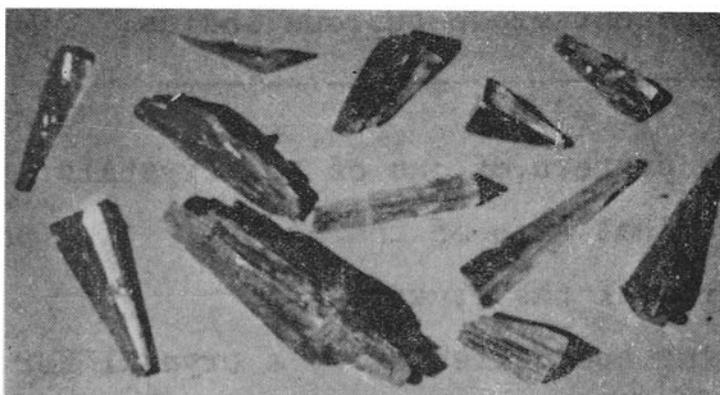
(8)

Figure 4. A few single crystals of ferroelectric lead monohydrogen phosphate (PbHPO₄) grown by reaction method (courtesy of Konak *et al* 1977).

Figure 6. A few single crystals of gold grown in a silica gel (courtesy of Kratochvil *et al* 1968).

Figure 8. A few single crystals of laser quality cuprous iodide (CuI) grown by complex dilution method (courtesy of O'Connor and Armington 1971).

(10)
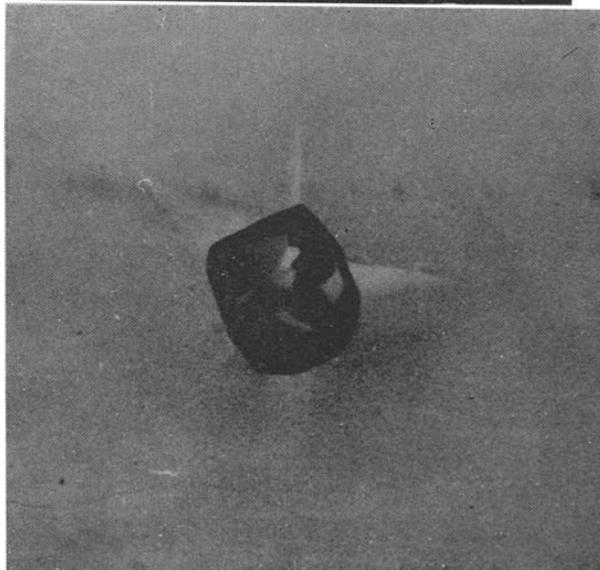
(11)

Figure 10. A few crystals of ferroelectric triglycina sulphate (TGS) are growing in test tube (courtesy of Henisch 1970).

Figure 11. Cusps around a growing crystals of $KClO_4$ (after Patel and Venkateswara Rao 1977).

is a matter of degree, quoted gelling times are always very approximate. The mechanical properties of fully developed gels can vary widely depending on the density and on the precise condition during gelling.

It has been observed that the time required for gelation is very sensitive to pH (Henisch 1970 ; Venkateswara Rao 1979). Because gelation is a gradual process, there is no unique definition of gelation time, but almost any definition will serve for comparative tests linked with a standard procedure. There is much that is still unclear about the mechanism of formation of silica gels, but it is known that two types of ions are in fact produced : H_3SiO_4 and H_2SiO_4, in relative amounts which depend on the hydrogen ion concentration. The latter is favoured by high pH values, is in principle more reactive, but the higher charge implies a greater degree of mutual repulsion. H_3SiO_4 is favoured by moderately low pH values and is held to be responsible for the initial formation of long-chain polymerization products. In due course, cross–linkages are formed between these chains, and these contribute to the sharp increase of viscosity that signals the onset of gelation. At very low pH values (below 3), the tendency towards polymerization is diminished, and chain formation is slowed.

Because gels are neither liquid nor solid, there is a great shortage of methods for quantitative investigations. As a result, one knows all too little about the relationships between gel structure and nucleation probability. From the SEM observations of dried silica gels (Halberstadt *et al* 1969) it has been found that gel consists of sheet-like structure of varying degrees of surface roughness and porosity, forming interconnected cells. The cell walls are ordinarily curved. From the SEM pictures of the silica gel it has been estimated that the cell walls seen in dense gels ($0 \cdot 4$ M Na_2SiO_3) have pores from less than $0 \cdot 1$ μ to $0 \cdot 5$ μ, compared with values from less than $0 \cdot 1$ μ to 4 μ in low density ($0 \cdot 2$ M Na_2SiO_3) gels. The cell walls are thicker for the dense gels. The pH during gelling has a profound influence on gel structure changes from a distinctly box like network to a structure consisting of loosely bound platelets which appear to lack cross-lin ages ; the cellular nature becomes less distinct (Halberstadt *et al* 1969).

The gel medium prevents turbulence and remaining chemically inert, provides a three-dimensional structure, which permits the reagents to diffuse at a desirable controlled rate. That the absence of turbulence is beneficial in growing good crystals has been demonstrated by repeating the experiments in an inert powder (TiO_2) instead of gel (Henisch *et al* 1965). In addition, the gel provides a frame work of nucleation sites and yet is soft enough to yield mechanically to the growing crystal. However, as soon as a crystal has reached a certain size, the gel splits off partially and forms one or more small cusp-like cavities, as shown in figure 11. It is interesting to note that the crystal does not cease to grow where these cusp-like cavities occur.

From the observation of the growth process, it was concluded that in the absence of convection, the only mechanism available for the supply of solute to the growing crystal is diffusion. Frank (1950) has developed equations which give a description of diffusion-controlled growth rates. Gel systems provide new applications of this theory. The growth kinetics of gel-grown crystals follow a parabolic law which is characteristic of one-dimensional diffusion controlled process (Hanoka 1969).

In the growth systems which depend on the diffusion of one reactant through a gel incorporating the other reagent it is observed that the growth rate is greatest near the gel-solution interface where the concentration gradients are high; away from the interface, the gradients are relatively low. Corresponding to different growth rates, the dislocation density is also different (Patel and Venkateswara Rao 1979a). This suggests strongly that the growth rate itself determines the number of defects grown into the crystal even in the absence of foreign impurities. Occasionally, crystals grown in gels are found to have dislocation densities less than $10^3/cm^2$. The high degree of perfection of these crystals has also been demonstrated by means of x-ray Laue diffraction patterns and etch patterns (O'Connor and Armington 1971 ; Patel and Venkateswara Rao 1979a).

It is apparent that crystals growing in a gel either displace the gel as they grow (Patel and Venkateswara Rao 1977) or incorporate the gel (Patel and Bhat 1973). In the case of gel displacing, cusps can be seen around the growing crystal as shown in figure 11, while in the other case, since the crystals incorporate the gel as they grow, final crystals turn turbid instead of being transparent. In the case of crystals growing in fissures in the gel, a clear boundary between opaque crystal grown in the gel and a clear crystal grown in the solution can be seen (Nickl and Henisch 1969). Normally the progressive deterioration of crystal quality indicates an increasing incorporation of gel in the passage of time which eventually leads to the destruction of the perfect facets observed on small crystals.

Crystals such as calcite grown in the normal way as reported by Nickl and Henisch (1969), are well-formed rhombohedra but are almost invariably turbid due mainly to silica inclusions. It is clear from these results that the silica network which constitutes the gel is incorporated into the growing crystals more or less in fact. In this way, calcite differs greatly from other gel–grown crystals (*e. g.* potassium perchlorate), which are surprisingly free from silica contamination. Crystals of calcite grow at the boundaries between gel and liquid are turbid to the extent to which they overlap the gel and clear to the extent to which they grow in solution. This suggests that calcite and other crystals which may behave in a similar way should not be grown in gels at all. They should be grown in solution, if possible without losing the general benefits of the gel method. The solution (*i.e.* H_2O) should thus be in a cavity so that solute concentrations within it may be regulated by the demands of the growing crystal. Nickl and Henisch (1969) have reproposed a hybrid method which uses gel as a diffusion barrier while the crystals grow in a gel-free region. An improved experimental design devised by Patel and Venkateswara Rao (1980) can also be used for the same purpose.

5. Nucleation control

Crystals growing in a gel system compete with one another for the solute atoms. This competition limits their size and perfection. It is therefore obviously desirable to suppress nucleation until only a few crystals are formed. There are some methods with which nucleation in gels can be controlled to some extent. They are devised by

(a) Using suitable reactants, (b) using gels prepared with various acids, (c) changing the gel structure, (d) using intermediate neutral gel, and (e) concentration programming.

5.1 *Using suitable reactants*

Out of various combinations of reactants which can be used to yield the required product crystal, only a few are found to be suitable to achieve controlled nucleation. In the case of growth of potassium perchlorate crystals, various reactants were used, however a combination of potassium chloride and perchloric acid has been found to considerably reduce the nucleation density. Even in this case, the nucleation centres are less and size of the crystals is bigger in gels mixed with perchloric acid than in gels mixed with potassium chloride (Patel and Venkateswara Rao 1979a). Tarun Bandyopadhyay and Asok de (1977) found that the nucleation density is reduced by using calcium chloride and ammonium carbonate as the reactants instead of calcium chloride and sodium carbonate for the growth of calcite crystals. Recently, Shiojiri *et al* (1978) reported that in the case of the growth of thallium iodide crystals, the nucleation density was much lower and the size of the crystals was much larger in the gels mixed with sodium iodide than in the gels mixed with thallium nitrate. The difficulties in growing single crystals of sulphides in gels can be traced to excessive nucleation when compounds such as sodium sulphide or hydrogen sulphide are used as the source of sulphide ions. The employment of an organic sulphur compound, thioacetamide, as sulphur ion donor overcomes this difficulty by its slow and controllable rate of hydrolysis which makes available only a limited number of sulphide ions at any time. Blank *et al* (1968b) have tried various organo-sulphur compounds to yield sulphide ions but crystals grown using thioacetamide are fewer in number, bigger and purer as compared to those grown with other sulphur compounds. In the case of the growth of selenides of lead and cadmium, nucleation density can be reduced to some extent using lead EDTA and cadmium EDTA instead of their respective chlorides or acetates (Blank and Brenner 1971).

5.2 *Using gels prepared with various acids*

After selecting the best combination of reactants with a particular acid set gel, it is necessary to use the same reactants with various acid set gels in order to reduce the nucleation density and grow bigger crystals. Only a few crystals have been grown in various acid set gels. Neodymium carbonate crystals have been grown in acetic and hydrochloric acid set gels (McCauley and Gehrhardt 1970). When acetic acid set gels were used to grow these crystals, only white-caked precipitate formed whereas hydrochloric acid set gels yielded good quality single crystals. For the growth of potassium perchlorate crystals (Patel and Venkateswara Rao 1979a), four mineral acids (perchloric, hydrochloric, sulphuric and nitric) and four organic acids (citric, tartaric, acetic and propionic) were used to form gels and it is found that the perchloric acid set gels yielded the best results. Regarding the growth of lead iodide crystals, the lowest nucleation density was obtained when acetic acid set gels were used (Patel and Venkateswara Rao 1981a).

5.3   *Changing the gel structure*

It is possible to change the gel structure and reduce the nucleation density by changing gel pH (McCauley and Gehrhardt 1970), gel density and gel aging (Patel and Venkateswara Rao 1978a). In general, increased gel density and gel pH decrease the nucleation density to a considerable extent but the final crystals are of poor quality. On the contrary, gel aging reduces the nucleation density and hence the total number of crystals, without affecting their quality. The decrease of nucleation centres at higher densities of gel and gels aged for longer periods is due to the fact that these two parameters reduce the cell size and consequently the rate of diffusion of ions into the gel. The decrease in nucleation density at higher pH values may be due to the improper formation of gel cells at higher pH values of gels (Patel and Venkateswara Rao 1978a).

5.4   *Using intermediate neutral gel*

This method involves the preparation of a gel containing one of the reactants in the bottom of a test tube as in the usual test tube method. However, a second gel, called the intermediate neutral gel or the reaction gel is formed over the first gel and the second reactant is then poured over it. The neutral gel will slow down the reaction between the reactants and reducing the number of nuclei. This method was first used by Blank and Brenner (1969) to grow lead and thallous and cuprous oxide single crystals. McCauley and Roy (1974) and McCauley and Gehrhardt (1970) have also used the same method to grow calcium carbonate, neodymium carbonate and calcium tungstate crystals. More recently Patel and Venkateswara Rao (1978) used this method to study the effect of intermediate neutral gel on nucleation and growth of potassium perchlorate single crystals. It has been found that the nucleation density decreases as the height of the intermediate gel increases.

5.5   *By concentration programming*

In this procedure, the concentration of diffusing reactant is initially kept below the level at which nucleation is known to occur and is then increased gradually in a series of small steps. It is considered that with very dilute reactants the amount of material diffused through the gel is small and hence smaller is the supersaturation rate. Under these circumstances, a few nuclei are formed. On increasing the concentration, further growth of the existing nuclei is preferred to the formation of additional ones. Crystals grown by this method are more perfect and larger than those grown otherwise. The method has been successfully applied for the control of nucleation in the case of calcium tartrate, cuprous tartrate, iodides of lead and thallium, calcium carbonate, cadmium oxalate, potassium perchlorates tungstates of barium and strontium etc. (Henisch 1970; Patel and Venkateswara Rao 1978a; Patel and Arora 1973).

6.   Morphologies of various gel grown single crystals

Crystals with various habits are important not only commercially but also in studying their physical properities. In gel growth, various habits of crystals can be

obtained by changing concentration of feed solutions, crystallization temperature and gel structure, by adding impurities and by using various types of gels. In addition to these, various habits in different regions of gel are also observed in some cases.

6.1 *Habit modification by changing the concentration of feed solution, crystallization temperature and gel structure*

In the case of calcium tungstate crystals grown in gels, high calcium concentrations favoured the growth of clear spherulites, whereas high tungstate concentrations resulted in opaque spherulites. During the growth of neodymium carbonate, sodium carbonate incorporated gel enhanced the formation of dendrites and spherulites, whereas neodymium chloride incorporated gel favoured the growth of rhombic plates and clusters of plates (McCauley and Gehrhardt 1970). With regard to calcium carbonate growth (Tarun Bandyopadhyay and Asok de 1977) when the strengths of feed solutions were from 0·2 to 0·3 M, the crystals were of rhombohedral habit and with the edges having wavy and ripple like features at concentrations of 0·4 to 0·6 M. Further increase in the strengths of feed solutions to 1·0 M and more, generated a large number of nucleation centres with dendritic crystallization. The morphology of both barium and strontium sulphate single crystals grown under similar conditions was the same. The change in the concentration of feed solutions had no effect on the morphology of the grown crystals. However, it was observed that there was a considerable effect of the growth temperature on their morphology. For example, in the case of strontium sulphate, all the crystals grown at about 35° C had {011} and {102} as their habit faces, whereas the crystals grown at about 20° C developed {022} habit faces in addition to the usual {011} and {102} faces (Patel and Bhat 1973). During the growth of potassium perchlorate (Patel and Venkateswara Rao 1979b) at lower concentrations of about 1 N of both the feed solutions, almost all the crystals developed predominant {101} and {210} faces and at higher concentrations (2N) of both the feed solutions, the crystals, were in the form of needles with predominant {210} faces. By increasing the concentration of one of the reactants to around 4 N and decreasing the concentration of the other to around 1 N, the crystals grown were of rhombic shape with two {001} faces bounded by four {210} faces. It was also observed that the growth rates along [010] direction increased with temperature. Cuprous chloride crystals grown in the temperature range 22-40° C were tetrahedral and those grown at 50° C were long needles (Armington and O'Connor 1968). The elongated C-axis growth was attributed to the relatively low pH of the gel medium in the case of ADP crystals (Glocker and Soest 1969). With respect to the growth of calcite crystals, decrease in the pH of gel resulted in the development of spherulites (pH 10·5) into feathery polycrystalline aggregates (pH 9 to 10·5) and finally into single crystals of rhombic habits (pH 7 to 9). (McCauley and Roy 1974).

6.2 *Habit modification by adding various impurities*

As in "solution growth" in gel growth also, it is possible to change crystal habit by adding impurities. Various habits of calcite were obtained by adding

impurities of Mg, Sr, Ni and Ba in various proportions during the growth of these crystals (McCauley and Roy 1974). Gypsum crystals grown in silica gel in the presence of inorganic compounds were needle-shaped, while the addition of organic compounds altered the habit into a more stubby modification (Rosmalen *et al* 1976). Crystals grown in pure agar gels were equally shaped. But when small amounts of hydrochloric acid were added, needles developed. Perfect rhombohedra-shaped crystals of calcite have been obtained by adding a saturated solution of sacroboise to the feed solutions (Barta and Zemlicka 1971). The addition of ammonium chloride to the gel system lead to the formation of single crystal needles of calcium tungstate (McCauley and Gehrhardt 1970).

6.3 *Habit modification by using various types of gels*

The morphology of minerals (for example gypsum) which have grown within muds (for example bentonite clay) and other sediments has assumed importance because of the possibility of a correlation between the physico-chemical parameters of the surrounding media and mineral habits. Since the primary concern in attempting to understand such a relationship is to simulate natural conditions in the laboratory, efforts have been made to grow crystals within natural muds (Cody 1976). A comparison of crystals of calcium sulphate dihydrate grown in two different gel media, sodium silicate gel and bentonite clay gel, showed that the two media affect crystal habit and surface topography differently. Those crystals grown in silica gel at 40° C and pH 6–7·5 consisted of elongated prisms with relatively smooth crystal faces, and they were often twinned. Crystals grown in bentonite gel at the same temperature and similar pH were tabular with a wide variety of kinks, steps and pits on their surfaces, and were never twinned. This suggests that bentonite gel more closely simulates natural mud as a support medium for crystal growth than silica gel (Cody and Shanks 1974).

6.4 *Various habits obtained at different regions of gel*

In the case of lead molybdate growth, there were different regions inside the gel where lead molybdate crystals of various habitats were formed. Near lead nitrate solution, polyhedral pyramidal crystals were formed. Octahedral bipyramidal crystals and platelets were formed in the central region and near the ammonium molybdate solution respectively (Sreedharan Pillai and Ittyachen 1977). The habit modification was explained to be due to the excess arrival of lead and molybdate ions in their respective zones. The morphologies of barium molybdate crystals in the U–tubes could be divided into three groups depending on all the crystallization zones where they formed in the tubes. The needle and cruciform-shaped crystals were formed towards the U-tube arm containing the barium chloride solution. The well-developed star-like dendritic and octahedral crystals formed very close to the central crystallization zone. The crystals formed near the sodium molybdate solution appeared to be aggregates of small crystallites (Cho *et al* 1977). In the growth of lead monohydrogen phosphate (LHP) crystals (Brezina and Havrankova 1976), crystallization zones were observed in which

crystals of various habits were obtained. In the region very close to lead nitrate reactant solution, lead nitrogen phosphate ($Pb_4 (NO_3)_2 (PO_4)_2 \cdot 2H_2O$) crystals were formed. After this region, platelets, spherulites and rosettes of LHP were observed. Near to phosphoric acid reactant solution, needle-like crystals were observed. In copper iodates also, a surprisingly wide variety of crystal morphology was observed at various regions in the gel (Nassau *et al* 1973).

7. Studies on gel grown single crystals

Much work has been done on lead iodide crystals to understand its band structure (Henisch 1970) and polytypism (Mahesh Chand and Trigunayt 1975; Meera Rao and Srivastava 1978). These studies had been greatly impeded because of lack of suitable specimens and besides many contradictory results were reported. With the gel technique, it was found possible to grow not only flat plates, but specimens thick enough to permit measurements of the refractive index in all crystal directions. The measurements showed that the dielectric polarization is mainly electronic in character. When gel–grown neodymium carbonate crystals were examined by transmitted light microscopy, they exhibited a highly symmetric domain structure and a strain birefringence (McCauley and Gehrhardt 1970). It was concluded that the domains might be magnetic in origin. The electrical resistivity of gel-grown lead sulphide crystals was found to be $8 \cdot 4 \times 10^{-4}$ ohm cm at 25° C (Blank *et al* 1968) in comparison with the values 8.0×10^{-2} ohm cm for untreated natural galena and $7 \cdot 0 \times 10^{-3}$ ohm cm for "synthetic" lead sulphide (Brebrick and Scanlon 1954). Test on a single filament of gel-grown silver acetate revealed stresses of $1 \cdot 25 \times 10^6$ psi in bending without any fracture or permanent deformation (Boulin and Ellis 1970). Silver trihydrogen periodate has been investigated because of its antiferroelectricity at low temperatures with a complicated phase transition near 231° K. Contrary to former heat anomaly measurements (Bartschi 1945), gel-grown crystals of $Ag_2H_3IO_6$ showed for the first time the two-stage character of transition (Arend and Perison 1971). Dendrites of metallic lead have been used for metallurgical studies by Bedarida (1964). Lead hydroxy iodide has been prepared for the first time in single crystal form by gel technique. Optical absorption spectra of the crystals have been studied at about 430μm. It also gives the spectral response of the photoconductivity. The low frequency (10^4 C/Sc) dielectric constant is about $10 \cdot 5$, and the magnetic susceptibility is $-0 \cdot 25$ b $\times 10^{-6}$ g. They showed a faint but stable bluish white cathodoluminescence (Henisch 1970). The quality of gel-grown potassium dihydrogen phosphate (KDP) crystals is judged according to dielectric properties measured in the vicinity of the ferroelectric phase transition. The values of maximum permittivity, spontaneous polarization and $\triangle T$ of these crystals (Brezina and Havrankova 1971) are comparable with those of very good samples of KDP grown by solution method. Nassau *et al* (1973) and Abraham *et al* (1973) have reported detailed studies on structural, optical and magnetic properties of transition metal iodates. Lead monohydrogen phosphate (LHP) is a typical representative of the family of ferroelectric schultemites undergoing a second order structural phase transition at $3 \cdot 75°$ C. Principal refractive indices, birefringence, indicatrix orientation data of the permittivity and spontaneous polarization of

dislocation free single crystals of ferroelectric LHP have already been reported (Konak *et al* 1977; Smutny and Fousek 1980). The temperature dependence of birefringence is found to be related to the ferroelectric transition. Studies on the gel-grown lead monohydrogen arsenate (LHA) crystals (Brezina *et al* 1975) suggest a ferroelectric transition similar to that of LHP. Detailed studies on the electrical and optical properties of gel grown AgI single crystals have been reported by Govindacharyulu and Bose (1978). The thermochromic compound, cuprous mercuric iodide, has been of great interest because of its usefulness as an erasable, high density infrared storage medium. The material exhibits hysteresis in its phase transition (Chivian 1976) which serves as the basis of infrared recording applications.

8. Conclusions

Considering the amount of data available on crystal growth in gel media and the importance of growing crystals at ambient temperatures, a survey of the method in general and subsequent modifications along with the experimental results reported so far are presented in this review article. The gel growth technique with its various modifications appears to be quite promising for the production of highly perfect single crystals of a variety of materials.

A general assessment of the method and its potentialities is not yet possible, but recent experiments have yielded results which should prove useful to other workers in this field. A great deal of work remains to be done to document and explain the detailed nature of gel structure which will be displaced by the growing crystal as in the case of potassium perchlorate or incorporation of gel into the new solid by crystal growth as in the case of calcite. Many important crystals such as $CaWO_4$, CaF_2. HgI, $CaCO_3$, PbS, ZnS, $PbHPO_4$, $Ag_2H_3IO_6$ etc. can be grown in various types of gels and by adding impurities in order to decrease nucleation density and to grow various shapes of highly perfect single crystals. Out of a large number of gel-grown single crystals, properties of only a few have been studied. Comparative studies of gel-grown single crystals with those grown by other method are worth attempting in order to probe into and take advantage of the characteristics and peculiarities of gel-grown crystals. The further development of the gel method will certainly depend on the extent to which its mechanism can be understood and controlled.

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