IN THE NAME OF GOD

THE COMPASSIONATE

THE MERCIFUL

دانشگاه سمنان
دانشکده فیزیک

Unidirection growth of crystals from aqueous solutions

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February 2021

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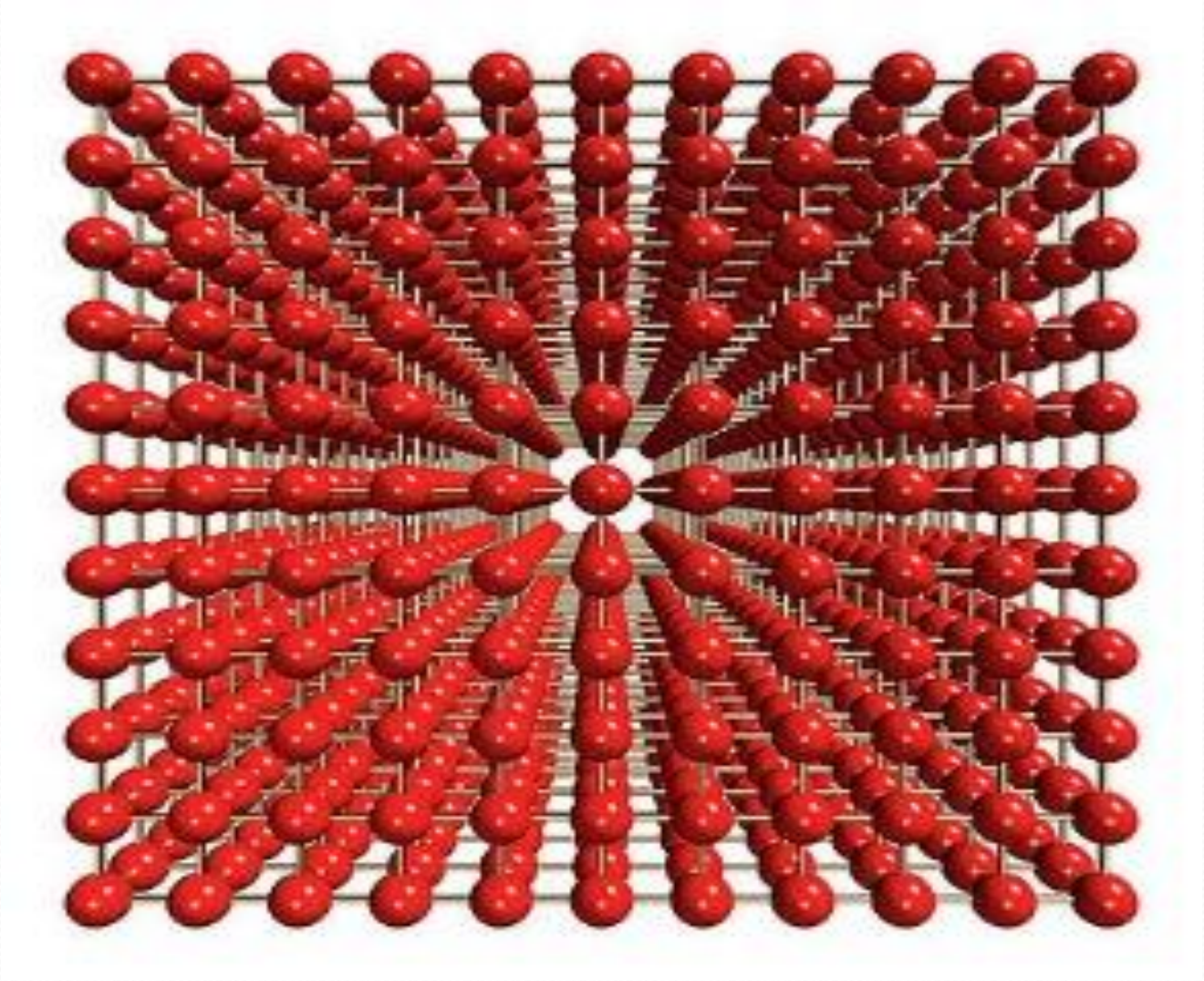
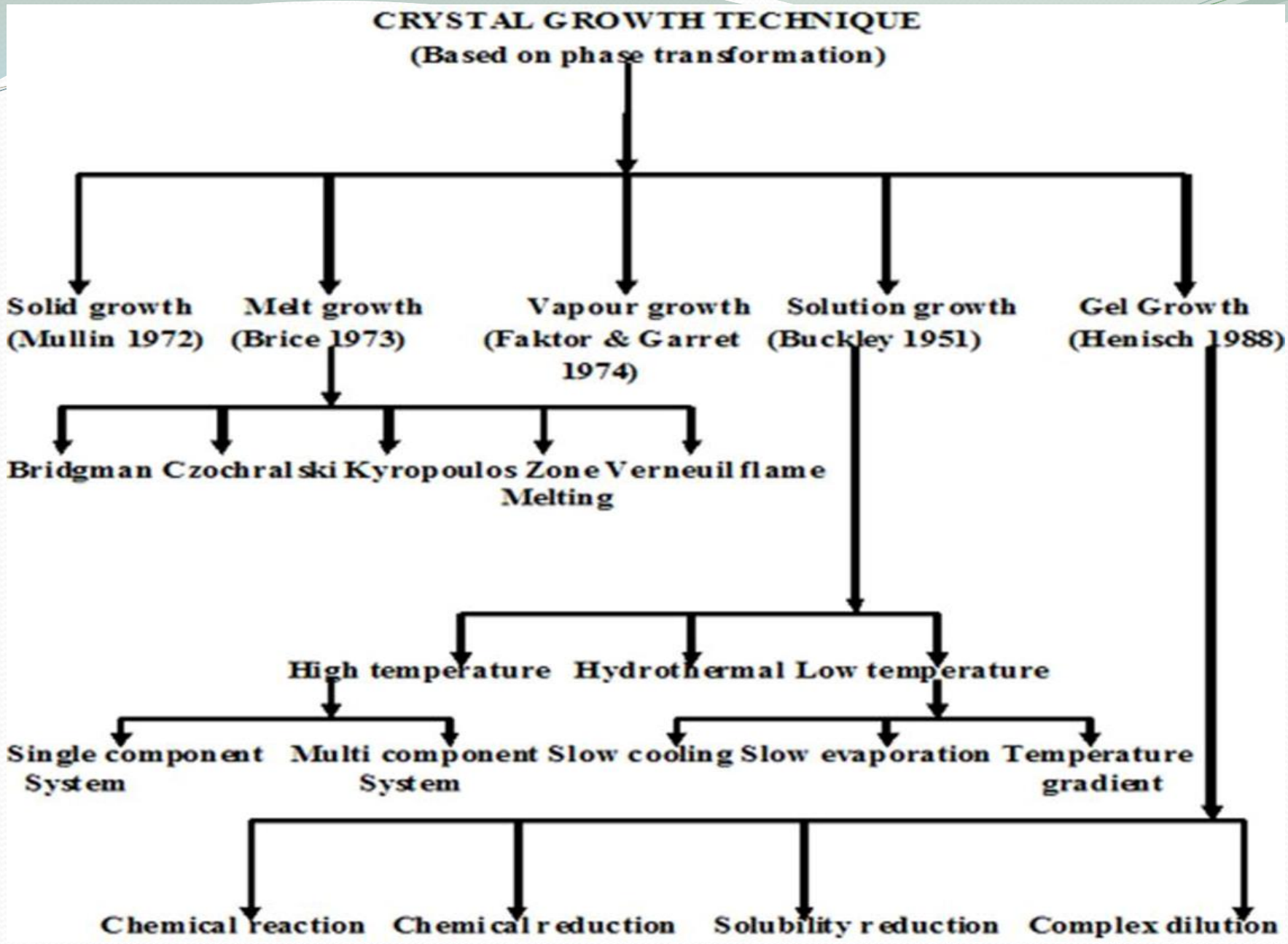
Introduction

What is a crystal?

The word ***crystal*** derives from the Ancient Greek word κρύσταλλος (*krustallos*), meaning both "ice" and "rock crystal".

A **crystal** or **crystalline solid** is a solid material whose constituents (such as atoms, molecules, or ions) are arranged in a highly ordered microscopic structure, forming a crystal lattice that extends in all directions.




CRYSTAL GROWTH TECHNIQUE
(Based on phase transformation)
Solid growth (Mullin 1972)
Melt growth (Brice 1973)
Vapour growth (Faktor & Garret 1974)
Solution growth (Buckley 1951)
Gel Growth (Henisch 1988)
Bridgman
Czochralski
Kyropoulos
Zone Melting
Verneuil flame
High temperature
Hydrothermal
Low temperature
Single component System
Multi component System
Slow cooling
Slow evaporation
Temperature gradient
Chemical reaction
Chemical reduction
Solubility reduction
Complex dilution

Low Temperature Solution growth

- Slow cooling method
- Slow evaporation method

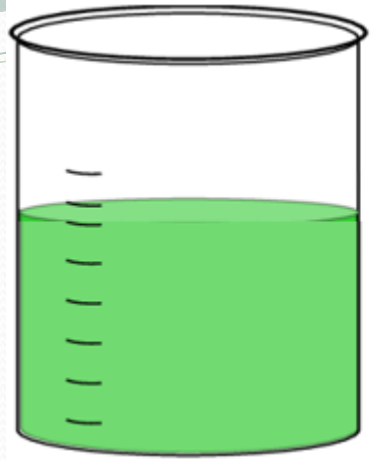
The following procedure is common in both techniques:

1- A saturated solution is made.

2- The solution is made supersaturated.

Here a saturated salt solution is being prepared.

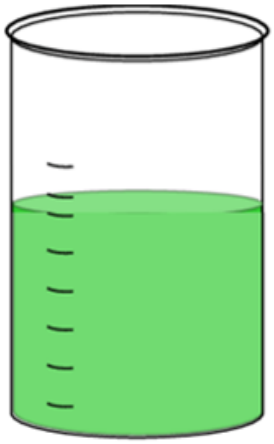
Transfer some amount of salt into a glass of water. Then stir it till the salt is completely dissolved. Do it again and again until the added salt is not dissolved. The solution is now saturated.



Solution volume = 300 cc

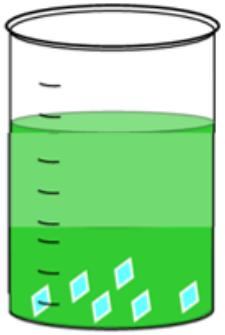
Temperature = 30°C

Weight of dissolved salt = 25 g



Saturated solution

Solution cooling



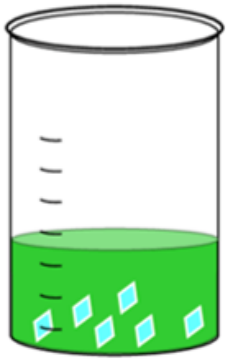
Solution volume = 300 cc

Temperature = 25°C

Weight of dissolved salt = 20 g

Weight of precipitated crystals = 5 g

Solution evaporation



Solution volume = 200 cc

Temperature = 30°C

Weight of dissolved salt = 20 g

Weight of precipitated crystals = 5 g

Solvent Evaporation method

- an excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and solute.
- the solution loses particles, which are weakly bound to other components, and therefore the volume of the solution decreases.
- the vapor pressure of the solvent above the solution is higher than that of the solute and, therefore the solvent evaporates more rapidly and the solution becomes supersaturated.
- The solute particles can be finally harvested.

Harvesting table salt
by salt farmers in Thailand (left) and in Iran (right)

What is the reason for growing crystals at certain directions?

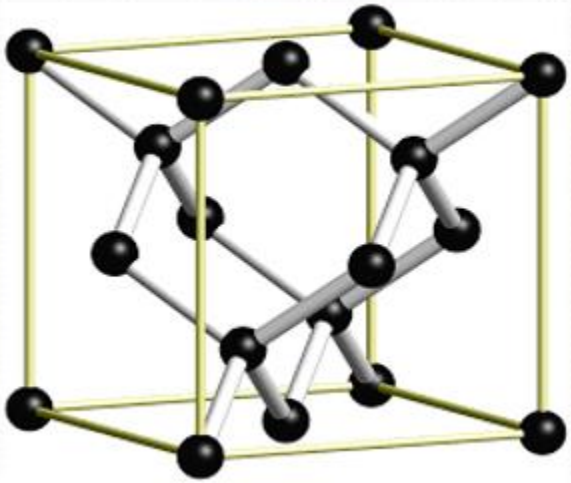
- Crystals are generally anisotropic.
- Crystals can have certain special electrical, optical, and mechanical properties.
- These properties are related to the anisotropy of the crystal, i.e. the lack of rotational symmetry in its atomic arrangement.

A good example may come across when comparing Aluminum with diamond.

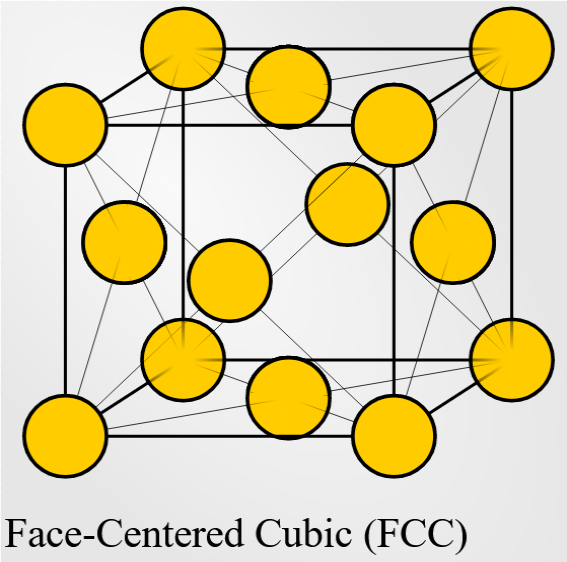
Which one is harder? Of course, the answer is, “diamond”.

Which one is more compact? The answer is, “Aluminum”.

Packing density of diamond is %34 and that of Al is %74. Therefore the Al unit cell is more compact than diamond.



Diamond structure



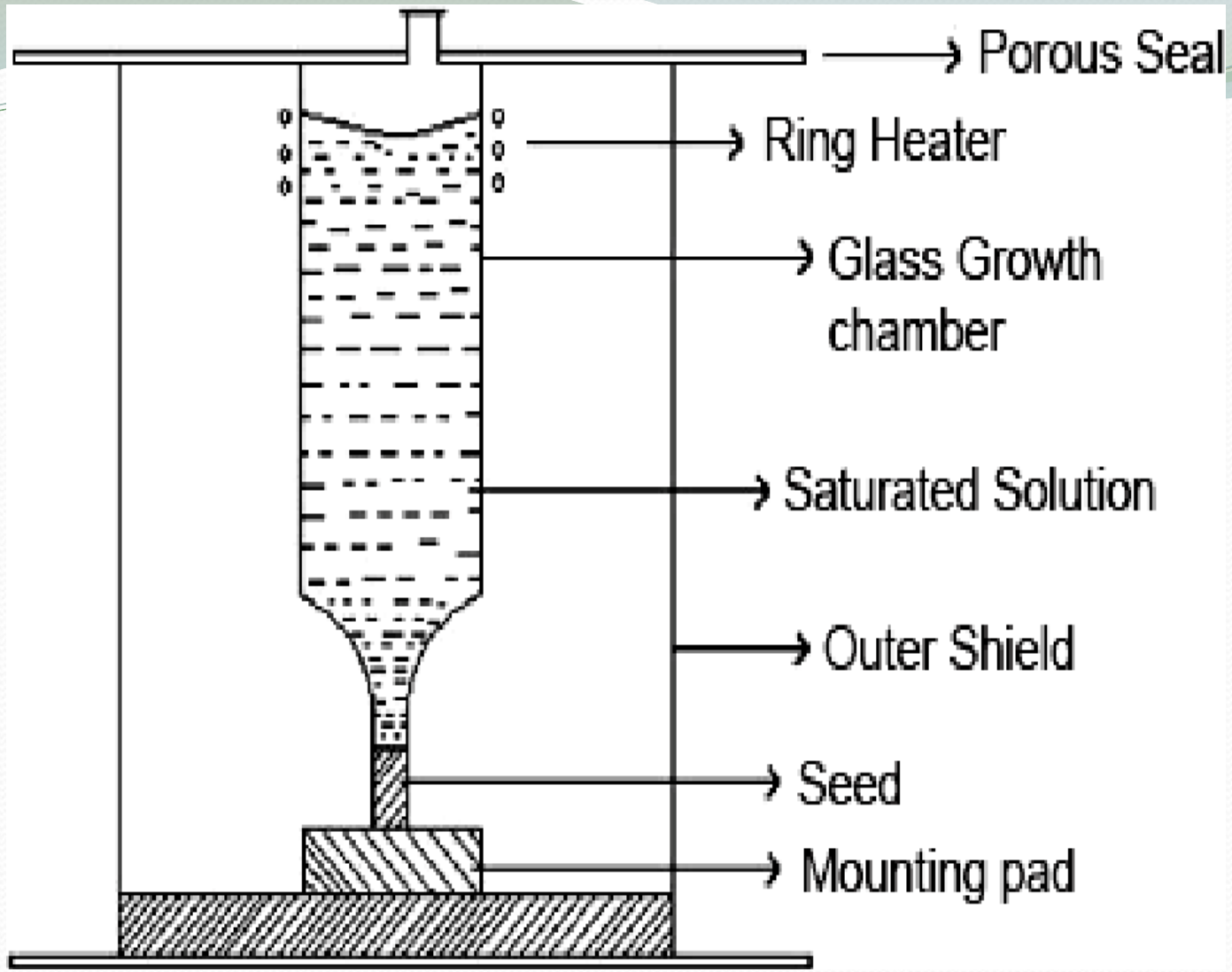
Face-Centered Cubic (FCC)

Few examples of anisotropic crystals:

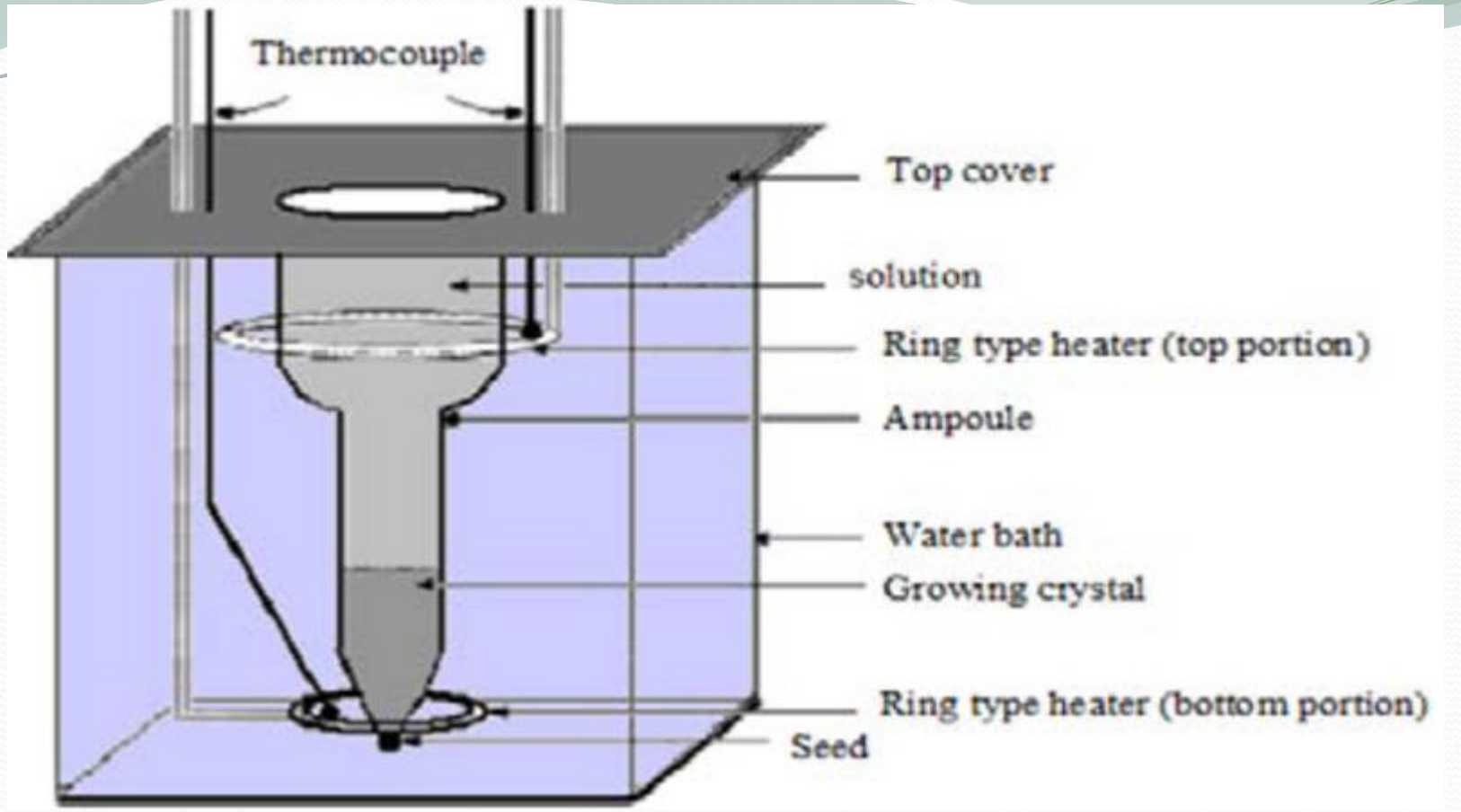
- The speed of light along different axes of crystals of the mineral calcite is different.
- When an alternating current is applied to selenium, it is transmitted in only one direction (rectified), thus becoming a direct current.
- Potassium dihydrogen phosphate (KDP) acts as a second harmonic generator at a certain direction.

Sankaranarayanan-Ramasamy Method

- Sankaranarayanan-Ramasamy (S-R) Method is the method by which one can grow a crystal in a desired direction from aqueous solution.
- S-R method was invented by Sankaranarayanan and Ramasamy in 2005.



K. Sankaranarayanan and P. Ramasamy, "Unidirectional seeded single crystal growth from solution of benzophenone", J. Cryst. Growth 280 (2005) 467-473.



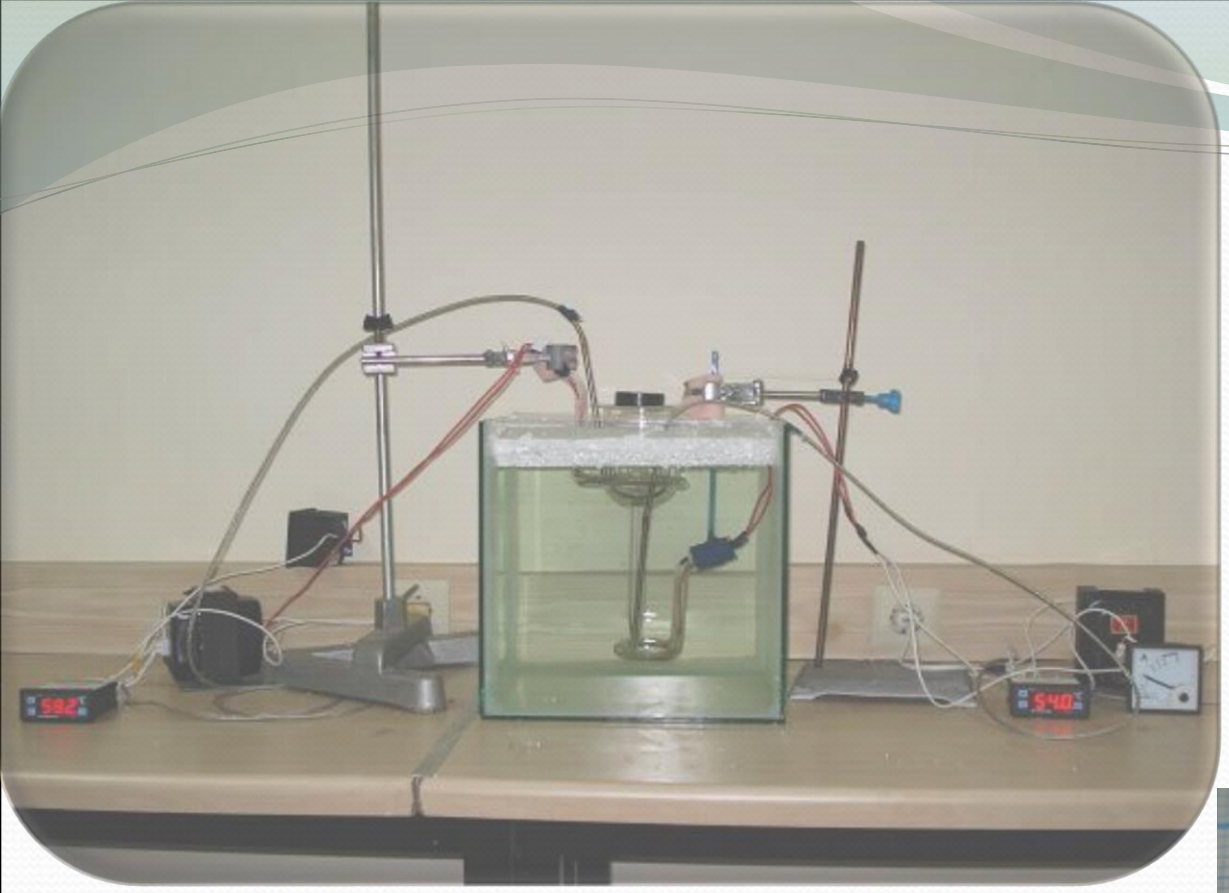
N. Balamurugan, M. Lenin, G. Bhagavannarayana and P. Ramasamy, “Growth of TGS crystals using uniaxially solution-crystallization method of Sankaranarayanan-Ramasamy”, Cryst. Res. Technol. 42 (2007) 151-156.

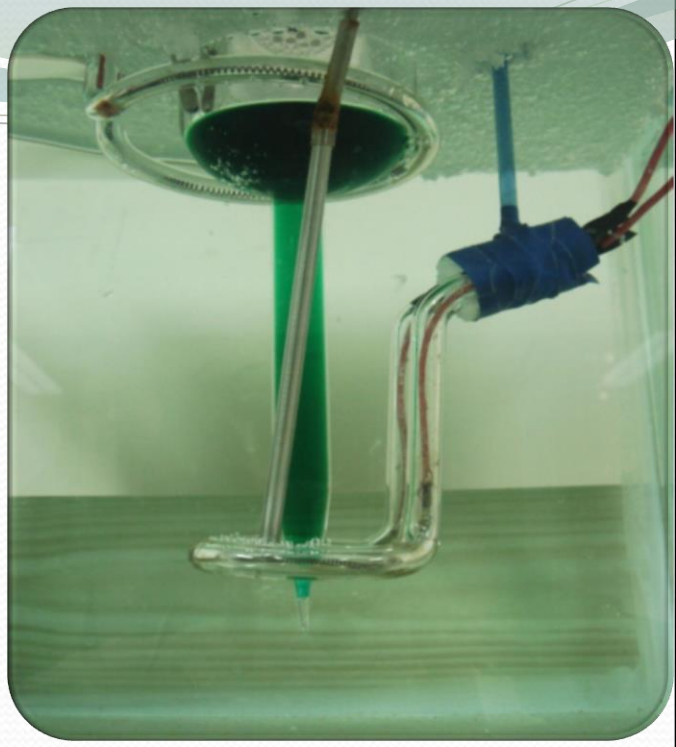
The advantages of S-R method

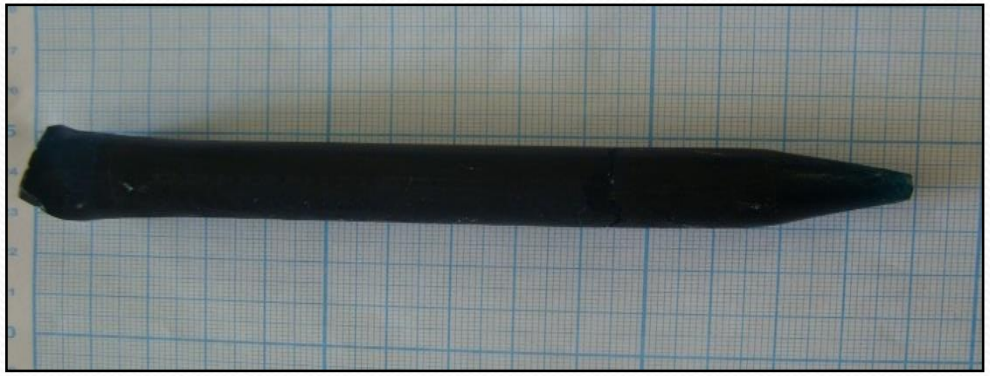
- The setup is very simple and inexpensive.
- 100% solute–crystal efficiency can be achieved.
- The experiment is performed at room temperature.
- The dislocation density in the crystal grown by this method is less than that grown by other methods.
- A big crystal can be grown in the desired direction.
- Since the fresh solution constantly feeds the growth ampule, the problem of microbial growth eliminated.

The disadvantages of S-R method

- The solution can not be stirred during the growth process.
- The growth time is long which can have effects such as fungus in the solution.
- Limiting the growth of the crystal in other directions may introduce tension to the crystal.

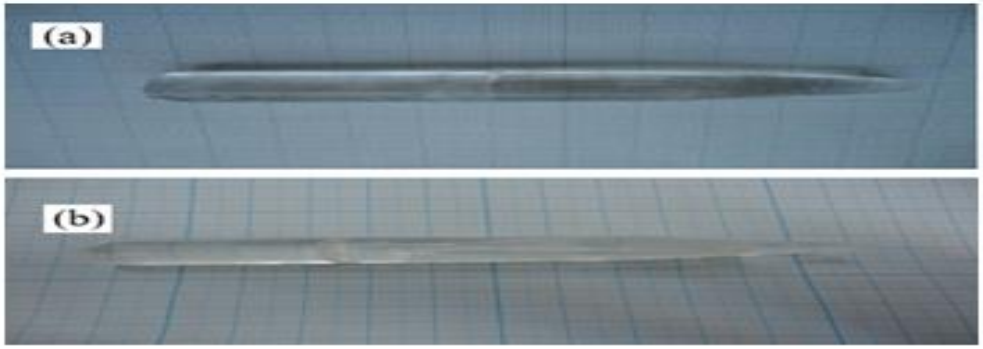
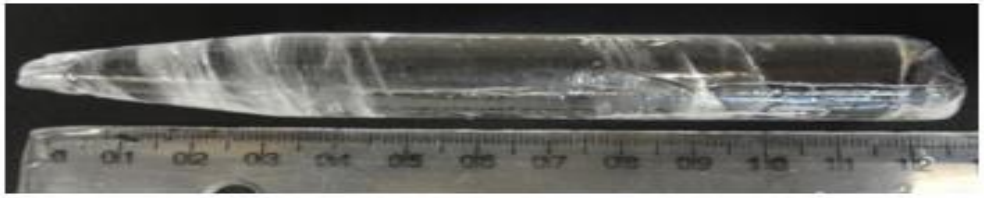
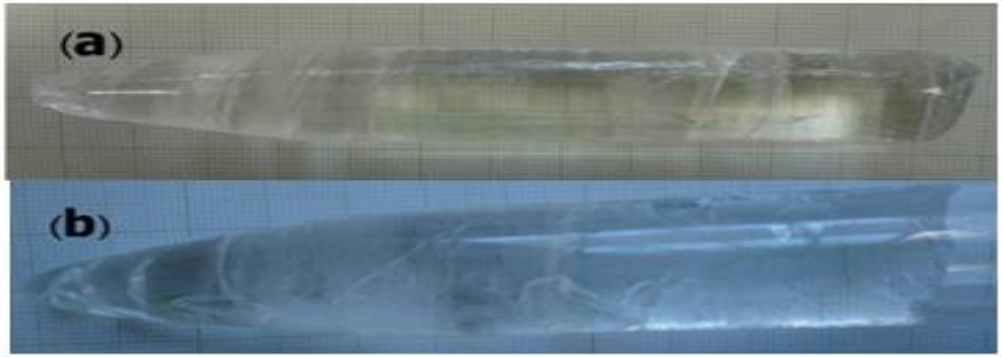






M. Hemmati and H. Rezagholipour Dizaji**, Unidirectional growth of *α*-NiSO4·6H2O crystal by Sankaranarayanan–Ramasamy (SR) method,** Cryst. Res. Technol. **47,** No. 7, 703–706 (2012).

Name of the crystal	Crystal photo
KDP	
EDTA doped KDP	
KCl doped KDP	
KCl + EDTA doped KDP	

(a) ADP (b) L-lysine doped ADP	
H_3PO_4 doped TGS	
(a)Pure TGS (b)NaCl doped TGS	
$NiSO_4$ doped TGS	

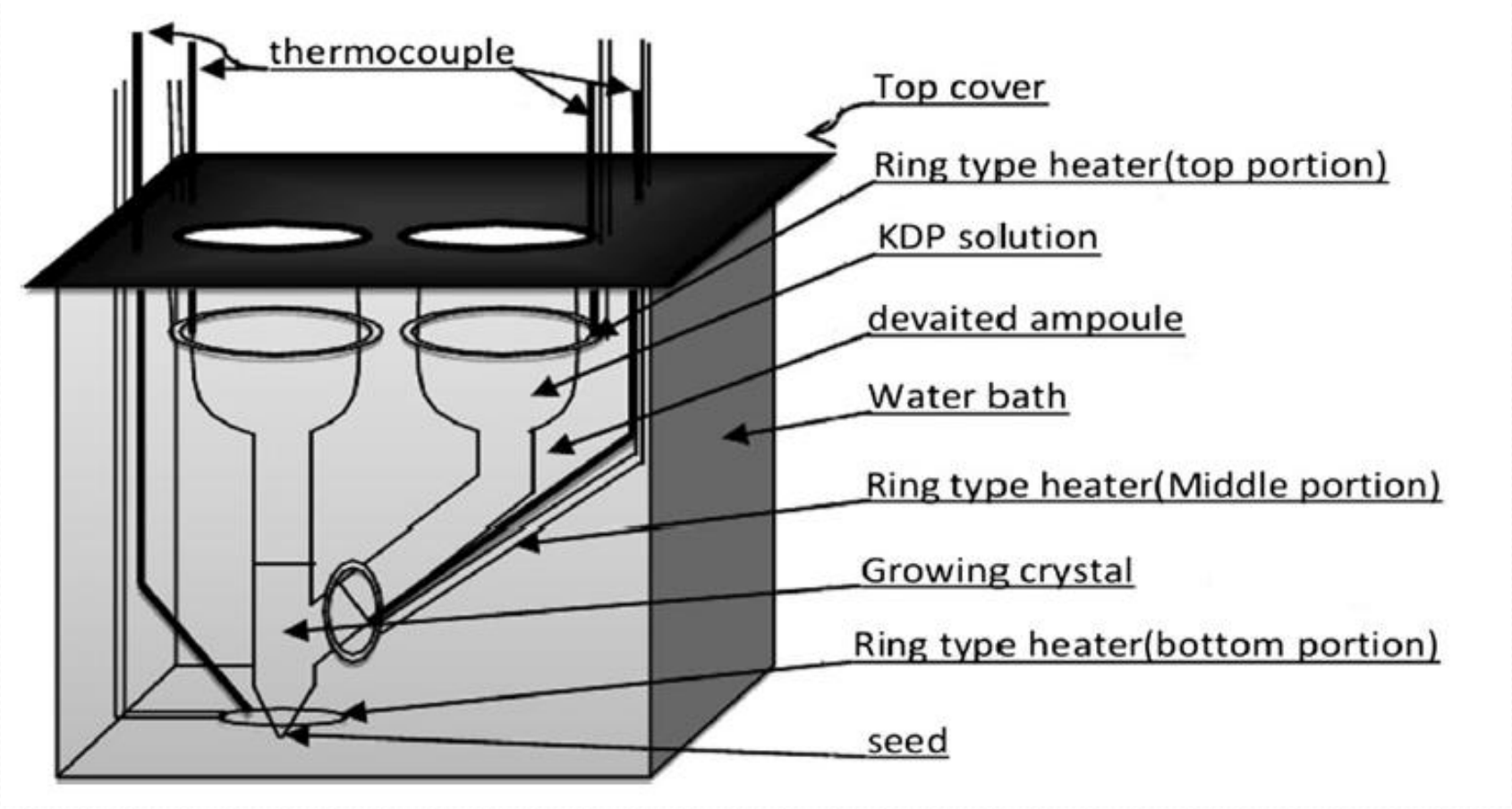
$NiSO_4 .6H_2O$ (NSH)	
$NH_4NiSO_4 .6H_2O$ (ANSH)	
$CoNiSO_4 .6H_2O$ (CNSH)	
$KNiSO_4 .6H_2O$ (KNSH)	

Growth of KDP crystal in 2nd harmonic direction by S-R method

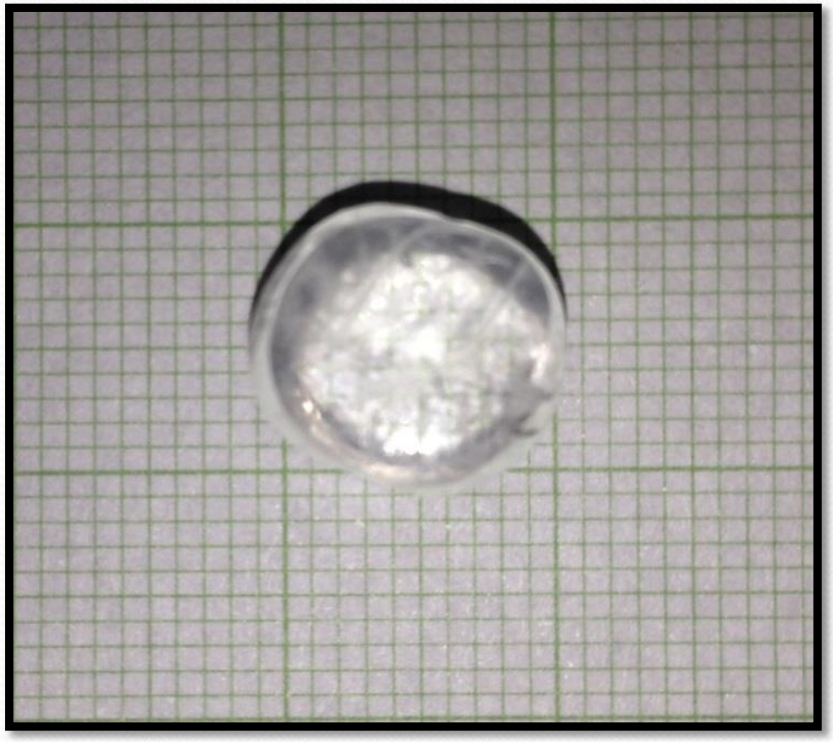
KDP crystal acts as a second harmonic generator (SHG) in the angle of 59.1° with respect to its optical axis.

Usually, for using KDP crystal as a SHG, one has to grow a large crystal. Then the crystal has to be cut in the desired direction in order to extract a crystal acting as an SHG.

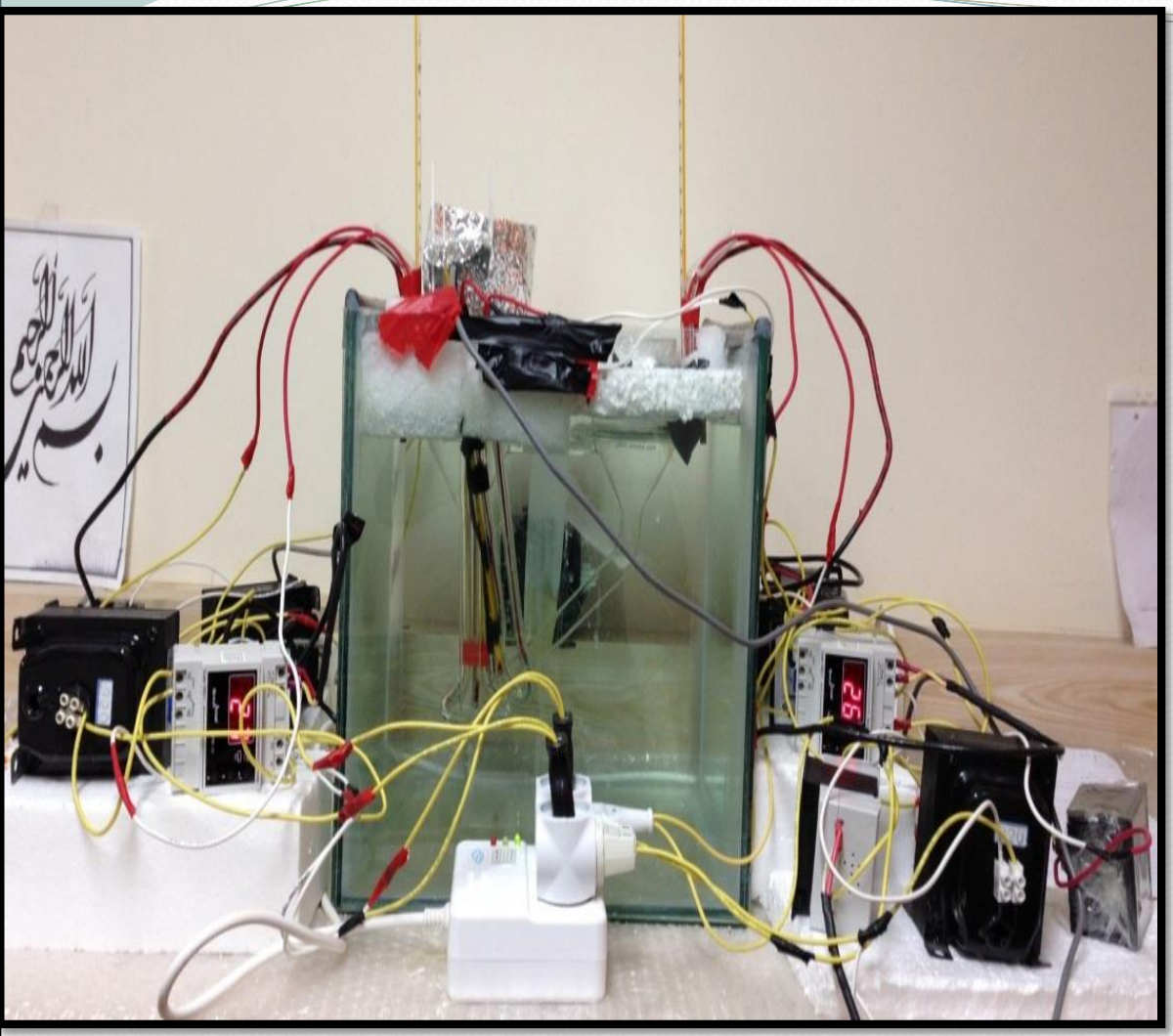
This leads to waste of time and material.

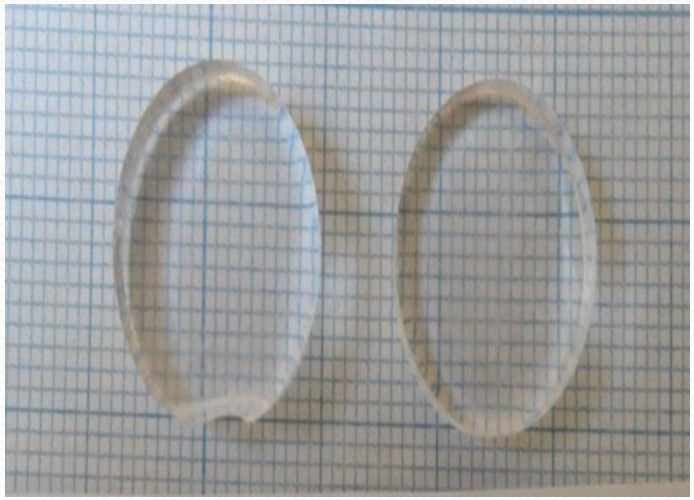


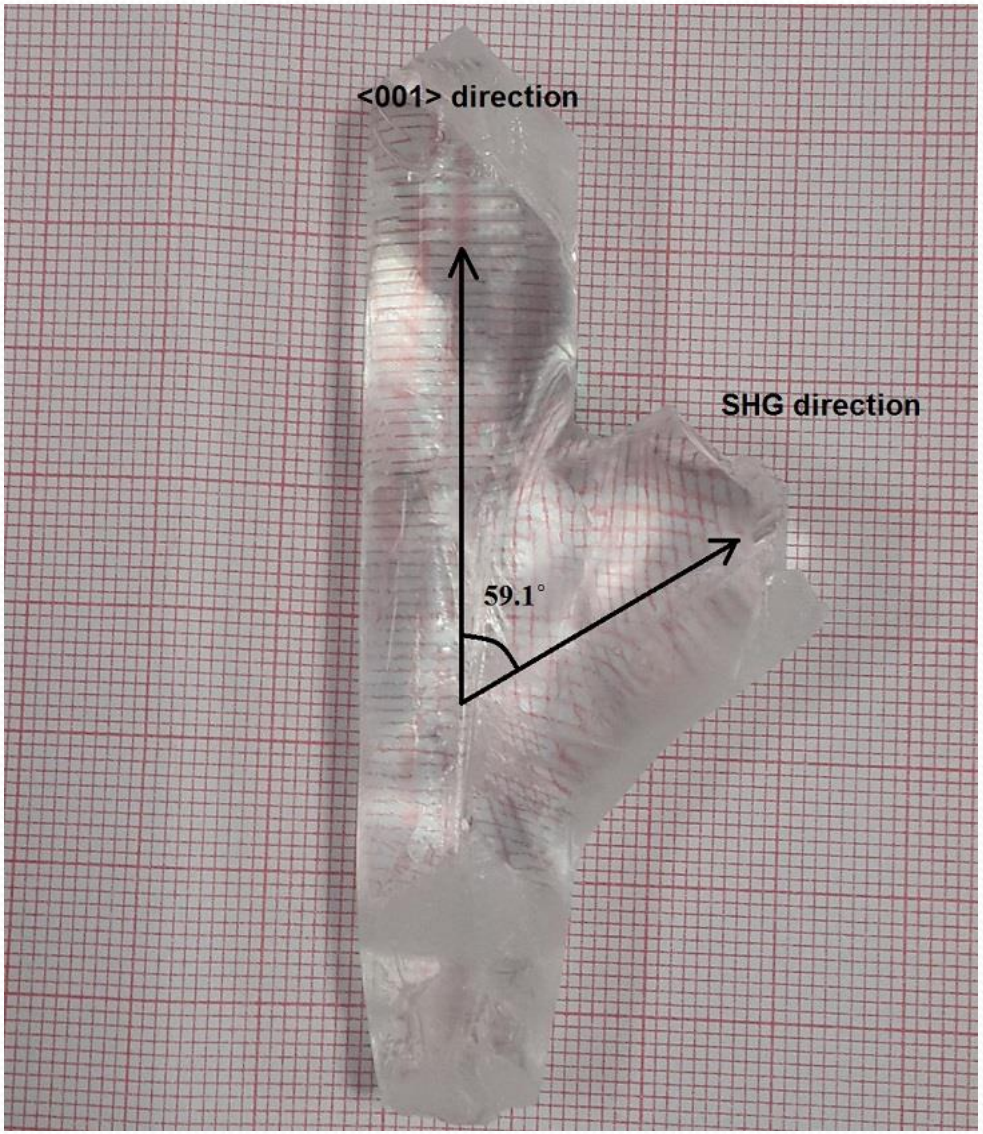
F. Barati and H. Rezagholipour Dizaji, "Growth of KDP single crystal in second harmonic direction by modified Sankaranarayanan–Ramasamy method", Opt Quant Electron (2016) 48:432.

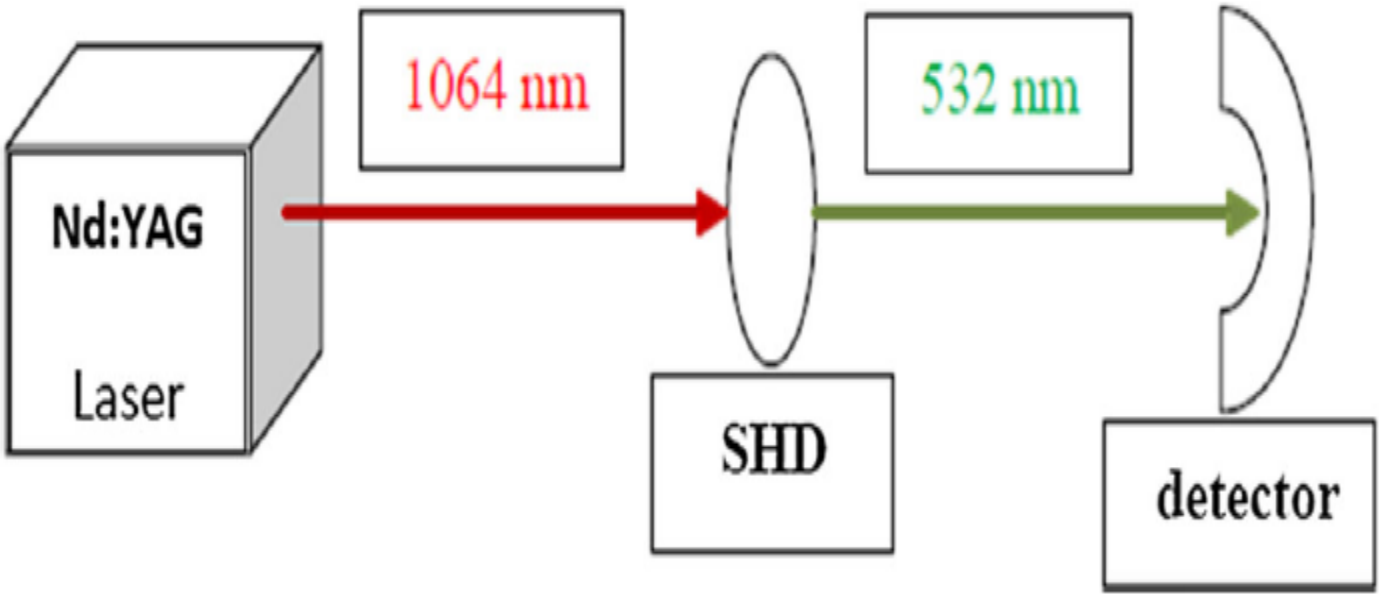


The crystal seed






<001> direction
SHG direction
59.1°



Sketch of the experimental setup for SHD specimen


Thanks for your attention