Crystal Growth from High-Temperature Solutions

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3.1. Introduction

Certain problems of the natural sciences survive all generations and demand more interest with increasing data and with increasing penetration into the knowledge of nature. The solutions represent such a fundamental problem: their role is likewise important in pure chemistry, in technology and in the processes in animated and unanimated nature, but their explanation belongs to the most difficult and challenging problems of chemistry.

These sentences have not yet lost their validity, although they appeared in a treatise on the historical development of solution theories by P. Walden (1910) which is recommended for anyone interested in the history of science. Solutions are certainly understood much less than are gases or crystalline solids, although simple liquids are now partially understood. Their structure is determined to a large extent by repulsive forces amongst the molecules, and the attractive forces (analysed by van der Waals and, using perturbation treatments, by Barker and Henderson, 1967, 1968) have a less important effect on the structure (Rowlinson, 1969, 1970; Bernal, 1968). Much further work, theoretical and experimental, is necessary to gain an understanding of polyatomic liquids and of solutions, and here especially systematic experiments and large-scale computer simulation studies promise to increase greatly the knowledge in this complex field (see Neece and Widom, 1969; Eyring and Jhon, 1969; Barker and Henderson, 1972).

In the case of high-temperature solutions the state of knowledge is even

smaller. A review of equilibrium theory of pure fused salts has been given by Stillinger (1964) and of thermodynamic properties of high-temperature solutions by Blander (1964). Some results of structural investigations of molten salts by neutron and X-ray diffraction, by electronic spectroscopy and by vibrational spectroscopy were reviewed by Levy and Danford (1964), Smith (1964) and James (1964), respectively. Reviews on all practical aspects of molten salts and molten-salt solutions are given by Belyaev and co-workers (1964), Bloom and Hastie (1965), Bloom (1967), Janz (1967), Mamantov (1969) and Janz and Tomkins (1972, 1973). A modern and comprehensive survey of theoretical and experimental aspects of ionic interactions in electrolyte solutions and in fused salts has been compiled by Petrucci (1971) and deals particularly with physicochemical properties of ionic high-temperature solutions and with crystal field and molecular orbit theories applied to fused-salt systems. Bloom and Bockris (1959) summarize the information necessary for a rough estimate of the structure of a molten salt as follows.

- 1. The type of entities present, i.e. ions, molecules, complex ions, etc.
- 2. The nature and effect of holes or vacancies.
- 3. Distribution functions relating to the relative positions of structural entities and holes.
- 4. The nature of the bonds or interionic forces amongst the various entities in the melt.

Of great importance is the presence of holes, free space, in the liquids. The presence of such holes is proved by the volume expansion when solids melt and by conductivity measurements. It is the presence of free space in liquids which favours transport processes.

Krasnov (1968) pointed out that the properties of solutions are closely related to the radii of the ions. These radii depend on the concentration: in highly concentrated solutions the ionic radii are similar to those known from corresponding crystal structures (Samoilov, 1957), whereas in dilute solutions they approximate to the radii of Böttcher (1943, 1952) which were derived from undeformed gaseous ions.

In the following a brief description of solution concepts, of solutesolvent interactions and solubilities and of equilibria in solutions will be given, followed by sections on "ideal" high-temperature solvents, on phase diagrams and on special solvents.

A rather detailed general discussion of solutions seems necessary with respect to the understanding of the processes occurring during crystallization from high-temperature solutions. The usual tendency is to consider only the reactions at the solid interface and to neglect the nature of the solution itself. From the following sections it will become clear that the type of solution and of the solute-solvent interactions may play a decisive role in the crystal growth process. In certain cases a systematic optimization of the solvent question may enable the experimentalist to decrease the tendency of unstable growth and to increase the width of the metastable region in order to prevent inclusions and multinucleation, respectively. The choice of solvent also determines the degree of solvent ion incorporation and therefore the purity of the grown crystals. It is interesting to note that many solvents chosen by experience are often optimum in many aspects, especially in flux growth of oxides, whereas for other compounds general rules are given in Section 3.6.1.

Preliminary experiments to synthesize new materials in crystalline form, as small crystals, do not require an exact knowledge of the corresponding phase diagram. For the systematic growth of large crystals and for the achievement of a high yield, the phase diagram has to be known to a sufficient degree. Therefore a discussion of phase-diagram determination as well as selected solubility data are given in the last part of this chapter.

3.2. General Solution Concepts

There is no fundamental difference between a solution and a mixture of liquids but it is convenient in a description of high-temperature solutions to consider the less refractory phase as the solvent while the solute is the phase which crystallizes first on cooling. The solute may have several components and solution behaviour may be extremely complex but the treatment given here will be restricted to basic considerations.

Since the total volume, entropy, enthalpy, etc. of the solution are, in general, not equal to the sum of the individual quantities prior to mixing it is necessary to use *partial molar* quantities. For example, in attempting to assign a fraction of the total volume to the separate constituents it is convenient to consider the partial molar volumes \overline{V}_1 and \overline{V}_2 which represent respectively the changes in volume of the solution on adding one mole of components 1 and 2 at constant temperature T and pressure p.

It may be readily shown that the Gibbs free energy of an ideal mixture (as of ideal gases) exceeds the value for the same unmixed material at constant T and p by an amount

$$\Delta G = RT \sum_{A} n_A \ln x_A,$$

where n_A is the amount of species A and x_A its fractional concentration $(x_A = n_A / \sum_i n_i)$. Thus the chemical potential $\mu_A = \partial (\Delta G) / \partial n_A$ of species A is given by

$$\mu_A = \mu_A^0 + RT \ln x_A, \tag{3.1}$$

where the superscript ⁰ refers to the pure liquid at the same temperature c2

and pressure. If a mixture (or solution) exhibits non-ideal behaviour, the departure from ideality may be expressed in terms of the relative activity a_A which is defined (see Guggenheim, 1967) by

$$\mu_A = \mu_A^0 + RT \ln a_A. \tag{3.2}$$

Comparison of Eqns (3.1) and (3.2) shows that, for an ideal mixture,

$$a_A = x_A. \tag{3.3}$$

The condition for a solution of material A to be ideal is that its chemical potential in the solution is the same as that of the pure substance in the solid state, so that

$$\mu_A(s) = \mu_A^0 + RT \ln a_A. \tag{3.4}$$

Division by T and differentiation with respect to temperature gives

$$\frac{\partial}{\partial T} \left[\frac{\mu_A(s)}{T} \right] - \frac{\partial}{\partial T} \left(\frac{\mu_A^0}{T} \right) = R \frac{\partial}{\partial T} \ln a_A.$$
(3.5)

Now it is a familiar relation that

$$rac{\partial}{\partial T} igg(rac{\mu}{T} igg) = rac{-H}{T^2},$$

where H is the enthalpy so that substitution in Eqn (3.5) gives

$$\frac{\Delta H_f}{T^2} = R \frac{\partial}{\partial T} \ln a_A,$$

where $\Delta H_f = H_A(s) - H_A^0$ is the enthalpy of fusion. Thus in an ideal solution where Eqn (3.3) holds,

$$\frac{\partial}{\partial T} \ln x_A = \frac{\Delta H_f}{RT^2}$$

$$x_A = x_{\infty} \exp(-\Delta H_f/RT). \qquad (3.6)$$

or

If $\ln x_A$ is plotted against reciprocal temperature for an ideal solution, a straight line of slope $(-\Delta H_f/R)$ is obtained with an upper limit of $\ln x_A = 0$ at the melting point T_M , as in Fig. 3.1. Thus if the heat of fusion and melting point are known the solubility curve can be plotted and will not depend on the solvent. Since the entropy of fusion of similar compounds is approximately constant, a high melting point is associated with a low solubility. This latter relation was recognized by Lavoisier (1794).

The assumption of an ideal solution also requires that $p_A \propto x_A$ (Henry's law) where p_A is the *fugacity* or vapour pressure of A. If the constant of



FIG. 3.1. Solubility curve for an ideal solution.

proportionality is the saturated vapour pressure p_A^0 of the pure liquid, the resulting relation

$$p_A = p_A^0 x_A \tag{3.7}$$

is known as Raoult's law.

Real solutions exhibit departures from Eqns (3.6) and (3.7) and these departures are often expressed by the deviation from unity of the activity coefficient a_A/x_A . According to Hildebrand and Scott (1970) non-ideal solutions may be divided into athermal, associated and regular solutions. In *associated solutions* departures from regularity are caused primarily by bonding between the molecules of one component in the solution, whereas

Type of solution	Enthalpy of mixing $\overline{H}_1 - H_1^o$	Entropy of mixing $\overline{S}_1 - S_1^o$	Remarks
Ideal	0	$-R\ln x_1$	$a_1 = x_1 \\ V_1 \cong V_2$
Regular	*	$-R\ln x_1$	$a_1 > x_1 \\ V_1 \cong V_2$
Non-ideal, athermal	0	$< -R \ln x_1$	$a_1 < x_1 \\ V_2 > V_1$
Irregular, associated	+	$> -R \ln x_1$	$a_1 > x_1$
Irregular, solvated	-	$< -R \ln x_1$	$a_1 < x_1$

TABLE 3.1. Classification of Solutions

in *solvated solutions* the principal bonding is between solute and solvent molecules. *Athermal solutions* represent a particular case in which the enthalpy of mixing is zero but the activity does not have the ideal value. This classification of solution types is indicated in Table 3.1.

Regular solutions approximately obey Raoult's law up to a solute concentration of about 15 m_{0}° . It has, however, been argued by Haase (1956) that "regular solutions" are somewhat hypothetical, or at least extremely rare (the possible exceptions being certain metallic solutions), and several definitions of a regular solution are in use.

Departures from ideal behaviour may also be displayed graphically on a plot of the Gibbs free energy of mixing versus composition, as shown in Fig. 3.2 (Darken and Gurry, 1953).



FIG. 3.2. Gibbs free energy of solutions with departures from ideal behaviour.

A positive deviation from Raoult's law corresponds to a smaller solubility for a solid and a negative deviation corresponds to a greater solubility than would be calculated from the melting point and the heat of fusion of the solid. The simplest possible model of a condensed system is based on the assumption that the total cohesive energy is the sum of interactions or "bonds" between neighbouring entities. The solution theory based on this model has been developed mainly by Rushbrooke (1938) and by Guggenheim (1952). A brief discussion has been given by Kleppa (1958). In general, the interaction energy W_{12} when species 1 and 2 form a solution will differ from the arithmetic mean of the individual bonding energies W_{11} and W_{22} so that there will be departure from Raoult's law.

Hildebrand has suggested that a useful parameter for characterizing the attraction between molecules is the solubility parameter δ , defined as

$$\delta = \Delta \omega_{\rm vap}^{1/2},\tag{3.8}$$

where $\Delta \omega_{\rm vap}$ is the energy of vaporization per unit volume of the solution.

The significance of this parameter is that the energy of mixing of a regular solution may be written in the form

$$\Delta W^M = V(\delta_1 - \delta_2)^2 \phi_1 \phi_2, \tag{3.9}$$

where ϕ_1 and ϕ_2 are the volume fractions of the components of the binary solution

$$\phi_1 = \frac{N_1 V_1}{N_1 V_1 + N_2 V_2} \qquad \phi_2 = \frac{N_2 V_2}{N_1 V_1 + N_2 V_2}$$

with V_1 and V_2 the molar volumes of the pure substances. The usefulness of the solubility parameter is not generally accepted and other semiempirical descriptions of non-ideal solutions have been proposed (see Haase, 1956).

The condition for complete miscibility of metals according to Hildebrand is that

$$\frac{V_1+V_2}{2}(\delta_1-\delta_2)^2 < 2RT.$$

However, Mott (1968) has shown that a better prediction of immiscibility can be obtained if the Pauling electronegativity difference W_B is included, so that

$$\frac{V_1 + V_2}{2} (\delta_1 - \delta_2)^2 - W_B \lesssim 2RT.$$
(3.10)

The value of W_B in calories is roughly 23,060 $\eta(\chi_1 - \chi_2)^2$, with χ_1 and χ_2 the electronegativities of metals 1 and 2 in volts and η the appropriate number of bonds between molecules of 1 and 2. Mott suggests that $\eta \simeq C.N./2$, where C.N. is the coordination number in the solution. Binary metals systems exhibiting liquid immiscibility are listed in Hildebrand and Scott (1964).

Immiscibility in oxide systems has been described by the screening concept of Weyl (1956), the electrostatic bond concept of Warren and Pincus (1940), the ionic field-strength concept of Dietzel (1942, 1948/1949) and related crystal chemical relations as reviewed by Levin (1970). A theory which predicts the extent of liquid immiscibility gaps in simple ionic systems has been derived by Blander and Topol (1965).

An obvious and well-known fact is the higher solubility at higher temperatures for most systems according to Eqn (3.4) for an endothermic dissolving reaction. The rare phenomenon of *retrograde solubility* (with the solubility decreasing with increased temperature) is connected with an exothermic dissolution process.

The effect of pressure on the solubility of solids can be discussed in terms of deviations from Raoult's law: ideal solutions and solutions with positive deviation will show a lowering of the solubility with higher pressure, whereas a negative deviation from Raoult's law is frequently associated with an increase in solubility with pressure.

For further details regarding the principles of solutions reference may be made to Garrels and Christ (1965), Darken and Gurry (1953), Kleppa (1958), Hildebrand and Scott (1970), Robinson and Stokes (1968), Rowlinson (1969, 1970), Prigogine (1957) and Petrucci (1971) and especially to Reisman (1970).

Ionic Solutions

According to Blander (in Mamantov, 1969) the models for molten salts are simpler than for most other liquids, since the structure of molten salts can as a first approximation be considered as a dense mass of ionic spheres with a strong tendency towards alternation of positive and negative ions. Thus, the total energy of ionic molten-salt systems is equal to the sum of the pair interactions between cations, anions, and each other, mainly given by the Coulomb interactions. The potential for a cation-anion pair is given by

$$U=-\frac{e^2}{r}+\frac{k}{r^n},$$

where *n* is of the order of 8 to 12. For a gaseous dipole $k = (e^2 r_0^{n-1}/n)$ with r_0 the internuclear separation. For a solid of the NaCl type,

$$\frac{U}{n} = -\frac{1.7e^2}{r} + \frac{6k}{r^n}$$

therefore the equilibrium value of r for the solid is about 19% larger than r_0 for the vapour molecule if n=8. Lowering the coordination leads to significant foreshortening and occurs when highly polarizable ions are stabilized in regions of high field intensity. A simple example is the ion-induced dipole interaction with $W=\frac{1}{2}\alpha E^2$ for weak fields where W is the energy, α the polarizability, and E the field intensity. Particular symmetries of anions around transition-metal cations are generated by ligand field effects which are dependent on interactions of nearest-neighbour anions as well as on next nearest-neighbour cations.

Cobb and Wallis (1969) discuss approaches to solubility with special

emphasis on ionic high-temperature (non-ideal) solutions. However their treatment, which follows standard thermodynamic theory and which is similar to the discussions of Garrels and Christ (1965), will not be given here since the necessary knowledge of the thermodynamic quantities is generally not available. The desired relationship between solubility and the change in Gibbs free energy is based on the partial molar free energy of mixing of the solute in the solvent, which itself is a function of the solute concentration. The calculation of the partial free energy of mixing from the solubility product concept is only possible when either the solutions are completely dissociated (which normally is not the case) or when the degree of dissociation (and association) are known as a function of temperature for the given system. For partially ionic systems the easiest approach is to determine the solubility at various temperatures experimentally and inter- and extrapolate the solubility curve. Some conclusions regarding the thermodynamic functions, the degree of dissociation and association might then be drawn from such experimental values.

In order to estimate oxide solubilities the Temkin (1945) model is frequently used. Concentrations are expressed in ionic fractions, and the ionic activity coefficients are assumed to be unity. Then the solubility product K' of a completely dissociated oxide is defined by $\ln K'(T) = \Delta G^F/RT$ and the solubility changes with temperature according to

$$\frac{\partial}{\partial T} [\ln K'(T)] \approx -\frac{\Delta H_m^F}{RT^2} + \frac{\Delta C_p}{RT^2} (T_m - T).$$

Here ΔC_p is the difference in the heat capacities of the solid and liquid oxide solute, ΔH_m^F its enthalpy of fusion and T_m its melting point.

The greatly simplified approach of Temkin assumes that the heat of mixing of the oxide in the flux is zero. Nevertheless this model often predicts thermodynamic properties of unknown flux systems with considerable accuracy.

Of the necessary data generally only T_m is known. Published thermodynamic data are summarized in Table 3.2. For oxides of which the enthalpies of melting and heat capacity changes are not known, some rules are available for estimating these quantities. For completely ionized salts ΔS_m^F might be estimated by *Richard's rule* where the entropy of melting is taken as roughly *R*, the gas constant (Darken and Gurry, 1953). Brice (1973), who gives expressions which may be used to estimate various parameters, quotes $\Delta S_m^F = 8.8 \pm 3.8 \, \text{J}(\text{g atom})^{-1} \,(^\circ\text{C})^{-1}$. Non-ionic solids can have much lower entropies of fusion, and also phase transitions in the solid near T_m will lead to low estimated enthalpies of fusion when the latter are determined using

$$\Delta H_m^F = T_m \, \Delta S_m^F.$$

Oxide	$T_m[K]$	<i>∆H^F</i> Kcal/mole	ΔS^F cal/degree mole	ΔC_p cal/degree mole
MgO	3173	18.5	5.8	
CaO	2873	12	4.2	
Al ₂ O ₃	2313	26	11	
TiO ₂	2106	11.4	5.4	
ZrO ₂	2950	20.8	7.0	
VO ₂ (V ₂ O ₄)	1815	27.21	14.99	10.1
Nb ₂ O ₅	1785	24.59	13.78	
WO ₃	1745	17.55	10.06	
Cu ₂ O	1502	13.4	8.9	
SiO ₂	2001	1.84	0.92	
SnO ₂	1898	11	5.8	

TABLE 3.2. Thermodynamic Properties of Oxides (Table 2, p. 26, Cobb and Wallis, 1969)

Cobb and Wallis (1969) estimated using Richard's rule the thermodynamic data for such oxides which are, according to the rules of Pauling, more than 70% ionic (and which are supposed to dissociate almost completely in solution). These data are given in Table 3.3. The difference in the heat capacities of the solid and liquid oxide are on average 1 cal deg⁻¹ gram atom⁻¹ of the oxide.

With these thermodynamic data and with Temkin's model the solubility behaviour of ionic systems can be estimated. However, the estimate is

Oxide	$T_m[K]$	ΔH_m^F Kcal/mole	ΔS_m^F cal/degree mole
Li ₂ O	2000	12.0	6.00
SrO	2688	10.8	4.00
BaO	2196	8.8	4.00
Y ₂ O ₃	2690	26.9	10.0
La_2O_3	2590	19.6	10.0
Ce ₂ O ₃	1960	19.6	10.0
Eu ₂ O ₃	2323	23.2	10.0
Dy ₂ O ₃	2613	26.1	10.0
MnO	2058	8.2	4.0
CoO	2078	8.3	4.0
NiO	2230	8.9	4.0

TABLE 3.3. Estimated Thermodynamic Properties of Pure Oxides(Table 3, p. 28, Cobb and Wallis, 1969)

very approximate as long as one is unable to take into account the solutesolvent interactions and the degree of covalency.

The solubility model described above for ionic oxides will also hold approximately for mixed oxides or other complex ionic compounds. The solubilities of incongruently melting compounds in novel solvents can be estimated (for the region below the incongruent melting point) by extrapolating from a known phase diagram or solubility curve to the hypothetical melting point and by estimating the heat of fusion of the compound by the use of Richard's rule.

Finally the theoretical approach to solutions should be mentioned. Although statistical mechanical treatments are potentially of great practical value this field has still remained a domain of theoretical physical chemists and has not found application in crystal growth from HTS, mainly because of the lack of understanding of solutions in general and especially at high temperatures. Future progress in this field should allow the calculation of solubilities from basic atomic and molecular data (Blander, 1964; Sundheim, 1964; Kaufman and Bernstein, 1970; Petrucci, 1971; Reisman, 1970).

3.3. Solute-solvent Interactions

The characteristic feature of a solvent is its ability to bring into a single phase (the liquid solution) one or more other (solid) compounds, the solutes. This dissolution process involves interactions of solvent and solute molecules which differ according to the types of bonding between solvent molecules and between solute molecules.

These various interactions and correspondingly the solubility cannot be connected with the thermal effects observed during dissolution. The heat of solution is the difference between the lattice energy and the solvation (hydration) energy, but this difference is small compared with each of the latter energies. As an example the lattice energy of KCl (corrected for 298°K) is 169 Kcal/mole, the heat of solution (in water) is $\Delta H = +4.1$ Kcal/mole, and therefore the total heat of hydration is the difference of 164.9 Kcal/mole.

The hydration energy can be roughly estimated for the case where an ion is brought from vacuum into water, which is taken as a continuous medium with a relative permittivity, ϵ , equal to 80. From electrostatics the amount of binding energy is $W_H = -\frac{1}{2}(e^2/r)(1-1/\epsilon)$, the energy of a charged sphere in a medium of relative permittivity ϵ being $\frac{1}{2}(e^2/r\epsilon)$ with r the ionic radius. For K^+ with r = 1.33 Å the hydration energy would be 122 Kcal/gram atom, and for Cl⁻ 89 Kcal/gram atom. Thus the sum for the idealized estimate of 211 Kcal/mole is much higher than the value of 164.9 Kcal/mole quoted above. The relations between the enthalpy of hydration of ions and the ionic radii have been reviewed by Morris (1968),

whereas Fajans (1921) and Fajans and Karagunis (1930) had already established the correlation between solubility, lattice energy, hydration energy and the tendency to form solid hydrates.

The silver halides would have a hydration energy similar to KCl but the lattice energy is much higher by the contribution of the Van der Waals-London attraction between the readily polarizable cations and anions, which explains the low solubility in water. However the silver halides are readily soluble in the more polarizable solvent liquid ammonia which forms donor bonds with the silver atoms.

It is also the large lattice energy which is responsible for the low solubility of the mainly ionic oxides (e.g. MgO 940 Kcal/mole, Al_2O_3 3618 Kcal/mole), sulphides (e.g. CuS, CdS), sulphates, phosphates, nitrides, etc. in water.

In high-temperature solutions, especially in those of oxides and oxide compounds in molten salts, the type of bonding is mainly ionic. For the case where both solvent and solute are ionic a separation (lowering the Coulomb attraction forces of the solute) and a solvation of the solute ions will occur. This solvation may be weak, irregular and constantly varying as in many aqueous solutions, and this case would correspond to the regular solution defined above. If the solvation action is strong, as in irregular solutions, there will be some additional short-range order, and relatively stable complexes or compounds may be formed.

The solvating or complexing action of an ionizing solvent involves electron or ion transfer processes. The acid-base concept of Lewis (1923) and the solvent-system concept of acids and bases developed by Gutmann and Lindquist (1954) enable us in simple cases to describe the above transfer processes. Lewis acids are defined as acceptors for electrons (or negative ions) and bases are electron donors. Gutmann and Lindquist distinguish cationtropic and aniontropic reactions depending on the charge of the transferred ion. In a cationtropic system an acid is a cation donor and a base a cation acceptor, whereas in an aniontropic system an acid acts as anion acceptor and the base as anion donor. For example, halide solvents are aniontropic favouring the transfer of fluoride or chloride ions. However, Payne (1965) raises the question of whether the terms "acid" and "base" are necessary for non-protonic solvents. Often there are uncertainties in the interpretation of the species present in the solution and so it is proposed to use the terms "acid" and "base" only with protonic solvents (e.g. in aqueous systems) and in such cases where there is a clear advantage.

The acid-base concept with respect to oxides and oxysalts has been discussed by Flood and Förland (1947) who apply the definition of Lux (1939)

 $base = acid + O^{2-}$

to a variety of reactions in high-temperature chemistry of oxides. The oxygen activity corresponds to the hydrogen activity of the classical protonic acid-base concept of Brönsted (1923, 1934). The acid-base relationship based on oxygen seems to be useful in glasses and in a discussion of high-temperature reactions and stabilities of oxides (Flood and Knapp, 1963). Thus the relative concentrations of the various silicate anions in the system PbO—SiO₂ could be estimated as a function of composition (Flood and Knapp), and phase diagrams could be calculated (Förland, 1955).

For oxide systems an earlier approach for finding relationships between properties and composition is that of the cationic field strengths (Weyl, 1932; Dietzel, 1942, 1948/1949). Compound formation, glass-forming and immiscible regions in phase diagrams, melting points and stabilities of oxide compounds, and other properties in oxide systems, especially silicate systems, were empirically related to the field strength, the attractive force $Z_c Z_0/a^2$ between cation and oxygen, with Z_c and Z_0 being the charges of the cation and oxygen, respectively, and *a* the distance between cation and oxygen. A revised form of the field-strength concept, the screening theory, and the acid-base relationships in aqueous solutions, fused salts and in glass systems was proposed by Weyl (1956) and Weyl and Marboe (1962). The field-strength concept was also used by Stoch (1968) to discuss the liquidus of oxide systems. He showed that the solubility of an oxide in a binary melt is approximately proportional to the difference in the reciprocals of the ionic potentials of the cations of the two components.

The higher the value of the field strength, the less ionic is the bonding. Thus the field strength is related to the ionicity of Pauling (1960) which is expressed in terms of the electronegativity differences χ_A and χ_B of cation and anion by $1 - \exp \left[-\frac{1}{4}(\chi_A - \chi_B)^2\right]$. According to the electrostatic valence rule of Pauling, the electrostatic bond strength of stable ionic compounds is defined as Z/C.N., where Z is the charge of the cation and C.N. is its coordination number. The concept of the electrostatic bond-strength has been widely applied to the study of ionic crystals in order to limit the number of possible structures and has been used, for example, by Block and Levin (1957) and by Levin (1970) to interpret immiscibility in oxide (glass) systems. Brown and Shannon (1973) reviewed recent bond-strength concepts and derived empirical bond-strength/bond-length curves for oxides.

These empirical or semi-empirical relationships are convenient for the experimentalist to get some idea of solute-solvent interactions in solutions, since exact theoretical treatments and thermodynamic data are normally missing. The initial approaches have been made in the application of crystal-field theory to ionic melts and of molecular orbital theory to

partially covalent fused systems. In addition, several experimental techniques such as ultraviolet and visible electronic spectroscopy, infrared and Raman spectroscopy, nuclear magnetic resonance and X-ray and neutron diffraction techniques have now been applied to obtain information on structural details of ion pairing and complexing and on association and dissociation in molten salts. An excellent compilation of recent approaches to the investigation of ionic solutions and melts has been given by Petrucci (1971). In addition Mamantov (1969) edited a book on experimental techniques for the investigation of molten salts.

Depending on the type of solute and solvent there are other forces between entities in the solutions in place of or in addition to the Coulomb forces between ions mentioned above. Large ions are polarized by small ions of high polarizing strength, thus deforming the electron shell of the former in such a way that electron pairs are formed (another way of describing the field-strength concept). The bond type is then partially covalent. In high-temperature solutions the forces between permanent dipoles (the origin of hydrogen bonding) and between permanent and induced dipoles (P. Debye) are not important. In non-ionic solutions, covalent bonds or the Van der Waals-London type of bonding between nonpolar molecules dominate. Metal and alloy solutions generally are mainly metallic with partially ionic character and many metallic solutions behave as regular solutions (Kleppa, 1958). Good agreement may be obtained between fairly simple theoretical models and experimental data, as shown in the case of solutions of the III-V semiconductors by Panish and Ilegems (1972).

3.4. Chemical Equilibria and Complexes in Solutions

The general principles of equilibria in solutions and the law of mass action, etc., which are applicable in principle also to high-temperature solutions, are treated in many textbooks on chemical thermodynamics and physical chemistry, and therefore will not be discussed here. The books of Garrels and Christ (1965), Smith (1963), Reisman (1970), Kubaschewski, Evans and Alcock (1967), Blander (1964), Petrucci (1971), Davies (1962), Nancollas (1966), Harned and Owen (1959), Friedman (1962), Darken and Gurry (1953), Lumsden (1966) and Mamantov (1969) deal especially with high-temperature solutions.

The principles of acid-base equilibria have been discussed in the previous section. In the following discussion on equilibria in solutions we shall merely discuss some selected topics in reaction and redox equilibria which are significant for crystal growth from high-temperature solutions. Complex formation in solutions needs a somewhat more detailed treatment because of its consequences in the crystal-growth processes. Further information on reaction and redox equilibria may be obtained from the many phase diagrams, of which the most important compilations are mentioned in Section 3.9.

3.4.1. Redox equilibria

Redox equilibria become important when oxides or other compounds of a lower valence state of the metal than that normally stable in air at the applied growth temperatures have to be grown. Examples discussed here are EuO and the other europium (II) chalcogenides, V_2O_3 , and the TiO_{2-x} phases. Such phases as well as complex compounds prepared from them often show interesting semiconducting or magneto-optic properties and occasionally other interesting effects such as metal-insulator transitions.

This type of compound, however, has generally been little explored, mainly because of the extreme difficulty encountered in the preparation of homogeneous crystals. This difficulty is encountered even for the cases where the "suboxides" have a relatively broad range of stability, as with EuO and V_2O_3 , but the difficulties are extreme for the suboxides in the systems Ti -O, Nb-O, and Ta-O. Bartholomew and White (1970) showed that Ti₃O₅ and the Magneli phases in the system Ti-O (see Fig. 3.3) can be grown from Na₂B₄O₇ $-B_2O_3$ fluxes under equilibrium conditions if the partial pressure of oxygen as well as the growth temperature are controlled within narrow limits.

Generally the oxygen partial pressure of the gas phase is achieved at the appropriate temperature by gas mixtures containing oxygen (for oxidizing conditions) and by H_2O-H_2 , CO_2-CO , and $CO-H_2$ mixtures according to Richardson and Jeffes (1948) as shown in Fig. 3.4. For sulphides the sulphur partial pressures of a variety of sulphides and the corresponding H_2S-S ratios as a function of temperature are shown in Fig. 3.5.

More recent thermodynamic data have been compiled by Kubaschewski, Evans and Alcock (1967), in the JANAF Thermo-chemical Tables, by Kelley (1961), by Reed (1972) (the latter with practical overlay charts for the various thermodynamic parameters—standard free energy, partial pressure, etc.), by Janz (1967) and by Mills (1974).

The characterization of the many possible phases, for example the determination of the exact stoichiometry, represents a major problem since the accuracy of chemical analytical methods is generally not sufficient to differentiate, for instance, between adjacent oxides in the Ti—O system and to determine the degree of solid solubility. An exact formula, however, can be derived from a careful X-ray structure determination, and later identification is then possible by comparison with the X-ray powder diagram taken with an instrument of good resolution (see Chapter 9).

If the compound (e.g. suboxide) forms a eutectic with its metal and has



FIG. 3.3. Stability regions of titanium oxides (Bartholomew and White, 1970).

only a limited solid solubility range then it may be grown from the excess metal. This method was used in the case of the europium chalcogenides (EuO, EuS, EuSe, EuTe) which were grown from excess europium by Eick *et al.* (1956), Shafer (1965) and by Reed and Fahey (1966). The stability range of EuO was estimated by McCarthy and White (1967) and recently the phase diagram of Eu—O was redetermined by Shafer *et al.* (1972), and is shown in Fig. 3.6.

On the other hand, however, low-melting oxides of a high valence state of the metal act as solvent for growth of the suboxide, as was demonstrated by the growth of VO₂ from V₂O₅ by Sasaki and Watanabe (1964) and by Sobon and Greene (1966). The phase diagram was obtained by Burdese (1957) and is shown in Fig. 3.7. In addition the epitaxial growth of CrO_2 from CrO_3 at high pressure was reported by DeVries (1966).

A special redox equilibrium has given problems to a number of crystal growers who required to grow chromium-doped compounds from leadcontaining fluxes in order to find candidates for replacement of the ruby



FIG. 3.4. Standard free energy of formation of metals oxides (Richardson and Jeffes, 1948; from Darken and Gurry, 1953).



FIG. 3.5. Standard free energy of formation of metal sulphides (Richardson and Jeffes, 1952; from Darken and Gurry, 1953).

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FIG. 3.6. Phase diagram of part of the Eu-O system (Shafer et al., 1972).



System V2O3-V2O5.

FIG. 3.7. Phase diagram of V2O5-V2O (Burdese, 1957).

laser (the only laser based on chromium transitions), and to grow rareearth orthochromites:

$$Cr_2O_3 + 1.5O_2 \xrightarrow[> \sim 1000^{\circ}C]{} 2CrO_3 (-5.3 \text{ Kcal}).$$

The oxidation of Cr^{3+} to Cr^{6+} in air in lead-containing solutions probably starts well above 1000°C as is evident from experiments to grow chromiumdoped Al₂O₃, GdAlO₃, MgAl₂O₄, ZnAl₂O₄, etc. by the slow-cooling technique: the centres of the larger crystals (grown between 1300° and about 1100°C) have the typical reddish ruby-colour of Cr^{3+} , whereas the outer region of the crystals (grown below 1050°C) and the small crystals (nucleated below 1050°C) are colourless—in other words, free from chromium.

In the determination of the system PbO-chromium oxide in air, Negas (1968) found the congruently melting (at 918°C) compound Pb_2CrO_5 , which gives a eutectic of 908°C with Cr_2O_3 and of 807° with Pb_5CrO_8 on the PbO-rich side. However, Fukunaga and Saito (1968) indicted that in the pure system Cr-O, CrO_2 is the only stable phase below approximately 300°C. This problem of the stability of six- or four-valent chromium at low temperatures has still to be clarified.

In this connection it should be mentioned that the preparation of the interesting (for magnetic recording) material CrO_2 is quite difficult since it seems to be stable only at low temperatures and since its solubility is very low at such temperatures due to its high lattice energy. Therefore the most promising method for such difficult compounds involves the use of high-pressure solutions (DeVries, 1966).

Six-valent chromium probably could not be incorporated into the above oxide compounds because of the difficulty of charge compensation. The reaction equilibrium and the formation of $PbCr_2O_7$ (Grodkiewicz and Nitti, 1966) are unlikely in view of the phase diagram mentioned above. In order to incorporate chromium homogeneously into crystals and to prepare chromium-containing compounds various methods have been proposed. Remeika (1956) proposed the use of Bi₂O₃ as solvent instead of lead-containing fluxes, and Grodkiewicz and Nitti (1966) proposed the solvent evaporation technique at high temperatures (for a detailed discussion of homogeneous doping, see Section 7.1.3).

The previously mentioned chromium oxide redox equilibrium, when modified for the case of alkali chromates according to Flood and Muan (1950):

$$2M_2Cr_2O_7 \rightleftharpoons 2M_2CrO_4 + Cr_2O_3$$
 (solid) + 1.5O₂

for M = Li, Na, K, and Tl could be used to grow Cr_2O_3 by slowly increasing

the temperature of a dichromate melt. The same principle of shifting the redox equilibrium has been used by McWhan and Remeika (1970) and by Foguel and Grajower (1971) in order to grow V_2O_3 crystals by reduction of V_2O_5 in the flux.

In several cases acid-base relationships influence the oxidation state of transition metals in such a way that an increase in concentration of a basic oxide favours a higher valence state of the transition metal ion. This was demonstrated, for example, for glass systems by Paul and Lahari (1966) and applied to growth of nickel ferrite (spinel) crystals from $BaO-B_2O_3$ fluxes by Smith and Elwell (1968): BaO-rich solutions produced $NiFe_2O_4$ crystals with less Fe^{2+} than B_2O_3 -rich fluxes. Redox equilibria in glasses have been discussed by Weyl (1951), Tress (1960, 1962), Holmquist (1966), Johnston (1966) and by Paul and Douglas (1966).

An important redox equilibrium is that of

 $2Fe^{3+} \rightleftharpoons Fe^{2+} + Fe^{4+}$

since it affects optical absorption and other properties of magnetic garnets of the type $R_3Fe_5O_{12}$. This equilibrium is shifted not only by the temperature but also by Ca and Si addition to the PbO— B_2O_3 solution. A model proposed by Nassau (1968) cannot explain all the experimental facts satisfactorily.

An appreciable number of redox equilibria have been studied in connection with phase-diagram determinations (see Section 3.8), and a classical paper on this topic has been published by Muan (1958) on the systems Fe—O, FeO—Fe₂O₃—SiO₂ and MgO—FeO—Fe₂O₃—SiO₂. The study of redox and other equilibria is one of the main fields of modern experimental and theoretical petrology, as discussed for example by Garrels and Christ (1965).

3.4.2. Reaction equilibria

Instead of a general discussion on phase equilibria and phase diagrams we wish to restrict the discussion to a few special groups of reactions, which are important for the experimentalist (and sometimes overlooked).

Temperature-dependent chemical reactions of the type (Barrer, 1949)

$$Al_2O_3 + 3CaF_2 \neq 3CaO + 2AlF_3$$

are worth mentioning since they can lead to an extreme loss by evaporation of the most volatile component (here AlF_3). A similar equilibrium was proposed by Morozewicz (1899):

$$SiO_2 + Na_2WO_4 \rightleftharpoons Na_2SiO_3 + WO_3$$

with WO₃ as the volatile compound. The shifting of the above equilibria

is obvious from the law of mass action and the principle of Le Chatelier. Other temperature-dependent equilibria are significant for the preparation of simple oxides or oxide compounds, respectively, for instance the reactions postulated by Grodkiewicz and Nitti (1966):

$$PbHfO_{3} \xrightarrow{1200^{\circ}C} PbO + HfO_{2}$$
$$PbTiO_{3} \xrightarrow{1200^{\circ}C} PbO + TiO_{2}.$$

These reactions suggest that HfO_2 and TiO_2 can be prepared from leadcontaining fluxes only by solvent evaporation above $1200^{\circ}C$, and $PbTiO_3$ and $PbHfO_3$ have to be grown at much lower temperatures.

These few examples of equilibria demonstrate their significance for crystal growth from high-temperature solutions, and the principles outlined in this chapter on solvents and solutions should be kept in mind when "inexplicable" results are obtained.

A special case of reaction equilibria in solutions is shown by the *reciprocal* salt systems. These are mixtures of salts containing at least two cations and two anions, which in the simplest case undergo the reciprocal reaction

$$AX + BY \rightleftharpoons AY + BX.$$

The thermodynamics of reciprocal systems, their deviation from ideal solution behaviour and its explanation, the reciprocal Coulomb effect, and some theoretical approaches with experimental evidence have been reviewed by Blander (1964) and Blander and Topol (1965). Several aspects of phase diagrams of reciprocal systems have been discussed by Ricci (1964).

Instead of losing reactants by evaporation, reactants can be transported to the system. As an example, for the growth of GaAs crystals or layers AsCl₃ is transported to the gallium solution. GaP is produced according to (Plaskett, 1969) $2Ga + 2PH_3 \rightarrow 2GaP + 3H_2$. This growth mechanism is similar to the VLS mechanism (Section 7.1.2.C) where crystal constituents are transported by vapour, enter the liquid solution in order to be transported to the growing (solid) crystal.

Another type of reaction involves reactive gases which decompose constituents of the solvent in order to form the required phase (Brixner and Babcock, 1968), for example,

$$BaCl_2 + 6Fe_2O_3 + H_2O \rightarrow BaFe_{12}O_{19} + 2HCl.$$

Further examples of reactions in high-temperature solutions are given in Section 7.1.2.C.

3.4.3. Complex formation in solutions

The solubility is increased by solvation and by complex formation in the solution as well as by other solute-solvent interactions. Complex formation and other forms of association generally result in maxima or minima when the following properties are measured and plotted *versus* composition: density, liquidus temperature, vapour pressure, viscosity, specific conductance, surface tension, etc. However, such maxima and minima are not necessarily indicative of complex formation and results must be interpreted with care. The deviation from the ideal solubility curve may indicate the degree of association as shown in Section 3.2. Valuable information on the coordination of many elements in molten salts or solutions is obtained by various other experimental and theoretical techniques as discussed by Petrucci (1971) and by Mamantov (1969).

Spectroscopic evidence for groups of ions of well-defined symmetry has often been established, especially of configurations of transition metal ions. Such spectroscopic studies are performed on a time scale orders of magnitude faster than the diffusion time. Therefore the observed local structure is often described as "configuration", "centre" or "group". The term "complex" or "species" should be used only for such groups which have a lifetime long with respect to the characteristic diffusion times. The lifetime is important with respect to the method of investigation, but also with respect to transport phenomena. The "holes" in liquids are small compared with the size of the species, and generally the quasilattice model gives a more realistic and preferable description of a liquid. Therefore, the motion of complexes as well as of other species is connected with a cooperative rearrangement in a volume (of the liquid) large compared to that of the complex. In the absence of applied fields this results in random diffusive displacements. However, the presence of an electric field in electrolysis, or of a concentration gradient ahead of the crystal growing from a supersaturated solution, imposes a directional bias so that large complexes can have an appreciable mobility. The presence of the field implies that the moving complex has to move against the stream of other particles (of opposite or neutral sign in electrolysis, of solvent in the case of solution growth) in such a way that no (large) holes are formed.

Vibrational spectroscopy, especially Raman spectra, can give more information on complexes in high-temperature solutions than electronic spectroscopy. However, the observed number and frequency of the Raman bands are dependent on the force constants, masses and geometrical arrangement of all the ions in the quasilattice of the solution. Only when the force constants of the complexes are large compared with those of the rest of the solution is it possible to relate the number of observed bands

by group theory to the symmetry of the complex in question. In several cases unambiguous information on the geometry of complexes has been obtained from vibrational spectra which in other cases are prone to misinterpretation.

In several solution systems which can be quenched as glasses, evidence on the type of complexes and on the coordination can be obtained from optical spectra of the glasses, as discussed by Berkes and White (1966), or by other techniques such as electron paramagnetic resonance or the Mössbauer effect.

However the difficulties of most of the above techniques increase at high temperatures and often make measurements impossible. Therefore little information on complex formation in high-temperature solutions is available for temperatures above 800°C which is a lower limit for most crystal growth. Reviews on complex ions in molten salts have been given by Van Artsdalen (1959), Blander (1964), Bloom (1967), in the review "Molten Salts as Solvents" by Bloom and Hastie (1965) and in the books of Mamantov (1969) and Petrucci (1971).

As an example of the dependence of viscosity on complex formation, Fig. 3.8 shows viscosity isotherms for the systems $KCl-MgCl_2$ (a) and NaF-AlF₃ (b). In both cases the complex formation as a precursor of compound formation (KMgCl₃, Na₃AlF₆) is indicated by singularities in the viscosity isotherms. Also the decreasing tendency of complex formation at higher temperatures is obvious from Fig. 3.8. Complex formation is to be expected frequently in molten compounds having a congruent melting



FIG. 3.8. Viscosity isotherms of (a) KCl-MgCl₂, (b) NaF-AlF₃ (Belyaev et al., 1964).

point as was shown above. Phase diagrams are therefore expected to give indications of complex formation in the melts in which, at least at not too high temperatures, the short-range order or the corresponding crystalline phase is preserved. Hence the many phase-diagram determinations play a major role in the study of complex formation. Cryoscopic measurements also indicate the degree of association as was demonstrated by a number of measurements by Rolin (1951) on the effect of a variety of oxides on the melting of cryolite (Na₃AlF₆). A review of cryoscopy and phase relations in dilute molten-salt solutions was given by Kozlowski (1970).

The formation of complexes in melts of congruently melting compounds increases significantly as the liquidus temperature is approached. This is proved by measurement of the specific conductance (Bloom, 1963). A mixture of PbCl₂ and NaCl shows the normal relation between specific conductance and temperature, i.e. an almost linear dependence on approaching the liquidus temperature to within a few degrees as shown in Fig. 3.9. The CdCl₂—KCl mixture (with the congruently melting compound KCdCl₃), however, shows a strong decrease of conductance at about 30–40° above the liquidus temperature, which may indicate a tendency to complex formation.



FIG. 3.9. Specific conductance near the crystallization front, which is indicated by the shaded line. (a) 50% NaCl + 50% PbCl₂ (molar), (b) 79.6% KCl + 20.4% CdCl₂ (Bloom, 1963).

Another factor favouring complex and compound formation is the difference between solute and solvent with regard to their acid-base character according to Lewis (1923, 1938). As an example, the difference in compound formation in molten-salt mixtures of AlCl₃ and of SbCl₃ is shown in Fig. 3.10 (Kendall *et al.*, 1923). In the little-reactive SbCl₃ the Cl as well as the Sb ions have a noble gas electron configuration, whereas in the case of AlCl₃ the aluminium is lacking two electrons from a noble gas electron configuration and therefore tends to react with other salts.

Molecules of high polarizability show a larger tendency to chemical combination and complex formation in the solution than those of low polarizability. This fact is well established from the phase diagrams of

• •	 3.9
:C2:	:C2:
•• ••	
Cl.Al	CLLALCL.K.
:Cl:	:C9:
• •	• •
:ci:	
.CR.Sb.	
C:	
••	

FIG. 3.10. Electron configuration of AlCl₃, SbCl₃ and of KAlCl₄.

lead chloride with the alkali halides which show an increasing degree of compound formation with increasing radius of the alkali ion. Thus PbCl₂—NaCl forms a simple eutectic, while in PbCl₂—KCl one congruently and one incongruently melting compound are formed, and in PbCl₂—RbCl three congruent compounds exist.

An interesting case of the utilization of complex formation was reported by Kunnmann *et al.* (1965) who described the crystallization of transition metal oxide compounds from sodium tungstate-sodium pyrotungstate solutions as will be discussed in Section 3.6.

Also discussed later (Section 3.6.2 and Chapter 7) will be the role of complex formation in determining not only the solubility but also the width of the metastable range. The effect of complex formation on mass transport and, through its effect on desolvation and interface kinetics, on

the stability of growth may also be appreciable. There are cases where complex formation is desirable in order to achieve a sufficient width of the metastable region in order to prevent multinucleation (as in growth of ZrO_2 , ThO_2 , $SrTiO_3$, TiO_2 , etc. from alkali fluoride fluxes). On the other hand, complex formation should be prevented in viscous solutions such as in borate fluxes.

The success of several complex solvent mixtures such as $PbO-PbF_2$ or $PbO-PbF_2-B_2O_3$ is due not only to their high dissolving power but also because these excellent solvent systems appear to show an optimum degree of complex formation and an optimum viscosity, therefore a sufficiently broad metastable region. On the other hand, the complexes formed are not stable enough to retard the interface kinetics.

Such statements are all qualitative. Further systematic experimental and theoretical work is necessary to find quantitative information on complex formation in solution and its effect on the crystal-growth processes. The role of complex formation ahead of the growing crystals and its influence on the habit is discussed in Section 3.6.3, in Chapter 5 and in Section 7.1.1.

3.5. High-temperature Solvents and Solutions

It is generally desirable that the aspects outlined in the first part of this chapter should be systematically applied to high-temperature solvents and solutions. Very little work has been done to date on the solubility of oxides in molten salts and on the structural interpretation of solutions of oxides (and chalcogenides generally) in molten salts. Other high-temperature solutions like metallic-ionic systems have also not been studied in detail. This may partially be attributed to the fact that the conditions (high temperatures, high volatility) are extremely unfavourable for experimental investigations. Another reason is that crystal growth from high-temperature solutions has become really active only in the past 15 years. Therefore it is no surprise that in most reviews and books on molten salts little (or no) attention has been given to solutions of oxides in molten salts. Crystal growers normally are unable to find the time for such basic investigations. However, information on such systems is urgently needed for the selection of the optimum solvents and growth conditions. What kind of interaction of solute and solvent is desirable for a high solubility, a reasonably broad metastable region and a small tendency to inclusion formation? This important question can only be answered by systematic studies of the structure and type of solution (deviation from ideality, degree of solvation) on a variety of molten salt-oxide systems and by comparison with crystalgrowth experiments.

Compilations of solvents used for crystal growth from high-temperature

solutions have been given by Laurent (1969), Wanklyn (1975) and in Chapters 2 and 10, and several aspects of HTS are discussed by Elwell (1975).

Fortunately, since about 1966 a new field of physico-chemical investigation has been directed towards ionic, covalent, and metallic melts at "high" temperatures. But the "high" temperatures of such investigations rarely reach 1000°C due to the principle of the method or to experimental difficulties, and so there is little direct relevance to crystal growth from high-temperature solutions which is mostly carried out above 1000°C. Nevertheless the results obtained in research on high-temperature melts are very valuable for crystal growers, and it would be of great interest to increase the research on high-temperature solutions to include systems of interest for crystal growth at temperatures above 1000°. There is a lack of basic information on high-temperature solutions, and a systematic investigation of such properties as density, expansion coefficient, viscosity, thermal and electrical conductivity, heat capacity and on structural properties (association, dissociation) needs to be carried out so that the data obtained can be correlated with crystal-growth phenomena. The few measurements which have been carried out will be discussed in Section 3.7.

3.6. Choice of Solvents

3.6.1. Properties of ideal high-temperature solvents

The wide variety of substances crystallized from high-temperature solutions make a generalized discussion of an ideal solvent difficult. The first indications of requirements for high-temperature solvents were given by Anikin (1958), and additional aspects have been listed in the several reviews on flux growth which were cited in Chapter 1. In the following we shall discuss the published criteria for the choice of solvents and add some of our own observations.

The main requirement of a solvent is that it will dissolve the solute to an appreciable amount, a practical minimum being of the order of one per cent. Generally one can say that crystal growth is facilitated by a high solute concentration if the required temperature is not too high and if the solution is not too viscous. A favourable viscosity of the solution is 1 centipoise to 1 poise, while the maximum practical viscosity would be about 10 poise. The solvent must not react with the solute to form solid compounds, or if it does, these compounds must not be stable in the crystallization temperature range of the phase required. Furthermore the range of solid solutions between solute and solvent should be as small as possible, and often it is the incorporation of solvent ions into the grown crystals which prevents the application of a particular solvent. The desirable properties of an ideal solvent are listed in Table 3.4.

THE THE TOPOLICO OF ALL THEORY COLUMN	TABLE	3.4.	Pro	perties	of an	Ideal	Sol	ver
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- 1. High solubility for the crystal constituents.
- 2. The crystal phase required should be the only stable solid phase.
- 3. Appreciable change of solubility with temperature.
- 4. Viscosity in the range of 1 to 10 centipoise.
- 5. Low melting point.
- 6. Low volatility at the highest applied temperature (except when the solvent evaporation technique is used).
- 7. Low reactivity with the container material (see Chapter 7).
- 8. Absence of elements which are incorporated into the crystal.
- 9. Ready availability in high purity at low cost.
- 10. Density appropriate for the mode of growth (see Chapter 7).
- 11. Ease of separation from the grown crystal by chemical or physical means (see Chapter 7).
- 12. Low tendency of the solvent to "creep" out of the crucible (see Chapter 7).
- 13. Low toxicity.

There is no solvent which fulfills all these ideal properties and a compromise is always necessary, depending on the type of the crystal and on the requirement of size and quality which makes some "ideal" property particularly important. The first three properties of Table 3.4 have to be fulfilled if a high yield of crystals is to be achieved by any of the normal techniques used to obtain supersaturation. A low viscosity is desirable to facilitate the achievement of a sufficiently homogeneous solution and of a fast stable growth rate as discussed in Chapter 6, so that crystal growth occurs uniformly at low supersaturation. A low melting point implies that crystal growth may occur at a convenient temperature in order to prevent destructive phase transitions, volatilization of solute or solvent constituents, and a high concentration of equilibrium defects. Often incongruent melting of the phase to be crystallized necessitates a low growth temperature. In addition, high temperatures are inconvenient with respect to furnace and power requirements. The other points will be discussed in the next sections except for the last "ideal" property, the low toxity, which is obviously desirable but very rarely fulfilled. For instance, the most popular solvents for oxides and oxide compounds contain lead and fluorine and are therefore very poisonous and most high-temperature solvent chemicals are poisonous to some extent. Therefore care must always be taken in handling chemicals, especially if they are in fine powder form, during the weighing and crucible-filling procedure. Poisonous vapours from the hot furnaces are also dangerous and may cause acute or chronic illnesses.

3.6.2. Crystal chemical aspects of choice of solvents

The various types of interaction between solute and solvent have been mentioned above (Sections 3.3 and 3.4). From the solubility point of view one would like to have a great chemical and crystal-chemical similarity between solute and solvent, but that generally favours mutual solid solubility. Therefore the optimum choice is a solvent which is chemically similar in the type of bonding to the solute, but crystal-chemical differences should exist in order to prevent solid solubility between solute and solvent. Most experience has been gained from flux growth of oxides which are therefore taken as examples for the discussion of many questions. Obvious crystal-chemical differences are established by differences in ionic size or in the stable valency states at the growth temperature. If these differences are large enough and if they are not compensated by solvent constituents

TABLE 3.5. Examples of Solvent-solute Pairs with Crystal-chemical Differences

Difference of Cationic and Anionic Radii	
CeO ₂ , ThO ₂ from Li ₂ WO ₄	
CoO, TiO ₂ from NaCl	
Difference of Cationic Radii	
MgO, MgAl ₂ O ₄ from PbF ₂ , Be ₃ Al ₂ Si ₃ O ₁₈ from Li ₂ MoO ₄ , Na ₂ MoO ₄ , etc.	
$Y_3Fe_5O_{12}$ from BaO.O.6B ₂ O ₃	
Al ₂ O ₃ from LaF ₃	
Difference of Anionic Radii	
BaTiO ₃ from BaCl ₂	
PbZrO ₃ from PbCl ₂	
BaWO ₄ from BaCl ₂	
CaO, CoO, CuO from NaCl	
Difference of Valency States of both Cation and Anion	
PbTiO ₃ , BaTiO ₃ from KF	
Al_2O_3 from PbF ₂	
Y ₄ Si ₃ O ₁₂ from KF	
TiO ₂ from Na ₃ AlF ₆ , NaCl	
Difference of Valency State of Cation	
VO_2 from V_2O_5	
ZrSiO ₄ from Li ₂ O-MoO ₃ , Na ₂ O-MoO ₃	
Al ₂ O ₃ from PbO	
Difference of Valency State of Anion	
Al ₂ O ₃ from LaF ₃ , PbF ₂	
MgAl ₂ O ₄ , MgO, TiO ₂ , MnO from PbF ₂	

BaTiO₃ from BaCl₂

or by impurities, little incorporation of solvent ions into the crystals grown can be expected.

Examples of crystal-chemical differences between solute and solvent ions are given in Table 3.5.

A clear correlation between crystal-chemical differences between solute and solvent and the concentration of incorporated impurity is not possible since most chemical analyses will be influenced by solvent inclusions due to unstable growth. Therefore only such analyses can be discussed which show low impurity concentrations, whereas high impurity concentrations of ions of different (from the solute) valence states indicate flux inclusions (not incorporation of flux ions into the crystal lattice) except for such cases where charge compensation is possible. As an example of the increase in impurity concentration in the presence of charge-compensating impurity, Barczak (1965) reported that the cosolubility of V₂O₅ and NiO in haematite, Fe₂O₃, was much higher than the separate solubilities of these compounds. Some examples of high impurity concentrations have been reported and these are plausible when the crystal-chemical differences are small. For example, it may be expected that rare-earth compounds grown from bismuth-containing fluxes, and niobates and tantalates grown from vanadate fluxes contain large amounts of bismuth and vanadium, respectively, as shown in Table 3.6.

Table 3.7 lists examples of low impurity contents of crystals grown from solvents which have large differences in ionic radii and/or valence state compared with the solute.

Care is necessary for those cases where either the solute or the solvent contains ions of variable valency state, especially the transition metal ions. Cations of V, Nb, Ta, Cr, Mo, W, Ti, Fe and the other iron-group elements and several rare-earth elements readily change their valency state and can therefore reduce or eliminate crystal-chemical differences between solute and solvent which arise from differences in the valency states (and ionic radii). In such cases unexpected incorporation of impurities (direct, or indirect through charge compensation) might occur and should be mini-

Crystal	Solvent	Impurity	Reference
GdAlO ₃	Bi ₂ O ₃ —B ₂ O ₃	5.5% Bi	Wanklyn (1969)
TbAlO ₃	Bi ₂ O ₃ -B ₂ O ₃	1.4% Bi	Wanklyn (1969)
TbNbO ₄	Bi ₂ O ₃ -V ₂ O ₅	2% V, 4% Bi	Garton et al. (1972)
GdVO,	Bi ₂ O ₃ -V ₂ O ₅	7% Bi	Garton et al. (1972)
Dy3Fe5O12	Bi ₂ O ₃ -V ₂ O ₅	20% Bi	Garton et al. (1972)

TABLE 3.6. Substitutional Bi³⁺ Concentration in Crystals Grown from Bi-containing Solvents

Crystal	Solvent	Impurity	Reference
LiFe,O,	РЬО	0.2% Pb	Folen (1960)
Al ₂ O ₃	PbF.	0.05% Pb	Giess (1964)
Al ₂ O ₃	PbO-PbF.	0.05-0.1% Pb	Chase and Osmer (1964)
NiO	PbF,	0.1% Pb	Hill and Wanklyn (1968)
B-Ga,Oa	PbO-PbF.	0.07-0.2% Pb	Katz and Roy (1966)
MgAl ₂ O ₄	PbF.	<10 ppm Pb	Cloete et al. (1969)
MgAl ₂ O ₄	PbF,	0.1% Pb	Wang and McFarlane (1968)
MgGa ₂ O ₄	PbO-PbF,	0.02% Pb	Giess (1962)
GdFeO ₃	PbO—PbF。	0.05% Pb	Wanklyn (1969)
Y ₃ Al ₅ O ₁₂	PbO-PbF ₂ -B ₂ O ₃	0.01% Pb	Van Uitert et al. (1965)
	with excess Al ₂ O ₃		
NpO ₂	PbF ₂ -B ₂ O ₂	0.02% B, 0.1% Pb	Finch and Clark (1970)
NpO ₂	Li2O-MoO3	10 ppm Mo	Finch and Clark (1970)
GdVO ₄	PbO-V ₂ O ₅	0.03% Pb	Garton et al. (1972)
ZnS	$Na_2S_X (X=2-5)$	35 ppm Na	Scheel (1974a)
CdS	$Na_2S_X (X = 2-5)$	30-50 ppm Na	Scheel (1973, 1974a)
FeS2	$Na_2S_X (X = 2-5)$	65 ppm Na	Scheel (1974a)
CdCr ₂ Se ₄	CdCl ₂ -PbCl ₂	< 50 ppm Pb	Kuse (1970)

TABLE 3.7. Impurity Concentration in Crystals Grown from Solvents with a Large Difference in Ionic Radii and/or Valence State

mized by proper control of the experimental conditions (temperature, oxygen partial pressure).

A few examples are given in Table 3.8 of high impurity concentrations in flux-grown crystals which could only be explained by:

- a. flux inclusions (which can be too small to be detected by the naked eye or which are difficult to detect in the opaque orthoferrites),
- b. unusual valence state of a cation (e.g. Fe⁴⁺, Pb⁴⁺),
- c. a high concentration of vacancies,
- d. a high concentration of charge-compensating impurities, or
- e. by a combination of these effects.

In case of HfO_2 a charge-compensated replacement of $Hf^{4+} + O^{2-}$ by $Bi^{3+} + F^-$ would be possible if the ionic radii of Hf^{4+} and Bi^{3+} were not too different. Such questions could be answered if complete impurity levels were determined and published. The possibility cannot be excluded that flux inclusions are responsible for some of the high impurity concentrations listed in Table 3.8. This is also indicated by the low lead incorporation (0.05% Pb) reported for GdFeO₃ grown from PbO—PbF₂ flux (see Table 3.7) compared to the 0.9\% Pb for the same compound listed in Table 3.8. It is questionable whether such a difference could be accounted for by different growth conditions. Remeika and Kometani (1968) suggested the com-

C	rystal	Solvent	Impurity	Reference
1. HfO,		BiF ₃ —B ₄ O ₃	5% Bi	Grodkiewicz and Nitti (1966)
2. Gd, 1	'iO ₅	PbO	4% Pb	Garton and Wanklyn (1968)
3. LaFe	O ₃	PbO-B ₂ O ₃	13% Pb	Remeika and Kometani (1968)
4. RFeC (R = 1) _a La—Lu)	PbO-B ₂ O ₃	0.08% to 13.4% Pb	Remeika and Kometani (1968)
5. GdFe	eO _a	PbO-B ₂ O ₃	0.9% Pb	Remeika and Kometani (1968)
6. Gd _{0.9}	Tm _{0.1} FeO ₃	PbO—PbF ₂ —B ₂ O ₃	0.72° o Pb	Giess et al. (1970)

TABLE 3.8. High Impurity Concentrations in Some Flux-grown Crystals

TABLE 3.9. Examples of Solvents Chosen for their Similarity with the Solute

Crystal	Solvent	Reference
1. Common cation	15	
and common and	ons:	
BaTiO ₃ , SrTiO ₃	TiO ₂	Belruss <i>et al.</i> (1971)
Ca ₅ (PO ₄) ₃ Cl	CaCl ₂	Prener (1967)
Pb ₃ MgNb ₂ O ₉	РЬО	Mylnikova and Bokov (1962)
Pb ₂ CoWO ₆	PbO—PbWO4	Bokov et al. (1965)
NaCrS ₂ , NaInS ₂	$Na_2S_X (X=2-5)$	Scheel (1974a)
KFeS ₂	$K_2S_x(X=2-6)$	Scheel (1974a)
ZnS	Ba_2ZnS_3	Malur (1966)
K(Nb, Ta)O ₃	K_2CO_3	for example: Wilcox and Fullmer (1966)
2. Common cation	15:	
ВаТіО _а	BaCl.	Blattner et al. (1947)
CdS	CdCl.	Bidnava et al. (1962)
FeS.	FeBr.	Wilke et al. (1967)
PbTiO,	PbCl.	Nomura and Sawada (1952)
PbZrO,	PbF	Iona et al. (1955)
CdCr ₂ Se ₄	CdCl ₂	Berger and Pinch (1967)
3. Common anion	s:	
CaWO ₄	Na ₂ WO ₄	Robertson and Cockayne (1966)
Oxides	PbO, Bi ₂ O ₃ , V ₂ O ₅ etc.	Many examples (see Chapter 10)
RVO,	Pb ₃ V ₃ O ₂	Feigelson (1968)
RPO	Pb.P.O.	Feigelson (1964)
RVO	V_2O_5	Brixner and Abramson (1965)

pensation of the Pb²⁺ incorporated into RFeO₃ by four-valent iron, whereas Lefever *et al.* (1961) proposed dendrite formation and trapping of flux.

If unusually high impurity concentrations are observed and if there is indication of the formation of solid solutions (for instance from the absence of inclusions) this should be checked by appropriate techniques (see Chapter 9) and in many cases an exact determination of the lattice constants clarifies the situation.

Another approach for the choice of good solvents is to look for those with anions or cations in common with the solute. The examples in Table 3.9 illustrate this possibility.

In many cases little solid solubility is to be expected (at not too high growth temperatures) when there are large differences in the type of bonding between solute and solvent. Normally this advantage has the great handicap of a low solubility, but in several cases this choice of solvent has been applied successfully as in the preparation of metals from ionic melts or in the crystallization of BaO using Ba as solvent (Sproull *et al.*, 1951; Libowitz, 1953).

In summarizing the choice of solvents by crystal-chemical principles it may be stated that, by a proper choice, impurity levels of less than 0.1%(often in the ppm range) can be achieved as long as stable growth (see Chapter 6) takes place and solvent inclusions are prevented, and high purity chemicals are used.

3.6.3. Additional criteria for choice of solvents

Several authors (J. W. Nielsen, E. A. D. White, and others) attributed the excellent solvent properties of PbO, PbF₂, Bi₂O₃, KF and BaO × $O.6B_2O_3$ to the high polarizability of the respective cations. But a number of excellent solvents are known which do not contain readily polarizable cations, for example Na₃AlF₆, LiF, Na₂B₄O₇, whereas several others show a medium degree of polarizability, such as the vanadates, molybdates and tungstates. One possibility seems to be that solute and solvent ions should not have too large a difference in their polarizabilities according to the similarity rule. On the other hand, large differences in polarizability, the solvent being readily polarizable (large ions) and the solute having a high polarizing strength (small ions), or *vice versa*, may have the effect of strong solvent-solute interactions and thus lead to higher solubilities unless stable compounds are formed (see Section 3.3).

Quite often the materials with good solvent properties are those which form compounds with the solute at lower temperature or in a different concentration range, or which can be considered as reciprocal salt systems (Scheel, 1974b). The relation between solute-solvent compound formation and solubility is analogous to the effect of hydration on solubility in water (see Section 3.3). Cases of this type are listed in Tables 3.10 and 3.11. In Table 3.10 only simple solute compounds are listed but the same arguments which hold, for instance, for Fe_2O_3 are also applicable to Fe_2O_3 -containing compounds ($R_3Fe_5O_{12}$, $M^{2+}Fe_2O_4$, RFeO₃, etc.). Complex solvents are excluded from the Table for simplicity. Table 3.10 shows that

Solute	Solvent	Compound	Melting point	Phase diagram ⁺
Solute	Solvent	Compound	Wiening point	I hase diagram
Al_2O_3	РЬО	PbAl₂O₄	980°C I	280
Fe ₂ O ₃	PbO	PbFe12O19	1315°C I	282
Cr_2O_3	PbO	Pb ₂ CrO ₅	918°C C	2134
TiO ₂	PbO	PbTiO ₃	1295°C C	2561
ZrO_2	PbO	PbZrO ₃	1570°C I	2330
$La_2O_3(R_2O_3)$	PbO	La ₂ Pb ₄ O ₇	1220°C C	2328
Al ₂ O ₃	B ₂ O ₃	Al ₄ B ₂ O ₉	1035°C I	2339
ZnO	B ₂ O ₃	Zn ₅ B ₄ O ₁₁	1045°C I	300
La_2O_3	B ₂ O ₃	La, B2O12	1386°C I	321
MgO	B ₂ O ₃	Mg ₃ B ₂ O ₆	1356°C C	261
Cr ₂ O ₃	V_2O_5	CrVO ₄	810°C I	333
Al_2O_3	V_2O_5	AlVO ₄	695°C I	320
NiO	V_2O_5	Ni ₃ V ₂ O ₈	1210°C I	279
ZnO	V_2O_5	Zn ₃ V ₂ O ₈	890°C C	2338
ZrO ₂	V ₂ O ₅	ZrV ₂ O ₇	750°C I	2405
Fe ₂ O ₃	Bi ₂ O ₃	Bi2Fe4O9	920°/960°C I	2358/2357

TABLE 3.10. Examples of Solute-solvent Pairs which Form Compounds (C = Congruent Melting, I = Incongruent Melting)

† Number of the phase diagram from the compilation of Levin et al. (1964, 1969).

TABLE 3.11. Examples of Solute-solvent Pairs which Tentatively can be Described as Reciprocal Systems

Solute	Solvent	Reaction
CuO (or CaO, CoO, NiO)	NaCl	$CuO + 2NaCl \rightleftharpoons CuCl_2 + Na_2O$
CaWO ₄	NaCl	$CaWO_4 + 2NaCl \rightleftharpoons CaCl_2 + Na_2WO_4$
BaSO4	NaCl	$BaSO_4 + 2NaCl \rightleftharpoons BaCl_2 + Na_2SO_4$
BaTiO ₃	KF	$BaTiO_3 + 2KF \rightleftharpoons BaF_2 + K_2TiO_3$
ZnS	PbCl ₂	$ZnS + PbCl_2 \rightleftharpoons ZnCl_2 + PbS$
Al ₂ O ₃	PbF ₂	$Al_2O_3 + 3PbF_2 \rightleftharpoons 2AlF_3 + 3PbO$
Y ₂ O ₃	PbF ₂	$Y_2O_3 + PbF_2 \rightleftharpoons 2YOF + PbO$
SrTiO ₃	PbF ₂	$SrTiO_3 + PbF_2 \rightleftharpoons SrF_2 + PbTiO_3$
Zn ₂ SiO ₄	Li2Mo2O7	$Zn_2SiO_4 + Li_2Mo_2O_7 \rightleftharpoons 2ZnMoO_4 + Li_2SiO_3$
CaSiO ₃	Na2WO4	$CaSiO_3 + Na_2WO_4 \rightleftharpoons CaWO_4 + Na_3SiO_3$
Y3Fe5O12	PbB ₄ O ₇	$12Y_{3}Fe_{5}O_{12} + 9PbB_{4}O_{7} \rightleftharpoons 36YBO_{3} + 5PbFe_{12}O_{19} + 4PbO_{10}O_{19} + 4PbO_{10}O_{1$
compound formation of solute-solvent pairs is very common, but a few exceptions are listed in Table 3.12.

Compound formation of a special type occurs in reciprocal salt systems in which equilibria of the type $AX + BY \rightleftharpoons AY + BX$ occur. The interactions in many solute-solvent systems can be formulated as reciprocal reactions, and supersaturation can be achieved by shifting the

Solute	Solvent	No. of phase diagram (Levin <i>et al.</i> , 1964, 1969)
BeO	WO ₃	2294
BeO	Li20.2.25MoO3	2425
ZnO	РЬО	2326
SiO ₂	V_2O_5	2401

TABLE 3.12. Examples of Solute-solvent Pairs which do not Form Compounds and which cannot be Described as Reciprocal

equilibrium in the required direction, for example by a change in temperature. Examples of such reciprocal crystal-growth systems are given in Table 3.11.

Aspects of the choice of solvents which have to be found out by experiment are the effects of the solvent on the width of the metastable region (prevention of uncontrolled nucleation) and on stable growth.

Complex solvent compositions have several advantages with respect to a low melting point and to lowering the vapour pressure of the most volatile solvent (or crystal) component. On the other hand, certain additions may lead to formation of undesired volatile compounds like SiF_4 , AlF_3 , etc.

Impurities in the solutions are generally undesirable since they may become incorporated in the crystal, or promote enhanced solvent ion incorporation by charge compensation, and frequently impurities cause deleterious growth. For example, Austerman (1965) reported that addition of 0.03 to 0.1 wt% SiO₂ to the lithium molybdate solvent caused a severe degradation of the perfection of the BeO crystals grown.

However, the addition of certain ions or compounds may sometimes have very favourable effects on growth or crystal habit and examples are listed by Wanklyn (1975). The most frequently used additive is B_2O_3 (1-5%) which is said to increase the width of the metastable region, to increase the solubility and to decrease the vapour pressure of the solvent, although high B_2O_3 additions are unfavourable due to an increase in the viscosity. In many cases, complex formation in front of the growing crystals is expected to be the reason for favourable growth. In the case of B_2O_3 , unstable complexes such as FeBO₃ and YBO₃ would be possible. Remeika (1970) reported a dramatic reduction in the number of crystals nucleated on adding 0.5-1% of V_2O_5 to PbO—PbF₂ solutions used for the growth of ferrites and garnets. Scheel (see Kjems *et al.*, 1973) observed a drastic increase in the size of inclusion-free LaAlO₃ crystals grown from PbO—PbF₂—B₂O₃ solvent when 0.7 wt% V₂O₅ was added to the flux, probably due to LaVO₄ complex formation. Other examples where complex formation by additives plays a favourable role are Al₂O₃ grown from Bi₂O₃—PbF₂ with the addition of La₂O₃(-LaAlO₃, Chase, 1967), Bi₄Ti₃O₁₂ grown from Bi₂O₃ with the addition of GeO₂ or MoO₃ (Epstein, 1970) and BeO grown from Li₂O—MoO₃ with the addition of LiPO₃ or LiBO₂ (Austerman, 1964).

The addition of monovalent ions is always advantageous when viscous fluxes like $Na_2B_4O_7$, $BaO \times 0.6B_2O_3$ and $PbO-B_2O_3$ are used because of the network-breaking action of alkali and halogen ions. As examples, LiF was reported by Anikin *et al.* (1965) and NaF by Baker *et al.* (1965) to be favourable for the growth of TiO₂ and ThO₂, respectively, from sodium borate flux. Similar arguments hold for the addition of Li or fluoride to very concentrated solutions.

The formation of large and high-quality crystals in nature from magmatic (especially from pegmatite) melts could not be understood without the presence of so-called "mineralizers" (Vogt, 1903/1904) like OH^- , F^- , Cl^- , CO_2 and SO_2 . Buerger (1948) has semiquantitatively described the role of such mineralizers which act by breaking Si—O—Si bridges in the silicate network of the mineral melts and thus increase the fluidity of the crystallizing magma. Both OH^- and F^- are most effective in doing this and, due to their small atomic weights, small weight fractions correspond to large atomic fraction and are thus very effective.

For several examples of the beneficial role of certain additives $(Al_2O_3 to Y_3Al_5O_{12}, CaO and SiO_2 to Y_3Fe_5O_{12})$ no good explanation has been found. A careful analysis of crystalline perfection by X-ray topography, of impurities and of microinclusions, of the habit, and of the surface morphology might help to find an explanation for the action of such additives.

3.7. Practical Solvents and their Properties

3.7.1. Solvents for growth of oxides, oxide compounds, silicates

Most of the common solvents like PbO, halides, borates, molybdates, tungstates and vanadates have been used for mineral synthesis in the last century (see Chapter 2). In the past twenty years many systems have been tried as high-temperature solvents, yet the few types of compound

Type of solvent	Solvent	Melting point °C	Boiling point °C	Density at 20°C	Viscosity (at °C, in cP)	Solubility of solvent	Examples of applications	Remarks
Lead-	РЬО	888°	1472°	9.53	Fig. 3.11	Hot HNO3-H2O	Perovskites, garnets, spinels	Corrodes Pt above 1300°C
and bismuth-	PbF ₂	855° (824°)	1293°	8.24	Fig. 3.11	Hot HNO ₃ —H ₂ O	Al_2O_3 , MgO, ZnO, MgAl_2O ₄	Corrodes Pt above 1300°C
compounds	PbCl.	498°	954°	5.8	Fig. 3.11	Hot H.O or acid	PhZrO, PhTiO,	Corrodes Pt
compoundo	PbO-Pb	$F_{\circ} \sim 500^{\circ} Eu$	it.	~9	Fig. 3.11	Hot HNOH.O	Garnets, perovskites, spinels	Corrodes Pt above 1300°C
	PbB.O.	\sim 500°		5.6	Fig. 3.11	Hot HNO,-H.O	Al.O., Fe.O., BeO. YIG. PbTiO.	Corrodes Pt above 1300°C
	Pb.P.O.	824°		5.8		Hot HNO,-H.O	RPO4, Fe.O3, MgFe.O4	
	Pb,V,O,	720°		~6		Hot HNO3-H2O	RVO4, TiO2, Fe2O3, Ga2O3	
	Bi ₂ O ₃	820°	1890° dec.	8.9		Hot HNO3-HO	Bi, Ti,O,,, Bi,Fe,O,, Fe,O3	Relatively corrosive for Pt
	Bi ₂ O ₃ -B	2O3 620-720) °			Hot HNO3-H2O	Fe ₂ O ₃ , FeBO ₃ , GaFeO ₃	Relatively corrosive for Pt
	BiF ₃	727°	1027°	5.32		Hot HNO ₃ —H ₂ O	HfO ₂ , MnCr ₂ O ₄	Relatively very volatile
Borates	B ₂ O ₃	\sim 460°	1860°	2.46	Fig. 3.11	Hot H₂O	LiFeO3, LiFe5O8	
	NaBO ₂	966°	1434°	2.464	-	H ₂ O	CdTiO ₃	
	Na2B4O7	741°	1575° dec.	2.367	Fig. 3.11	H ₂ O, hot H ₂ O- acid	BeO, Al ₂ O ₃ , Fe ₂ O ₃ , TiO ₂	
	KBO ₂	950°				$H_{2}O$	RFeO ₃ , CdTiO ₃	
	$K_2B_4O_7$	815°		1.74		H ₂ O, hot H ₂ O- acid	Cr_2O_3 , Fe_2O_3 , TiO_2	
	BaB4O7	910°			Fig. 3.11	Hot HNO3-H2O		
	BaB ₂ O ₄	1105°				Hot HNO3-H2O	YIG, YAG, RFeO ₃ , BaTiO ₃	
	Ba2B2O5	~ 915° Eut.				Hot HNO ₃ -H ₂ O	$YIG, Ba_2Zn_2Fe_{12}O_{22}$	
	LiBO ₂	845°		1.4		Hot HNO3-H2O		Slightly soluble in hot H ₂ O
	Li ₂ B ₄ O ₇	930°				Hot HNO ₃ —H ₂ O	Cr_2O_3 , Fe_2O_3	Slightly soluble in hot H ₂ O
Vanadates,	V ₂ O ₅	690°	1750° dec.	3.36		Acids, alkali	VO ₂ , V ₂ O ₃ , RVO ₄	
molybdates,	LiVO ₃	616°						
tungstates	NaVO ₃	630°				H ₂ O, hot acid	YVO4, (Y, Eu) VO4	
1.1	MoO ₃	795°	1151° subl.	4.69		Acid		
	Li2MoO4	705°		2.66	Fig. 3.11	Hot alkali	ZrSiO ₄ , Zn ₂ SiO ₄ , TiO ₂	
	Li2Mo2O	600°			Fig. 3.11	Hot alkali	BeO, TiO ₂ , ZrSiO ₄	

TABLE 3.13. Properties of Solvents used for Growth of Oxides and	Oxide Compounds
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Vanadates, molybdates, tungstates (cont.)	Na2M0O4 Na2M02O7 K2M02O7 Li2WO4 Li2W2O7 Na2WO4	687° 612° 500° 742° 720° 698°		3.28 3.71 4.18	Fig. 3.11 Fig. 3.11 Fig. 3.11 Fig. 3.11 Fig. 3.11 Fig. 3.11	H ₂ O Hot acid Hot alkali Hot alkali Hot alkali H ₂ O	TiO ₂ , Be ₂ SiO ₄ , ZrSiO ₄ SrMoO ₄ , NiFe ₂ O ₄ TiO ₂ CeO ₂ , ThO ₂ , TiO ₂ LiR (WO ₄) ₂ , ThO ₂ Al ₂ O ₃ , SiO ₂ , Fe ₂ O ₃	
	$\mathrm{Na_2W_2O_7}\ \mathrm{K_2W_2O_7}$	730° 650°			Fig. 3.11 Fig. 3.11	Hot alkali	(Ca, Sr, Ba, Cd etc.) WO ₄	
Sulphates, phosphates, hydroxides	Na2SO4 Zn3(PO4)2 NaOH KOH	884° 900° 318° 360°	1390° 1320°	2.68 4.0 2.13 2.0	Fig. 3.11 450:1.7, 600:0.8	H_2O acid H_2O H_2O	NiO: Li (Zn, Sb) ₃ O ₄ α-Ga ₂ O ₃ (high pressure) KNbO ₃	
Halides	LiF LiCl NaF NaCl KF KCl CaCl ₂ SrCl ₂	842° 610° 988° 801° 856° 772° 782° 873°	1676° 1382° 1695° 1413° 1502° 1407° 1627° 1250°	2.64 2.1 2.56 2.2 2.5 1.9 2.2 3.05	650:1.6, 850:0.7 Fig. 3.11 800:1.1, 900:0.9 800:4.25, 850:3.65	$\begin{array}{c} HF-H_{2}O\\ H_{2}O\\ H_{2}O, HF-H_{2}O\\ H_{2}O, HF-H_{2}O\\ H_{2}O, HF-H_{2}O\\ H_{2}O\\ H_{2}O\\ H_{2}O\\ H_{2}O\\ H_{2}O\end{array}$	LiFePO ₄ , LiNiPO ₄ BaTiO ₃ , Cd ₂ Nb ₂ O ₇ TiO ₂ , CaWO ₄ , BaSO ₄ BaTiO ₃ , KNbO ₃ , CeO ₂ KNbO ₃ Ca ₅ (PO ₄) ₃ Cl, Ca ₂ Nb ₂ O ₇ Sr ₂ NiWO ₆ , SrSnO ₃	Also soluble in methanol Soluble in glycerine Soluble in methanol
	BaF ₂ BaCl ₂ ZnF ₂ CdCl ₂ LaF ₃ LaCl ₃ Na ₃ AlF ₆	1280° 1354° 962° 872° 568° 1493° 860° 1000°	2137° 1560° 1502° 960° 1862°	4.9 3.9 4.9 4.05 5.94 3.84 2.9	Fig. 3.11 Fig. 3.11 Fig. 3.11	Hot acid H ₂ O Hot H ₂ O or acids H ₂ O Hot acid H ₂ O Hot acid (slightly)	MgAl ₂ O ₄ , BaFe ₁₂ O ₁₉ BaTiO ₃ , BaWO ₄ , BaTi ₃ O ₇ Al ₂ O ₃ LaOCl Al ₂ O ₃ , TiO ₂ , WO ₃	Slightly soluble in methanol

commonly utilized have remained the same and can be classified as follows:

- a. Lead and bismuth compounds.
- b. Borates.
- c. Vanadates, molybdates and tungstates, particularly of the alkali metals.
- d. Alkali halides, carbonates, etc.

This classification is not exact and rarely used solvents are not included; many solvent systems are combinations of two categories, for example, PbO— B_2O_3 , PbO— V_2O_5 , etc. We now consider some examples in detail since their use illustrates the factors influencing the choice of a solvent. The important properties of these fluxes are listed in Table 3.13. The literature data of the examples given in Table 3.13 and further applications



FIG. 3.11(a). Viscosity of high-temperature solvents: (a) low viscosity solvents. (b) high viscosity solvents, (c) alkali molybdates and tungstates.





Composition (mole%)

FIG. 3.12. Viscosity isotherms for Na₃AlF₆/Al₂O₃ solutions (Belyaev et al., 1964).

of the common as well as of unusual solvents may be obtained from the Tables in Chapters 2 and 10. The viscosities are given in Figs 3.11(a) and 3.11(b) for solvents of low and high viscosities, respectively, and in Fig. 3.11(c) for alkali molybdates and tungstates. The viscosities of the solutions are quite different and generally higher, as is shown with the example cryolite-Al₂O₃ in Fig. 3.12. Cobb and Wallis (1967) determined the viscosity of a solution of 20 mole % Al₂O₃ in LaF₃ to vary between 10.6 cp at 1360°C and 9.3 cp at 1500°C, while Bruton and White (1973) measured the viscosity of an 8 mole % PbTa₂O₆ solution in Pb₂V₂O₇ solution as about 2 cp at 1200°C. Tolksdorf *et al.* (1972) reported that the viscosity of a solution of 5.91 wt% Fe₂O₃ + 0.70 wt% R₂O₃ in 91.37 PbO + 2.02B₂O₃ (wt%) varies from 83 cp at 900°C to 63 cp at 1100°C.

Lead Oxide PbO

Lead oxide was already used as a solvent in 1877 by Fremy and Feil and was rediscovered by Remeika (1956) and applied to the growth of crystals of ferrites and several other compounds. It is still widely used mainly as a constituent of a binary or ternary flux composition, and such lead-based fluxes have been the most widely used of all fluxes. The high solubility of refractory oxides in lead-containing melts is attributed to the strong polarizability of the Pb²⁺ ions, and dissolution is presumably effected by the formation of complex ionic species between solute and solvent. The ionic nature of molten PbO is indicated by its high electrical conductivity, which has a value of about 1 Ω cm at its melting point (McKenzie, 1962).

Disadvantages of PbO are its toxicity, its tendency to attack platinum under reducing conditions or at temperatures above 1300° and, for certain techniques, its high volatility. Lead-based solvents are not practical for compounds containing large divalent cations (Ca²⁺, Sr²⁺, Ba²⁺) since solid solutions will be formed.

Lead Fluoride PbF₂

Lead fluoride has a lower melting point and generally a higher solvent power than PbO. Some high-quality crystals have been grown from PbF₂ solution by the evaporation technique [for example, Al_2O_3 : Cr by White and Brightwell (1965) and MgAl₂O₄ by Wood and White (1968), Robertson and Taylor (1968), Wang and McFarlane (1968)]. The high vapour pressure of PbF₂, useful in the evaporation technique, has severe disadvantages in crystal growth by slow cooling since it causes uncontrolled supersaturation if the crucibles are not completely sealed. Therefore in the latter technique, cobinations of PbF₂ with oxides to decrease the volatility are often used.

PbO-PbF2

The solvent system $PbO-PbF_2$ offers improvements over the individual components due to its low eutectic temperature (at around 500°C). Nielsen (1960) found that better-quality crystals of yttrium iron garnet were formed from this system than from PbO alone, and attributed this improvement to the lower melting point and viscosity. However, other factors such as complex formation (for instance of YOF) as discussed in Section 3.4 might also contribute to the improved growth.

The lower viscosity of mixed PbO—PbF₂ melts compared to the components has been confirmed by Oliver (1965). The viscosity data for PbO, PbF₂, PbO—PbF₂-mixtures and for Pb(BO₂)₂ are included in Figs 3.11(a) and (b). These data may not be very accurate but they do give some idea of the viscosities of these popular solvent systems. The viscosities of solutions of oxides in these solvents will generally be much higher than those of the solvents, but few viscosity determinations of saturated hightemperature solutions have been published. Such measurements are necessary for a full understanding of the hydrodynamics in the solutions

and of the growth mechanism. Evaporation losses from this mixed system are mainly of PbF₂. This causes a change in the PbO—PbF₂ ratio (and therefore in the solute-PbO and solute-PbF₂ ratios) so that frequently inhomogeneities may occur in the crystals grown. As was shown by Nielsen *et al.* (1967) the preferred evaporation of PbF₂ is especially harmful for the growth of $Y_3Fe_5O_{12}$ — $Y_3Ga_5O_{12}$ and relatively homogeneous solid solutions can be prepared if the PbF₂ evaporation is suppressed by sealing the crucibles.

PbO-PbF₂-B₂O₃

As discussed previously (Sections 3.4.3 and 3.6.3) the addition of relatively small amounts of B_2O_3 to PbO—PbF₂ generally improves the quality of the crystals grown and decreases the tendency to uncontrolled nucleation, probably by increasing the width of the metastable region and by complex formation in front of the growing crystal. Also B_2O_3 is thought to decrease the volatility of the PbF₂ in the solution. The effect of small additions of B_2O_3 on the viscosity of PbO—PbF₂ and of solutions (including 15–30% solute) is complex (Coe and Elwell, 1974).

This complex solvent system has been used for growth of a large variety of oxides and oxide compounds.

PbO-B₂O₃

Fluxes in this system are clearly worthy of investigation since they combine the advantages of borate and of lead-containing solvents. There are four compounds of low melting point in this system (Levin *et al.*, 1964, Fig. 281) of which PbB₄O₇ has the highest melting point of 768°C. On the B₂O₃-rich side a large liquid immiscibility region exists up to 800°C. PbO—B₂O₃ might be used for seeded growth (for example, top-seeded solution growth) and for the working temperature a compromise has to be found between the high viscosity at low temperatures (below 1000°) and the high volatility at high temperatures (above 1200°). Linares (1962a) demonstrated that the crystallization field of Y₃Al₅O₁₂ is extended appreciably with increasing B₂O₃ concentration (relative to the stability fields of Al₂O₃ and YAlO₃). Schieber (1967) proposed PbO—B₂O₃ as a fluorine-free solvent for rareearth garnets, and for several magnetic rare-earth garnets of the type R₃Fe₅O₁₂, the optimum mole ratio of Fe₂O₃: B₂O₃ was said to be 3:1.

Pb₂P₂O₇, PbO—As₂O₃, PbO—V₂O₅

 $Pb_2P_2O_7$ was proposed as a solvent by Wickham (1962) since its volatility is less than that of PbO or PbF₂. It is particularly useful for the growth of phosphate crystals but has quite a high solubility for Fe₂O₃ and was used to grow ferrite crystals. Accordingly, lead arsenates and lead vanadates are useful solvents for growth of rare-earth arsenates and vanadates, respectively. However, other rare-earth compounds cannot be grown from solvents rich in P_2O_5 , As_2O_3 or V_2O_5 because of the stability of the corresponding rare-earth compounds. For growth of TiO₂ the solvent PbO— V_2O_5 was used by Belyaev and Chodakov (1952), and Linares (1967) used this flux successfully for growth of emeralds. PbO— V_2O_5 fluxes are found to have a very low volatility and have been used to grow a wide range of crystals. One special advantage of this solvent is that V⁵⁺ prevents reduction of the PbO to metallic lead by its reduction to V⁴⁺ or V³⁺ (Wanklyn, 1970).

Bi₂O₃-based Solvents

In many respects bismuth compounds show similarity to lead compounds with respect to solvent properties although solubilities in the bismuth compounds are generally lower. One reason that Bi₂O₃-based solvents have not found so much use as the PbO fluxes is the valence state of Bi³⁺: it cannot be used for the many cases where compounds containing large trivalent cations have to be grown, such as the rare-carth compounds. Other disadvantages of Bi₂O₃-based fluxes are their relatively high viscosity and corrosiveness. As proposed by Remeika (1956) PbO should be replaced when Cr^{3+} -containing compounds or chromium-doped crystals have to be grown by the slow-cooling technique. Of the many Bi-containing compounds, Bi₂O₃ fluxes are an obvious choice. The addition of Bi₂O₃ to BaO-B2O3 fluxes (see "BaO-B2O3") can produce a marked decrease in the liquidus temperature (down to $\sim 600^{\circ}$ compared to approximately 900° for the BaO-B2O3 eutectics) and compositions around the eutectic composition 23.4% BaO: 62.4% Bi2O3: 14.2% B2O3 have been found to be preferable to BaO-B2O3 solvents for the growth of spinel ferrites (Elwell et al., 1972). This nonvolatile system can be used with advantage for seeded growth, for instance, by the top-seeded solution-growth technique.

Alkali Borates

 B_2O_3 is not suitable as a solvent due to its high viscosity (see Fig. 3.11b). The viscosity is greatly lowered when the glassy network is broken up by the addition of monovalent metal ions such as alkali ions, and the alkaline earth ions decrease the viscosity of B_2O_3 to a lesser degree. The alkali borates and especially molten borax, $Na_2B_4O_7$, have been well known as fluxes for over a century and have found applications in various fields.

An investigation of the solvent behaviour of the alkali borates was undertaken by Berkes and White (1969a). Accurate liquidus curves were determined and the departures from ideality were attributed to clustering of the boron and oxygen atoms. This model led to the conclusion that, in

 $Na_2B_4O_7$, for example, $8.5B_2O_3$ units formed the average-sized cluster at 820°C, decreasing to $2B_2O_3$ units at 1120°C. A similar tendency was exhibited by the $K_2B_4O_7$ and $Rb_2B_4O_7$ solvents. The B_2O_3 clusters exclude the Ni²⁺ ions which are weakly bonded in large interstitial sites in the boron-oxygen network. The weak interaction of Ni²⁺ was confirmed by optical spectroscopy of the borate liquids after quenching to glasses. The crystal-field splitting of the Ni²⁺ ions was found to be small, and to decrease as the atomic weight of the alkali increases.

Solutions in $Na_2B_4O_7$, $K_2B_4O_7$ and $Rb_2B_4O_7$ of NiO show a positive departure from ideality and therefore a tendency to immiscibility. In the system $Li_2B_4O_7$ —NiO a negative departure from ideality was observed, that is, the solubility of NiO was remarkably greater than that of an ideal solution and therefore indicates compound (complex) formation.

Although NiO has not been grown as good-quality crystals from alkali borates, similar materials such as Fe_2O_3 have been grown by Barks and Roy (1967). Berkes and White conclude that a good high-temperature solvent is one in which the solute does not form a tightly bound complex with the solvent but is excluded by clusters or complexes formed by the solvent atoms. However, we feel that this is not a generally valid rule, on the contrary it was proposed in Sections 3.4.3 and 3.6.3 that complex formation in the solutions and in front of the growing crystals generally has a beneficial effect. The conclusion of Berkes and White holds for the case where the solvent or the solution has a high viscosity.

Sodium tetraborate has been used as a solvent for the growth of a wide variety of crystals and it is a useful solvent for the rapid growth of small crystals. However, larger high-quality crystals have not been grown from this flux which is very viscous and volatile.

Potassium borate KBO₂ with a melting point of 950° C was used by Marezio *et al.* (1970) for growth of small crystals of RFeO₃ and by Sholokhovich *et al.* (1970) for CdTiO₃, CdTiO₃—SrTiO₃ solid solutions and for PbTiO₃, but probably KBO₂ is not the best solvent for growth of large crystals due to its high viscosity.

BaO-B₂O₃

The use of barium borate fluxes was advocated by Linares (1962a) who used this system to grow several iron-containing oxides as well as CeO_2 , TiO_2 , ZnO and a variety of other oxides. The advantages of $BaO-B_2O_3$ fluxes are a very low volatility, low rate of attack on platinum crucibles and low density compared with the lead fluxes. The latter property means that crystals tend to grow at the base of the crucible rather than the surface (in an appropriate temperature gradient), where excessive nucleation may result from foreign bodies or evaporation. The viscosity of these fluxes is high and spontaneous nucleation often yields a large number of tiny crystals. Barium borates are of particular value for seeded-growth methods in which the crystal grows just below the surface of a solution in an open crucible. The typical composition range used is from $BaO \times 0.5B_2O_3$ to $BaO \times 0.6B_2O_3$.

The low volatility permits the use of these fluxes at temperatures higher than those normally used, and a considerable reduction in viscosity might be achieved by growth at $1400^{\circ}-1500^{\circ}$ C provided that this is not compensated by the increase in solute concentration. Lowering of the viscosity may also be achieved by addition of Bi₂O₃ as discussed earlier, or of BaF₂ (Burmeister, 1972), and the ternary BaO—BaF₂—B₂O₃ has been proposed as a solvent for rare-earth garnets and orthoferrites by Hiskes *et al.* (1972) and its properties are discussed by Elwell *et al.* (1974) and Hiskes (1975).

Vanadates, Molybdates, Tungstates

The oxides V₂O₅, MoO₃ and WO₃ have all been used as fluxes but are very volatile. Therefore the alkali vanadates, molybdates and tungstates are generally preferred and a wide variety of crystals has been prepared from them. In particular, many silicates and germanates are preferably grown from these solvents. A well known example is emerald which was grown from lithium molybdate and lithium vanadate as early as 1888, and in the recent commercial production by various companies of emerald (for gem purposes) this group of solvents has been used with success. The high valence state of vanadium, molybdenum and tungsten prevents significant incorporation into most compounds, although the easy reducibility of these three ions might cause problems in certain cases. For growth of vanadates, molybdates and tungstates the corresponding solvents are obviously well suited as solvents containing the same anions and as can be seen from the Tables of Chapter 2 and Chapter 10. Many properties of the alkali molybdates and tungstates have recently been published by Gossink (1971), and the viscosity data from this work are given in Fig. 3.11(c).

A systematic study of the alkali vanadates, molybdates and tungstates for the growth of BeO was carried out by Newkirk and Smith (1965). The solubility is highest for the lithium compounds, and the solubility in the Li_2O-MoO_3 system increases regularly with the MoO_3 concentration. Dissolution was considered to be due to the formation of $(BeO)_X(MoO_3)_T$ complexes. This complexity is indicated, for example, by the observation of crystal growth at 1400°C, which is above the melting point of pure MoO_3 . For a given alkali metal, the solubility increases in the order $V \rightarrow Mo \rightarrow W$. However, the usefulness of the alkali-vanadate fluxes for growth of BeO is obviated by a very strong tendency to creep.

Kunnmann et al. (1965) described the solvent action of the sodium-

tungstate fluxes in terms of Lewis acid-base theory. The Lewis acid WO_3 (an electron pair acceptor) dissolves the basic oxides which form the crystal, and crystallization could be promoted by the addition of the Lewis base Na_2WO_4 (electron donor). The dissolution and growth of a metal oxide MO in sodium pyrotungstate can be represented by the equation

$$x$$
MO + y Na₂W₂O₇ $\xrightarrow{\text{heating}}_{\text{cooling}}$ x (MO × n WO₃) + ($y - nx$)Na₂W₂O₇ + nx Na₂WO₄.

The MO × nWO₃ complex must be stable only in the liquid phase so that the oxide is crystallized on cooling. The principles proposed have been verified by the application of these fluxes to grow a range of vanadium spinels such as Co_{1+δ}V_{2-δ}O₂ by an electrolytic method (Rogers *et al.*, 1966).

The system $K_2O - V_2O_5$ has been studied by Holtzberg *et al.* (1956) and according to Shannon (private communication) the low-melting KVO₃ (mp 520°C) is a suitable flux not only for many vanadates but also for other compounds.

Miscellaneous Solvents for Growth of Oxides

Of the alkali halides only the fluorides dissolve an appreciable amount of oxides whereas, for instance, NaCl dissolves generally less than 1% oxide at 1000°C, at which temperature it already has a relatively high vapour pressure. Occasionally, small crystals of oxide compounds have been prepared from NaCl.

The most popular alkali halides are KF and Na₃AlF₆. The latter, cryolite, has been used for a long time as a flux, and because of its technological importance its properties as a solvent have been studied in some detail. The solubilities of oxides at 1000°C in cryolite after Belyaev et al. (1964) are given in Table 3.14 and show interesting regularities. The solubility of the alkaline earth oxides increases from BeO to BaO according to the increasing degree of ionicity, and the low solubility of the transition metal oxides may be attributed to their partial covalent character. B₂O₃ and WO₃ are exceptions probably due to some form of complex formation. In Table 3.14 the solubilities of the oxides in a cryolite melt containing 5% Al₂O₃ are also given because they indicate the decrease in the oxide solubilities. Potassium fluoride KF, known as solvent already in the last century, was reintroduced by Remeika (1954) for the growth of the first large BaTiO₃ "butterfly" crystals and since then it has often been used (occasionally in combination with other halides) for the growth of titanate perovskites, and also for several other compounds. KF is volatile at high temperatures and has a very low viscosity. Generally, small crystals are obtained from KF-based fluxes due to uncontrolled spontaneous nucleation.

LaF₃ has been investigated systematically by Cobb and Wallis (1967)

Oxide	Solubility in Na3AlF6	Solubility in Na ₃ AlF ₆ + 5% Al ₂ O ₃
B ₂ O ₃	x	ø
WO ₃	87.72	86.14
BaO	35.75	22.34
Al ₂ O ₃	19.77	
CaO	13.12	8.46
MgO	11.65	7.02
BeO	8.95	6.43
SiO.	8.82	
TiO,	4.87	4.15
Mn ₃ O ₄	2.19	1.22
CuO	1.13	0.68
CdO	0.98	0.26
V ₂ O ₅	0.05	0.21
ZnO	0.51	0.004
NiO	0.32	0.180
Co ₃ O ₄	0.24	0.140
Fe ₂ O ₃	0.18	0.003
Cr ₂ O ₃	0.13	0.050
SnO.	0.08	0.010

TABLE 3.14. Solubilities of Oxides in Molten Cryolite and Cryolite Containing 5% Al₂O₃ at 1000°C (mole %)

as a potential solvent for the preparation of homogeneous ruby-laser crystals, but it seems that LaF_3 has not found a wider application since it needs a protective atmosphere.

The alkali carbonates have been successfully used for the growth of the corresponding niobates, tantalates and solid solutions of potassium tantalate-niobate (KTN), sometimes by the top-seeded solution-growth technique. With this technique (for which solvents of low volatility are a necessity) large $SrTiO_3$ and $BaTiO_3$ crystals were grown from excess TiO_2 , and excess GeO_2 was used as solvent for seeded growth of complex germanates (Belruss *et al.*, 1971).

Only the most popular and useful fluxes for the growth of oxides have been mentioned. Other solvents might be found in the Table (Chapter 10), from Laurent (1969), Wanklyn (1975) or, of course, by reasoning according to the criteria for the choice of solvents described in Section 3.6. Other solvents might be chosen with the help of phase diagrams, of which for the oxide field the most complete compilation is that of Levin *et al.* (1964, 1969) and for the field of metals and semiconductors those of Hansen and Anderko (1958), Elliott (1965) and Shunk (1969).

3.7.2. Solvents for growth of metals, alloys, semiconductors

Molten salts are not only common solvents for ionic compounds like many oxides but can also act as solvents for metals. In particular, the solubility behaviour of metal halides has been investigated, especially for their parent metals.

When there is no appreciable chemical interaction between the salt and the metal, the solution becomes partially metallic, and particularly the solutions of the alkali, the alkaline-earth and the rare-earth metals in their respective halides are prone to this behaviour. Solutions with strong metal-salt interactions show relatively small changes in conductivity upon addition of metal to the molten salts, and this type of behaviour is frequently found in the systems of the transition and post-transition metals.

In industrial electrolysis another type of metal solutions is of importance, namely, solutions of metals in salts of another metal. According to the electrochemical series of metals in molten salts (see Delimarskii and Markov, 1961) the one metal displaces the other according to the example

$$Cd + PbCl_2 \rightleftharpoons CdCl_2 + Pb.$$

The equilibrium constant for this reaction may be obtained from the solubility behaviour of the metals in unlike salts. In the above example cadmium will displace lead below 650°C and lead will displace cadmium above 650°C due to a change in the equilibrium constant with temperature. The principles of solutions of metals in molten salts have been reviewed by Fischer (1954), Delimarskii and Markov (1961) and by Bredig (1963).

Metallic solutions as the medium for crystal growth of elements and a variety of compounds have been reviewed by Luzhnaya (1968). Metallic solvents can be used for the growth of many metals and alloys which do not form stable compounds or solid solutions and show miscibility in the liquid state. Liquid immiscibility in metallic systems has been discussed in Section 3.2.

Comparitively few metals and intermetallic compounds have been systematically grown from metallic solutions, notable exceptions being the growth of silicon from gallium and indium solutions by Keck (1953) and by Keck and Broder (1953), from tin solutions by Goss (1953), from silver and zinc solutions by Hartenberg (1951) and from gold by Carman *et al.* (1954). Germanium and silicon crystals have been grown from Al, Ga, Sn, Cd, Sb, Ag and Zn solutions by Faust and John (1964) and the superconductor Nb₃Sn has been crystallized by Hanak and Johnson (1969) from tin solution. However, many more binary metallic systems are simple eutectics (Reisman, 1970, p. 158) and are thus suitable for crystal growth of either component.

Intermetallic compounds can often be prepared from one of the components in the appropriate temperature range. For example, the III–V semiconductors GaP, GaAs, GaSb have been grown from gallium solutions in many laboratories either as bulk crystals or as thin layers, and intermetallic compounds such as V₂Ga₅, VGa₅, MnGa_{5.2}, NbGa₃, Ta₅Ga₃, CrGa₄, FeGa₃ have been prepared as small crystals by R. Reinmann (unpublished). It is obvious from the phase diagrams (of which many are still unknown) that AuGa₂, PrGa₂, MgGa₂, UGa₃ and several other compounds could also be crystallized from gallium solutions. Several metals and many of their intermetallic compounds can be grown from lowmelting metals such as gallium, aluminium, bismuth, silver and gold. From bismuth solutions the following compounds have been crystallized by Teitel *et al.* (1954) and by Barton and Greenwood (1958): BaBi₃, CaBi₃, CeBi₂, Mg₃Bi₂, BiSe, SrBi₃, Bi₂Te₃, Th₃Bi₅, UBi₂ and ZrBi₂, and large crystals of MnBi have been obtained by Ellis *et al.* (1958).

Solvents for III-V and II-VI Semiconductors and for Chalcogenides generally For the growth of III-V compounds the most popular solvents are the corresponding metals (e.g. gallium, indium), especially for layer growth and device fabrication by liquid phase epitaxy. However, other metals like zinc, tin, lead, mercury and cadmium have been used by several authors for III-V and the isoelectronic II-IV-V2 compounds as reviewed by Luzhnava (1968), by Faust and John (1964) and by Spring-Thorpe and Pamplin (1968). Faust et al. (1968) discussed the effect of solvents (Ag, Al, Au, Cd, Ga, In, Pb, Sn, Zn) and of added impurities on the habit of the semiconductor crystals grown (Si, Ge, III-V compounds). II-VI compounds (the sulphides, selenides, tellurides) are rarely grown from the constituent elements; they are generally grown either from metallic solutions (gallium, indium, bismuth, thallium, tin), from halides or from chalcogenides as solvents. For example, ZnS has been grown from ZnF, and ZnCl₂, and CdCl₂ acts as solvent for CdS, CdSe and CdTe. A high solubility (at moderate temperatures) for several sulphides is shown by lead chloride (Linares, 1968; Wilke et al., 1967), thus PbCl₂ could play the same important role in flux growth of sulphides as does PbF₂ for growth of oxides. Koutaissoff (1964) has prepared europium sulphide EuS crystals using LiCl-KCl eutectic as solvent for the reaction

$$EuCl_2 + Li_2S \rightarrow EuS + 2LiCl.$$

Many chalcogenides and pnictides have been prepared as crystalline products with the addition of the corresponding halides (Kweestroo, 1972).

Although several chalcogenides have been used for the growth of II–VI compounds, for example Ba_2ZnS_3 for the growth of ZnS by Malur (1966), they have not found wide application except for alkali polysulphides (for example, Na_2S_2 — Na_2S_5) which have been used by Garner and White (1970) for the growth of cinnabar (HgS) and by Scheel (1974a) for the growth of many sulphides: ZnS, CdS, CuS, α -MnS, FeS₂, NiS₂, CoS₂, PbS, Cu₃VS₄, KFeS₂, NaInS₂, NaCrS₂, etc. Sodium polysulphides have low melting temperatures and eutectics (200° to 450°C), a common anion, are easily dissolved in water or alcohols, and alkali ions are incorporated into the crystals only as ppm traces (Scheel, 1974a). Information on the sodium polysulphide melts was obtained by Cleaver and Davies (1973), South *et al.* (1972) and Bell and Flengas (1966); and Garbee and Flengas (1972) studied the structural and electrical properties of PbS—PbCl₂ and of Cu₂S—CuCl and FeS—FeCl₂ solutions, respectively.

Solvents for Borides, Carbides, Pnictides

Owing to the extremely high melting points of many of the borides, carbides, etc., crystal growth by direct techniques (Czochralski, Bridgman, sublimation) at those high temperatures is extremely difficult due to container problems and precise growth control. In the crucible-free electron-beam zone melting, arc-imaging and plasma flame-fusion techniques, the stoichiometry as well as crystal quality (strain, grain boundaries, dislocation densities) present still unsolved problems.

For crystal growth of these classes of compounds often with very high melting points (e.g. $TiB_2 2800^{\circ}C$, $TaC_{0.98} 3983^{\circ}C$) those transition metals which form compounds of relatively "low" melting point with the corresponding non-metal (B, C, etc.) may act as solvents.

Rowcliffe and Warren (1970) were able to grow 2 mm crystals of TaC_{0.96} by the technique of Robins (1959) using solutions of Ta and C in iron which were slowly cooled from 2200°C to 1450°C, and Gerk and Gilman (1968) grew WC crystals of 1 cm diameter from cobalt solutions by the top-seeded solution-growth technique (see Chapter 7). Silicon carbide, one of the most intensively studied crystals with potential applications in many fields, has been prepared from several metal solutions which are listed in Table 3.15. The solubility of carbon in silicon at 1600°C is only 0.03 at %, but it can be enhanced by the addition of several transition elements. Of the transition metals, cobalt, nickel and chromium have been applied as thin molten layers for epitaxial vapour-liquid-solid (*VLS*) growth. The *VLS* growth mechanism often acts in the growth of whiskers (see Chapter 7), and a variety of droplets on the top of whiskers of many compounds have been analysed. These droplets act as a solvent for thin-layer transport growth and even for growth of bulk crystals of the whisker

Solvent	Melting point of metal	Melting points of compounds	References of SiC growth
Silicon	1410 C		Hall (1958), Halden (1960), Beckmann (1963), Nelson <i>et al.</i> (1966), Bartlett (1969)
Silicon + Chromium	1900 C	$Cr_3Si \sim 1750^\circ, Cr_2Si 1600^\circ, CrSi 1640^\circ, CrSi_2 1540^\circ, CrSi_2 1540^\circ, Cr_3C_2 1890^\circ, Cr_7C_3 1780^\circ, Cr_4C 1520^\circ$	Griffiths and Mlavsky (1964), Wright (1965), Knippenberg and Verspui (1966), Silva <i>et al.</i> (1967), Comer and Berman (1970), Kalnin and Tairov (1966), Kunagawa <i>et al.</i> (1970)
Silicon + Cobalt	1492°	Co ₂ Si 1330°, CoSi 1400°, CoSi ₃ 1306°	Marshall (1969), Comer and Berman (1970)
Silicon + Iron	1536	FeSi 1420 [°] , Fe ₃ C 1227°	Halden (1960), Ellis (1960)
Silicon ± Nickel	1455	Ni ₂ Si 1318 , NiSi 992 , Ni _a C	Baumann (1952), Ellis (1960), Berman and Comer (1969), Comer and Berman (1970)
Silicon + Silver	961 ^o	no compound formation	Pickar (1967)
Silicon + Gold	1063	no compound formation	Berman and Comer (1969)

TABLE 3.15. Solvents used for Growth of Silicon Carbide (m.p. >2700°C)

material. A variety of carbides and carbide solid solutions have been prepared from metallic solvents by Jangg *et al.* (1968), and this technique has found industrial applications.

As for the carbides, transition metal elements or compounds have been used for the preparation and growth of borides and the pnictides. For example, B₆P has been formed from Ni solution (Burmeister and Greene, 1967), AlB₂ from Al solution (Horn *et al.*, 1952) and BP and BAs have been grown from Cu₃P solution by various groups (see Chapter 10). Silicon diphosphide has been crystallized from Sn and Sn—Mg solutions (Spring-Thorpe, 1969). A variety of borides, carbides, silicides, germanides,

phosphides, arsenides, etc., have been prepared by electrolytic reduction of the corresponding salts dissolved in a molten salt stable at the preparation conditions (see for instance Aronsson *et al.*, 1965; Delimarskii and Markov, 1961; Wold and Bellarance, 1972; Kunnmann, 1971).

Tin was found to be a powerful solvent for the growth of $II-IV-V_2$ compounds as reported by Rubenstein and Ure (1968) for $ZnSnP_2$, and by Faust and John (1964) for $ZnSnAs_2$ and as reviewed by Spring-Thorpe and Pamplin (1968) for several $II-IV-V_2$ compounds. The latter authors claim that indium, lead, bismuth, cadmium and zinc could also be used for the growth of ternary phosphides and arsenides.

3.7.3. Solvents for miscellaneous elements and compounds

A peculiar effect of the role of solvent in the crystallization of diamond and graphite was described by Wentorf (1966). In the stability field of diamond (60 kb, 1600°C) carbon crystallizes in its high-pressure modification from solutions in the transition metals of groups VI, VII and VIII (best from Ni, Fe and Fe-Ni alloys, see Chapter 7) and as graphite from oxides, sulphides, halides and silicates such as Cu₂O, CuCl, Cu₂S, AgCl, AlCl₃, ZnO, ZnS, CdO, FeS and silicates containing hydroxyl such as serpentinite, biotite, muscovite and hydrous alkaline alumino-silicates (Wentorf, 1966). This fact was explained by the formation of positively charged carbon ions in solvents of the first group (Fe, Ni), whereas the second group shows a smaller solubility for carbon and dissolves it probably as a nearly neutral species. In Li₂C₂ and Ca₂C₂ the carbon is negatively charged. Wentorf attributes the effect of the charge of the dissolved carbon species (having different partial atomic volumes) on the crystallization of either diamond or graphite to the rates of nucleation of the two forms which is mainly determination by the change (with pressure) of the free-energy content of the crystalline phase relative to its state in solution, which depends on the differences in partial atomic volumes. When crystallizing graphite or diamond from iron solutions the addition of a small amount of silicon or aluminium is helpful in suppressing the formation of the iron carbide Fe₃C (Strong and Chrenko, 1971; Sumiyoshi et al., 1968). The solubility behaviour of carbon in nickel at high pressure has been discussed in detail by Strong and Hanneman (1967). In the diamond synthesis by the Swedish group, iron carbide was used as solvent (Liander and Lundblad, 1960). It is still not certain under which conditions crystallization of the large high-quality diamonds has occurred in nature. Borazon BN, the III-V analogue of diamond, has been prepared by Wentorf (1957, 1965) and by DeVries and Fleischer (1972) from Li₃BN₂(Mg₃N₂, Ca₃N₂) solutions at pressures of 40 to 60 kb and temperatures of about 1600 and 1900°C. Wentorf (1957) states that with increasing atomic number of the metal component of the solvent the process of crystallization of cubic boron nitride requires higher pressures, and DeVries and Fleischer assume that the structure of the Li₃BN₂—BN solutions consists of B—N chains cross-linked by lithium ions.

3.8. Determination of Solubility Curves and Phase Diagrams

A large number of high-temperature solution growth experiments have been performed with little or no knowledge of the appropriate phase diagram. The normal procedure for the growth of a new material is to select a suitable solvent on the basis of past experience, taking into account any special requirements of the material. A number of trial experiments using small quantities of chemicals and fairly rapid cooling rates are then carried out, with solute concentrations normally in the range 10-25%. If one or more compositions are found to yield crystals of the required phase, the experiment is repeated with such compositions on a larger scale and with much slower cooling rates in order to obtain crystals of the desired size.

However, if the conditions of any crystal-growth experiment are to be optimized and crystals of high quality grown, some knowledge of the phase diagram is necessary. It will be clear from the previous discussion that many high-temperature solutions contain five or more components, and the determination of a complete phase diagram in such cases is totally impractical. As stressed by Roy and White (1968) the solution is treated as a pseudo-binary system with the phase to be crystallized as one component (solute) and the solvent as the other. The information required for crystal growth is the solubility curve of the phase to be crystallized and the stability field of this phase—the range of composition and temperature over which it is stable.

A purely theoretical approach for determination of phase diagrams is possible only for cases where the solutions fulfill the conditions of a simple model and where the appropriate thermodynamic data of the components are known. Generally, the experimental determination of the phase diagrams is necessary and in the following the various approaches to determine the solubility curves are briefly presented. However, the role of phase diagrams on solid solubility and in the type of dopant incorporation as reviewed by Reisman (1970) and by Panish (1970a) will not be discussed here; the liquidus curves will be the only aspect covered.

Knowledge of the phase diagrams is not only helpful or necessary for planning crystal-growth experiments, it is also indicative of the type of solution, and of the solute-solvent interactions as outlined in Sections 3.2–3.4 and as discussed in detail by Reisman (1970). A review of thermoanalytical investigations of crystal-growth problems has recently been presented by Schultze (1972).

3.8.1. Direct techniques

Phase-diagram investigations should be performed under equilibrium conditions and it is important to allow sufficient time for equilibration prior to measurement. This time depends on the mobility of the components (thus on diffusion constants, viscosity and convection) and can be shortened by continuous mixing and by stirring.

The simplest method for determination of a solubility curve is to introduce excess crystals or even a polycrystalline mass of the solute into the solvent at a controlled temperature. After dissolution has proceeded for several hours, the undissolved material is separated from the saturated solution and weighed, and the loss in weight due to dissolution represents the solubility at that temperature. Solubility values are normally quoted as a function of the whole solution, either in mole (atomic) % or in weight %.

Some investigators have recovered the undissolved material by removal of the solution after equilibration by dissolution in some reagent after cooling to room temperature. This method is clearly very time-consuming and the construction of a solubility curve can occupy several weeks. Separation of the saturated solution from excess solute may be done by careful decanting or by using sieve arrangements, and Hall (1963) has removed excess floating compounds from the saturated melts by a quartz glass loop in his determination of solubilities of III–V compounds in gallium and indium.

An alternative but related approach is to remove a sample of the solution after equilibration and to determine the solubility by chemical analysis of this solution. If the quantity of solution removed is small compared with the total mass of solution, a solubility curve may be constructed fairly quickly by taking samples over a range of equilibrium temperatures. In this way Ray (1969) determined the solubilities of NiO, CoO, FeO and Cu_2O in neutral silicate melts.

Seed crystals may be introduced into the approximately saturated solution. If the seed is put into an unsaturated solution it will dissolve and if put into a supersaturated one it will grow (Timofeeva and Kvapil, 1966; Manzel, 1967). Instead of facetted seed crystals the use of spheres has the advantage that growth (supersaturation) can be more easily detected by the formation of facets (Timofeeva and Konkova, 1968). By this technique the solubility curves can be determined as accurately as $\pm 10^{\circ}$ C if care is taken of the experimental parameters (homogeneous solution, dipping time, no interfering heat transfer, etc.) and if the volatility of any components of the solution is negligible.

Wagner and Lorenz (1966) simply used the disappearance and the

formation of solid ZnSe and ZnTe on the surface of highly reflecting gallium and indium melts for solubility determination, and by temperature cycling, the liquidus temperatures could be measured very precisely. However, due to thermal gradients in the furnace with a full length viewport, the accuracy is estimated to be only $\pm 10^{\circ}$ C.

Quenching methods. The main disadvantage of the above dissolutionextraction methods is that they give no direct information on changes in the phase which is crystallized, and are therefore unsuitable for investigations of novel systems or for stability field determinations.

The most popular method of performing more detailed investigations involves quenching the solutions to room temperature followed by examination of the quenched sample or a polished section of it by optical microscopy. This method relies on the ability to detect undissolved particles, but optical microscopy is an extremely sensitive means of detection, and a second phase can normally be distinguished at concentrations as low as 0.05%.

The solubility of a material at a known temperature is determined by quenching samples containing a range of different solvent-solute ratios following equilibration at that temperature. If the solubility is below the solubility limit, no undissolved material will be present on quenching and the accuracy of determination of any point on a solubility curve may be increased by the use of samples having progressively smaller differences in solute concentration. Solidus temperatures may be determined by a similar method. Since several samples are required for the determination of a single point of the liquidus curve, it is desirable to quench several samples at the same time. These samples may either be of different compositions quenched from the same temperature, or of the same composition equilibrated at different temperatures in a furnace of which the temperature gradient is accurately known. A multiple-sample apparatus has been described by Cobb and Wallis (1969).

3.8.2. Hot-stage microscopy

The methods described above, though simple, are all very laborious and lengthy. Alternative methods normally involve the application of a varying temperature and so do not yield equilibrium values. However, since crystallization does not occur under equilibrium conditions, the values obtained are normally sufficiently accurate for the determination of conditions for crystal growth, and any inaccuracy is more than compensated by the great saving in time and possibly materials and the additional information which may be obtained.

The ideal method, in principle, is the visual polythermal hot-stage

microscopic method in which the heated sample is located near the objective of a microscope by means of which it may be observed continuously. The amount of heat supplied to the sample must necessarily be small to prevent damage to the objective and it is normally found preferable to locate the sample at the junction of a thermocouple which is used for temperature determination. The region of the thermocouple in the immediate vicinity of the junction is made of much finer wire than the rest of the thermocouple so that heating is localized to this region. Heating may be performed by passing an alternating current through the thermocouple wire, with temperature sensing through the same thermocouple.

After a period of dissolution the sample is slowly cooled, and the formation of small crystals observed through the microscope when the solution becomes supersaturated. By temperature cycling the precision might be increased. In practice the observation of crystallization may be extremely difficult particularly if the melt is opaque or if crystallization occurs below the surface of the melt or if the crystals possess optical properties not substantially different from the solution. The main source of inaccuracy is, however, preferential volatilization of one component of the solution which can cause rapid changes in composition. Even with "non-volatile" fluxes such as $BaO \times 0.6B_2O_3$, the increase in solute concentration with time due to evaporation is very marked, due to the high area-to-volume ratio of the sample.

The solubility of sodium niobate in a borax flux was determined by this method by Burnett *et al.* (1968) but the liquidus temperatures quoted could be in error by 100°C due to solvent evaporation. Hot-stage microscopy is, however, valuable for rapid determination of the phase diagram of novel solvent systems (Elwell *et al.*, 1972).

3.8.3. Differential thermal analysis

In differential thermal analysis (DTA) two samples of similar thermal capacity are located in a furnace heated or cooled at a uniform rate. Thermocouples are inserted into the two samples and are connected in opposition so that the temperature difference ΔT between the samples is measured. If neither sample undergoes a phase change in the temperature range investigated, the value of ΔT will ideally be zero throughout the whole range. However, if one sample is inert while the other undergoes a phase change, the evolution or absorption of latent heat will result in a temperature difference between the samples. If ΔT is recorded for an unknown sample, any thermal effect such as crystallization or dissolution may be detected.

Several problems are encountered in the application of DTA to crystallization from high-temperature solutions, and these have been discussed by Elwell *et al.* (1969). Apart from the corrosive nature of the fluxes, the main problem is that crystallization occurs rather slowly and the solute concentration does not normally exceed 25%, so the values of ΔT are rather low. Also, at temperatures above about 1000°C, electrical conduction in the ceramic specimen holders may become appreciable and this can provide the main contribution to electrical noise on the ΔT signal as the temperature is increased. In the apparatus of Elwell *et al.* (1971) the



FIG. 3.13. DTA apparatus for fluxed melts (Elwell et al., 1971).

noise due to conduction in ceramic components is reduced by mounting each crucible containing a sample or reference material (normally α -Al₂O₃ powder) on an independent support. The thermocouples are also mounted independently of each other and the junctions are immersed just below the surface of the solutions. In order to protect the thermocouple junctions from flux attack, they are enclosed in a sheath of very fine platinum foil. This platinum sheath is electrically earthed and so acts as a screen against stray electric fields. The signal-to-noise ratio with this apparatus is higher by an order of magnitude than that obtained from the more usual arrangement in which the thermocouple is inserted in a well in the base of the crucible. Figure 3.13 shows the layout of the apparatus in diagrammatic form. A typical record of ΔT versus T for a crystallizing solution is shown in Fig. 3.14. The signal due to crystallization persists throughout the crystallization range and a very large signal normally appears on solidification. In any apparatus the signal will be accompanied by a gradual



FIG. 3.14. DTA thermogram for 18 wt% NiFe₂O₄ crystallizing from a BaO— Bi₂O₃—B₂O₃ flux (Elwell *et al.*, 1971).

drift of the base line due to mismatch between the thermal capacities of the sample and the reference material, and particularly to changes in the thermal properties of the sample due to the formation of a layer of solute around the thermocouple sheath during cooling.

Since crystallization proceeds as the temperature is lowered rather rapidly, some supercooling inevitably occurs and so the liquidus temperatures indicated on cooling will be low. The magnitude of the error may be estimated by comparison of the curves obtained during heating and cooling; in the crystallization of nickel ferrite from barium borate, this was normally 10–20°C at a cooling rate of 2–3°C/minute. Karan and Skinner (1953), in their DTA investigation of the phase diagram BaTiO₃— KF, found a difference of $65 \pm 5^{\circ}$ C for the heating and cooling curves, respectively, with a cooling rate of 3–4°C/minute.

One advantage of DTA is that the crystals which form during cooling are normally large enough for identification by X-ray crystallographic or other means. It is, in principle, a good technique for volatile samples, which may be contained in sealed crucibles to which the thermocouple junctions are welded.

3.8.4. Thermogravimetry and other methods

Thermogravimetry involves a determination of the changes in weight in a sample during heating or cooling. Application of this method to crystalgrowth studies from aqueous solutions was reported by Bennema (1966), and apparatus for the application of thermogravimetry to high-temperature solutions was described by Smith and Elwell (1967) and by Nielsen (1969).

In the determination of crystallization temperatures, a long platinum wire is suspended so that its tip is immersed just below the surface of the solution as shown in Fig. 3.15. As the solution is cooled below the liquidus temperature, the end of the wire acts as a nucleation centre for the growth of crystals. Provided that the density of the crystals is different from that of the solution, crystallization is then indicated by a change in weight of the wire. Usually this weight is measured on an electrobalance and is indicated on a chart recorder simultaneously with the temperature, measured as near as possible to the tip of the wire.

This method is more accurate than DTA since the rate of cooling can be reduced to an arbitrarily low value. The main source of error is that of the temperature measurement but this can be minimized by replacing the wire by a thermocouple so that crystals are formed directly on the junction.

If the solution is cooled slowly below the crystallization temperature, crystals typically up to 1-2 mm in diameter can be obtained for identification of the stable phase. The stability field can be determined readily from the weight-change record and any changes in the crystal phase can be



FIG. 3.15. Thermogravimetric apparatus for crystallization temperature determination (Smith and Elwell, 1967).

confirmed by periodic removal of the wire for inspection. The main limitations of the method are that it is difficult to homogenize the solution by stirring and that it is inaccurate when applied to volatile solvents since the solution must be contained in an open crucible.

Resistivity. In general, the electrical resistivity of a crystal is higher than that of its solutions and this difference could be used as a means of measuring crystallization temperatures. This method does not appear to be very accurate in practice (Smith, 1970) since the fractional area of even a fine wire electrode which is covered by a crystal immediately after nucleation is small. Optimization of this geometrical problem might produce a feasible method which would have the advantage of cheapness and ease of recording. Resistivity changes may be conveniently used to measure the melting points of novel solvent compositions.

Identification of crystalline phases will be discussed in Section 9.3, but frequently morphology and colour suffice to identify crystals of simple or well-known systems.

3.8.5. Solid phase metastability

A discussion of phase-diagram determination would be incomplete without mention of the possibility that identical systems under nominally identical conditions may not always yield the same crystal phase. Perhaps the best example of this phenomenon is encountered in the growth of garnets from PbO/PbF, fluxes with and without B₂O₃ addition. An attempt to ascertain the stability field of yttrium iron garnet, Y3Fc3O12, has been made by Timofeeva and Lukyanova (1970). Several other phases can crystallize from this system, notably YFeO₃, Fe₂O₃ and PbFe₁₂O₁₉, and van Uitert et al. (1970), after a great deal of experience, reported that the probability of garnet formation from a favourable composition was only 50%, and this statement was re-emphasized by Tolksdorf and Welz (1972). However, by systematic studies necessary for reproducible growth of garnet films for magnetic bubble domain devices, this situation was clarified. It was shown by Levinstein et al. (1971) that supercoolings up to 120°C can be achieved, and Blank and Nielsen (1972) reported that a garnet-PbO-B₂O₃ solution can be saturated with respect to orthoferrite, and supersaturated with respect to garnet, simultaneously. If no seeds of either phase are introduced and nucleation occurs spontaneously, minor effects such as trace impurities or a slight volatilization of one of the solution components might accidentally determine the crystallizing phase which could thus grow in a metastable field.

Another example of metastable growth has been discussed in Section 3.7.3 where the crystallization of graphite in the stability field of diamond was explained by solute-solvent interactions; at high pressures and temperatures graphite or diamond could be crystallized depending on the type of solvent.

According to Ostwald's law of successive transformation a metastable phase may transform step by step (Ostwald'sche Stufenregel) to the stable phase. Thus metastable phases are frequently observed as low-temperature crystallization products in glasses (metastable viscous solutions of which

the supersaturation is frozen in), and as shown by Scheel (1968) it is possible even to obtain relatively large crystals of metastable quartz solid solutions.

Other phases which are not the stable phases of the pure compounds can be stabilized by traces of impurities. Thus anatase and brookite may be obtained in the stability field of rutile (TiO_2) and tridymite stabilized by traces of alkali crystallizes instead of quartz (Flörke, 1955, 1956). However, one cannot speak of metastability in the latter cases since the trace-stabilized phases are thermodynamically stable. All the examples of growth of metastable phases mentioned above are exceptional, and one would expect that in almost all cases the thermodynamically stable phases crystallize from high-temperature solutions. However, Roy and White (1968) pointed out that the highest probability for growth of metastable phases is obtained in high-pressure solution growth.

3.9. Selected Solubility Data and Phase Diagrams

For the convenience of experimentalists, literature data are listed in Tables 3.16, 3.17 and 3.18 which contain solubility data and phase diagrams. However, phase diagrams which are contained in one of the following works are generally not listed:

Levin et al. (1964, 1969): Oxides, salts. Landolt-Börnstein (1956): Metals, oxides, salts, etc. Hansen and Anderko (1958): Binary alloys. Elliott (1965): Binary alloys. Shunk (1969): Binary alloys. Smithells (1962): Alloys. Delimarskii and Markov (1961): Salts and metals. Stephen and Stephen (1963): Solubilities of inorganic and organic compounds. Kaufman and Bernstein (1970): Computer calculations of phase diagrams. Alper (1970): Many aspects of phase diagrams. Panish and Ilegems (1972): Ternary III–V systems. Gschneidner (1961): Rare earth alloys.

Table 3.16 gives solubility data of oxides and oxide compounds, Table 3.17 of metals, alloys and semiconductors, and Table 3.18 of miscellaneous elements and compounds. Further solubility data may be found in several of the original publications which are listed in the Table of Chapter 10. However, Tables 3.16–3.18 are not complete, and any published or unpublished solubility data submitted to the authors would be appreciated.

3. SOLVENTS AND SOLUTIONS

Solute	Solvent	Exper.	Theor.	References
Al ₂ O ₂ and	Na-AIF.	x		Foster (1960)
Al ₂ O ₃ :Cr	PbF ₂	X		Giess (1964), Airtron (1963), Wilke (1968),
				Adams et al. (1966)
	PbF ₂	х		Timofeeva and Lukyanova (1967),
				White and Brightwell (1965)
	РЬО	X		Torkar <i>et al.</i> (1966), Wilke (1968)
	PbO-B ₂ O _a	х		Timofeeva and Konkova (1968),
				Timofeeva and Lukyanova (1967),
				Timofeeva (1968)
	Li-, Na-, K-, Sr- and	x		
	Ba-tungstates	X		Voronkova et al. (1967)
BaTiO ₃	KF	х		Karan and Skinner (1953), Karan (1954)
	TiO ₂	x		Rase and Roy (1955)
	BaCl ₂	X		Rase and Roy (1957)
(Ba, Pb)TiO ₃	$(Ba, Pb)B_2O_4$	X		Perry (1967)
BaWO ₄	Na ₂ SO ₄	X		Wilke (1968)
	NaCl	X		Wilke (1968),
		10000		Voigt and Neels (1971)
	WO ₃	X		Chang et al. (1966)
$Ba_{\mathfrak{z}}(Y, Ta)_{4}O_{1}$	s BaB2O4	x		Layden and Darby (1966)
BaTa ₂ O ₆	B_2O_3 , BaB_8O_{13}	X		Layden and Darby (1966)
Ba ₅ Ta ₄ O ₁₅	BaB ₂ O ₄	X		Layden and Darby (1966)
BeO	$L_{12}MoO_4 \cdot 1.25MoO_3$	X		Austerman (1963)
	PbO PLO PLE	X		Newkirk and Smith (1965)
	PbO—PbF ₂	X		Newkirk and Smith (1965)
	S102	X		Morgan and Hummel (1949)
	GeO2	X		Cobb and Wallis (1969)
D 010	WO3	X		Chang et al. (1966)
Be25104	$L_{1_2}O-MoO_3$	X		Ballman and Laudise (1965)
C WO	Na ₂ O-MoO ₃	X		Ballman and Laudise (1965)
Caw04	CaCl ₂ —LICI Eut.	X		Barta <i>et al.</i> (1968)
	Na ₂ SO ₄	х		Schultze <i>et al.</i> (1967), Wilke (1968)
	Na ₂ WO ₄	X		Schultze <i>et al.</i> (1967), Cobb and Wallis (1967a)
	LiCl	X		Wilke (1962)
	NaCl	X		Voigt and Neels (1971)
	WO ₃	X		Chang et al. (1966)
CaSO4	Na ₂ SO ₄	X		Wilke (1968)
	NaCl	x		Wilke (1968)
CaMoO4	Li ₂ SO ₄	x		Parker and Brower (1967)
Cu ₂ O	(Na, K) ₂ SiO ₃	X		Ray (1969)
CoO	(Na, K) ₂ SiO ₃	X		Ray (1969)

TABLE 3.16. Solubilities (Phase Diagrams) of Oxides and Oxide Compounds

124	CRYSTAL	GROWTH	FROM	HIGH-TEMPERATURE	SOLUTIONS

124	CRY	STAL	0
TABLE	3.16	cont.	

Solute	Solvent	Exper.	Theor.	References
CoFe ₂ O ₄	PbO-PbF ₂ -B ₂ O ₂	x		Kvapil et al. (1969)
Cr ₂ O ₃	$PbO \cdot PbF_2 \cdot 0.35B_2O_3$	х		Timofeeva and Konkova (1968).
		x		Timofeeva et al. (1969)
		x		Timofeeva (1968)
	PLO	Ŷ		Negeo (1068)
E.O	FBO	A N		Shafan et al (1072)
EuO	Eu	A		Shafer et al. (1972)
Fe ₂ O ₃	NaCI	X		Wilke (1964, 1968)
	$PbO \cdot PbF_2 \cdot 0.35B_2O_3$	х		(1968),
		x		Timofeeva (1968)
	РЬО	X		Mountvala and Ravitz (1962)
	Na2B4O7, K2B4O7	x		Barks and Roy (1967)
	Na ₂ B ₄ O ₇	x		Nielsen (1969)
	B _a O _a	x		Makram et al. (1972)
FeO	(Na K) SiO	x		Ray (1969)
FeBO.	B.O.	Ŷ		Makram et al (1972)
KNbO ₃	$K_2CO_3(K_2O)$	x		Reisman and Holtzberg
VT.O	K CO (K O)	V		(1955)
LiFe5O8	$\begin{array}{c} \mathbf{R}_{2}\mathbf{CO}_{3}(\mathbf{R}_{2}\mathbf{O})\\ \mathbf{B}_{2}\mathbf{O}_{3} \end{array}$	X		Anderson and Schieber
				(1963)
MgO	PbF ₂	x		Webster and White (1969)
	MgWO ₄	X		Chang et al. (1966)
MgFe ₂ O ₄	PbMoO ₄	Х		Viting and Khomyakov (1965)
MgWO ₄	WO ₃	X		Chang et al. (1966)
Mn ₃ O ₄	Na ₂ B ₄ O ₇	X		Nielsen (1969)
Nd_2O_3	$PbO \cdot PbF_2 \cdot 0.35B_2O_3$	X		Timofeeva and Konkova (1968).
		x		Timofeeva et al. (1969)
		x		Timofeeva (1968)
NIO	AL: O FR O	÷		Parkes and White (1060a)
MO	$P_{12}O \cdot 3B_2O_3$	2		Derkes and White (1969a)
	B_2O_3 , LIBO ₂	2		Berkes and White (1969a)
	$L_{1_2}B_4O_7, L_{1_4}B_6O_{11}$	A		Berkes and White (1969a)
	$(Na, K)SiO_3$	\mathbf{X}	22	Ray (1969)
	$Na_2B_4O_7, K_2B_4O_7$	X	X	Berkes and White (1969b)
	$Rb_2B_4O_7$	X	X	Berkes and White (1969b)
NiFe ₂ O ₄	РЬО	X		Remeika (1955), Manzel (1967)
	PbO-PbF2-B2O3	X		Kvapil et al. (1969)
	BaO · 0.62B • O3	X		Smith and Elwell (1968)
NiWO,	Na ₂ SO ₄	X		Schultze et al. (1967)
0.000.000.000	Na.WO. Na.W.O.	x		Schultze et al. (1967)
PhTiO.	PbCl.	x		Nomura and Sawada (1952)
101103	KE NaVO KVO	Ŷ		Belvaev et al (1954)
	K Mao NaF	A V		Belveev et al. (1954)
	N ₂ WIOO ₄ , Nar	A		Delyaev et al. (1954)
	$Na_2 NOO_4$, $Na_2 WO_4$	X		Belyaev et al. (1954)
	$Na_4P_2O_7, K_4P_2O_7$	X		Belyaev et al. (1954)
PbZrO ₃	PbO	X		Fushimi and Ikeda (1967)
SrTiO ₃	LiF—KF	X		Sugai et al. (1968)

Solute	Solvent	Exper.	Theor.	References
SrSO,	Na.SO,	x		Wilke (1968)
	NaCl	X		Wilke (1968)
SrWO.	NaCl	X		Voigt and Neels (1971)
2010-10-10-10-10-10-10-10-10-10-10-10-10-	WO,	X		Chang et al. (1966)
TiO.	K.B.O.	X		Naumova and Anikin (1966)
	LisB.O. NaBO. K.B.O.	X		Anikin et al. (1965)
Y_2O_3	PbO—PbF ₂ —0.35B ₂ O ₃	Х		Timofeeva and Konkova (1968),
				Timofeeva (1968)
YBO3	$BaO - B_2O_3$	X		Linares (1962a)
Y ₃ Al ₅ O ₁₂	$PbO = 0.35B_2O_3$	X		Timofeeva and Kvapil (1966)
	PbOPbF ₂ 0.35B ₂ O ₃	Х		Timofeeva and Kvapil (1966),
		Х		Timofeeva and Konkova (1968),
		X		Timofeeva et al. (1969),
		x		Timofeeva (1968)
	PbO—PbF ₂	X		Bakradze <i>et al.</i> (1968), Timofeeya (1967)
	BaO-B ₂ O ₃ , PbO-B ₂ O ₃ ,			
	PbO-PbF,-B,O, etc.	X		Timofeeva (1967)
$Y_3Fe_5O_{12}$	РЬО-РЬГ ₂ -0.35В ₂ О ₃	х		Timofeeva and Konkova (1968),
		X		Timofeeva (1968)
	BaO-B,O3	X		Linares (1962a, 1964)
	PbF ₂ —YF ₃	X		Sato and Hukudo (1963)
	РЬО	X		Nielsen and Dearborn (1960)
	PbO—PbF ₂	X		Kvapil et al. (1969)
	PbO-PbF ₂ -B ₂ O ₃	X		Kyapil et al. (1969),
		Х		Timofeeva and Lukyanova (1970)
YVO4	NaVO3, NaVO3-Na3B4O7	X		Phillips and Pressley (1967)
0.000	V ₂ O ₅	X		Levin (1967)
ZnFe ₂ O ₄	РЬО	X		Manzel (1967)
ZnAl ₂ O ₄	PbF,	X		Giess (1964)
ZrO,	Li,Mo,O,	X		Kleber et al. (1966)
na ann an tha ann an th	PbF,	X		Anthony and Vutien (1965)
ZrSiO ₄	Li ₂ O-MoO ₃	X		Ballman and Laudise (1965)
	Na ₂ O-MoO ₃	X		Ballman and Laudise (1965)

TABLE	3.16	cont.

Solute	Solvent	Exper.	Theor.	References
Ag.S	AgCl	x	· · · ·	Garbee and Flengas (1972)
AlaEr	Al	X		Meyer (1970)
CdS	CdCl.	X		Izvekov et al. (1968)
1.11.11.1	CdICdCl.	X		Izvekov et al. (1968)
	Cd	x		Woodbury (1963)
	Cd. Sn. Bi	X		Rubenstein (1968)
CdSe	Cd. Sn. Bi	X		Rubenstein (1968)
CdTe	Cd Sn Bi	x		Rubenstein (1968)
(Cd Zn)Te	Cd Zn	x	x	Steininger et al (1970)
CuS	CuCl	x		Garbee and Flengas (1972)
E ₂ S	FaCl	x		Garbee and Flengas (1972)
Call	Co.	Ŷ		Hall (1963)
GaAs	Ca Aa Ca Sa	Ŷ		Panich (1965)
	Ca Sa Di Dh Ca	Ŷ		Parish (1900)
	Ga, Sn, Bi, PD, Ge	Ŷ	v	Rubenstein (1900)
~ ~	Zn, Sn, Ge, Cu, Ag, Au, Te	A	A	Panish (1970a)
Ga(P,As)	Ga	х	л	Broder and Wolff (1963),
				Antypas (1970), see also Stringfellow and Antypas (1971)
(Ga, Al)As	Ga, Al	х	х	Panish and Sumski (1969), Woodall (1971)
(Ga. In)As	Ga. In	X		Kovaleva et al. (1968)
(01)		X	X	Panish (1970b)
GaP	Ga	X		Hall (1963)
Uar	Zn	x	x	Panish (1970a) Panish (1966)
	Ga-GaAs	x		Shib (1970)
(Ca In)P	Ga In	x	x	Marbitt (1970) Blom (1971)
(Ga, III)	Ga, m	(X)	Ŷ	Stringfellow (1970)
CLCL	Ca	(A)	~	Hall (1963)
Gaso	Ga Ca Ia Sh	Ŷ	v	Plan and Plashatt (1071)
(Ga, In)5b	Ga, In, SD	÷	~	We man (1069)
Ge	Au	~		Wagner (1908)
HgS	Na ₂ S ₄	A.		Garner and White (1970)
HgTe	Hg	A		Dziuba (1971)
InAs	In	X		Hall (1963)
	CdI ₂	X		Luzhnaya <i>et al.</i> (1966)
	In, As, Cd	X		Luzhnaya et al. (1966),
				Koppel et al. (1965)
	Sn, Zn, Pb	X		Koppel et al. (1967a)
	KCl, InI, CuCl, AgCl, AgI, ZnI ₂ , CdCl ₂ , CdBr, SnCl, PbCl, PbL	х		Koppel et al. (1967b)
In(As, Sb)	In, Sb, As	х	Х	Stringfellow and Greene (1971)
In(As, P)	In	Х	X	Antypas and Yep (1971),
InP	In	х		Ugai et al. (1968) Hall (1963).
		12210		Shafer and Weiser (1957)
InSb	In	X		Hall (1963)
PbS	PbCl ₂	x		Garbee and Flengas (1972)
	1721	X	X	Bell and Flengas (1966)

TABLE 3.17. Solubilities of Metals, Alloys and Semiconductors

Solute	Solvent	Exper.	Theor.	References
SnTe	Sb	х		O'Kane and Stemple (1966)
ZnS	ZnF,	x		Linares (1962b)
	ZnCl ₂	х		Gashurov and Levine (1960), Garbee and Flengas (1972)
	Sn, Bi	X		Rubenstein (1968)
ZnSe	Ga, In Zn, Sn, Bi	х		Wagner and Lorenz (1966) Rubenstein (1968)
$ZnSiP_2$	Sn	х		Spring-Thorpe and Pamplin (1968)
ZnTe	Ga, In Zn, Sn, Bi	Х		Wagner and Lorenz (1966) Rubenstein (1968)

TABLE 3.17 cont.

TABLE 3.18. Solubilities of Miscellaneous Elements and Compounds

Solute	Solvent	Exper.	Theor.	References
BN	Li ₃ BN ₂ (50 kb)	х		DeVries and Fleischer (1971)
BaF,	LiF	X		Neuhaus et al. (1967)
C (graphite,	Fe (57 kb)	X		Strong and Chrenko (1971)
diamond)	Ni (1 atm., 54 kb)	x		Strong and Hanneman (1967)
	Fe, Ni	х		Strong and Chrenko (1971)
KMgF ₃	MgF ₂	х		Neuhaus et al. (1967)
K,MgF	KF	х		Neuhaus et al. (1967)
LiBaF,	LiF	X		Neuhaus et al. (1967)
RF ₃	NaF	X		Thoma and Karraker (1966)
(R = rare eart	h)			
Si	Au	X		Hansen and Anderko (1958)
ThF.	LiF-BeF ₂	x		Thoma et al. (1960)
UF,	LiF-BeF,	X		Jones et al. (1962)
WC	Co	x		Gerk and Gilman (1968)

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APPENDIX B

lowed by several others but serve to illustrate a need for intensive development so that this important technology of LPE can achieve its true potential. This requires the education of crystal/epitaxy technologists (Scheel 2003&2004).

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