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# Crystal Growth : An experimental aproach

## Summer School S3++

**Gimnazija Požega**

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# Introduction

Crystals are found almost everywhere in the world. They have wide use in medicine and industry, but their properties are still being researched. The aims of our project are to grow a perfect crystal, fully understand what a perfect crystal really is and also get to know for which applications crystals are used. In order to discover properties of crystals, their structure and lattice must be known. Solid materials with microscopic organized repeating units forming crystal lattice are considered crystals. Every crystal has its unique arrangement of atoms, ions or molecules forming symmetrical patterns.

## 1. What is a perfect crystal

### a. Lattice and symmetry

A crystal's structure plays a vital role in determining many of its physical properties, such as cleavage, conductivity and optical transparency. There are 14 main types of lattices, called Bravais lattices. These are obtained by combining one of the seven lattice systems with one of the four lattice types. The lattice systems can be characterized by their shapes according to the lengths of the cell edges (a, b, c) and the angles between them (α, β, γ). The lattice types describe different position of atoms, ions or molecules in the unit cell (P, I, F, C/A).

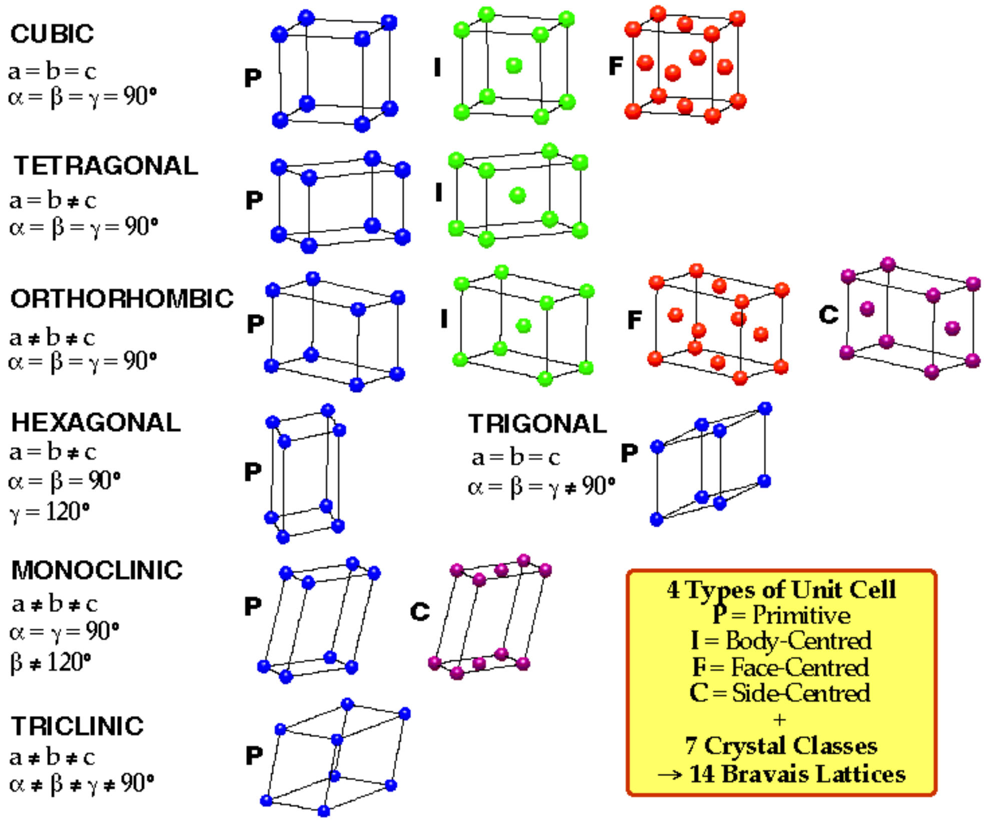
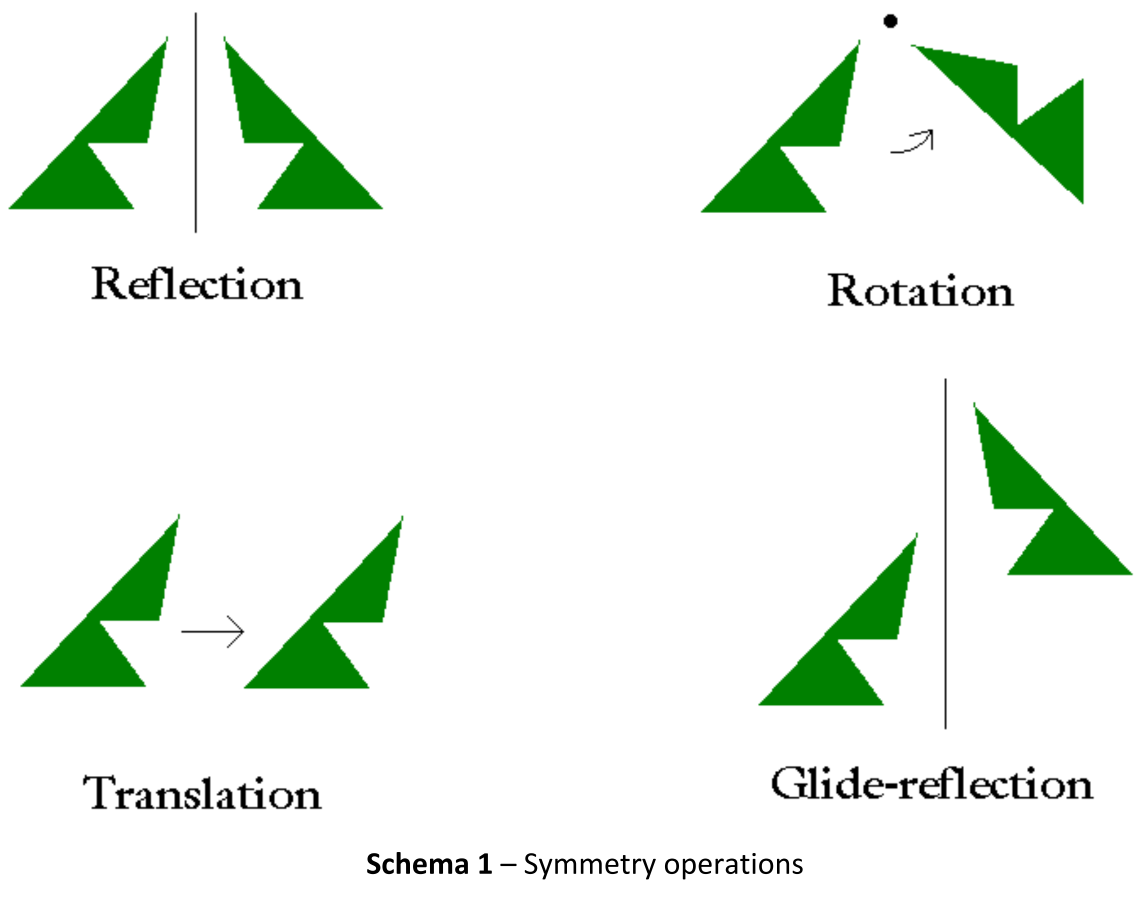



**Table 1** – 14 Bravais Lattice

Crystals can be divided into two groups: monocrystals and polycrystals. Monocrystals are crystals with continuous and unbroken crystal structure and with no grain boundaries. Polycrystals are crystals that are composed of many monocrystals that vary in size and orientation. Thanks to lack of defects, monocrystals have many unique mechanical and optical properties. In contrast, polycrystals are useless in optical industry but are still applied in other fields of science. Perfect crystal is obviously a monocrystal, one that contains no point, linear, or planar imperfections. Growing a perfect crystal in theory is incredibly hard and in reality it´s impossible as even the slightest impurity or gravity force can completely change its shape.

Symmetry is essential in crystallography. It can be described as a correspondence in size, form, and arrangement of parts on opposite sides of a plane, line, or point. There are three main types of symmetry; reflection symmetry-when the object has an identical reflection along the line of symmetry, rotation symmetry-when the objects is turned around its center point for a certain number of degrees and looks the same, and finally translation-when the object is moved without rotating or reflecting it. Knowing the symmetry of a crystal we can identify it as well as discover its thermal conductivity and optical activity.




**Schema 1** – Symmetry operations

## b. Compounds used

During our project we used mainly three types of different inorganic salts; copper (II) sulfate hydrate with chemical formula $CuSO_4 \cdot 5H_2O$ because of its spectacular blue color and rhombic shape, monopotassium phosphate $KH_2PO_4$ (also known as KDP) widely used in optical industry thanks to its unique property of nonlinear conversion of light, and hydrated potassium aluminum sulfate with formula $KAl(SO_4)_4 \cdot 12H_2O$ (alum). As various impurities we used Rochelle salt (KNaC4H4O6·4H2O) with very useful piezo electric properties, iron and aluminum ions.

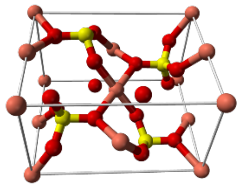
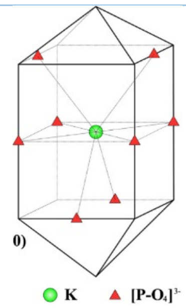
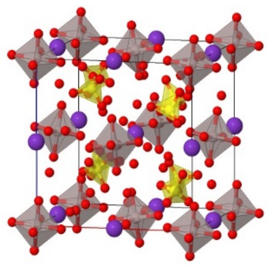
| Name of the crystal | Chemical formula | Symmetry | Space group | Parameters | Lattice image |
|---|---|---|---|---|---|
| copper (II) sulfate | $CuSO_4 \cdot 5H_2O$ | triclinic | P1 | a=0.5986 nm<br>b=0.6141nm<br>c=1.0736nm |  |
| monopotassium phosphate | $KH_2PO_4$ | tetragonal | I42d | a=b=0.744nm,<br>c= 0.697nm |  |
| potassium aluminum sulfate | $KAl(SO_4)_2 \cdot 12H_2O$ | cubic | Pa3 | a=b=c=<br>12.133nm |  |

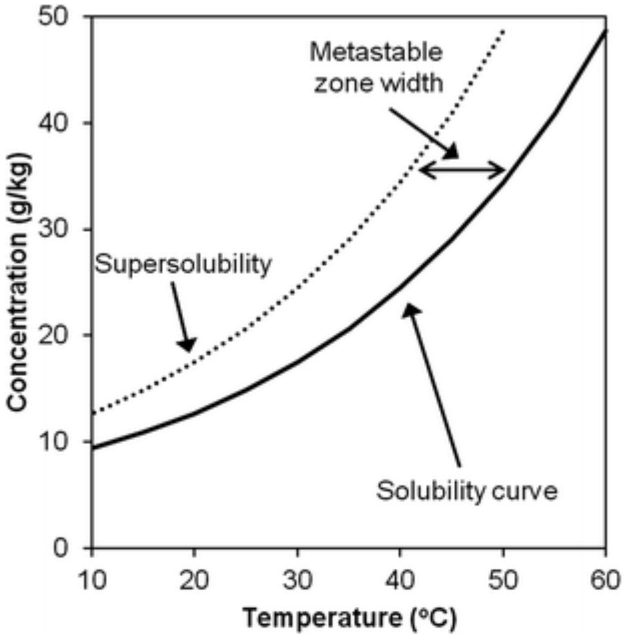
**Table 2**– Compounds used

## 2. How can we grow a perfect crystal

### a. Crystal growth and supersaturation

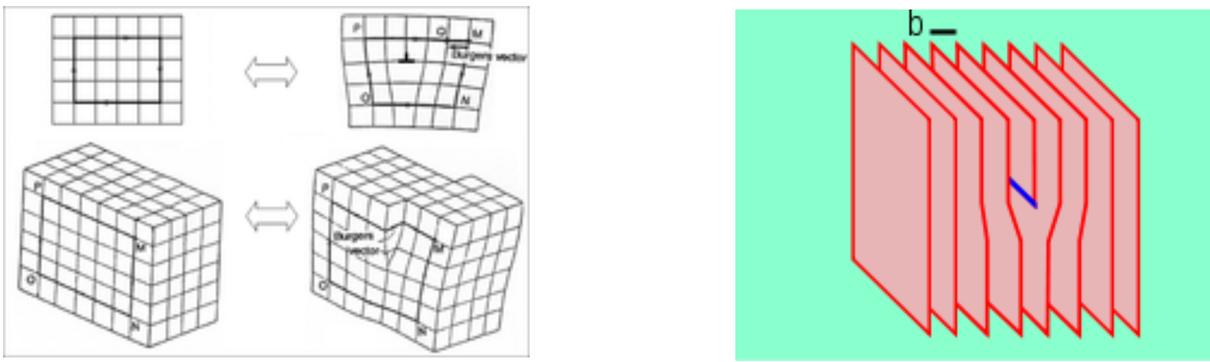
Crystals are usually made by crystallization process. It consists of two steps: nucleation and crystal growth. Nucleation is the step where the solute molecules start to gather into stable clusters, which do not dissolve, and are considered as nuclei. Formation of these clusters is thermodynamically favorable when the certain conditions are met e.g. supersaturated solution.

Supersaturated solution is a solution that contains more dissolved substance than water can dissolve at certain temperature. As it can be seen from the graph below, supersaturation area (above solubility curve) consists of spontaneous nucleation zone (nuclei begin to form, so crystallization is spontaneous) and metastable zone (it is necessary to have a nucleation center in order for crystallization to begin).




**Graph 1** – Correlation between Concentration and temperature

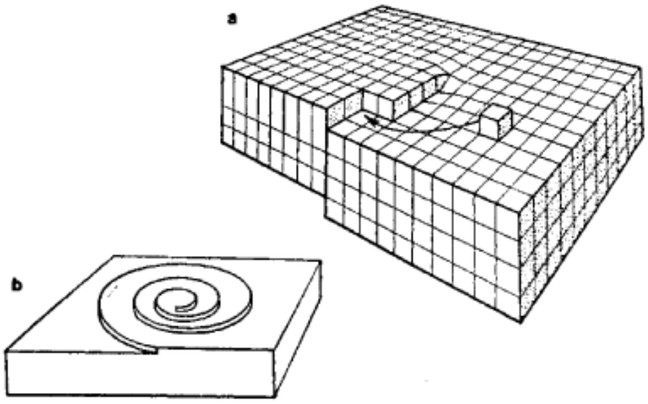
Crystal growth is referred to adding new atoms, ions or molecules to the existing nuclei. So, crystal growth precedes nucleation or adding of the "seed" crystal. In order to understand crystal growth, certain linear defects in crystal structure, called dislocations, must be considered. They are generated when stress is applied to the crystal and here will be considered two types: edge and screw dislocations (these are the basic ones, the extreme forms; most dislocations are mixed)

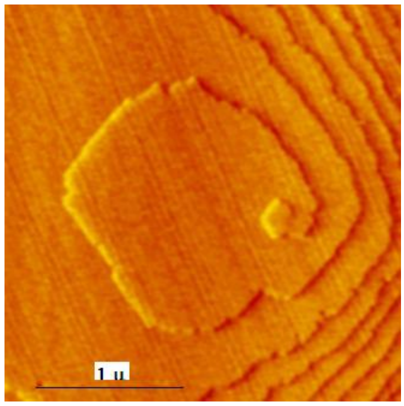



**Schema 2** – Different types of dislocation

Edge dislocation is linear defect which occurs when an extra half of the plane is inserted in the crystal structure (picture 2). It can be viewed as when a half sheet of paper is added into the stack of sheets, so papers around that one curve to maintain the structure (picture 3). Screw dislocations are far more important for crystal growth. These defects can be imagined like cutting the crystal in one plane from the side to the center, sheared along the cut and stacked together again (picture 2).

Crystals grow by adding new atoms, ions or molecules to the nuclei so they are fitting and completing regular shape of the crystal. They are adding to the places where the layer of crystal structure is incomplete. That means once the layer is completed, crystal growth stops, because there aren't any incomplete places left. However, that's not the case with real crystals, because they have dislocations. The screw dislocation doesn't allow for a layer to be completed (picture 4a). New atoms are adding around that dislocation, but instead of completing it, they are going in what looks like a spiral spreading layers (picture 4b). These layers could be seen with atomic force microscopy (AFM) (picture 5).




*Slika 1 Calcite crystal growing and AFM monitoring its growth*

**Schema 3** – Illustration of crystal growth

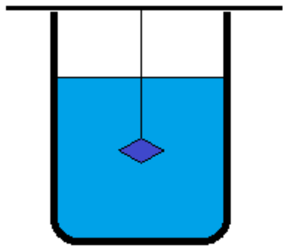
## b. General process to grow a crystal

General procedure of crystal growth is not as simple as it looks like. There are so many elements and variables that need to be considered and looked after during the process. The procedure itself can be divided into two stages.

The first part is making the seeds and the second part is the actual crystal growth. First of all, to make seeds we need to mix the right amount of water and compound so we could get the saturated solution. It is very crucial for the crystallization process that compound is fully dissolved and that does not have any impurities. After heating the solution and cooling it down to the room temperature the solution starts to crystallize.

The procedure continues by picking the seeds that are more symmetrical than the others. It is very important to use perfect seeds because of the growth itself. If we use merged or damaged seeds they will continue to grow without any regular shape and most of the time they are useless in industry in general. Also it is very important to know how to make a perfect supersaturated solution for the seed growth. The ratio of water and compound matters and it is a crucial factor in growing crystals. Usually it is better to tide up the seed with the string, put it on the stick and immerse it in the supersaturated solution because that is the proper way to grow a perfectly shaped crystal (picture below). If the seed is on the bottom of the beaker it will just merge with the bottom and start to crystallize in disorganized and useless way. In stable conditions and clean environment the crystal should grow regularly and normally expanding its shape and size.

The procedure continues for few days, just waiting the crystal to grow as well as paying attention to the surrounding factors that we can control. The process may seem very simple and easy, but there are so many factors that need to be carefully analyzed and monitored as well.



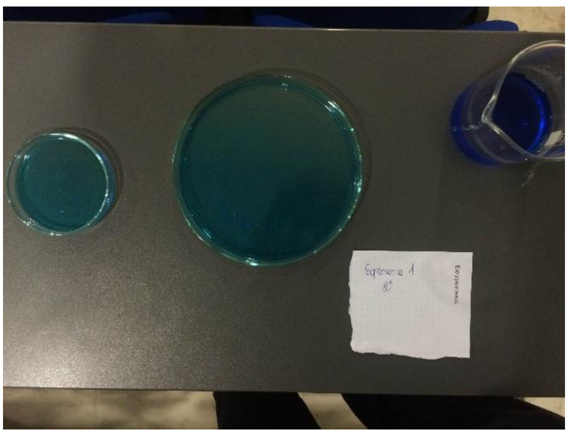
**Schema 4** - Beaker with growing crystal in copper (II) sulfate solution

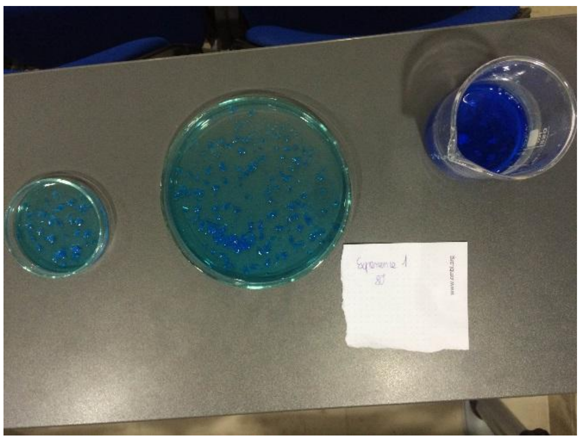
## c. Influence of the different parameters on the crystal growth

In our first experiment we tried to see how the different temperature of the copper (II) sulfate solution affects the crystal growth itself. Firstly, we made three solutions with the same concentration of copper (II) sulfate but heated on various temperatures (40°C ,60°C and 80°C).

Then we let the solutions cool down to the room temperature and tried to realize if this differences would change numbers of shapes of the seeds or the . Finally, we came to conclusion that the most seeds appeared in a beaker that contained a solution cooled down from 80C (pictures 1 and 2), little less from 60°C (pictures 3 and 4) and just one seed appeared in solution that had 40°C. We also realized that even though we can quickly get many seeds on higher temperature, in that process we do not get very symmetrical and useful seeds.

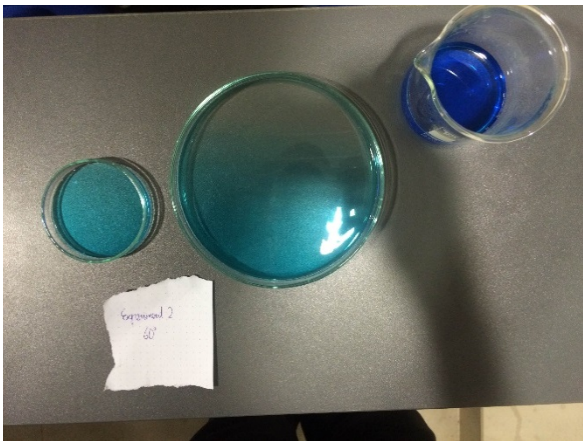
Often they are merged and we cannot use them to grow a bigger monocrystals used in optical industry. The most perfectly symmetrical and useful seed was actually from the solution of 40°C. The procedure was much slower but we got a monocrystal which was bigger that the other ones as well as suitable for growing larger crystals.

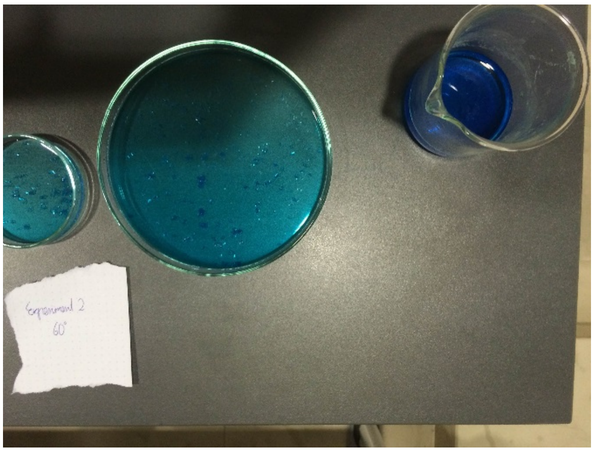




experiment 1 (80°C) **Picture 1** **Picture 2**

In the second experiment we were trying to see the differences in shapes, sizes and structure of several compounds that we have used in the lab (copper (II) sulfate, KDP, alum, Rochelle's salt, natrium thiosulfate ). We made five different solutions containing five different compounds. Through time the solution started to crystalize and the seeds started to grow. We realized that all the seeds have different shapes (Rochelle's salt-cube…) and sizes associated with their structure.





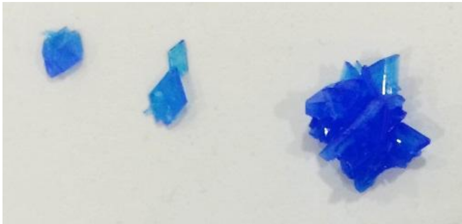
experiment 2 (60°C) **Picture 3** **Picture 4**

Also we tried to find the exact type of lattice for each compound to connect the molecular structure of materials to the shapes that we can see. In the picture we can actually see the shape, size and colour differences between four crystals (picture 5. -1. Rochelle's salt, 2. KDP, 3. alum and 4. copper (II) sulfate)

**Picture 5** – Seeds of Rochelle's salt, KDP, alum and copper (II) sulfate - comparison

Those seeds were just a starting point for growing a bigger crystals. We tried to grow a perfect monocrystal with no impurities that it can be used in optical industry. Firstly, we made a supersaturated solution on 45C in which we put our seeds and let them cool down to the room temperature. Also we attempted to mix the right ratio of water and compound to grow a perfect crystal. It was very challenging to get the right amount of components because too much water leads to dissolution of the seed and too much compound leads to uncontrolled crystallization not just on the seed but on the bottom of the beaker as well. Unfortunately because of the unstable temperature, dirty glassware and mechanical movements that we were not able to control we managed to grow polycrystals which are mostly used in medicine. In the first picture below we can see the seeds of copper (II) sulfate which we used for growing bigger copper crystals (polycrystals) which we can analyze on the second picture.

**Picture 6** – Seeds of copper (II) sulfate



**Picture 7** – Polycrystal of copper (II) sulfate

Our third experiment was to see what happens if we mix two concentrated solutions. We realized that the shape of that seed is actually a mixture of shapes of both (copper (II) sulfate and Rochelle's salt) seeds as you can see on the photo. Importantly all those seeds did not have the same shape and size. Some of them looked more similar to the copper (II) sulfate seeds and some of them to the Rochelle's seeds. That difference depends on the ratio of each component in the mixture and that is the main reason why some of them resemble more to the copper (II) sulfates seeds and some to the Rochelle's salt seeds. The difference can also be seen in the color (light blue).

**Picture 8** – Seeds of copper (II) sulfate, Rochelle's salt and their mixture between

In the end we wanted to see and analyze what happens if we add some impurities in our solution. In KDP solution we added $Fe^{3+}$ (picture b) ) and in the alum solution we put potassium chromium (picture a) ).We did the same procedure which we can divide in two parts (seed and crystal growth).

It is interesting to see how impurities in the solution incorporated in crystal affect its shape and color. Crystal growth of KDP in solution with $Fe^{3+}$ as impurities will be used as example. A KDP crystal consists of prismatic and pyramid part (picture 6). Because of more $K^+$ ions on the surface of the pyramid part, positive iron ions will more likely be incorporated in the prismatic part and so lengthen it (picture 7). Another interesting example is growth of potassium alum in presence of $Cr^{3+}$ ions in the solution. Because of the similar size of $Al^{3+}$

and $Cr^{3+}$, chromium ions can replace aluminum in the crystal lattice and, because chromium is d-element, crystal color is changed from colorless to purple. Intensity of color depends on concentration of $Cr^{3+}$ in the solution.

Also by mixing the impurities with the clean solution we got the change of colour.

**Picture 9** – crystals with impurities (1. alum + potassium chromium, 2. KDP + $Fe^{3+}$)

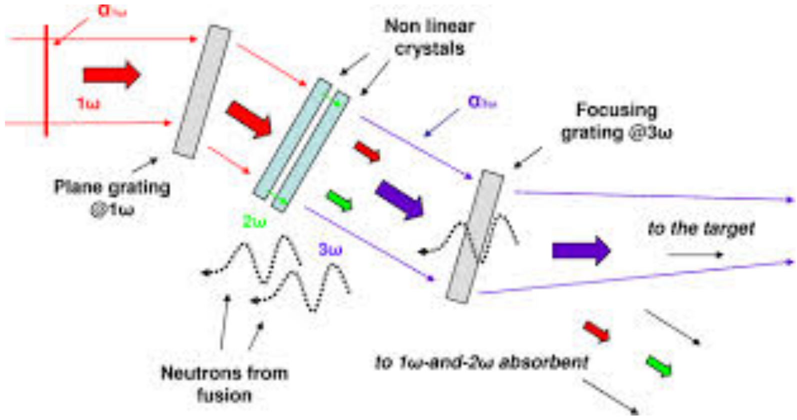
**Picture 10** – alum + potassium chromium crystal

## 3. For which applications are used the crystals

### a. Description of LMJ

As mentioned before crystals have many important unique optical properties that are essential for many parts of scientific processes and technology. KDP thanks to its non-linear optical properties, is able to convert visible light to UV.

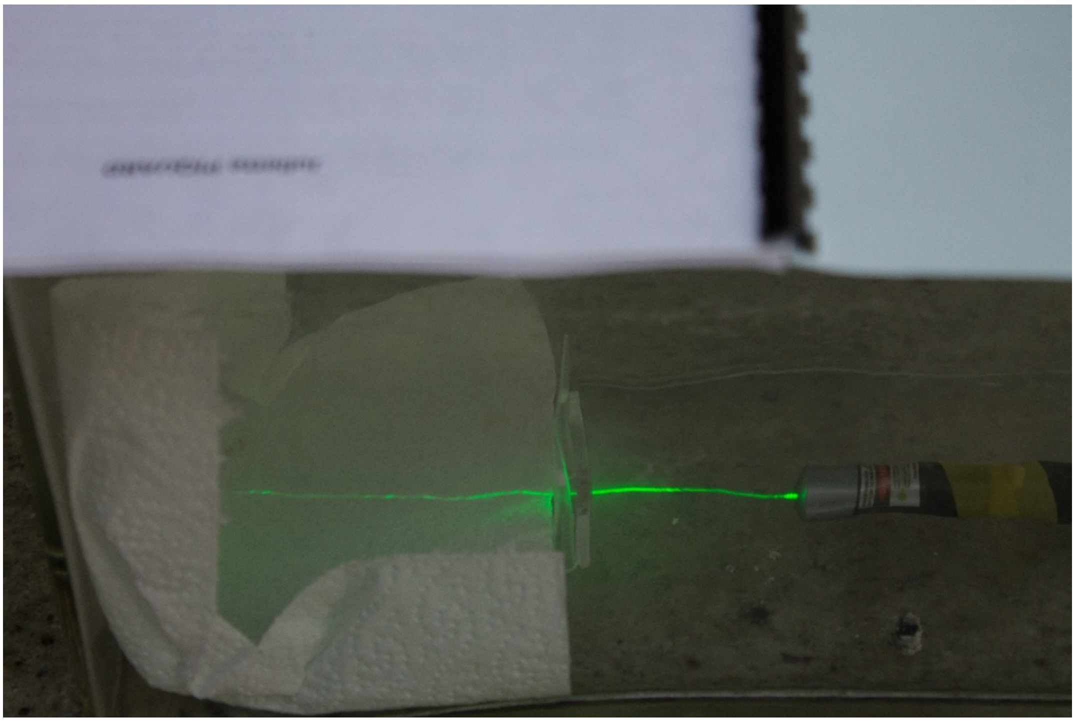
That's why it is used in lasers such as American NIF and French LMJ, large laser-based inertial confinement fusion (ICF) research device being built near Bordeaux.




**Picture 11** – Illustration of frequency conversion and a laser line in LMJ

## b. Experience

Using tank willed with cigarette smoke and small laser (wavelength : 532 nm), we tried to examine the properties of KDP. We could observe that after passing through a KDP layer the beam of laser became diffused and much less visible. This experience shows that after the crystal, we have lost a part of the intensity from the initial beam, which is a result of the frequency conversion. Indeed, when we have frequency conversion, only a part of the laser is converted and the other part keeps the same frequency. So, in our experience, we can suppose than the resulting green beam is the non-converted part resulting from the frequency conversion. Afterwards we used light spectrometer to find out how exactly KDP influences the light.



**Picture 12** – frequency conversion of a laser beam (532 nm) by a KDP crystal

# Conclusion

All things considered, we can say that crystallography is very delicate and precise job. The actual procedure of making crystals is not that easy as it looks like.

There are many variables that need to be considered such as temperature, purity as well as knowledge of each material used during the process. In theory making a perfect crystal is very hard, but in reality is not really possible. Even the smallest impurities can affect the properties of crystals and they change the outcome of the crystal growth. So we can conclude that a perfect crystal is a crystal grown in very specific conditions including very clean glassware and materials and specific parameters (temperature, sursaturation).

Because of their specific and unique structure we can conclude that crystals are very important in various fields of science and are crucial part for technological development in general, for physic simulation and optical application for KDP for example. Crystal is also very used in the fabrication of semi-conductors.