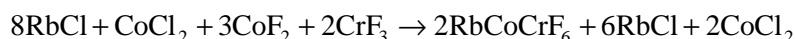


#### 4. Flux growth

The principle of flux growth does not differ significantly from that of growth in solution : temperature is higher and related to the melting temperature of the flux (solvent). Simple metals (Ni, Fe...), oxides ( $B_2O_3$ ,  $Bi_2O_3$ ), hydroxides (KOH, NaOH), salts (BaO, PbO,  $PbF_2$  and other halides ...) can be used as solvents. However, eutectics, found in binary ( $PbO$ - $PbF_2$ ,  $Li_2O$ - $MoO_3$ ,  $Li_2O$ - $B_2O_3$  ...) or ternary diagrams, are generally preferred as a reason of their low temperature of melting and, frequently, their low viscosity. This fact explains that garnet growth is realised in  $PbO$ - $PbF_2$ - $B_2O_3$  fluxes though the crystallisation of  $Y_3Fe_5O_{12}$  is theoretically possible from the BA liquidus line of figure 4.c.

Low temperature varieties can be obtained and the growth rate is generally high (the diffusion coefficient  $D$ , in equation 10, is large); for example, the orthorhombic variety of  $YF_3$  is grown from a  $LiF$ - $YF_3$  melt (figure 4.b) by the Czochralski pulling technique (see III.2). Generally, the flux composition at the end of crystal growth has to be close of a eutectic composition. Therefore, the amount of crystals and the temperature range of crystallisation are maximum. Exchange reactions must be taken into account for the calculation of the weights of starting materials.

Such an exchange reaction leads, for example, to the pyrochlore  $RbCoCrF_6$  :



The final proportion of  $RbCl$  and  $CoCl_2$  (3/1) is close to the eutectic composition :  $RbCl$  72%,  $CoCl_2$  28%,  $T_m \approx 490$  °C).

Sometimes, the exchange reactions result in the formation of mixed anionic compounds. It is the case of chlorofluorides (table 1). Very important examples are found in the growth of diamond in a (Fe-Co-Ni) flux at high pressure (discussed for this reason in 5.2), of ferrites (spinel, garnet) for magnetic applications, of  $LiNbO_3$ ,  $BaNbO_3$ ,  $KTiOPO_4$  (KTP) for applications in optics and of fluorides (perovskite, weberite, pyrochlore). The experimental synthesis conditions of several materials are listed in Table 1.

Table 1 - Conditions of synthesis of selected materials by flux growth.

	Material	Structure type	Flux	Temperature range (°C)	Cooling rate (°C/h)
Oxides	$BaTiO_3$	Perovskite	$30BaTiO_3$ -70KF	1200-850	1-5
	$GdAlO_3$		$PbO$ - $PbF_2$ - $B_2O_3$	1300-900	0.3-0.5
	$CoFe_2O_4$	Spinel	$Na_2B_4O_7$	1300-1100	1-2
	$Y_3Al_5O_{12}$	Garnet	$4PbO$ - $3.5PbF_2$ - $0.4B_2O_3$	1300-1050	0.2-0.5
	$Be_3Al_2Si_6O_{18}$	Beryl	$PbO$ - $4V_2O_5$	1250-800	0.5-5
	$ZnBaFe_6O_{11}$		$Ba_2B_2O_5$	1000-800	0.5
	$YAl_3(BO_3)_4$	Huntite	KF- $MoO_3$	900-700	1-1.5
	$MgWO_4$	Wolframite	$25MgWO_4$ - $75Na_2W_2O_7$	1250-700	2-3
Fluorides	$Na_2Ca_3Al_2F_{14}$		$10NaCl$ - $5ZnCl_2$ - $2CaCl_2$ - $4NaF$ - $2CaF_2$ - $2AlF_3$	650-RT	5
	$RbCoF_3$	Perovskite	$5RbCl$ - $3CoF_2$	850-600	5
	$RbCoCrF_6$	Pyrochlore	$8RbCl$ - $CoCl_2$ - $3CoF_2$ - $2CrF_3$	950-560	5
Mixed anions	$CaClF:Sm^{2+}$		$40CaCl_2$ - $60CaClF:Sm^{2+}$	750-645	5
	$Sr_{10}Al_2F_{25}Cl$		$5.4NaCl$ - $3.5ZnCl_2$ - $NaF$ - $3SrF_2$ - $AlF_3$	700-RT	5

Several variants of the flux method were devised and are presented below.

*The ACRT method.*

Alternate rotations of the crucible accelerate the diffusion of the species ( $h$  decreases in  $\{10\}$ ). The Accelerated Crucible Rotation Technique (ACRT) consists of accelerated counter clockwise and anti counter clockwise rotations during  $t_1$  and  $t_2$  with a maximum rotation speed of  $n$  rotations per minute. A temperature gradient can be created by cooling the crystal with a cold gas flow (figure 11).

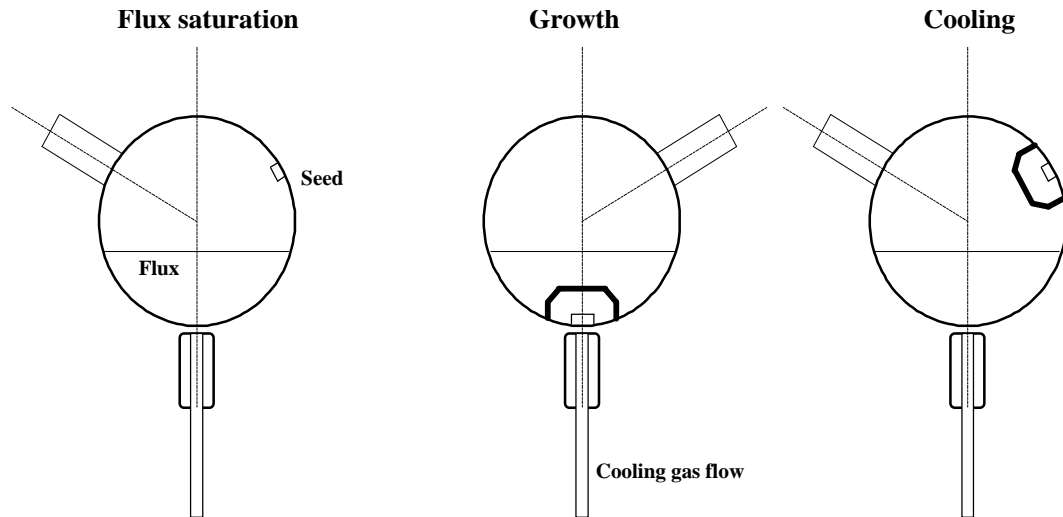


Figure 11. - Flux growth of  $Y_3Fe_5O_{12}$  garnet from a seed in a spherical crucible.

This method has been applied to the growth of  $Y_3Fe_5O_{12}$  in a spherical crucible. The crystal seed is fixed in the upper part of the crucible; the melt is homogenised at  $1260\text{ }^\circ\text{C}$  for one day and supersaturated by cooling at  $1075\text{ }^\circ\text{C}$ . The crystal seed is rotated downward and the growth is performed with ACRT between  $1075\text{ }^\circ\text{C}$  and  $1000\text{ }^\circ\text{C}$  by cooling at  $0.2\text{ }^\circ\text{C/h}$  during 175 h and  $0.5\text{ }^\circ\text{C/h}$  during 80 h. Finally, the crystal is rotated upward in order to avoid the adhesion of the flux at the crystal surface.

The observed mass increase (from 5.3 g to total 66.5 g for example) corresponds to average growth speeds of  $80\text{ }\mu\text{m/h}$  at  $1075\text{ }^\circ\text{C}$  (cooling rate  $0.2\text{ }^\circ\text{C}$ ),  $60\text{ }\mu\text{m/h}$  at  $1030\text{ }^\circ\text{C}$  and  $40\text{ }\mu\text{m/h}$  at  $1000\text{ }^\circ\text{C}$  (cooling rate  $0.5\text{ }^\circ\text{C}$ ). The dissolution enthalpy ( $\Delta H_d = +46\text{ kJ mol}^{-1}$ ) is obtained from the estimation of solubility  $s = x_B^1$  which varies according to the relation :

$$\ln x_B^1 = -\frac{\Delta H_d}{RT} + K \quad (\text{derived from } \{3\}).$$

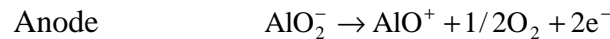
*The growth of emerald by the diffusion method.*

Green emerald is a substituted beryl  $Be_3Al_2Si_6O_{18,x}H_2O$  ( $x < 1$ ). Both silicon and aluminum sites are substituted, according to  $Si^{IV} \rightarrow Na^+ + Al^{3+}$ ,  $H_2O \rightarrow Na^+$  and  $Al^{3+} \rightarrow Cr^{3+}$  (0.1-2 %). Diffusion from the top ( $SiO_2$   $\rho = 2.65\text{ g cm}^{-3}$ ) and the bottom ( $Al_2O_3 + BeO + \epsilon Cr_2O_3$ ,  $\rho \approx 3.5\text{ g cm}^{-3}$ ) of the crucible allows for the deposition of green emerald on seeds or on low value incolore beryls (placed in the intermediate zone).

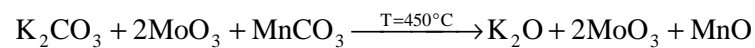
The  $\text{Li}_2\text{O-MoO}_3$  flux (which contains also a small amount of  $\text{V}_2\text{O}_5$ ) has a composition close to  $\text{Li}_2\text{Mo}_2\text{O}_7$  ( $\rho = 2.8 \text{ g cm}^{-3}$ ). The temperature is kept constant ( $T=800 \text{ }^\circ\text{C}$ ) during several weeks.

### 5. Electrolysis

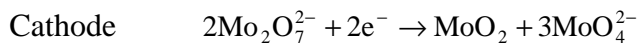
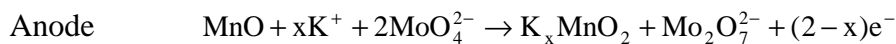
Electrolysis is a very important industrial process for metal elaboration (Zn) or purification (Cu). Aluminum industry is also based on electrolysis:  $\text{Al}_2\text{O}_3$  alumina, obtained from bauxite ore, is dissolved in a fused fluoride flux of  $\text{Na}_3\text{AlF}_6$  cryolithe and  $\text{CaF}_2$ . Electrolysis, at  $T\approx 950^\circ\text{C}$  with a current density of  $\approx 1 \text{ A cm}^{-2}$  and a potential of 4.5V, leads to the redox reactions at the electrodes :



This topic is not much concerned with metals. Consequently, electrolysis in solid state chemistry will be illustrated by the preparation of a bronze type oxide (at a laboratory scale) : cryptomelane  $\alpha$ - $\text{K}_x\text{MnO}_2$  with  $0.12 < x < 0.16$ . This phase is prepared by electrolysis of a solution of  $\text{MnO}$  in a molybdate flux. After the decomposition of the starting carbonates, the oxide mixture is fused at  $T=465 \text{ }^\circ\text{C}$  in air and electrolysed at  $T=485\text{-}500 \text{ }^\circ\text{C}$  during 4-8 days with a stabilized current intensity  $I < 12 \text{ mA}$  :



The following reactions at the platinum electrodes indicate the solids which crystallise :



The overall reaction is :  $\text{MnO} + (1-x)\text{K}_2\text{Mo}_2\text{O}_7 \rightarrow \text{K}_x\text{MnO}_2 + (1-x)\text{MoO}_2 + (1-1.5x)\text{K}_2\text{Mo}_2\text{O}_4$