

3. Hydrothermal synthesis

The physical properties of water are strongly influenced by temperature or pressure (figure 28) : the density and the ϵ dielectric constant of liquid water decrease with a temperature increase and increase with pressure. The coefficient of self-diffusion D increases with T , at the opposite of viscosity η (η), which decreases from $\eta=1.0 \cdot 10^{-3}$ at 300 K to $\eta=3.0 \cdot 10^{-4}$ at 373 K and $\eta=3.14 \cdot 10^{-5}$ at 647 K. All these variations are much larger than density variation of the fluid which decreases from 1 to 0.322 ($T=647$ K) at best. Water mobility and reactivity are enhanced at high temperature and the diffusion of the dissolved species is faster.

At $T > 647$ K, $P > 2.205 \cdot 10^5$ Pa and $\rho > 0.322$ g.cm⁻³, supercritical water is a solvent of materials which are, in normal conditions, insoluble (see Box 4 : the critical solvent). It is the case of α -SiO₂ quartz, grown at $T=400^\circ\text{C}$, below the $\alpha \rightarrow \beta$ quartz transformation at $T=570^\circ\text{C}$.

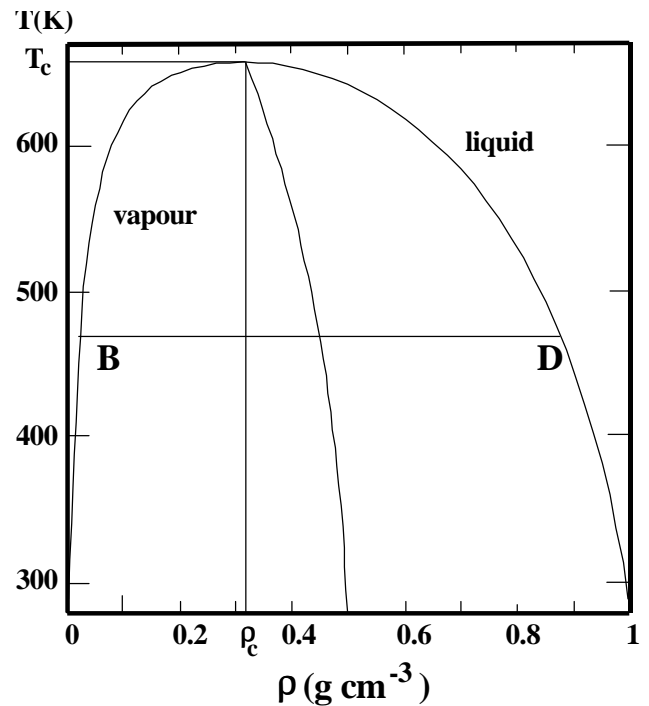


Figure 28. - Variation of mass with temperature for liquid and vapour water.

Various experimental devices for hydrothermal growth have been designed. The autoclave, shown in figure 29, is built in allied steel (PER7H...) and holds pressure up to 250 MPa at 750 °C with a limited rate of creeping. The cone set closure is kept at a lower temperature, outside of the furnace. Then, a temperature gradient ΔT is created between the bottom (hot zone) and the top (cold zone) of the autoclave. The resulting solubility gradient Δs ensures the transport of materials with a direct solubility (s increases with T) from the nutrient (bottom) to the crystallisation zone (top). In the case of inverse solubility, the nutrient is solubilised at low temperature which is, then, slowly increased.

Agressive solutions or materials are inserted in noble metal tubes (gold, platinum or silver) which are sealed; in this case, an external pressure must be applied in order to compensate the internal water pressure (figure 29). A lining of the autoclave is also possible.

When the crystal growth conditions are optimised, crystal seeds can be installed in the growth zone of larger autoclaves. Oriented crystallisation is then promoted. Diffusion and convection flows are limited by baffles (aperture τ) in order to separate the dissolving and growth zones and to obtain low and uniform growth rates for all seeds.

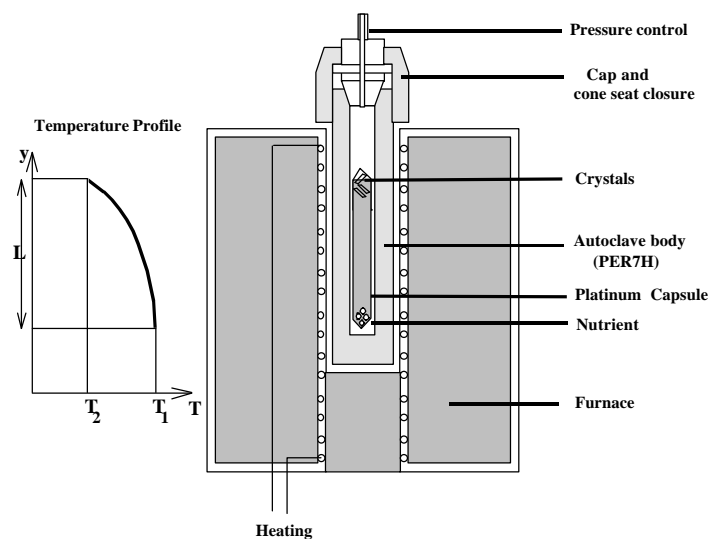
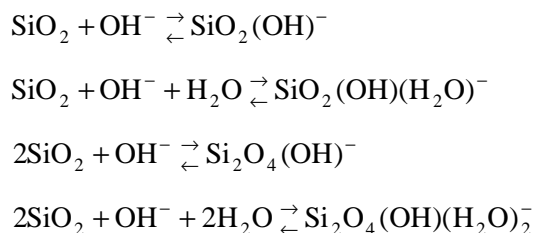
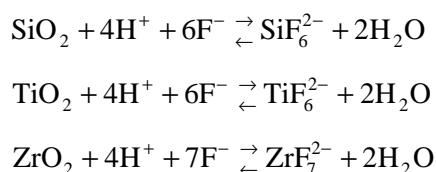


Figure 29. - Principle of the hydrothermal growth technique.

Complexing agents (mineralisers) are frequently dissolved in the solution. These salts increase the solubility of the nutrient and favour the formation of transport species. For example, quartz dissolution and recrystallisation in aqueous solutions are thought to proceed through several acid-base reactions :



Fluoride ions are supposed to form complexes :



At large alkaline fluoride concentrations, these last reactions lead to the crystallisation of Na_2SiF_6 , K_2TiF_6 or K_3ZrF_7 .

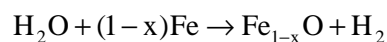
Numerous materials were synthesised by the hydrothermal method : piezoelectric SiO_2 quartz, AlPO_4 berlinite (negative solubility coefficient at $T < 300$ °C). The main industrial production is dedicated to SiO_2 quartz. Very large autoclaves ($\phi=65$ cm, $h=7.5$ m) have been built for quartz crystallisation. They operate at 425 °C (hot zone), 375 °C (growth zone), 175 MPa with 0.1M NaOH solutions and yield several hundred kilograms of crystals after 2 or 4 weeks.

The hydrothermal method has proved its advantages to grow :

- low temperature varieties (α - SiO_2 quartz, α - FeF_3 , $(\text{H}_2\text{O})_{0.33}\text{FeF}_3$ (hexagonal tungsten bronze type)) ;
- compounds which decompose at low temperature, hydrates ($\text{MnFeF}_5 \cdot 2\text{H}_2\text{O}$, β - $\text{FeF}_3 \cdot 3\text{H}_2\text{O}$, $\text{MnFeF}_5 \cdot 2\text{H}_2\text{O}$), ammonium phases ($\text{NH}_4\text{MnFeF}_6$, NH_4AlF_4 , NH_4MnF_3), hydroxides ($\text{La}(\text{OH})_3$), carbonates (CoCO_3 , $\text{Ln}(\text{CO}_3)\text{F}$ Ln=La, Y, rare-earth) ;
- mixed cationic valence (Fe_3O_4 , $\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{F}_8(\text{H}_2\text{O})_2$, $\text{NH}_4\text{Fe}^{\text{II}}\text{Fe}^{\text{III}}\text{F}_6$, Ag_6O_2 , Na_xTiO_2) or mixed anionic phases ($\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ azurite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$ hydroxyapatite, $\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$ sodalite, fluoride carbonates).

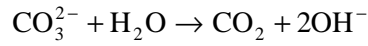
A very large range of materials (table 5), including metals (Te), has been successfully synthesised and solubility studies have greatly improved the knowledge of mineral formation. Most of the oxides, important for applications, are grown : MO_2 (M=Si, Ti, Cr, Mn, Zr, U), Fe_2O_3 , Fe_3O_4 . The crystal size and the quality (mosaicity...) can be sufficient for stringent optical applications (AlPO_4 berlinite).

The hydrothermal medium is frequently reducing. Water reacts with the steel wall of the autoclaves and hydrogen is evolved from the reaction :



Decomposition of amines or HCOOH plays an identical reducing role. At the opposite, the addition of H_2O_2 or platinic acids $\text{PtO}_{2,n}\text{H}_2\text{O}$ gives an oxidising medium.

High pressure helps to prevent the reactions which lead to gaseous species :



This influence (Clapeyron equation 19) is illustrated by the growth of fluoride carbonates : $\text{KCu}(\text{CO}_3)\text{F}$ crystals are obtained at $T=740^\circ\text{C}$ and $P=200\text{ MPa}$ while they decompose at $T=340^\circ\text{C}$ at atmospheric pressure !

Table 5 Hydrothermal growth of selected materials.

	Material	Structure type	Solvent	T °C	ΔT	P 10^5 Pa	τ	t h	f	Starting material
Hydroxyde	$\text{La}(\text{OH})_3$		30m NaOH	400	20-50	400	0.8			
	$\text{YbO}(\text{OH})$		0.1 M NaOH	540		700		24		$\text{Yb}(\text{OH})_3$
Carbonate	CaCO_3	Calcite	4m Rb_2CO_3	600	10-50	1700	0.7	200		CaCO_3
	$\text{Y}_2(\text{CO}_3)_3 \cdot 2\text{H}_2\text{O}$	Tengerite	HCOOH	190				80		$\text{Y}(\text{OH})_3$
Oxide	SiO_2	Quartz	0.1M NaOH	400	50	1750	0.8		0.05	SiO_2
	TiO_2	Anatase	5 % NH_4F	400		1900	0.8	60		TiF_3
	Fe_2O_3	Hematite	5M NaOH	445	5	1500	0.77			Fe_2O_3
	Fe_3O_4	Magnetite	HCOOH	250		400		80		Fe_2O_3
	$\gamma\text{-Bi}_2\text{MoO}_6$	Koehnlinite	1.5 M KF	450	30	800		120		Bi_2MoO_6
	$\text{Fe}_2(\text{MoO}_4)_3$		6 % FeCl_3	475			0.5	120		$\text{Fe}_2\text{O}_3\text{-MoO}_3$
Sulfide	HgS	Cinabar	0.5M Na_2S	260	5	250	0.86	650	0.05	HgS
	$\beta\text{-Ag}_2\text{S}$		$\text{H}_2\text{S}(\text{C}_2\text{H}_5)_3\text{NHCl}$							
Silicate	ZrSiO_4	Zircon	3M KF-1M LiF	650	20	2000	0.65	600		ZrSiO_4
	$\text{Be}_3\text{Al}_2\text{Si}_6\text{O}_{18}$	Beryl	8M NH_4Cl	550	15	1000	0.62	400		$\text{Al}(\text{OH})_3\text{-Be}(\text{OH})_2\text{-SiO}_2$
Phosphate	AlPO_4	Berlinite	1.5 M HCl	150-290			0.82			AlPO_4
	$\text{Ca}_5(\text{PO}_4)_3(\text{OH})$	Apatite	$\text{Ca}(\text{OH})_2$	800		700				$\text{Ca}_3(\text{PO}_4)_2$
	Te		4M KOH	240	1	100	0.82	250	0.05	Te
Fluoride	FeF_3		28M HF	380		2100	0.7	100		FeF_3
	$\text{Na}_3\text{Al}_2\text{Li}_3\text{F}_{12}$	Garnet	H_2O	300		30	0.25	150		$3\text{NaF}\text{-}2\text{AlF}_3\text{-}3\text{LiF}$
	$\text{Fe}_3\text{F}_8(\text{H}_2\text{O})_2$		28M HF	450		2300	0.7	300		$\text{FeF}_3\text{-H}_2$
Mixed anionic systems	$\text{Ba}_5\text{Nb}_3\text{O}_3\text{F}_{18}(\text{HF}_2)$		5M HF	200		15		48		$\text{BaF}_2\text{-NbO}_2\text{F}$
	BaTiOF_4		5M HF	350		1300	0.5	24		$\text{BaF}_2\text{-TiOF}_2$
	$\text{Co}_2(\text{PO}_4)\text{F}$	Triplidite	15M H_3PO_4	700		2000	0.5	30		CoF_2
	$\text{BaCu}(\text{CO}_3)\text{F}_2$		2.5M NaF	740		2000	0.5	20		$\text{BaCO}_3\text{-CuF}_2$
	$\text{Na}_3\text{La}_2(\text{CO}_3)_2\text{F}_2$		5M NaF	740		2000	0.5	20		$\text{BaCO}_3\text{-LaF}_3$
	$\text{Na}_4\text{Al}_3\text{Si}_3\text{O}_{12}\text{Cl}$	Sodalite	NaCl-NaOH	475	25	1000				$\text{Al}_2\text{O}_3\text{-SiO}_2$