International Journal of Pure and Applied Mathematics
Volume 119 No. 12 2018, 5743-5758
ISSN: 1314-3395 (on-line version)
url: http://www.ijpam.eu
Special Issue

ijpam.eu

DIFFERENT TYPES OF CRYSTAL GROWTH METHODS

K.Seevakan[1], S.Bharanidharan[2]
Assistant Professor [1 2]
Department of Physics, BIST, BIHER, Bharath University, Chennai.
seevakan.phy@bharathuniv.ac.in

ABSTRACT:

To grow a crystal, the basic condition to be attained is the state of super saturation, followed by the process of nucleation. The information of super saturation and nucleation forms the basis of crystal growth.The growth of crystals from liquid and gaseous solutions, pure liquids and pure gases can only occur if some degree of super saturation or super cooling has been first achieved in the system. The attainment of the supersaturated state is essential for any crystallization operation and the degree of super saturation or deviation from the equilibrium saturated condition is the prime factor controlling the deposition process.

INTRODUCTION:

Crystals are used in semiconductor physics, engineering, as electro-optic devices etc., so there is an increasing demand for crystal[1-5]. For years, Natural specimens were the only source of large, well formed crystals.

The growth of crystals generally occurs by means of following sequence of process.

- Diffusion of the molecules of the crystallizing substance through the surrounding environment.
- Diffusion of these molecules over the surface of the crystal to special sites on the surface.

Today almost all naturally occurring crystals of interest have been synthesized successfully in the laboratory[6-9]. It is now possible only by crystal growth techniques.

The growth aspect differs from crystal depending as their physics and chemical properties such as solubility, melting point[10-15], decomposition, phase change, etc,This chapter gives a brief account of the methods of crystal growth.

BASICS OF CRYSTAL GROWTH:

To grow a crystal, the basic condition to be attained is the state of super saturation, followed by the process of nucleation[16-21]. The information of super saturation and nucleation forms the basis of crystal growth.

CONDITIONS FOR GROWING CRYSTAL:

The growth of crystals from liquid and gaseous solutions, pure liquids and pure gases can only occur if some degree of super saturation or super cooling has been first achieved in the system[22-27]. The attainment of the supersaturated state is essential for any crystallization operation and the degree of super saturation or deviation from the equilibrium saturated condition is the prime factor controlling the deposition process. Growth of crystals can be considered to compress these steps[28-35].

1. Achievement of super saturation or super cooling.
2. Formation of crystal nucleus of microscopic size.
3. Successive growth of crystals to yield distinct faces.

CRYSTAL GROWTH TECHNIQUES:

Crystal growth is a challenging task and the technique followed for crystal growth depends upon the characteristics of the materials under investigation[36-43], such as its melting point, Volatile nature, solubility in water or other organic solvents and so on.

The basic growth methods available for crystal growth are broadly.

- Growth from melt.
- Growth from vapour.
- Growth from solution.
- Growth from solid.

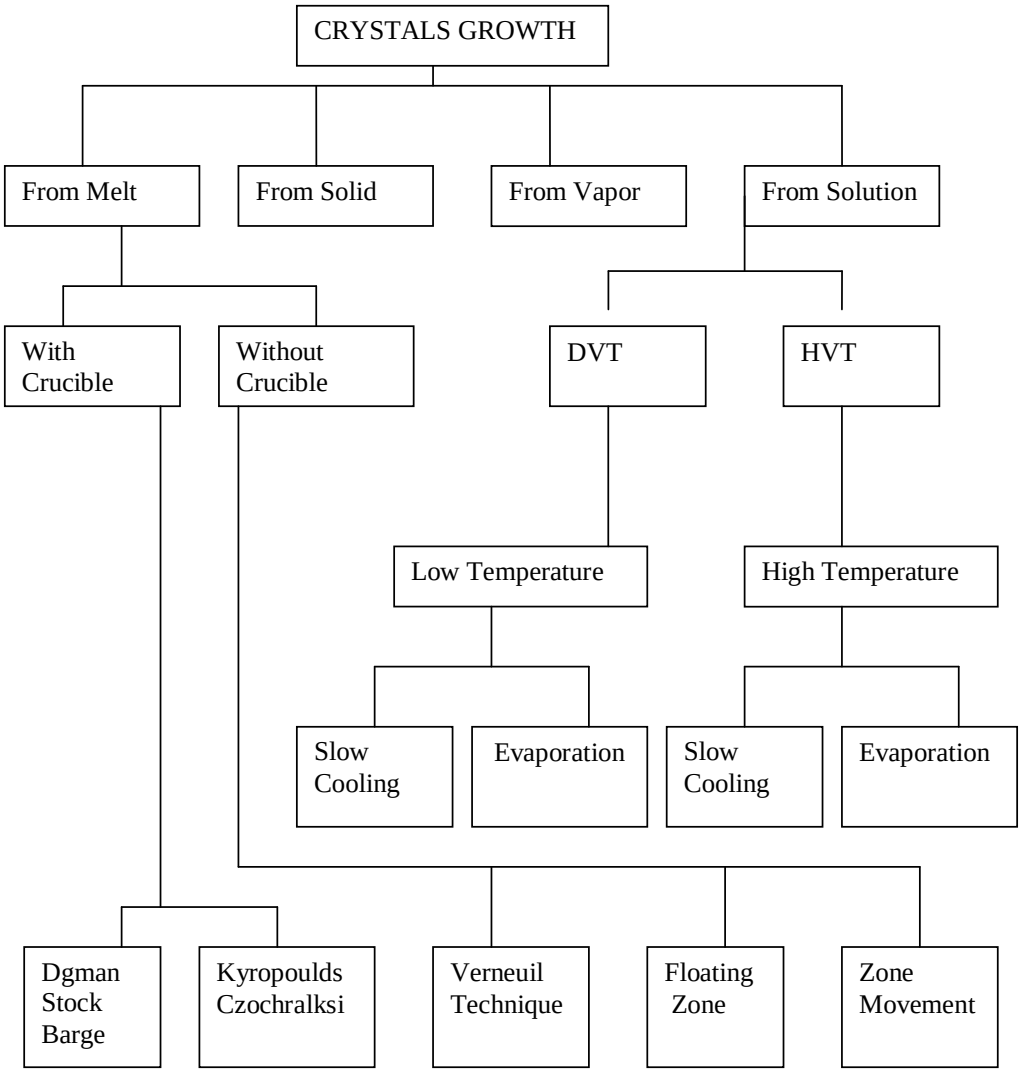

Figure. 1. Classification of Crystal growth methods

GROWTH FROM THE MELT:

Melt growth is the process of crystallization of fusion and resolidification of the pure material, crystallization from a melt on cooling the liquid below its freezing point. In this technique apart from possible contamination from crucible materials and surrounding atmosphere[44-50], no impurities are introduced in the growth process and the rate or growth is normally much higher than possible by other methods. Melt growth is commercially the most important method of crystal growth. The growth from melt can further be sub-grouped into various techniques.

a) Bridgmann method.
b) Czochralski method.
c) Vernuil method.
d) Zone melting method.
e) Kyropoulos technique.
f) Skull melting.

Bridgmann method:

This technique was named after its inventor Bridgemann in 1925, Stockbarger in1938.

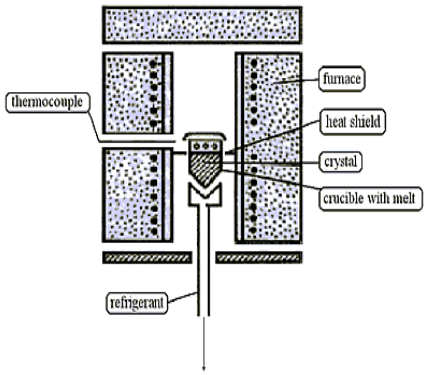

Figure.2.Bridgmann method

The Bridgmann technique is a method of growing single crystal ingots or boules. The method involves heating polycrystalline material in a container above its melting point and slowly cooling it from one end where a seed crystal is located. Single crystal material is

progressively formed along the length of the container,the process can be carried out in a horizontal or vertical geometry.

Advantage:

- This method is technically simple.
- This technique is low cost.
- Selecting the appropriate container can produce crystal of pre assigned diameter.

Disadvantage:

- The compression of the solid by the contracting container during cooling can lead to the development of stresses high enough to nucleate dislocations in the material.

Czochralski method (or) Pulling Technique:

This method is widely used for growing semi conducting material crystal. The shape of the crystal is free from the constraint due to the shape of the crucible. In this method the charge is melted and maintained at a temperature slightly above the melting point.

The pulling rod is lowered to just touch the melt. Since the rod is at lower temperature of melt occurs at the point tip of the pulling rod. The crystal is pulled slowly.

The rate of pulling upon various factors like thermal conductivity, latent heat of fusion of charge and rate of cooling of the pulling rod. The seed is rotated to keep the grow crystal uniform and cylindrical.

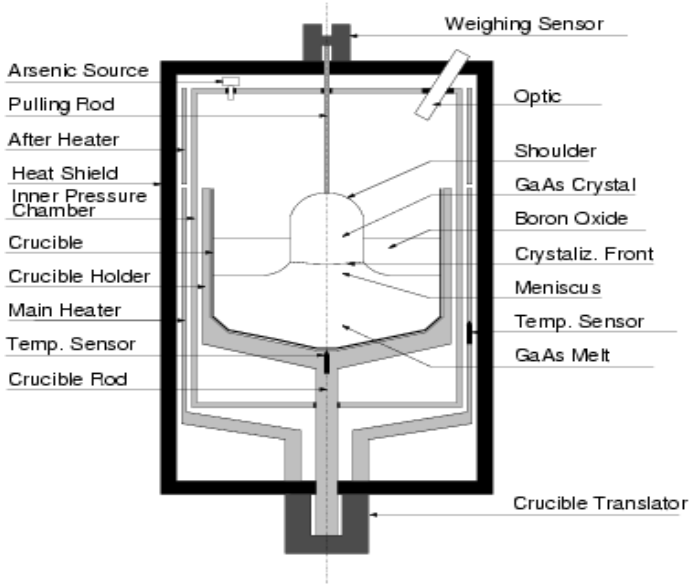

Figure. 3Czochralski method

Advantage:

- This method is used to grow large single crystals. Thus it is used extensively in the semiconductor industry.
- There is no direct contact between the crucible walls and the crystal which helps to produce unstressed single crystal.

Disadvantage:

- In general this method is not suitable for incongruently melting compounds and of course the need for a seed crystal of the same composition limits is used as tool for exploratory synthetic research.

Vernuil method:

The basis of vernuils method is as follows. Chemically pure fine powder which emerges through an Oxygen-hydrogen flame and falls onto the fused end of an oriented single crystal seed fixed to a lowering mechanism. The powder charge is fed from bankeei by mean of a special tapping mechanism. Coordinating the consumption of the charge, hydrogen and oxygen with the rate of descent of the seed ensures crystallization at a prescribed level of the apparatus.

Advantage:

- There is no container which eliminates the problem of physical-chemical interaction between the melt and the container material.
- It is technically simple and the growth of crystal can be observed.
- Single crystal of ruby, sapphire etc., can be grown by this method. Single crystal in various Shapes like plates, disc, hemi-sphere and cones can be grown by this method.

Zone Melting Method:

In this technique a liquid zone is created by melting a small amount of materials in a relatively large or long solid charge. Zone melting techniques basically enable one to manipulate distribution of soluble impurities or phases through a solid.

Advantage:

- Zone melting technique is that impurities tend to be concentrated in the melted portion of the sample.
- The process sweeps them out of the sample and concentrates them at the end of the crystal bowl, which is then cut off and discarded.
- Thus this method is sometimes used to purify semiconductor crystals.

2.7.5 Kyropoulos Technique:

In this technique, a cooled seed to initiate single crystal growth within the melt containing crucible. Heat removal continues by controlling the furnace temperature to grow the crystal.

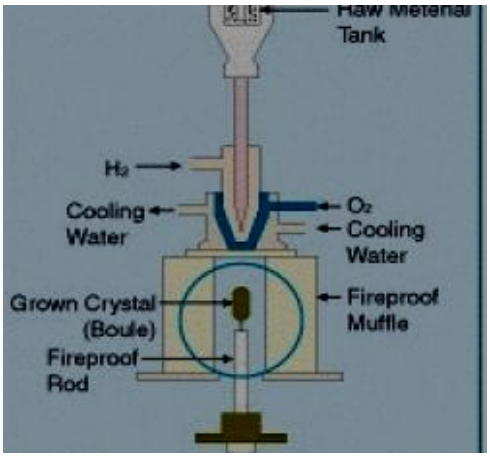

Figure.4Kyropoulos Technique

Advantage:

- The crystal is grown in a larger diameter.

- With the large diameter crystal we can make prisms, lenses and other optical components.

Skull Melting Process:

Skull melting process is used for the growth of high melting point materials. Cubic zirconium is made using a radio-frequency "Skull crucible" system, a specialized melt process. This is a type of super-hot melt process used to produce the most widely accepted diamond imitation: Cubic zirconia(cz). Zirconium oxide, the main component in cubic zirconias has an extremely high melting point (4980'F). Conventional (low) melt crucibles cannot be used. Therefore a crucible free technique is inevitable. The Skull melting process is used to produce Zirconia up to 10cm long.

VAPOUR GROWTH:

Crystallization from Vapour is widely adopted to grow bulk crystal, epitaxial films, and thin coatings. Techniques for growing crystals from vapour is divided into two types they are,

a. Chemical transport method.
b. Physical transport method.

a. Chemical transport method:

This method involves a chemical transport in which material is transported as a chemical compound (halide), which decomposes in the growth area. In this case depending on the nature of the reaction involved. The growth region may be either hotter or cooler than the source.

b. Physical transport method:

This method involves in the direct transport of materials by evaporation or sublimation from a hot source zone to a cool region II-VI compounds (Zns, Cds) are widely grown by this method either in vaccum or with a moving gas stream. In both cases the growth can be suitable with seed crystals, which can either be of the material being grown or some other

material with similar lattice spacing. In this case the substance evaporates and diffuses from hot end to a cooler growth end. In then, deposits in the form of single crystals.

Advantages:

- Films can obtain by the close spaced transport method and decomposition of compounds.
- Crystal of silicon, diamond, gas, semiconductor compounds can be grown by this method.

SOLUTION GROWTH:

In this method, Crystals are grown from aqueous solution. This method is also widely practiced for producing bulk crystals. The four major types are

A. Low temperature solution growth.
B. High temperature solution growth.
C. Hydro Thermal growth.
D. Gel Growth.

A. Low temperature solution growth:

This is a widely practiced method; the techniques used here are,

- Slow cooling method.
- Solvent Evaporation method.
- Temperature Gradient method.

The solvent used here are water, ethy1 alcohol, acetone, etc.,

- **Slow cooling method:**

A saturated solution above the room temperature is poured in a crystallizer and thermally sealed. A seed crystal is suspended in the solution and the crystallizer is kept in a water thermostat, whose temperature is reducing according to a pre assigned plan, which results in the formation of large single crystals. The need to use a range of temperature is the origin of

disadvantages. The possible range is usually small so that much of the solute remains in the solution at the end of run. To compensate for this effect, large volumes of solution are needed.

- **Solvent Evaporation method:**

` In this method, an excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and solute. In contrast to the cooling method, in which the total mass of the system remains constant, in the solvent evaporation method, the solution loses particles, which are weakly bound to other components, and therefore the volume of the solution decreases. In almost all cases, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and, therefore the solvent evaporates more rapidly and the solution becomes supersaturated(Petrov1969). Usually, it is sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. This is the oldest method of crystal growth and technically, it is very simple. Typical growth conditions involve temperature stabilization to about $\pm 0.0005^{o}C$ and rates of evaporation of a few mm^3/hr.

- **Temperature Gradient method:**

The transport of material forms a hot region containing the source of the material to be grown, to a cooler region where solution is super saturated result in the crystal growth. A smaller variation in the temperature between the source and the crystal has larger effects on growth rate.

B. High Temperature Solution Growth:

- The solvents are considered generally effective at temperatures above room temperature. Also the concepts of low temperature solution growth are applicable equally well. In the growth of crystals from high-temperature solutions, the constituents of the material to be crystallized are dissolved in a suitable solvent and crystallization occurs as the solution becomes critically supersaturated. The most widely used high temperature solution growth technique is the flux growth.

C.Hydro Thermal Growth:

This is regarded as an intermediate case between growths from the vapour and solution. Growth occurs from aqueous solution at high temperature and pressure. The liquids from which the process starts are usually alkaline aqueous solutions. Temperatures are typically in the range 400-600^{o}C and the pressure involved is large (100-1000 of atmospheres). Growth is usually carried out in steel auto claves with gold or silver linings. The concentration gradient required to produce growth is provided by temperature difference (usually 10-100^{o}C) between the nutrient and growth areas. Those materials like calcite, alumina, antimony, etc., can be grown by this technique.

Advantages:

- It occurs in air at a temperature much lower than the melting of the crystallizing substance.
- Single crystals of diamond, barium titanates are to be grown by using this method.

Disadvantages:

- At elevated temperature of crystal growth there are some disadvantages.

D. Gel Growth Method:

The principle used in this crystal growth techniques is very simple solution of two suitable compounds give rise to required crystalline substance by mere chemical reactions, crystallization takes place according to chemical reaction equation as shown below,

$$X \text{ (in solution)} + \text{Gel medium} \xrightarrow[\text{Atm .Pressure}]{} X\text{(crystal)}$$

Various types of gels

1. Physical gel

Gel which is obtained by Physical process such as cooling is called physical gel.Eg. Gelatin, clay.

2. Chemical gel:

Gels formed by chemical reaction such as hydrolysis (or) polymerization are called chemical gels. E.g. Silica, Polyacryalamide.

Advantages:

1 It prevents turbulence and formation of good crystals by providing a framework of nucleation.

2 The convection is absent in growth experiments

3 The high degree of perfection and lesser number of defects have been observed in gel growth.

4 The Gel method has also been applied to the study of crystal formation in human system such as cholesterol stores, Sex hormones.

CONCLUSION:

Crystal growth is a challenging task and the technique followed for crystal growth depends upon the characteristics of the materials under investigation, such as its melting point, Volatile nature, solubility in water or other organic solvents and so on.Skull melting process is used for the growth of high melting point materials. Cubic zirconium is made using a radio-frequency “Skull crucible” system, a specialized melt process.Crystallization from Vapour is widely adopted to grow bulk crystal, epitaxial films, and thin coatings.

REFERENCES
References

1. R. N. Singh, Madhu, R. Awasthi, S. K. Tiwari, Int. J. Hydrogen energy. 34, 4693 (2009).
2. S. D. M. Jacques, O. Leynaud, D. Strusevich, A. M. Beale, G. Sankar, C. M. Martin, P. Barnes, Angew. Chem. Int. Ed. 45, 445 (2006).
3. W. X. Kuang, Y. N. Fan, Y. Chen, Langmuir, 16, 5205 (2000).
4. A. W. Sleight, B. L. Chamberland, Inorg. Chem. 7, 1672 (1968).
5. U. Kersen, L. Holappa, Appl. Phys. A: Mater. Sci. Process. 85, 431 (2006).
6. Ramamoorthy, R., Kanagasabai, V., Kausalya, R., Impact of celebrities' image on brand, International Journal of Pure and Applied Mathematics, V-116, I-18 Special Issue, PP-251-253, 2017

7. Ramamoorthy, R., Kanagasabai, V., Vignesh, M., Quality assurance in operation theatre withreference to fortis malar hospital, International Journal of Pure and Applied Mathematics, V-116, I-14 Special Issue, PP-87-93, 2017
8. Ramya, N., Arthy, J., Honey comb graphs and its energy, International Journal of Pure and Applied Mathematics, V-116, I-18 Special Issue, PP-83-86, 2017
9. Ramya, N., Jagadeeswari, P., Proper coloring of regular graphs, International Journal of Pure and Applied Mathematics, V-116, I-16 Special Issue, PP-531-533, 2017
10. Ramya, N., Karunagaran, K., Proper, star and acyclic coloring of some graphs, International Journal of Pure and Applied Mathematics, V-116, I-16 Special Issue, PP-43-44, 2017
11. Ramya, N., Muthukumar, M., On coloring of 4-regular graphs, International Journal of Pure and Applied Mathematics, V-116, I-16 Special Issue, PP-491-494, 2017
12. Ramya, N., Muthukumar, M., On star and acyclic coloring of graphs, International Journal of Pure and Applied Mathematics, V-116, I-16 Special Issue, PP-467-469, 2017
13. Ramya, N., Pavi, J., Coloring of book and gear graphs, International Journal of Pure and Applied Mathematics, V-116, I-17 Special Issue, PP-401-402, 2017
14. Ramya, P., Hameed Hussain, J., Alteration framework for integrating quality of service in internet real-time network, International Journal of Pure and Applied Mathematics, V-116, I-8 Special Issue, PP-57-61, 2017
15. Ramya, P., Sriram, M., Tweet sarcasm: Peep, International Journal of Pure and Applied Mathematics, V-116, I-10 Special Issue, PP-231-235, 2017
16. Sabarish, R., Meenakshi, C.M., Comparision of beryllium and CI connecting rod using ansys, International Journal of Pure and Applied Mathematics, V-116, I-17 Special Issue, PP-127-132, 2017
17. Sabarish, R., Rakesh, N.L., Outcome of inserts for enhancing the heat exchangers, International Journal of Pure and Applied Mathematics, V-116, I-17 Special Issue, PP-419-422, 2017
18. Sangeetha, M., Gokul, N., Aruls, S., Estimator for control logic in high level synthesis, International Journal of Pure and Applied Mathematics, V-116, I-20 Special Issue, PP-425-428, 2017
19. Sangeetha, M., Gokul, N., Aruls, S., Image steganography using a curvelet transformation, International Journal of Pure and Applied Mathematics, V-116, I-20 Special Issue, PP-417-422, 2017
20. Saraswathi, P., Srinivasan, V., Peter, M., Research on financial supply chain from view of stability, International Journal of Pure and Applied Mathematics, V-116, I-17 Special Issue, PP-211-213, 2017
21. Saravana Kumar, A., Hameed Hussain, J., Expanding the pass percentage in semester examination, International Journal of Pure and Applied Mathematics, V-116, I-15 Special Issue, PP-45-48, 2017
22. Saravana, S., Arulselvi, S., AdaBoost SVM based brain tumour image segmentation and classification, International Journal of Pure and Applied Mathematics, V-116, I-20 Special Issue, PP-399-403, 2017

23. Saravana, S., Arulselvi, S., Dynamic power management monitoring and controlling system using wireless sensor network, International Journal of Pure and Applied Mathematics, V-116, I-20 Special Issue, PP-405-408, 2017
24. Saravana, S., Arulselvi, S., Clustered morphic algorithm based medical image analysis, International Journal of Pure and Applied Mathematics, V-116, I-20 Special Issue, PP-411-415, 2017
25. Saravana, S., Arulselvi, S., Networks, International Journal of Pure and Applied Mathematics, V-116, I-20 Special Issue, PP-393-396, 2017
26. Saritha, B., Chockalingam, M.P., Adsorptive removal of heavy metal chromium from aqueous medium using modified natural adsorbent, International Journal of Civil Engineering and Technology, V-8, I-8, PP-1382-1387, 2017
27. Saritha, B., Chockalingam, M.P., Adsorptive removal of brilliant green dye by modified coconut shell adsorbent, International Journal of Pure and Applied Mathematics, V-116, I-13 Special Issue, PP-211-215, 2017
28. Saritha, B., Chockalingam, M.P., Photodegradation of eriochrome black-T dye from aqueous medium by photocatalysis, International Journal of Pure and Applied Mathematics, V-116, I-13 Special Issue, PP-183-187, 2017
29. Saritha, B., Chockalingam, M.P., Photodradation of malachite green DYE using TIO<inf>2</inf>/activated carbon composite, International Journal of Civil Engineering and Technology, V-8, I-8, PP-156-163, 2017
30. Saritha, B., Chockalingam, M.P., Synthesis of photocatalytic composite Fe-C/TiO2 for degradation of malachite green dye from aqueous medium, International Journal of Pure and Applied Mathematics, V-116, I-13 Special Issue, PP-177-181, 2017
31. Saritha, B., Chockalingam, M.P., Removal of heavy X`X`l from aqueous medium using modified natural adsorbent, International Journal of Pure and Applied Mathematics, V-116, I-13 Special Issue, PP-205-210, 2017
32. Saritha, B., Chockalingam, M.P., Degradation of malachite green dye using a semiconductor composite, International Journal of Pure and Applied Mathematics, V-116, I-13 Special Issue, PP-195-199, 2017
33. Sartiha, B., Chockalingam, M.P., Photocatalytic decolourisationoftextileindustrywastewaterby TiO2, International Journal of Pure and Applied Mathematics, V-116, I-18 Special Issue, PP-221-224, 2017
34. Sartiha, B., Chockalingam, M.P., Study on photocatalytic degradation of Crystal Violet dye using a semiconductor, International Journal of Pure and Applied Mathematics, V-116, I-18 Special Issue, PP-209-212, 2017
35. Shanthi, E., Nalini, C., Rama, A., The effect of highly-available epistemologies on hardware and architecture, International Journal of Pharmacy and Technology, V-8, I-3, PP-17082-17086, 2016
36. Shanthi, E., Nalini, C., Rama, A., Drith: Autonomous,random communication, International Journal of Pharmacy and Technology, V-8, I-3, PP-17002-17006, 2016
37. Shanthi, E., Nalini, C., Rama, A., A case for replication, International Journal of Pharmacy and Technology, V-8, I-3, PP-17234-17238, 2016

38. Shanthi, E., Nalini, C., Rama, A., Elve: A methodology for the emulation of robots, International Journal of Pharmacy and Technology, V-8, I-3, PP-17182-17187, 2016
39. Shanthi, E., Nalini, C., Rama, A., Autonomous epistemologies for 802.11 mesh networks, International Journal of Pharmacy and Technology, V-8, I-3, PP-17087-17093, 2016
40. Sharavanan, R., Golden Renjith, R.J., Design and analysis of fuel flow in bend pipes, International Journal of Pure and Applied Mathematics, V-116, I-15 Special Issue, PP-59-64, 2017
41. Sharavanan, R., Jose Ananth Vino, V., Emission analysis of C.I engine run by diesel,sunflower oil,2 ethyl hexyl nitrate blends, International Journal of Pure and Applied Mathematics, V-116, I-14 Special Issue, PP-403-408, 2017
42. Sharavanan, R., Sabarish, R., Design of built-in hydraulic jack for light motor vehicles, International Journal of Pure and Applied Mathematics, V-116, I-17 Special Issue, PP-457-460, 2017
43. Sharavanan, R., Sabarish, R., Design and fabrication of aqua silencer using charcoal and lime stone, International Journal of Pure and Applied Mathematics, V-116, I-14 Special Issue, PP-513-516, 2017
44. Sharmila, G., Thooyamani, K.P., Kausalya, R., A schoolwork on customer relationship management with special reference to domain 2 host, International Journal of Pure and Applied Mathematics, V-116, I-20 Special Issue, PP-199-203, 2017
45. Sharmila, S., Jeyanthi Rebecca, L., Anbuselvi, S., Kowsalya, E., Kripanand, N.R., Tanty, D.S., Choudhary, P., SwathyPriya, L., GC-MS analysis of biofuel extracted from marine algae, Der Pharmacia Lettre, V-8, I-3, PP-204-214, 2016
46. Sidharth Raj, R.S., Sangeetha, M., Data embedding method using adaptive pixel pair matching method, International Journal of Pure and Applied Mathematics, V-116, I-15 Special Issue, PP-417-421, 2017
47. Sidharth Raj, R.S., Sangeetha, M., Android based industrial fault monitoring, International Journal of Pure and Applied Mathematics, V-116, I-15 Special Issue, PP-423-427, 2017
48. Sidharth Raj, R.S., Sangeetha, M., Mobile robot system control through an brain computer interface, International Journal of Pure and Applied Mathematics, V-116, I-15 Special Issue, PP-413-415, 2017
49. Sivaraman, K., Sundarraj, B., Decisive lesion detection in digital fundus image, International Journal of Pure and Applied Mathematics, V-116, I-10 Special Issue, PP-161-164, 2017
50. Sridhar, J., Sriram, M., Cloud privacy preserving for dynamic groups, International Journal of Pure and Applied Mathematics, V-116, I-8 Special Issue, PP-117-120, 2017