

## Solid State Synthesis Methods: A brief review

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**Abstract:** The synthesis of various materials is now a common practice in materials science research. As single crystals maintain translational symmetry over macroscopic distances, it is possible to study directional dependence of various properties and compare with theoretical predictions. Growth 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 article describes the most common synthesis methods of single crystal in the solid-state chemistry: solid-state method, hydrothermal, and slow evaporation at room temperature. 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.

**Introduction:** The solid state materials may be prepared as single crystals, polycrystalline powder, thin films and amorphous. Single Crystals preferred for characterization of structure and properties. Polycrystalline Powder (Highly crystalline) used for characterization when single crystal cannot be easily obtained, preferred for industrial production and certain applications.

Polycrystalline Powder (Large Surface Area) are desirable for further reactivity and certain applications such as catalysis and electrode materials. Thin Films have widespread use in microelectronics, telecommunications, optical applications, coatings, etc. Amorphous (Glass) solids have no long range translational periodicity used or studied in electrophotography, thin film electronics, solar voltaic cells and many other areas [1,13-18].

Single-crystal X-ray diffraction is most commonly used for precise determination of a unit cell, including cell dimensions and positions of atoms within the lattice. Single crystal shows intense and sharp narrower peaks in XRD pattern but polycrystalline materials shows less intense and broad XRD peaks.

Conventional solid state synthesis techniques involve heating mixtures of two or more solids to form a solid phase product. Unlike gas phase and solution reactions, the limiting factor in solid-solid reactions is usually diffusion. To obtain good rates of reaction you typically need the diffusion coefficient to be larger than  $\sim 10^{-12}$  cm<sup>2</sup>/s.

The diffusion coefficient increases with temperature, rapidly as you approach the melting point. This concept leads to Tamman's Rule; it suggests a temperature of about two-thirds of the melting point (K) of the lower melting reactant is needed to have reaction to occur in a reasonable time. Thorough grinding is necessary to achieve a homogeneous mixture of reactants. Extensive reaction will not occur until the temperature reaches at least  $2/3$  of the melting point of one or more of the reactants. Rates of Reaction depends on by three factors:

1) The area of contact between reacting solids, 2) The rate of diffusion, 3) Rate of nucleation of the product phase

In this article, 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.

**Solid-state method:** In this method, the number of affecting 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. The crystallization generally occurs during phase change and it is accompanied by a thermal effect. It is carried out in two stages: germination and growth. The germination begins at a non-equilibrium point where the phases are not in, a condition can be favored by several factors such as impurity, crucible wall, 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 porcelain basket and preheated between 500°C and 2000°C for a few hours. This operation allows the decomposition of the starting reagents and removes the volatile products such as NH<sub>3</sub>, NO<sub>2</sub>, CO<sub>2</sub>, and H<sub>2</sub>O, 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 some 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 then by using the polarizing microscope. This choice is confirmed by the intensity and the width of the diffracted X-rays. The different parameters of the synthesis reagents, pre-treatment temperature, temperature of synthesis, pre-treatment time, synthesis time, and cooling rate. 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)

**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 or a sealed glass tube. 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 hydro-thermal method. The hydrothermal conditions of an aqueous medium

correspond to temperatures and pressures above 100°C and 1bar, respectively. These conditions allow to considerably modifying 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 [1,2]. 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 [1]. Quantitative data are collected in numerous review articles [1-4]. There are three essential points to remember.

The dielectric constant of water drops when the temperature increases. It increases by pressure increase [5]. 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 [6], which leads to greater mobility of the dissolved species than under normal conditions. The ionic product of water increases strongly with temperature [7]. The conductivity measurements allow establishing the law of variation of the ionic product as a function of temperature

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

The phosphate  $\text{AgNi}_3\text{PO}_4(\text{HPO}_4)_2$  [8] has been obtained after 3 weeks of heating at 300°C in sealed glass tube filled with the mixture to about 25% in volume. The phase has been prepared from an aqueous solution of  $\text{AgNO}_3$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , and  $\text{H}_3\text{PO}_4$  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 route. Kniep et al. [9] have prepared a lot of new borophosphates as a single crystal and they have developed an approach of the 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 boron [9]. It is possible to obtain hybrid (organic/inorganic) materials by using this synthesis method. For example, the hybrid material with general formula  $\text{Bis}[4,4'-(\text{propane-1,3-diyl})\text{dipiperidinium}]\beta\text{-octamolybdate (VI)}$  [10] has been synthesized as single crystals by using the hydrothermal method in an autoclave at 150°C for 2 days

**Reaction at high pressure** : Increase of pressure increases the coordination number during crystallization e.g. by applying pressure the NaCl type crystal structure having 6:6 coordination

number changes to CsCl type crystal having coordination number 8:8. 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 [11]. Upon high pressure conditions (6GPa, 173K) olivine-like  $\text{LiMAsO}_4$  ( $M=\text{Fe, Co, Ni}$ ) transforms to spinel-like compounds where  $\text{Li}^+$  and  $M^{+2}$  ions randomly occupy 16d octahedral positions and the  $\text{As}^{+5}$  cations occupy the tetrahedral 8a sites [11]. 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 [12] by Oganov et al. The code may be used with to predict many new crystal structures. This 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.

### **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 in aqueous solution forms entities in which cations, identical or different, are linked by different types of oxygenated bridges,  $\text{HO}^-$  or  $\text{O}^{2-}$ . 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. 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  $100^\circ\text{C}$  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. In this type of materials, the organic part and the inorganic part are linked via hydrogen bond and  $\pi$ - $\pi$  bond. The obtaining 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  $\pi$ - $\pi$  bond.

**Flux method:** This method, usually applied to grow materials as single crystals. 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. 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.

**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 [13,14]. 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 [17]. 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 dis-solved 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.

### Conclusion:

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 yields crystalline materials of different sizes returning to the synthesis conditions. The change of one of the parameters such as temperature, pressure, and reactional environment and time can influence the crystallinity and the size of the sample obtained. By the control of these parameters is essential in the synthesis of crystalline materials.

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