GROWTH & CHARACTEIZATION OF INORGANIC POTTASSIUM PENTA BORATE TETRA HYDRATE (PPBTH) SINGLE CRYSTAL

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ABSTRACT

Single crystal of pottassium penta borate tetra hydrate an organic material: have been grown by slow evaporation technique at room temperature .The crystalline nature of grown crystal was confirmed by power x ray diffraction analysis (XRD). The structure of LKS consists of Li+ and lying on threefold axes and K+ ion has a tetrahedral coordination with Li-O distances 1.909 - 1.923 Ǻ. The UV- Vis study was performed to know optical behaviour of the grown crystals.

Key Words: Single crystal,XRD,UV

1.1 Introduction

In the recent past, extensive studies have been made on the synthesis and crystal growth of nonlinear optical (NLO) materials due to their potential application in the field of telecommunication, photonics and opto electron-ics technology. Presently, numerous inorganic NLO ma-terials have been developed to increasing the variety of these applications by the researchers [1]. The significant attention is currently being paid to these crystals due to their physical properties such as ferroelectricity, piezoelectricity and ionic conductivity. During the past two decades, extensive studies have been carried out for the growth, structural and phase transition of LKS crystal. At room temperature, it exhibits a hexagonal system with $P6_3$ space group [5]. In addition, it undergoes several structural phase transitions below [6] and above room temperature [2].

In the present investigation is aimed at the growth of lithium potassium sulphate single crystals by slow evaporation method at room temperature. The grown crystals have been subjected to single crystal X-ray diffraction analysis, UV-Vis-NIR spectral analysis, optical band gap measurements.

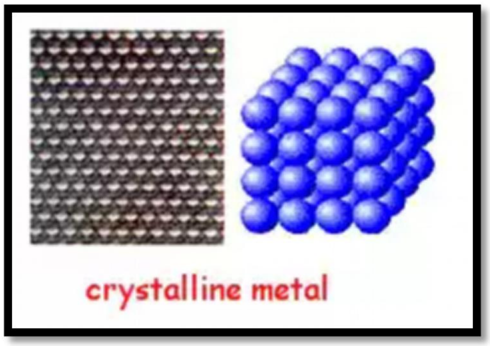
1.2.Types of solids:

When a substance is at such a low temperature that the thermal agitation of its molecular (or constituent particles) is not strong enough to move them all around the inter-molecular forces tend to hold the molecular together in more or less positions. The material acquires a shape and is then said to be in the solid state. The so called "solid" material may be divided into two distinct classes.

1.2.1.Amorphous solid:

An amorphous solid differs from a crystalline substance in being without any shape of its own and has a completely random particles arrangement no regular arrangement of amorphous substance in many aspects resembles liquids, which flow very slowly at room temperature. Strictly speaking amorphous substances are regarded as super cooled liquids.

In single-crystals the regularity of arrangement of the pattern extends throughout the solid and all points are completely equivalent. In other words if the points under consideration is given any amount of displacement in any direction. The points finds itself in the same environment as that in which it was previously thus the most important and the essential feature of a crystal is the periodicity of the arrangement along with regularity. Some examples are



- If we examine grains of ordinary table salt under a magnifier we shall find most of them to have the shape of regular cubes.
- In many solid we may not clearly see the shape of the crystals because many small sized crystals are tightly packed together without any specific order an ordinary copper wire does not look like a crystalline substance but when its surface is examined under a microscope its crystalline nature becomes visible thus a copper wire is said to have a microcrystalline structure whenever.

1.3.Reasons for growing single crystals:

State simple the job of the crystal grower is to prepare large specimens of crystalline material such that there is complete crystallography continuity across a given specimen in all direction. There are two principle reasons for the deliberate growth of single crystal.

- Many physical properties solids are obscured or complicated by the effect of grin boundaries.
- The full range of tensor relationships between applied physical cause and observed effect can be obtained only if the full internal symmetry of the crystal structure is maintained throughout the specimen.

1.4.Application of crystal:

Modern technology requires physicists, chemists, electrical engineers, metallurgists and growers to assist each other at many levels. Crystal growth is a vital and fundamental part of materials science and engineering. Since crystals of suitable size and perfection they are required for fundamental data acquisition and for practical devices such as detectors, integrated circuits and for other millions and millions of applications. Behind every new solid state device there stands a single crystal and the explosion in solid state device development, which followed the invention of the transistor in 1948. This means that many new crystals had to be grown and fabricated in order to assess their device properties. The ever increasing application of semiconducting, ferroelectric, piezoelectric, oxide single crystals. The volume of silicon single crystals production, the most commonly used in domestic electronic materials is about $6*10^4$ metric tons a year. The piezoelectric quartz is $2.5*10^3$ metric tons a year. The high technology GaAs crystal is about $1*10^3$ metric tons and the new promising in crystal is about 10 metric tons.

SYNTHESIS METHODS AND CHARACTERIZATION TECHNIQUES

2.1.Need for crystals:

The growth of single crystals has been developed over the years to meet needs for basic research and applications. Basic crystal growth methods have been modified and refined to enhance their applicability to specific materials or classes of materials. The development and refinement of the methods and of the crystal products have relied heavily on empirical engineering and on trial and error. Striking advances in solid state electronics have been based on single crystal of semiconductors, as well as magnetic and optical materials, further technological advance await the availability of suitable single crystals. For example, potentially pro-found electro-optical applications cannot be realized fully because suitable single crystals of III-V, IV-VI, components and their alloys cannot be yet reliably obtains.

Solvent:

It is known that the choice of solvent provides some control over crystal habit and this effect depends on the interaction of the surface of the crystal as it grows and the solvent molecules. Sometimes this is sufficient to result in the precipitation of a new crystalline phase. Also this effect is related to the influence of impurities or additives upon habits, solvents commonly used include water, both light (H_2O) and heavy (D_2O) ethanol, methanol, acetone, carbon tetrachloride, hexane, xylene and many other solvents having all the above characteristics together, however don’t exist.

Mechanics:

Mechanical disturbance of the crystal growing vessel results in smaller crystals. Let the crystals growth with a maximum of the disturbance we should not pick up the vessel every day to check on how the crystals are growing. Set up the crystals growing attempt, in a quiet, out of the way place and forget about it for a week.

Time:

This is related to mechanics. Crystals fully recognize that patience is a virtue and will reward those who practice it.

2.2 NUCLEATIONS:

Nucleation is an important phenomenon in crystal growth and is the precursor of crystal growth and of the overall crystallization. Before crystals can grow there must exist in the solution a number of minute solid bodies known as centres of crystallization, seeds embryos of nuclei. Nucleation may occur spontaneously or it may be induced artificially; based on these nucleation is classified as two kinds.

- **Homogeneous nucleation**
- **Heterogeneous nucleation**

Homogeneous nucleation:

The spontaneous formation of crystalline nuclei in the parent phase is called homogeneous nucleation, though the spontaneous formation of nuclei in the bulk of supersaturates systems is a comparatively rare occurrence, its basic principles from the necessary background for the understanding of numerous processes in science and technology as well as in nature when phase transitions are involved.

Heterogeneous nucleation:

On the other hand if the nuclei from heterogeneously around ions, impurity molecules or on dust particles, on surface or at structural singularities such as dislocations or other imperfections, it is called heterogeneous nucleation. The nucleation process was understand after realizing the under cooling and supersaturated phases, which refer the unstable conditions.

2.3 METHODS

(i) Slow Cooling Methods:

This is the best methods among others to grow bulk single crystal from solution. In this method, super saturation is produced by a change in temperature usually throughout the whole crystallization. The crystallization process is carried out in such a way that the point on the temperature dependence of the concentration moves into the metastable region along the saturation curve in the volume of the crystallization is the finite and the amount of substance placed in its limited. The super saturation requires systematic cooling. It is achieved by using a thermo stated crystallizer and the volume of the crystallizer is selected based on the desired size of the crystals and the temperature dependence of the solubility at the substance the temperature at which such crystallization can being is usually within the range 45-75^{0}C and the lower limit of cooling is the room temperature.

(ii) Slow Evaporation Method:

In this method, an excess of a given solute is established by utilizing the difference between the rates of evaporation 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 solute and therefore the solvent evaporates more rapidly and the solution becomes supersaturated usually it is sufficient to allow the vapour format above the solution to escapes freely into the atmosphere. This is the oldest method of crystal growth and technologically. It is very simple typical growth conditions involve temperature stabilization to about 0.005^0C and rates of evaporation of a few mm^3/hr.

(iii) Temperature Gradient Method:

This method involves the transport of the materials from a hot region containing the source materials to be grows to a cooler region, where the solutions is supersaturated and the crystal grows, the main advantages of the method are that.

- Crystal grows at fixed temperature,
- This method is insensitive to changes in temperature, provide both the sources and the growing crystal undergo the same change,
- Economy of solvent and solute

(iv) Melt Growth:

Melt growth is the process of crystallization by 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, no impurities are introduced in the growth process and the rate of growth is normally much higher than that possible by other methods, mainly for latter reason. Melt growth is commercially the most important method of crystal growth. The growth from melt can further be sub-grouped into various techniques.

The main techniques are

- Bridgman technique
- Czochralski technique
- Verneuil technique

- Zone melting technique
- Heat exchanger method
- Shaped crystal growth

The major practical factors to be considered during growth of crystals from the melt are

- Volatility of dissociating
- The chemical reactivity and
- The melting point

The volatility or dissociability is probably the most important factor, those materials which exhibit volatility of one or more of their components require special melt growth techniques to prevent evaporation loss during growth. The chemical reactivity of a material with the crucible and its gaseous environment. Additionally in the growth chamber accessible to the volatile vapours must be checked. Many oxides and ceramics particularly high melting point materials require one of the noble metals as crucible materials. High melting point inevitably cause problems with high temperature gradients and these can bring seven convention problems. High temperature gradients can be responsible for thermal shock and stress in materials, which can be severe problems on oxide materials.

(v)Vapour growth:

The growth of single crystal materials from the vapour phase is probably the most versatile of all crystal growth processes. Although the large number of variables involved tends to make it a relativity difficult process to control. In addition, the lower density of molecules in the crystal growth environment leads to a lower growth rate than achieved from stochiometric metals. The driving force for the great evolution of vapour growth method in the past year has been unquestionably, the demand of physics and electronics for single crystal of all possible materials.

Crystal growth techniques from the vapour can be classified into various categories depending on the way in which the vapour is obtained.

- Physical vapour deposition
- Chemical vapour deposition
- **Physical vapour deposition:**

Traditional vacuum evaporation may involve either direct evaporation of the source material onto a substrate or reactive evaporation where the evaporated materials reacts with a component intentionally added to the vapour phase to produce the desired deposit. This technique is frequently employed where direct evaporation of compounds yields deposits deficient in non-metallic species. Thus the evaporation is carried out in an ambient containing the deficient species in gaseous from. A relatively new and elegant evaporation technique, molecule beam epitaxial has been developed for this purpose.

Chemical vapour deposition:

Chemical vapour deposition could be identified as process of the different from physical sputtering or wet chemical process even though the end objective is similar viz. Obtaining a thin film surface or coating.

The major impact of chemical vapour deposition on this film technology took place when it was demonstrated nearly three decades ago that epitaxial layers of silicon and germanium could be grown by this method. Since then it has been successfully used for the formation of a variety of layers, compound semiconductor such as **GaAs, Gap, Sic**, and others, various insulators like **Si_3N_4, Sic,**etc… conductors and resistors particularly those which become important in connection with semiconductors integrated circuit technology and ferrites

(vi) Gel growth:

The gel growth technology has gained considerable importance due to its simplicity and effectiveness in growth single crystals of certain compounds. Gel growth is an alternative technique to solution growth with controlled diffusion on and the growth process is free from convection. The growth of single crystals in gel is a self-purifying process, free from thermal strains which are common in crystal growth from the melt.

The principle of gel growth technique is a simple and elegant method of growing single crystals under controlled growth and at room temperatures. Solution of two suitable compounds which give rise to the required insoluble crystalline substance by mere chemical reaction between them are allowed to diffuse into the gel medium and chemically react as follows.

$$\mathbf{AX + BY \quad AB + XY}$$

A gel is a two compound system, highly viscous, semi-solid in nature and having fine pores through which diffusion takes place and gel can be classified as follows.

Physical gel:

Gel which is obtained by physical process such as cooling is called physical gel.

E.g. Gelatine agar agar and clay.

Chemical gel:

Gels formed by chemical reaction such as hydrolysis is called chemical gels.

E.g. Silica, polycrylamide, tetramethoxsysilane.

Solution growth:

Gibbs-Thomson equation can also be applied when a crystal (second phase) is Formed in a supersaturated solution (first phase). The solubility of a crystal increases as the size of the crystal decreases. If Ci and Cα are the concentrations of solution with a small crystal of radius r and with a large crystal of radius r=α respectively then

$$\mathbf{KT\ In\ CI/CI=2\sigma V\pi/r}$$

A supersaturated solution with a super saturation ration of CI/CI can be equilibrium with a crystal if the size r satisfies equation. Any crystal large then r will grow in this supersaturated solution since its solubility is smaller than CI: any crystal smaller then r will dissolve in this supersaturated solution since its solubility is greater than CI.

There are two types of solution growth are

- Low temperature solution growth
- High temperature solution growth

Low temperature solution growth:

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth from low temperature aqueous a solution is extremely popular in the production of many technology important crystals. The crystal by low temperature solution growth involves weeks, month and sometimes years. Much attention has been paid to understand the growth mechanism of the process detailed theories are now available, and this great work of scientists like Bennema, Chernov and others during the past several decades. Though the technology of growth of crystals from solution has been well perfected, it involves meticulous work, much patience and even a little amount of luck. A power failure or a contaminated batch of material can destroy months of work.

High temperature solution growth:

The high temperature crystal growth can be divided into two major categories:

First one is growth from single component system and the second one is that from multi-components, in the single component method only the chemical compo forming the crystal is present in the growth system, while in the multi-components method another component is added to the growth system.

2.4. Characterization techniques

2.4.1. Powder X-ray diffraction (XRD)

X-ray diffraction technique is the most common and efficient method for the determination of structure, crystallainity and material identification. XRD examines whether a resultant material has amorphous or crystalline nature. Crystalline phases can be identified by just comparing the interplanardistance ‘d’ values obtained from XRD data with the fundamental data in Joint Committee on Powder Diffraction Standards (JCPDS). X-ray diffraction is based on constructive interference of monochromatic X-rays from a crystalline sample. The X-rays, generated by a cathode ray tube are filtered to produce monochromatic radiation, collimated and directed towards the sample. X-ray primarily interact with electrons in atoms, collide and some photons from the incidentbeam are deflected away from original. The X-rays interfere constructively and destructively producing a diffraction pattern on the detector. The incident X-ray radiation produces a Bragg peak if their reflections from the various planes interfered constructively. The interference is constructive, when the phase shift is a multiple of 2π, this condition can be expressed by Bragg's law ($n\lambda = 2d \sin\theta$) where, n is an integer, λ is the wavelength of incident wave, d is the spacing between the planes in the atomic lattice and s is the angle between the incident ray and the scattering planes. Fig. 2.3 shows the principle of X-ray diffraction.

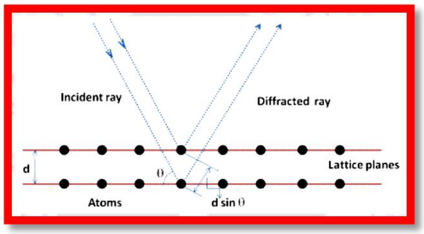


Fig. 2.1: Principle of X-ray diffraction

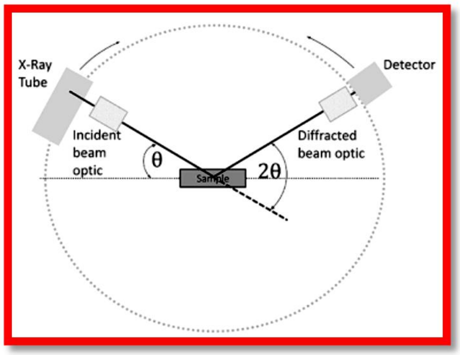


Fig. 2.2: Schematic diagram of X-ray diffractometer

A typical powder X-ray diffractometer consists of a source of radiation, a monochromator to choose the wavelength, slits to adjust the shape of the beam, a sample and a detector. A goniometer is used for fine adjustment of the sample and the detector positions. The goniometer mechanism supports the sample and detector, allowing precise movement. The source of X-rays contains several components; the most common being K_α and K_β. The specific wavelengths are the characteristic of the target material (Cu, Fe, Mo and Cr). Monochromators and filters are used to absorb the unwanted emission with wavelength K_β, while allowing the desired wavelength, K_α to pass through. The X-ray radiation most commonly used is that emitted by copper, whose characteristic wavelength for the $K_\alpha$radiation is equal to 1.54 Å. The filtered X-rays are collimated and directed onto the sample. When the incident beam strikes a powder sample, diffraction occurs in every possible orientation of 2θ. The diffracted beam may be detected by using a moveable detector such as a Geiger counter, which is connected to a chart recorder. The counter is set to scan over a range of 2θ values at a constant angular velocity. Routinely, a 2θ range of 5 to 70 degreesis sufficient to cover the most useful part of the powder pattern. The scanning speed of the counter is usually 2θ of 2° min^{-1}. A detector records and processes this X-ray signal and converts the signal to a count rate which is then fed to a device such as a printer or computer monitor. Fig. 2.4 shows the schematic diagram of X-ray diffractometer. The sample must be ground to fine powder before loading it in the glass sample holder. Sample should completely occupy the square glass well. The structural property of prepared Co_3O_4 nanoparticle was studied by X-ray diffraction.

2.4.2. UV-Visible Spectroscopy

UV spectroscopy is a type of absorption spectroscopy in which light of ultra-violet region (200-400 nm) is absorbed by the molecule. Absorption of the ultra-violet radiations results in the excitation of the electrons from the ground state to higher energy state. UV spectroscopy obeys the Beer-Lambert law, which states that when a beam of monochromatic light is passed through a solution of an absorbing substance, the rate of decrease of intensity of radiation with thickness of the absorbing solution is proportional to the incident radiation as well as the concentration of the solution. The expression ofBeer-Lambert law is

$$A = \log (I_0/I) = \mathcal{E}cl$$

where,

- A= absorbance.
- I_0 = intensity of light incident upon sample cell.
- I = intensity of light leaving sample cell.
- l = length of sample cell.
- $\mathcal{E}$ = molar attenuation coefficient.

From the Beer-Lambert law, it is clear that greater the number of molecules capable of absorbing light of a given wavelength, the greater the extent of light absorption. The basic principle of UV spectrophotometer is shown in the Fig. 2.5.

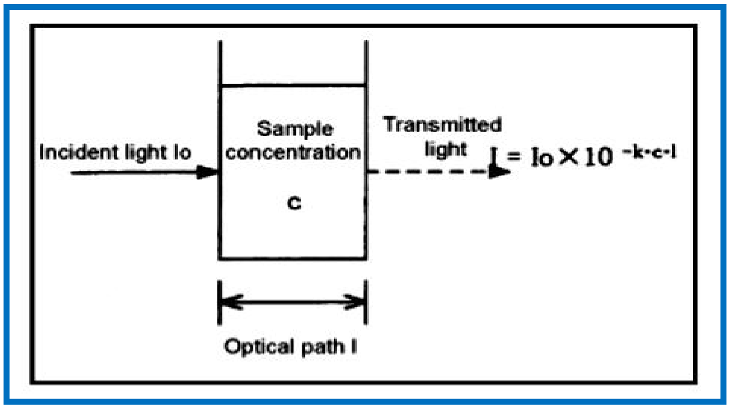


Fig. 2.3: Principle of UV-Vis Spectrophotometer

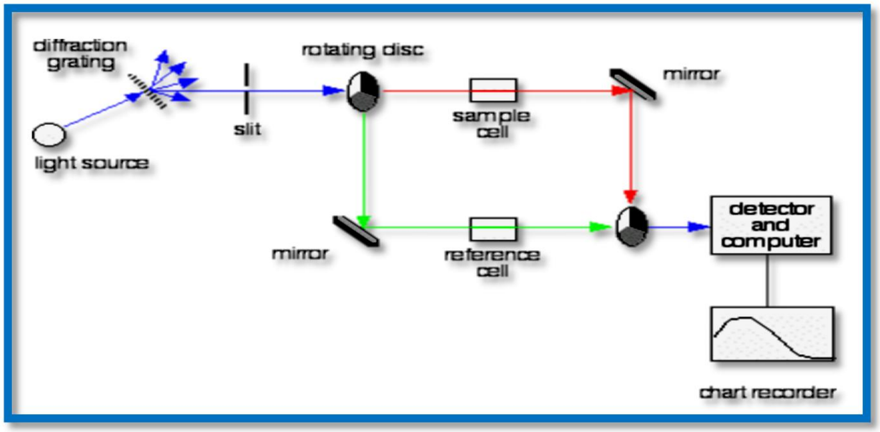


Fig. 2.4: Schematic diagram of UV-Vis spectrophotometer

The main components of the UV-Vis spectrophotometer are a light source, double beams (reference and sample beam), a monochromator, a detector and a recording device. The source is usually a tungsten filament lamp for visible and deuterium discharge lamp for UV measurements. The light coming out of the source is split into two beams - the reference and the sample beamas shown in the Fig. 2.6.The sample and reference cells are rectangular quartz / glass containers; they contain the solution (to be tested) and pure solvent, respectively. The spectrophotometer records the ratio between the reference and sample beam intensities. The recorder plots the absorbance (A) against the wavelength (λ). The sample is prepared into a paste and then dissolved into the solvent to make a dilute sample solution. This sample solution is filled up to mark line of the sample cell. The optical properties of samples were studied by UV-Vis spectrophotometer.

3. Experimental Procedure

3.1. Synthesis of the Material

Lithium potassium sulphate was synthesized by the che- mical reaction of commercially available Lithium sul- phate (Analar grade-E. Merck) with Potassium sulphate (Analar grade-E. Merck) taken in the stoichiometric ratio 1:1 by dissolving double-distilled water (solvent) at room temperature and the chemical reaction is given below

3.2. Growth of Single Crystals

A saturated solution of LKS was prepared by double- distilled water. The solution was allowed to slow evapo-ration in the vibrational and dust free atmosphere. After the growth period of 25 days, colourless and transparent crystals were harvested. The harvested crystals were recrystallized repeatedly to achieve good quality as shown in **Figure 1**.

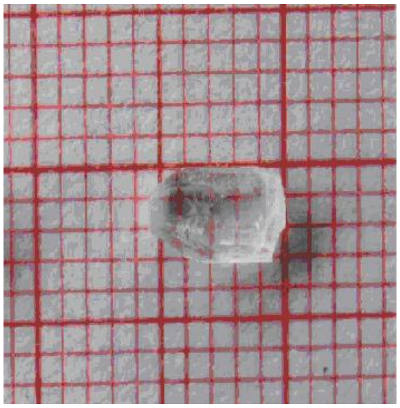
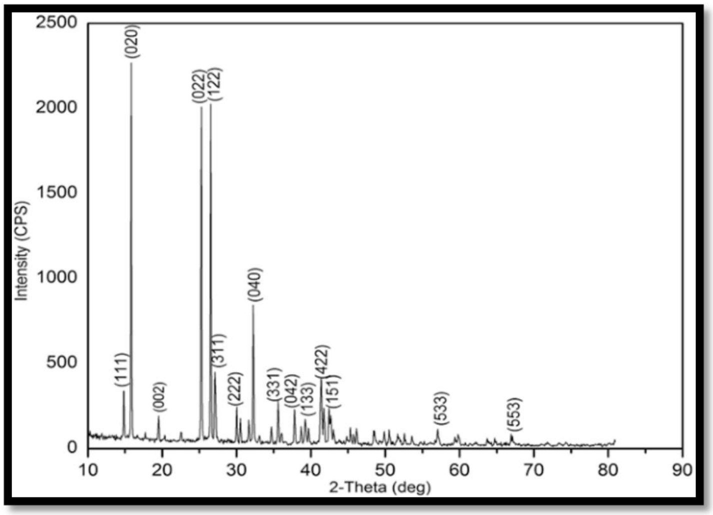


Figure 1. As the grown single crystal of lithium potassium sulphate.

3.3. Results and discussion

3.3.1. Structure of the Crystals

The single crystal **X**-ray diffraction (XRD) studies of LKS were carried out using Enrafnonius CAD4 single **X**-ray diffractometer with MoKα (λ = 0.717 Å) radiation. The UV-Vis-NIR spectrum was recorded using Perkin elmmerLamda 35 spectrophotometer in the range of 190 - 1100 nm. The SHG efficiency and the phasematching studies were carried out by the Kurtz and Perry powder technique using a Q-switched, mode locked Nd:YAG laser. Microhardnessbehaviour of the grown crystal was carried out using Vicker's hardness tester



The single crystal XRD study indicates that $LiKSO_4$ crystallize in hexagonal system with P63 space group at room temperature. The unit cell dimensions are a = b = 5.1453(2) Ǻ and c = 8.6342(7) Ǻ. These values are good agreement with the reported values [4]. There are two molecules in the unit cell. The structure of LKS consists of Li+ and lying on threefold axes and K+ ion has a tetrahedral coordination with Li-O distances 1.909 - 1.923 Ǻ (**Figure 2**).

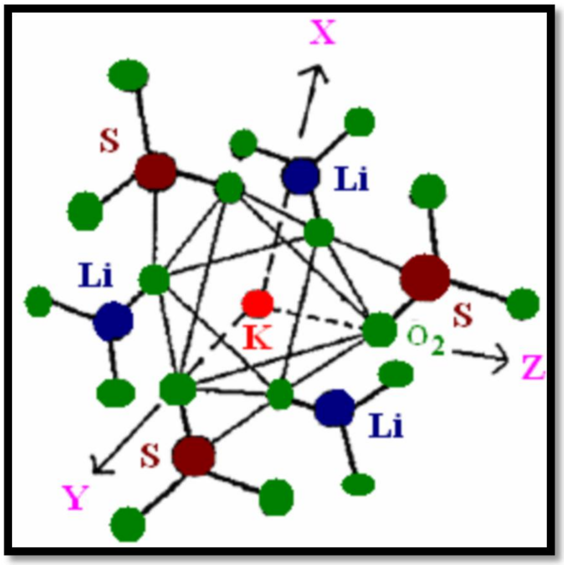


Figure 2. Coordination polyhedron of K+ viewed along c- axis.

3.3.2. Optical Transmittance Study

The optical transmittance spectrum of LKS crystals is shown in **Figure 3**. The optical transmittance study may be assisted in understanding the electronic structure of the optical band gap of the crystal. The study of the ab-sorption edge is essential in connection with the theory of electronic structure, which leads to the prediction of whether the band structure is affected near the band extreme. From the transmittance spectrum, it was observed that the grown crystals have high transmittance in the entire visible-NIR region and the lower cut-off wave-length (253 nm) facilitates LKS crystals to be potential nonlinear optical material for second harmonic generation of Nd:YAG laser. Using the formula, the value of optical band gap of LKS is calculated to be 4.24 eV. The observed behaviour of the optical spectrum and band gap value found in this work is in good agreement with the spectrum of LKS crystal.

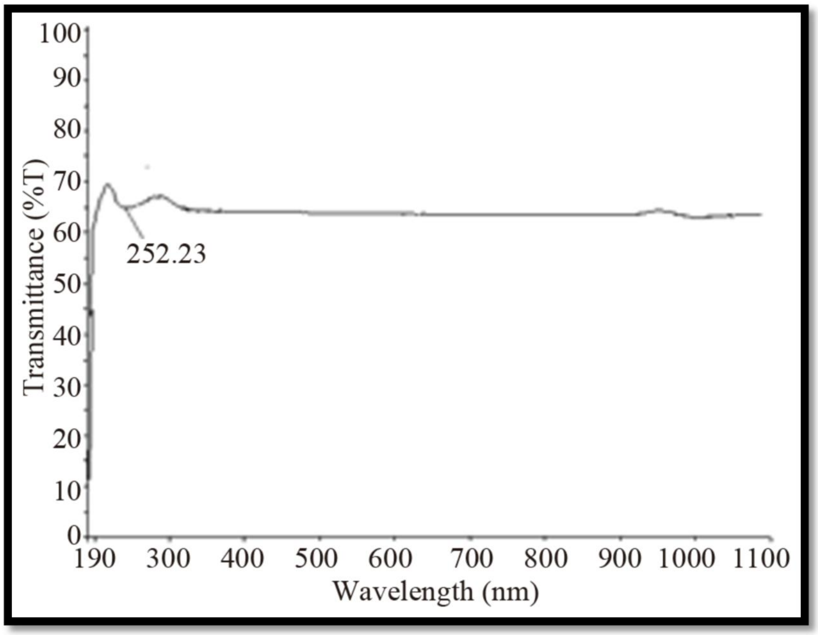


Figure 3. Optical transmittance spectrum of LKS.

SUMMARY AND CONCLUSIONS

4. Conclusion

Single crystals of lithium potassium sulphate, an inorganic nonlinear optical material, were grown by slow evapora- tion method at room temperature. The single crystal X-ray diffraction analysis confirms the grown crystal belongs to hexagonal system. The optical transmittance study shows the crystal has good transmittance in the entire visible-NIR region and wide band gap.

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