CRYSTAL CROWTH OF ZINC SULPHATE DOPED L – TARTARIC ACID BY NLO MATERIAL

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Abstract - Growth of crystals ranges from a small inexpensive technique to a complex sophisticated process and crystallization time ranges from minutes, hours, days and to months. Crystal growth needs the careful control of a phase change. In this project, an organic nonlinear single crystals of L – tartaric acid and a 5 mol % ZnSO4 doped L-tartaric acid crystals were grown in double distilled water by slow evaporation method. This method of crystal growth is very simple. The grown sample materials were characterized by XRD analysis, UV–Vis-NIR analysis and dielectric studies.

Keywords: Graph, Crystal, Vertex, Path and Growth

I. INTRODUCTION

Technology of today is seeing a rapid change and its reflection on mankind is splendid. The technology development is mainly due to the development of crystal growth technology. Crystals have fascinated men and women for many thousands of years. The use of gems for ornamental purposes appears in the practice since the birth of humankind. Crystals are formed in many natural processes, for example, crystallization of salt, and sugar from sugarcane juice etc.

Crystals are those in which the atoms, molecules or ions are arranged in a very regular and orderly fashion in a three dimensional pattern. Each molecule is fixed at a definite point in space at a definite distance and in a definite angular orientation to all others surrounding it. A crystal appears when a substance changes from one state to another. They have different physical properties in different directions. Crystallization is a general term for the process that results in the formation of crystals. Crystal growth specifically is the enlargement of crystals at the expense of materials in contact with them. The specific properties of crystals have considerably widened various field in science and technology. Crystals are used in transistors, oscillators, polarizers, radiations detectors, lasers etc. Materials like titanium doped sapphire are being developed as tunable lasers which promise longer life and more stable output than the present day lasers photorefractive crystals are used in storage and processing of data.

Crystals are divided into macro, micro and nano crystals. Macro crystals are ordered crystals of mm (= 10^{-3} m and above) size. They are visible crystals. Micro crystals are microscopically small crystals. Nan0 crystals are crystals of dimensions = 10^{-7} m or below. If a crystal is having inner boundaries along with the external boundary it is called polycrystalline. It is equivalent to the combination of a number of single crystals attached together at some point. If only two crystals are attached together it is called twinned and if more crystals are connected together it is called multiplex. A single crystal consist of atomic, ionic or molecular arrays that are periodic in three dimensions with equal repeated distance in a given direction. An ideal single crystal is one in which the surroundings of any atom would be exactly the same as the surroundings of every similar atom. Single crystals are solids in the most uniform condition that can be attained and this is the basis for most of the uses of the crystals.

1.1 General methods of growing single crystals

Crystal growth is a non-equilibrium process and thought must be given to the temperature and concentration and other gradients and the fact that heat of crystallization is process must be kept as near equilibrium and as near to a steady state process as possible. This is why control of the crystal growth environment and a consideration of growth kinetics both at the macroscopic

and atomic levels are of vital importance to the success of a crystal growth experiment.

We may define three main categories of crystal growth methods.

Growth from Solid-S →S process involving
Solid-Solid phase transformation

Growth from Melt-L →S processes involving
Liquid–Solid phase transformation

Growth from Vapour-V →S processes involving
Vapour – Solid phase transformation

A fourth main category which is strictly already included in the above definitions is

Solution growth -Growth of solute from solutions or melt

This is done primarily because growth from the melt is such a large and important category and because solution growth methods differ from methods used for pure melt growth. So we have four main categories of crystals growth techniques. They are solid growth, vapor growth, melt growth and solution growth.

II. PROPOSED METHOD

An organic nonlinear single crystals of L – tartaric acid and a 5 mol % $ZnSO_4$ doped L-tartaric acid crystals were grown in double distilled water by slow evaporation method. The grown sample materials were characterized by XRD analysis, UV–Vis-NIR analysis and dielectric studies.

2.1 Different methods in solution growth

The quality of the crystal grown depends upon the quality of the seed crystal used. Small seed crystals can be obtained by spontaneous nucleation. The seed crystal is used to grow large uniform crystal and it must be a single crystal free of inclusions, cracks, block boundaries, twinning and any other obvious imperfections. A defect-free crystal must be used for various studies.

Low temperature solution growth can be subdivided into the following methods:

(i) Slow cooling method

(ii) Slow evaporation method and

(iii) Temperature gradient method

(i) Slow Cooling Mothed

This is the best method to grow bulk single crystals from solution. In this method, super saturation is created by a change in temperature usually throughout the who9le crystallizer. The crystallization process is carried out in such a way that the point on the temperature dependence of the concentration moves into the meta stable region along the saturation curve in the direction of lower solubility. Since the volume of the crystallizer is finite and the amount of substance placed in it is limited, the super saturation requires systematic cooling. It is achieved by using a thermo stated crystallizer. Volume of the crystallizer is selected based on the desired size of the crystals and the temperature dependence of the solubility of the substance.

(ii) Slow (Free) Evaporation Method

In this method the solution loses particles which are weakly bound to other components and, therefore, the volume of the solution decreases. An excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and the solute. Normally, the vapour pressure of the solvent above the solution is higher than the vapor pressure of the solute and, therefore, the solvent evaporates more rapidly and the solution becomes supersaturated. It is sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. This method of crystal growth is the oldest and technically it is very simple. For nontoxic solvents such as water, evaporation is permissible into the atmosphere but for toxic and inflammable solvents precautions are taken to avoid the leakage of solvent vapour in the atmosphere.

The simplest apparatus for growth by this method a beaker covered with a few holes in the lid to allow solvent evaporation. The rate of crystallization depends on the rate of solvent evaporation which may be governed by changing the total area of the holes. In sophisticated crystallizers, evaporation is controlled by passing air or an inert gas at a controlled rate over the solution. Good

control of evaporation rate can also be obtained by using some sort of condenser to allow the removal of condensed solvent at a controlled rate.

(iii) Temperature Gradient Method

In this method, the materials are transported from a hot region containing the source material to be grown to a cooler region where the solution is supersaturated and the crystal grows. The main advantages of this method are (i) crystal grows at fixed temperature, (ii) It is insensitive to change in temperature, provided both the source and the growing crystal undergo the same change and (iii) Economical use of solvent and solute etc.

III. RESULTS AND DISCUSSION

3.1 Growth of L (+)- Tartaric Acid and $ZnSO_4$ doped single crystals

L(+)-tartaric acid (LTA) (Merck-extra pure) ($C_4H_6O_6$) was dissolved using deionised water as the solvent in a 100ml beaker. The solution was stirred well for about two hours at 32^oC and the saturated solution was filtered with Whattman filter paper in clean vessel. The vessels containing the solutions were covered with perforated polythene sheets. The solution was allowed for slow evaporation. The nucleation was observed in 5 days and it was allowed to grow further for two weeks. To get $ZnSO_4$ doped LTA crystals the 5 mol % of $ZnSO_4$ was added in the saturated solution of LTA. The dimensions of grown crystals are 10 x 5x3mm^3 (LTA) and 8x6x6 mm^3 (ZnSO4 doped LTA).

3.2 Powder XRD analysis

The powder X-ray diffraction analysis were revealed that the grown LTA and 5 mol % ZnSo4 doped LTA are of monoclinic structure. The obtained lattice parameter values of LTA crystal were a = 6.201Å , b=6.017Å , C= 7.719 Å α=γ=90^{o}β=100.10^o and volume V=283.54. The 5 mol% $ZnSO_4$ doped LTA crystal has a lattice parameter values of a = 6.100Å, b=6.017Å c=7.720Å α=γ=90^o β= 100.36^o and volume V =278.733 Å^3. The TREOR software is used to ensure the PXRD results.

The obtained PXRD results are in good agreement with reported Single Crystal XRD results of LTAcrystal(23, 24)

3.3 UV-Vis-NIR analysis

The UV-visible spectral studies of grown tartaric acid crystals were carried out using perkin Elmer spectrophotometer. The spectrum was recorded in the wave length region from 200 to 800 nm. The transmittance of the grown samples LTA and $ZnSO_4$ doped LTA. It was found that the grown crystal has convenient transparency range from 291 to 750 nm, with maximum transmission in the visible region. It indicates that the crystal is suitable for electro-optic modulation. The spectrum revealed that in the grown crystals the absorbtion is absent in the visible region, hence tartaric acid crystals are more transparent and may be used as potential candidates for NLO applications. The lower cut-off wavelength for 5 mol% $ZnSO_4$ doped LTA crystal is 238 nm and the same for LTA crystal is 237 nm.

Calculation of band gap energy for $ZnSO_4$ doped LTA crystal:

E_g = 1240/λ eV
= 1240/234 eV
=5.2991 eV

For LTA crystal

E_g =1240/237 eV
=5.232 eV

3.4 Dielectric studies:

The dielectric parameters depend on the applied frequency and temperature of the samples. The variations of dielectric parameters of the samples with temperatures and frequencies are presented. Dielectric parameters like dielectric constants and loss factors decrease with increase in frequency and their values increase with increase in temperature. The high values of dielectric constant at low frequencies may be due to presence of space charge polarization and its low value at high frequencies may be due to the loss of significance of the four type of

polarizations viz. space charge, orientational, ionic and electronic polarization. The low value of dielectric constant at of the applied field and is a suitable parameter for the enhancement of SHG coefficient and the sample may be used in photonic, opto electronics and NLO devices.

IV. CONCLUSION

An organic L- Tartaric acid crystal and a 5 mol% of $ZnSO_4$ doped L-Tartaric acid crystal were grown successfully by slow evaporation method at room temperature. It was observed that the grown crystals have a good structures optical and electrical behaviour. The materials may be used in NLO based on applications.

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