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Synthesis Methods in Solid-State Chemistry

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Abstract

The synthesis of single crystal is an area of intense activity in the materials science. The obtaining of the single crystal with sufficient dimension for X-ray diffraction depends on several factors including the chemical composition, crystal structure of the reagents, and physical parameters (temperature and pressure). In this context, this chapter is dedicated to the description of the most common synthesis methods of single crystal in the solid-state chemistry: solid-state method, hydrothermal, and slow evaporation at room temperature. Same other materials can be obtained at high pressure. There are also some physical techniques to grow single crystal, each technique is specific for specific materials.

Keywords: synthesis, single crystal, hydrothermal, evaporation, crystal growth

1. Introduction

Synthesis is the most important step in solid-state chemistry research and in materials science. The samples may be prepared as single crystals, polycrystalline powder, or a thin film. Glass and amorphous samples are from another class of materials. In this chapter, we discuss only the methods of synthesis of single crystals.

The discovery of new materials passes necessarily by the X-ray single crystal method. Usually, the polycrystalline powder and thin film are designed for the known materials, where their structures have been determined by X-ray single crystal diffraction. It is possible to determine the crystal structure of the polycrystalline samples, but generally it shows some difficulty. However, powder XRD is generally dedicated to materials that cannot be prepared as single crystals like some pharmaceutical compounds.

The four most adopted methods of synthesis of single crystals are solid-state, hydrothermal, slow evaporation at room temperature, and flux methods. Here, we discuss also the crystal structure prediction method at high pressure. Each method is controlled by several controllable and/or uncontrollable parameters. The parameters influence the obtaining of phase, morphology, and size of single crystals. The most important criterion in determining the crystal structure is the size of the single crystal and the crystallinity. These two parameters may be checked before the X-rays single crystal diffraction by using the binocular magnifying glass and the polarizing microscope.

2. Solid-state method

The solid-state method is the simplest method. The number of acting parameters is relatively few but difficult to control. This method is commonly used for the synthesis of the single crystals and polycrystalline powders of phosphates and arsenates of transition metals and monovalent cations [1–17].

The crystallization is a phenomenon which generally occurs during a phase change and accompanied by a thermal effect. It is carried out in two stages: germination and growth. The germination begins at a point where the phases are not in equilibrium, a condition can be favored by several factors such as crucible wall, impurity, amorphous. This step consists of the appearance within the reaction mixture of “germs.” The growth takes place in several stages: reorganization of the atoms, adsorption on the surface of the solid, diffusion, and fixation of the atoms on their final sites. Successive layers therefore aggregate on the faces of the crystal which sees its volume increase.

The solid-state synthesis can be done into two steps:

Preliminary treatment: This step consists in weighing the desired quantities of the precursors and then grinding them in an agate mortar. The powder obtained is placed in a crucible or a porcelain basket (**Figure 1**) and preheated between 350 and 400°C for a few hours (**Figure 1**) This operation allows the decomposition of the starting reagents and removes the volatile products such as NH_3 , NO_2 , CO_2 , and



Figure 1.
Equipment used in solid-state synthesis.



Figure 2.
Image of a single crystal of the phase $\text{Na}_{1.25}\text{Co}_{2.187}\text{Al}_{1.125}(\text{AsO}_4)_3$ [9] seen under the binocular magnifying glass.

Single crystal	Reagents	T1 (°C)	T2 (°C)	t1	t2	R	Ref.
LiCo ₂ As ₃ O ₁₀	Li ₂ CO ₃ + CoCl ₂ ·6H ₂ O + NH ₄ H ₂ AsO ₄	350	730	12 h	3days	5 K/h	[2]
NaCo ₂ As ₃ O ₁₀	NaNO ₃ + Co(NO ₃) ₂ ·6H ₂ O + As ₂ O ₅	400	670	24 h	3 days	5 K/h	[3]
Na ₄ Co ₇ (AsO ₄) ₆	NaNO ₃ + Co(NO ₃) ₂ ·6H ₂ O + NH ₄ H ₂ AsO ₄	350	750	24 h	3 days	5 K/h	[4]
K _{0.13} Na _{3.87} MgMo ₃ O ₁₂	Na ₂ CO ₃ + K ₂ CO ₃ + (NH ₄) ₂ Mo ₄ O ₁₃ + Mg(NO ₃) ₂ ·6H ₂ O	400	600	12 h	5 days	5 K/h	[5]
Na _{2.77} K _{1.52} Fe _{2.57} (AsO ₄) ₄	Na ₂ CO ₃ + K ₂ CO ₃ + Fe(NO ₃) ₃ ·9H ₂ O + NH ₄ H ₂ AsO ₄	400	850	24 h	3 days	5 K/h	[6]
K _{0.86} Na _{1.14} CoP ₂ O ₇	NaNO ₃ + KNO ₃ + Co(NO ₃) ₂ ·6H ₂ O + NH ₄ H ₂ PO ₄	400	660	12 h	4 days	5 K/h	[7]
Na ₂ CoP _{1.5} As _{0.5} O ₇	NaNO ₃ + Co(NO ₃) ₂ ·6H ₂ O + NH ₄ H ₂ PO ₄	350	620	12 h	3 days	5 K/h	[8]
Na _{1.25} Co _{2.187} Al _{1.125} (AsO ₄) ₃	Na ₂ CO ₃ + Co(NO ₃) ₂ ·6H ₂ O + NH ₄ H ₂ AsO ₄	350	800	12 h	3 days	5 K/h	[9]
Na ₃ Co ₂ (As _{0.52} P _{0.48})O ₄ As ₂ O ₇	Na ₂ CO ₃ + Co(NO ₃) ₂ ·6H ₂ O + NH ₄ H ₂ AsO ₄ + NH ₄ H ₂ PO ₄	350	700	12 h	3 days	5 K/h	[10]
K _{0.405} Bi _{0.865} AsO ₄	K ₂ CO ₃ + Bi ₂ O ₃ + NH ₄ H ₂ AsO ₄	400	850	12 h	30 days	5 K/h	[11]
(Na _{0.71} Ag _{0.29}) ₂ CoP ₂ O ₇	NaNO ₃ + AgNO ₃ + Co(NO ₃) ₂ ·6H ₂ O + NH ₄ H ₂ PO ₄	400	620	24 h	5 days	5 K/h	[12]
Ag ₄ Co ₇ (AsO ₄) ₆	AgNO ₃ + Co(NO ₃) ₂ ·6H ₂ O + As ₂ O ₅	400	1005	24 h	5 days	5 K/h	[13]
Na ₄ Li _{0.62} Co _{5.67} Al _{0.71} (AsO ₄) ₆	Na ₂ CO ₃ + LiOH·H ₂ O + Co(NO ₃) ₂ ·6H ₂ O + Al ₂ O ₃ + NH ₄ H ₂ AsO ₄	400	870	24 h	5 days	5 K/h	[14]
Ag _{3.68} Co ₂ (P ₂ O ₇) ₂	AgNO ₃ + Co(NO ₃) ₂ ·6H ₂ O + NH ₄ H ₂ PO ₄	350	610	12 h	3 days	5 K/h	[15]
Na ₂ Co ₂ (MoO ₄) ₃	NaNO ₃ + Co(NO ₃) ₂ ·6H ₂ O + (NH ₄) ₆ Mo ₇ O ₂₄	350	650	24 h	4 days	5 K/h	[16]
Na ₇ Li _{0.8} K _{0.2} Co ₅ (As ₃ O ₁₀) ₂ (As ₂ O ₇) ₂	NaNO ₃ + Co(CH ₃ COO) ₂ ·4H ₂ O + As ₂ O ₅	400	670	12 h	7 days	5 K/h	[17]

T1, pre-treatment temperature; T2, temperature of synthesis; t1, pre-treatment time; t2, synthesis time; R, cooling rate.
The different parameters of the synthesis (reagents, pre-treatment temperature, temperature of synthesis, pre-treatment time, synthesis time, and cooling rate) are regrouped in the table.

Table 1.
Same materials have been obtained as single crystals by the means of solid-state reaction.

H₂O, only the oxides remain. The mixture is again ground at the outlet of the oven to make it more homogeneous and to minimize the grain size.

Crystal growth: After the germination phase, and under the effect of a concentration gradient, the cations have just migrated to the germs, forming well-ordered layers. This migration is favored by heating at very high temperature. After cooling, the crystals are separated from the stream by hot and sometimes boiling water.

The disadvantages of this method are that it is very slow and needs a lot of energy. In fact, the reaction occurs at high temperatures (500–2000°C) for several hours and for same time for several days. The heating at these temperatures may decompose the desired compound.

Experimentally, oxides and nitrates are bad reagents in the synthesis of single crystals, and they often give crystals with small size which is insufficient to do the x-ray single crystal diffraction. The mechanical grinding can be used to decrease the grain sizes and increase the specific surface then increase the reactivity.

The cooling rate is a very important factor to obtain a single crystal with good crystallinity. The cooling rate should be as slow as possible and at least up to 50°C below the crystallization temperature. The choice of the size and the confirmation of the crystallinity of single crystals are initially done using a binocular magnifier (**Figure 2**) then by using the polarizing microscope. This choice is confirmed by the intensity and the width of the diffracted X-rays.

Table 1 summarized that same materials have been obtained as single crystals by the means of solid-state reaction. The different parameters of the synthesis (reagents, pre-treatment temperature, temperature of synthesis, pre-treatment time, synthesis time, and cooling rate) are regrouped in the table.

The resolution of the structure same crystals needs the knowledge of its compositions by using elementary analysis such as the energy-dispersive X-ray spectroscopy (EDX) (**Figure 3**).

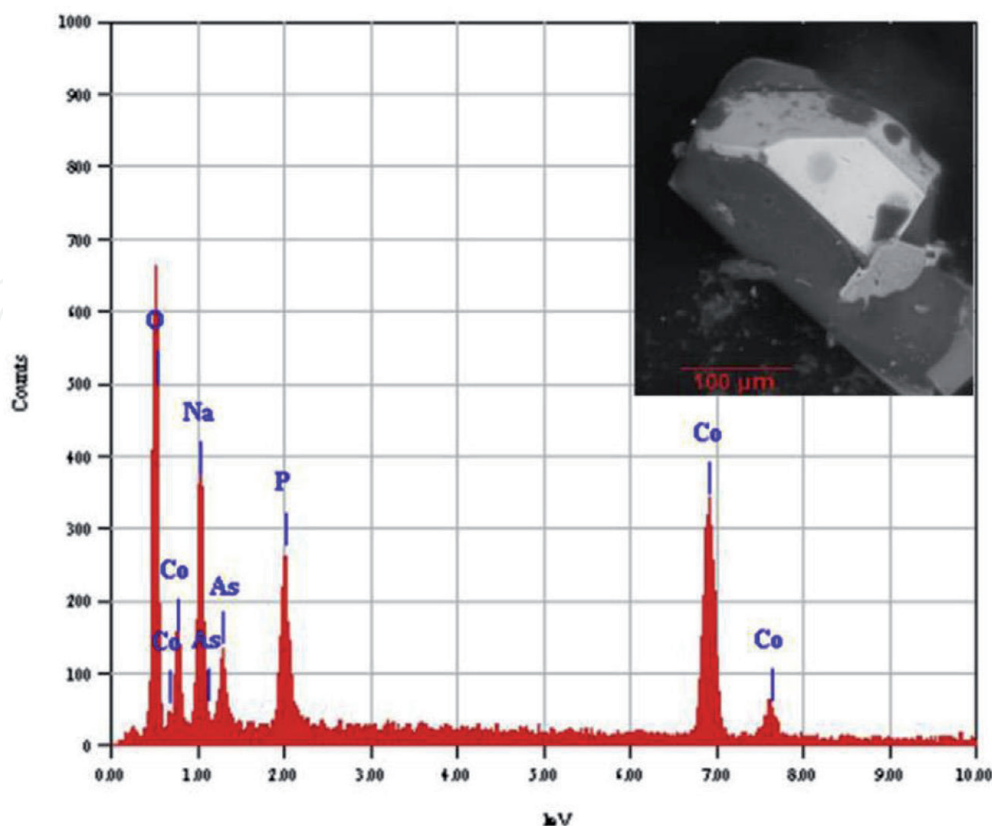


Figure 3. SEM micrograph and EDX analysis of a single crystal of Na₂CoP_{1.5}As_{0.5}O₇ [8] showing the morphology, size, and composition of the single crystal.

3. Hydrothermal method

The synthesis of the single crystal by the means of hydrothermal method occurs usually in water at temperatures between 180 and 300°C. The reactor can be an autoclave (**Figure 4**) or a sealed glass tube (**Figure 5**). The pressure is controlled by the gas law [$P = f(T)$]. The pressure of some reactors can be controlled, and it can reach a value of 850 GP. Several materials have been synthesized using the hydrothermal method.

The hydrothermal conditions of an aqueous medium correspond to temperatures and pressures above 100°C and 1 bar, respectively. These conditions allow to considerably modify the chemistry of the cations in solution. They favor the formation of complex metastable structures of lower symmetry and involving smaller variations in enthalpy and entropy than under “normal” conditions [18, 19]. Hydrothermal conditions are also those of the geological processes during which many minerals were formed. In the laboratory, such conditions are achieved by heating a solution in a closed enclosure (autoclave and sealed glass tube) at temperatures of the order of 200–400°C.

The thermodynamic properties of water up to temperatures of 1000°C and pressures of several tens of kilobars are well known [18]. Quantitative data are collected in numerous review articles [18–21]. There are three essential points to remember.

- The dielectric constant of water drops when the temperature increases. It increases by pressure increase [22] (**Figure 6**). The hydrothermal solutions are therefore characterized by low dielectric constants and the electrolytes which are completely dissociated under normal conditions preferentially form pairs of ions or complexes of low electrostatic charge.
- The viscosity of water decreases with the increase of temperature [23], which leads to greater mobility of the dissolved species than under normal conditions.
- The ionic product of water increases strongly with temperature [24] (**Figure 7**). The conductivity measurements allow establishing the law of variation of the ionic product as a function of temperature

$$\log K_e = -(3018/T) - 3.55 \quad (1)$$



Figure 4.
 Autoclave.



Figure 5.
Sealed glass tube.

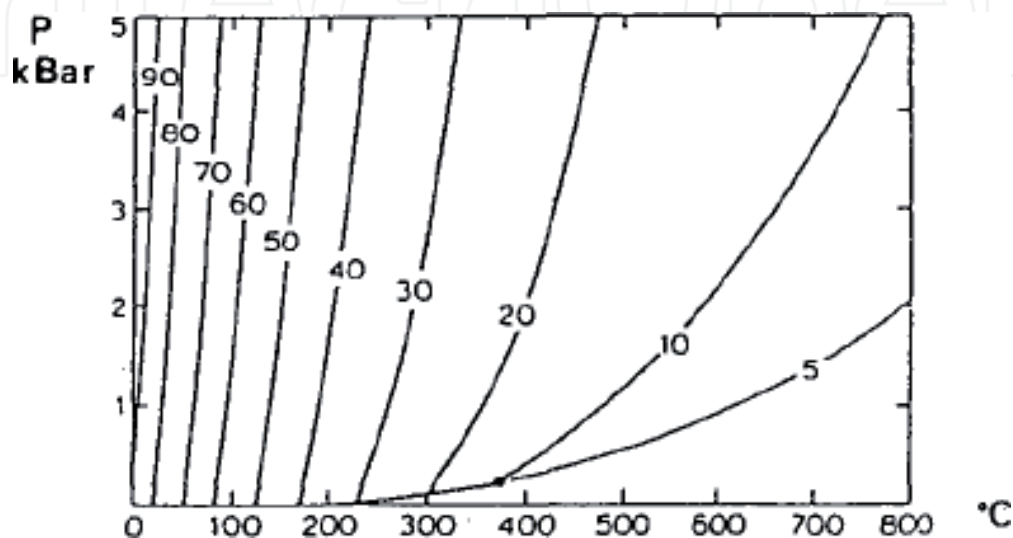


Figure 6.
Variation of the dielectric constant of water as a function of the temperature and the pressure [22].

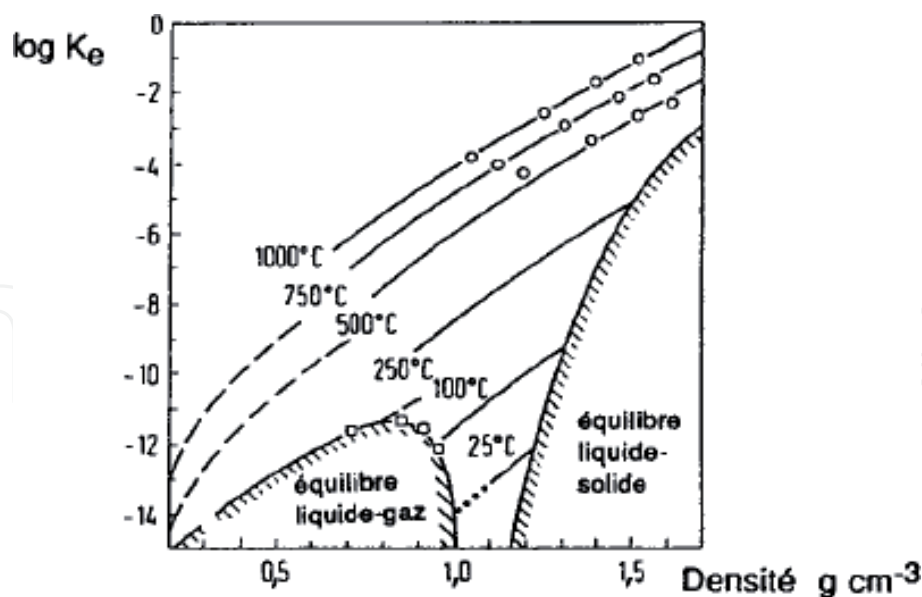


Figure 7.
Variation of the ionic product K_e of water as a function of the temperature and the density of the liquid [24].

The phosphate $\text{AgNi}_3\text{PO}_4(\text{HPO}_4)_2$ [25] has been obtained after 3 weeks of heating at 300°C in sealed glass tube filled with the mixture to about 25% in volume (**Figure 5**). The phase has been prepared from an aqueous solution of AgNO_3 , $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and H_3PO_4 in the atomic ratio $\text{Ag}:\text{Ni}:\text{P} = 2:1:2$.

In the other hand, most of the single crystals of the borophosphate family have been obtained by the hydrothermal rout. Kniep et al. [26] have prepared a lot of new borophosphates as a single crystal and they have developed an approach of the

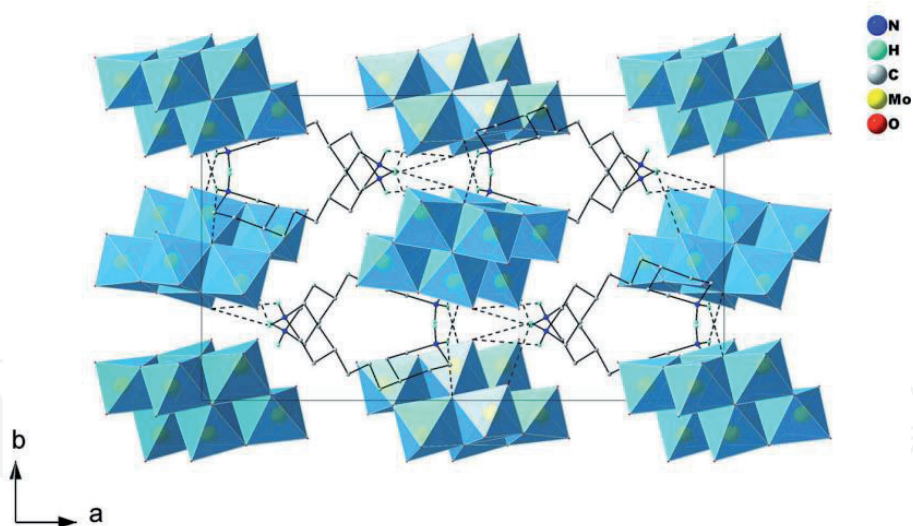


Figure 8.
 Projection of the crystal structure of $(C_{13}H_{28}N_2)_2[Mo_8O_{26}]$ along c -axis [27].

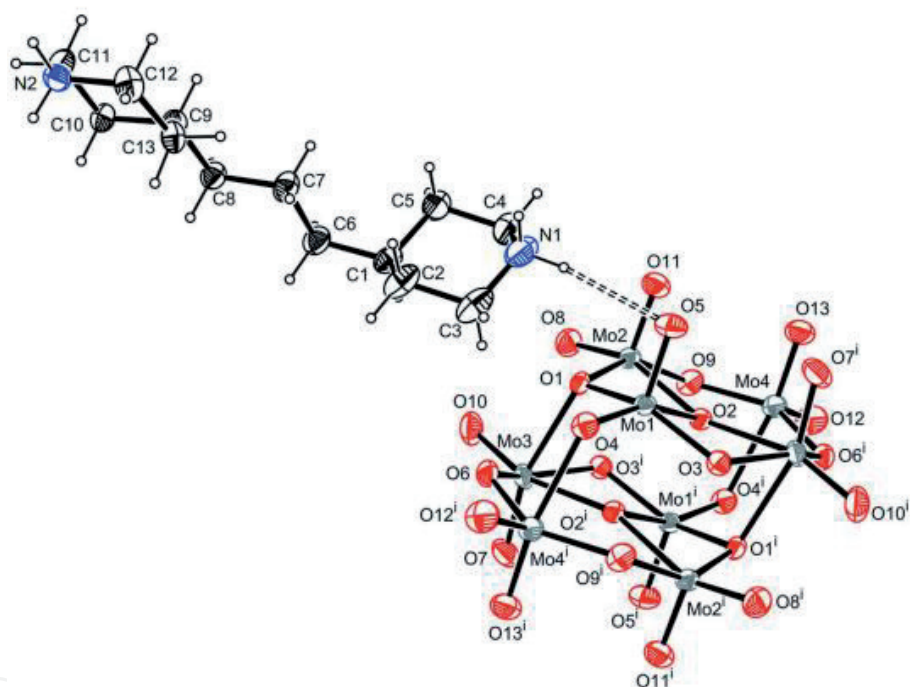


Figure 9.
 Representation of the inorganic part $[Mo_8O_{26}]^{4-}$ and the organic part $(C_{13}H_{28}N_2)^{2+}$ of $(C_{13}H_{28}N_2)_2[Mo_8O_{26}]$ [27]. The two parts are linked by a hydrogen bond.

borophosphate crystal chemistry. They have classified the different existing materials in this family as the B/P ratio and as the coordination number of the bore [26].

It is possible to obtain hybrid (organic/inorganic) materials by using this synthesis method. For example, the hybrid material with general formula Bis[4,4'-(propane-1,3-diyl)dipiperidinium]β-octamolybdate (VI) [27] (**Figures 8 and 9**) has been synthesized as single crystals by using the hydrothermal method in an autoclave at 150°C for 2 days.

4. Reaction at high pressure

The effect of pressures on the crystal structure of same materials as the transformation of the ZnO from wurtzite to rock salt from 9 to 13 GPa is well known [28]. Another example is the transformation of the olivine structure at high pressure

from the hexagonal close packing into the cubic close packing of the spinel structure [29]. Upon high pressure conditions (6 GPa, 1173 K) olivine-like LiMAsO_4 ($M = \text{Fe, Co, Ni}$) transforms to spinel-like compounds where Li^+ and M^{+2} ions randomly occupy 16d octahedral positions and the As^{+5} cations occupy the tetrahedral 8a sites [29] (**Figure 10**).

Since 2006, the prediction of the structure at high pressures became an area of intense activity thanks to the development of the new computer program USPEX [30] by Oganov et al. The code was used with success to predict many new crystal structures, and the results were confirmed by the synthesis of same predicted materials such as Na-Cl system: Na_3Cl , Na_2Cl , Na_3Cl_2 , Na_4Cl_3 , NaCl_3 , and NaCl_7 [31] and H-Cl system: H_2Cl , H_3Cl , H_5Cl , and H_4Cl_7 [32, 33]. This result allows the discovery of new generation of materials where the core electrons can participate in the formation of chemical bonds. Thus, obviously, we will have very interesting physical and chemical properties.

5. Synthesis by slow evaporation at room temperature

It is the simplest method, but it is suitable only for certain materials. The preparation protocol consists in weighing the reagents in the desired proportion and adding water or an organic base in a ratio that should be determined experimentally. Then the solution must be heated to reach the saturation.

This method takes a few hours to obtain crystals as in the synthesis of $\text{NH}_4\text{H}_2\text{AsO}_4$ or $\text{NH}_4\text{H}_2\text{PO}_4$, and for other materials, it needs a few days. The condensation of ions

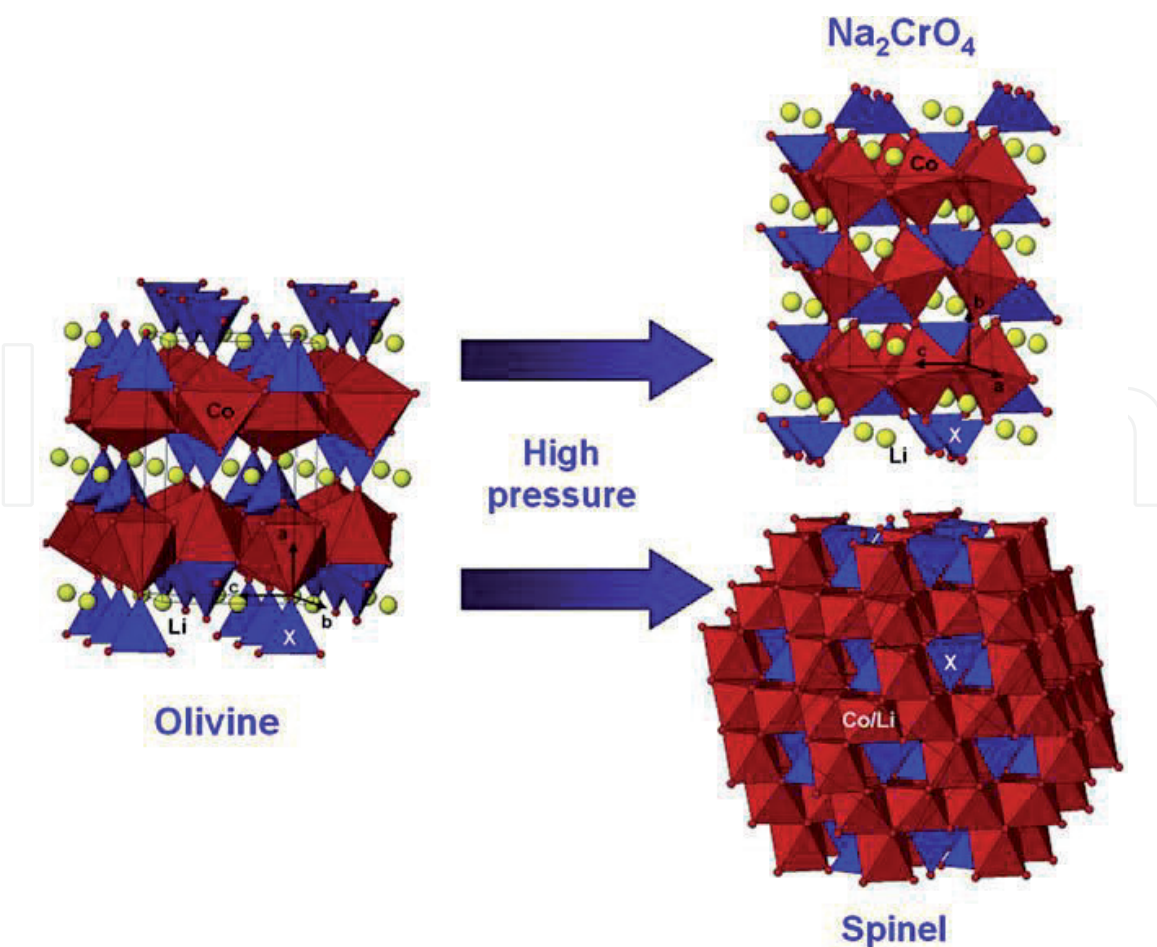


Figure 10. Structures of olivine-, Na_2CrO_4 -, and spinel-like LiCoXO_4 ($X = \text{P, As}$) [29].

in aqueous solution forms entities in which cations, identical or different, are linked by different types of oxygenated bridges, HO^- or O^{2-} . Thus, the value of pH is a very important factor in this method. In fact, the choice of pH must be chosen to co-precipitate the various reagents simultaneously. For example, in the ternary system $\text{H}_2\text{O}-\text{NH}_3-\text{As}_2\text{O}_5$, the adjusting of the pH at 4.3 allows the formation of $\text{NH}_4\text{H}_2\text{AsO}_4$, and for a basic value of pH, the preparation gives a second phase: $(\text{NH}_4)_2\text{HAsO}_4$.

The following phosphate $\text{KCdHP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ (**Figure 11**) [34] has been obtained by slowly evaporation at room temperature. The method consists in the preparation of a saturated solution containing the reagents in the desired proportion. The reagents are dissolved in water then heated at 100°C for a few minutes to have a saturated solution. The solution obtained is transferred into a petri dish and left in a corner in the laboratory.

The hybrid materials (organic base+ salt) may be synthesized by slow evaporation at room temperature. The best solvent can be used is the water. It is possible to add other solvent with water such as alcohol like in the preparation of $(\text{C}_7\text{H}_7\text{N}_2)_2[\text{CuCl}_4] \cdot 2\text{H}_2\text{O}$ [35]. In this type of materials, the organic part and the inorganic part are linked via hydrogen bond and $\pi-\pi$ bond as shown in **Figure 12**.

Another example may be cited in this section, the synthesis and the crystal structure of $(\text{C}_3\text{H}_6\text{N}_3)_4\text{Bi}_2\text{Cl}_{10}$ [36] which was grown by a slow evaporation of an aqueous solution of bismuth chloride (BiCl_3) and 3-aminopyrazole ($\text{C}_3\text{H}_5\text{N}_3$) in molar amount (1: 2) with a small excess of hydrochloric acid (HCl). The single crystals were obtained after 7 months of slow evaporation (**Figure 13**).

Many organic compounds also have been crystallize by slow evaporation at room temperature such as alkyl-2-(2-imino-4-oxothiazolidin-5-ylidene) acetate [37], 3,4-*cis*-disubstituted pyrrolidin-2-ones [38] ethyl 2-(4-chlorophenyl)-3-cyclopentyl-4-oxo-1-propylimidazolidine-5-carboxylate ($\text{C}_{20}\text{H}_{27}\text{ClN}_2\text{O}$) [39]. The obtaining

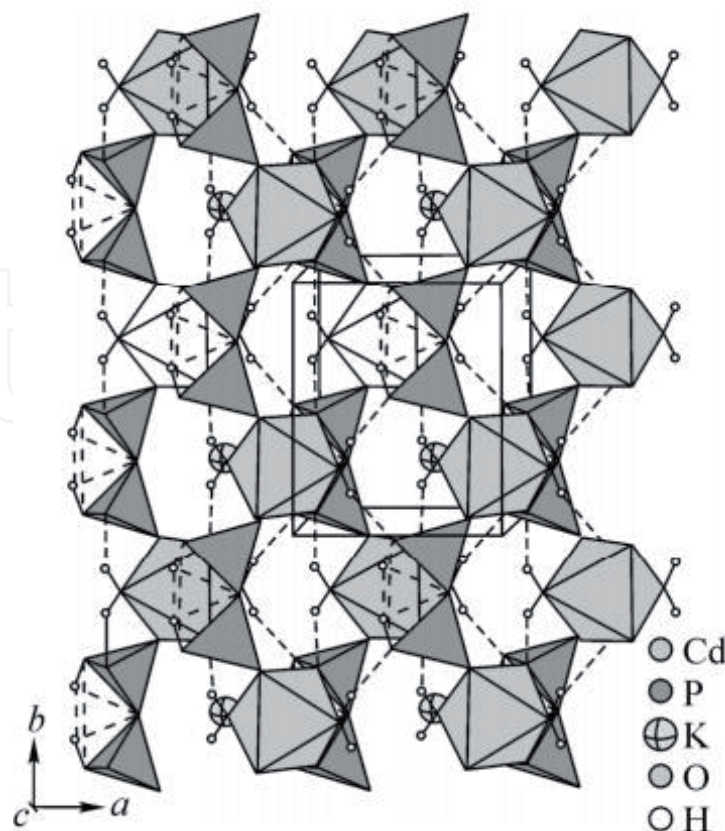


Figure 11.
 Perspective view of the structure of $\text{KCdHP}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ showing the hydrogen bonds (dashed lines) and the location of the alkali metal cations [34].

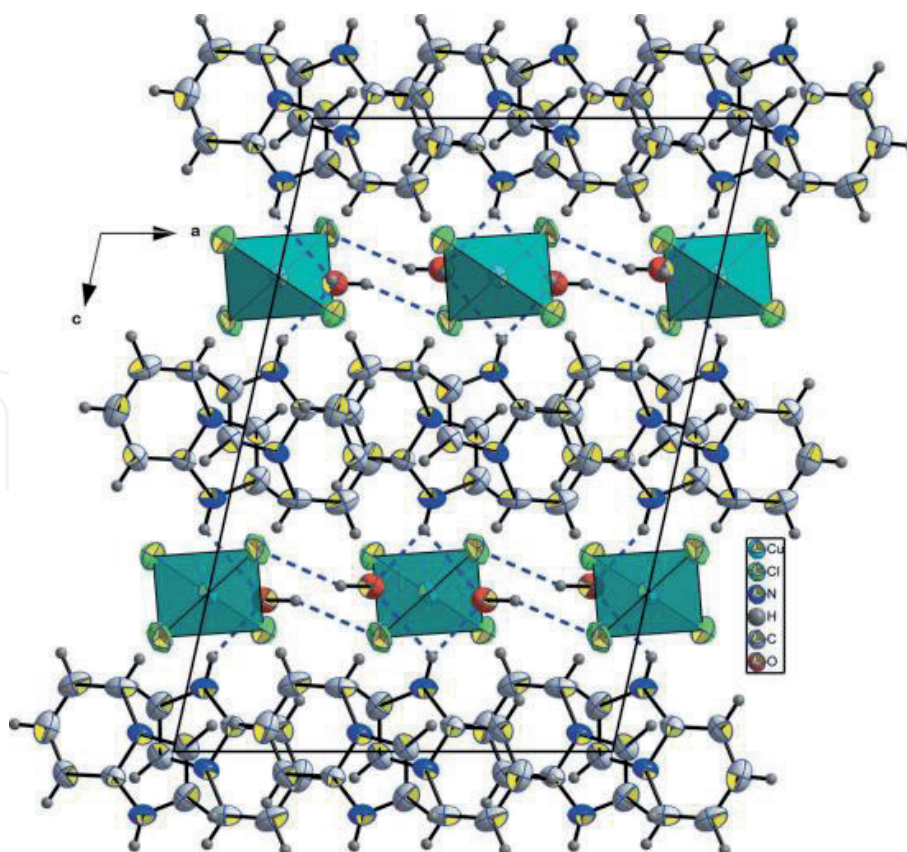


Figure 12.

Projection of the structure of $(C_7H_7N_2)_2[CuCl_4] \cdot 2H_2O$ showing the alternating stacking of the organic and inorganic layers connected through hydrogen bonds. The face-to-face π - π stacking between parallel organic molecules is noteworthy with a centroid-centroid distance of 3.968 (3) [35].

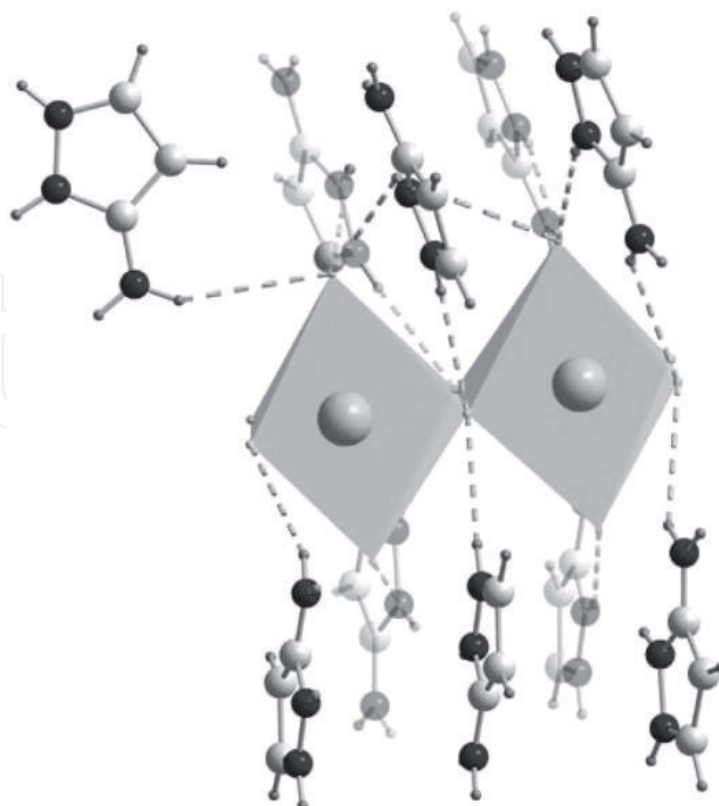


Figure 13.

Bi_2Cl_{10} octahedron surrounded by aminopyrazolium entities, showing the H-Cl contacts [36].

of single crystals depends in the case on the nature of the organic compounds and solvent. The presence of heterocyclic group in the organic molecule promotes the crystallization by the formation of hydrogen and π - π bond.

6. Flux method

Usually, the flux method is used to grow materials as single crystals [40]. The main objective of this method is to decrease the crystallization temperature. This technique has been used to grow high melting phosphate crystals, arsenates, oxides, minerals, and ceramic crystals which cannot be obtained by the conventional solid-state method (Section 1). In this growth technique, the basic materials (solute precursors to crystallize) are reduced to a liquid form in an appropriate flow and the growth process starts when the solution reaches critical supersaturation. The resulting supersaturation and crystal growth are achieved by flow evaporation, solution cooling, or a transport process in which the solute is caused to flow from the hottest region to the coldest region.

The understanding of the phase information about the materials is indispensable to optimize the crystal growth of multi-component system. Practically, binary or other above compositional systems can be easily described using the phase diagram. The phase diagram shows the crystallization or solidification within a material as a function of the material composition (% elements) and material temperature.

The solvent can be a single element, compound, or combination of chemical compounds. The solute is an element or a compound with a melting point generally higher than that of the solvent but in principle it is quite possible to grow crystals from eutectic systems in which the “solvent” has a higher melting point.

For more clarification, taking the example of $\text{LiPr}(\text{PO}_3)_4$ [40]. The material has been synthesized as a single crystal by the means of flux method. A mixture of Li_2CO_3 and Pr_6O_{11} with stoichiometric ratio was dissolved in an excess of phosphoric acid H_3PO_4 (85%). The mixture was heated to 200°C for 12 h, then to 325°C for 5 days. Finally, the mixture was cooled slowly to room temperature. The single crystal was separated from the excess phosphoric acid by washing in boiling water [40].

7. Crystal growth

When a solid is heated, some physical and chemical changes sintering, melting, and thermal decomposition can be observed. Sintering process results from crystal growth at the contact area between adjacent crystallites. As to conclude, the crystallites connect to each other, and the size increases [41–43].

In high temperatures, as a result of ion movements, melting occurs. The ordered lattice array is replaced by the short-range order of the liquid state. Crystallization may proceed in the light of several different ways:

1. Vapor-solid (condensation)
2. Solution-solid (precipitation)
3. Melt-solid (freezing)
4. Solid A-Solid B (transformation)

It is well-known that there is a remarkable correlation between stability and energy. Stable states have low energy values. For the processes, final energy values of solids must be lower from the free energy of initial state of the systems. It should be noted that crystal formation process forms from two steps. First step is the formation of a new nucleus. Second step is the growth of the nucleus formed to form a particle of appreciable size. Crystals may contain some defects. In terms of the determination of crystal properties, these defects are quite important. In addition to these defects, distortion of lattice also may be possible. This condition is called as dislocation. Many important properties of crystals are due to the regions and numbers of these dislocations. Crystal growths can be via the following types:

- growth from melt
- high-temperature solution growth
- flux growth
- chemical vapor transport
- hydrothermal synthesis
- high-pressure synthesis
- electrolytic reduction of fused salts

In high-temperature solution growth, the constituents of the crystals are dissolved in a suitable solvent and then when the solution becomes over saturated, crystallization occurs. In flux growth, crystals like ceramics and ferrites have been grown by the slow cooling of a solution in a molten flux. Chemical transport reactions are widely considered in the preparation of single crystals like magnetite.

8. Conclusion

In this chapter, the methods of synthesis of crystalline materials and their stages are discussed. These methods are the most adopted and the most common in solid-state chemistry. Each synthesis method brings back to crystalline materials of different sizes returning to the synthesis conditions. The change of one of the parameters such as temperature, pressure, and reactional environment can influence the crystallinity and the size of the sample obtained. For this, the control of these parameters is essential in the synthesis of crystallized materials and in their reproducibility.

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