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UNIDIRECTIONAL GROWTH AND CHARACTERIZATION OF NLO CRYSTAL: POTASSIUM DIHYDROGEN ORTHOPHOSPHATE

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ABSTRACT

A System is reported for evaporation controlled crystal growth of potassium dihydrogen orthophosphate (KDP) from aqueous solution by the Sankaranarayanan-Ramasamy (SR) method. KDP (KH_2PO_4) single crystal of 10 x 3 x 4 mm^3 has been grown at an average rate of 5 mm/day from the point seed in a glass crystallizer. The growth rate formula is derived for the SR method. The grown crystals were characterized by UV-Vis, Laser Raman, Second harmonic generation efficiency X-ray diffraction and FTIR studies. The SR method is an efficient method to grow crystals of good optical quality.

Key words: Crystal growth, SR method, X-ray diffraction, FTIR.

INTRODUCTION

One of the obvious requirements for a non linear optical crystal is that it should have excellent optical quality. Potassium dihydrogen orthophosphate, KH_2PO_4 (KDP) is a good nonlinear crystal material due to its interesting electrical and optical properties, structural phase transitions and its easy crystallization. The study of KDP is of great interest because of its unique non linear optical properties and vast applications in the field of high power laser systems. Potassium dihydrogen orthophosphate is a model system for a non linear optical device application. Large single crystal of KDP is used for frequency conversion and as parts of large aperture optical switches in the laser fusion systems.

The novel uniaxial Sankaranarayanan-Ramasamy (SR)[1,2] solution growth method attracted the researchers due to the growth of defect free transparent bulk single crystals along a particular axis. Simple experimental techniques, unidirectional growth, 100% solute –solid conversion, minimum thermal stress and prevention of the microbial growth are the interesting features of this technique[3,4]. Though potassium dihydrogen phosphate KDP is a

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classical material, the growth aspects and properties such as transparency, dielectric nature, wide frequency conversion, high damage threshold against high power laser etc.[5] attracted material scientists in improving the crystal size for the desired applications. KDP is a well-known non-linear optical crystal, belongs to tetragonal crystal system having tetra molecular unit cell with lattice parameters a = b = 7.448 Å and c = 6.977 Å[6]. In the present work, the single crystal of KDP was grown by Sankaranarayanan-Ramasamy method. The grown crystals have been analyzed by different characterization techniques.

EXPERIMENTAL

The experimental setup is shown in Fig. 1 and is basically the same as that described by Sankaranarayanan and Ramasamy[7]. It was employed in-house by a controllable heating assembly, transparent growth vessel made out of borosilicate glass. An outer glass shield tube protects and holds the inner growth ampoule. A ring heater positioned at the top of the growth ampoule was connected to the temperature controller. In this experiment, the temperature around the growth ampoule was selected based on the solvent used and was controlled with aid of the temperature controller. In this experiment, the temperature around the growth region is maintained at 40^{o}C with ± 0.05^{o}C accuracy. Depending on the evaporation rate of the solvent, the freshly prepared solution was periodically (drop by drop) added. The addition of just a few drops does not seriously alter the supersaturation, evaporation rate, etc. The solution was made from Analar-grade (Alfa) chemical reagents dissolved in twice-distilled water.

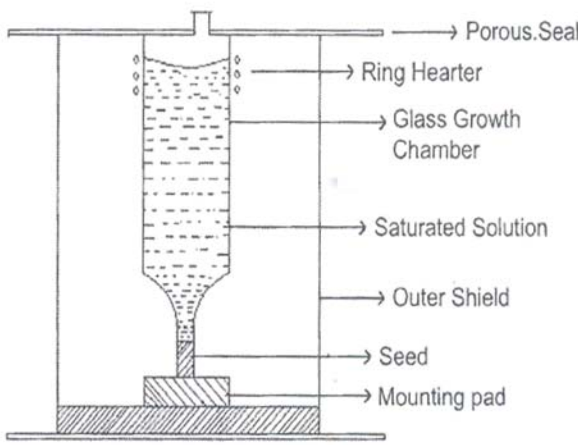

Fig. 1: SR method experimental setup

The solution was contained in conical glass tubed (growth vessel), with the tip of the cone slightly flattened to accommodate small single-crystal seeds. The top of the solution in the growth vessel was maintained above room temperature about 42^0C to increase the evaporation rate. Depending on the actual growth rate of the crystals, the evaporation rate was varied by varying the temperature. In the bottom of the vessel, there is an oriented seed, and it grows as a single crystal in oriented growth direction. Growth was carried out along the c-axis as well as along the (110) direction. The average growth rate was 5 mm/day. The grown crystals are shown in Fig. 2.

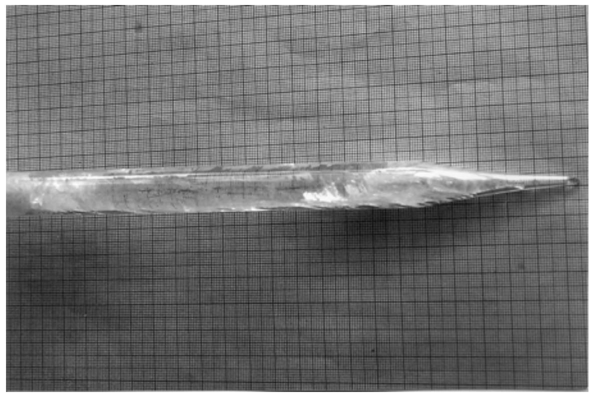

Fig. 2(a): As grown crystal of KDP with ampoule

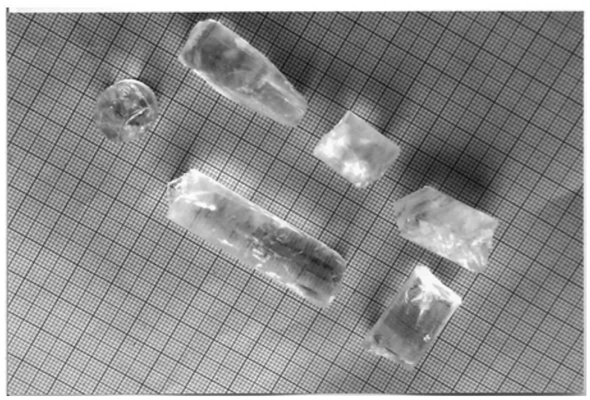

Fig. 2(b): As grown crystals of KDP

Growth rate formula for the SR method

It is well-known that the evaporation rate of water into the atmosphere is a function of temperature, humidity, and air velocity. It has been understood that the evaporation process in the atmosphere is the diffusion of water molecules coming out of a water surface through the air layer covering the water surface. To calculate theoretically the absolute evaporation rate, we must know the diffusion coefficient of water vapour in air and the thickness of the boundary layer accurately. Therefore, more careful studies are needed to determine the absolute evaporation rate exactly to find out the growth rate. Kazuo Histake et al.[8] reported a detailed study on the evaporation rate experimentally as well as theoretically.

A relation can be given for the growth rate for the SR method based on the solubility of the material, evaporation rate, size of the growth vessel, and the density of the material.

$$R_{(T)} = 0.318k\ (SE)/r^2 d\ \text{(cm/day)}$$

Where k is the proportionality constant, S is the solubility of the material (g/mL of solvent), E is the evaporation rate of solvent (mL/day), r is the radius of the vessel (for cylindrical) (cm), d is the density of the material (g/cm^3), and T is the temperature (K).

Using the above parameters, the growth rate (R) of the crystal can be calculated. For successful growth of the crystal, the amount of solute obtained by solvent evaporation should not exceed the mass transfer rate of solute by diffusion. The evaporation rate of solvent in a vessel was measured by observing the lowering rate of the top surface of the solution level.

Characterization studies

The grown crystals have been analyzed by different characterization techniques. The lattice parameters of grown crystals were confirmed by X-ray diffraction analysis. The presence of functional groups in the grown crystal was confirmed using FTIR studies. The optical transparency of the grown crystal was measured. The Laser Raman study was also carried out.

RESULTS AND DISCUSSION

X-ray diffraction analysis

The crystal system was identified from the powder X-ray diffraction pattern analysis and found that it belongs to tetragonal system. The calculated lattice parameters are given Table 1. The recorded powder XRD spectrum is given in Fig. 3.

FTIR studies

Fourier transforms infrared transmission (FTIR) spectra of KDP crystal was carried out in the mid IR region 400-4000 cm^{-1} in order to confirm the presence of functional groups. The spectrum (Fig. 4) shows absorptions bands at 1299.51 cm^{-1} and 1100.28 cm^{-1} which could be assigned to P = O stretching and P-O stretching mode of vibration. The O-H stretching modes have intense broad absorption band between 3500 and 2400 cm^{-1}. The absorption bands at 2443 and 2773 cm^{-1}, is assigned to O-H stretching vibrations. The $(PO_4)^{3-}$ symmetric bending is at 541.73 cm^{-1} and P-O and $(PO_4)_3$ plane bending at 114.61 cm^{-1}. The broad absorption bands appearing at 1683.02 cm^{-1} and 906.56 cm^{-1} are assigned to P-O-H stretching vibrations.

Table 1: Unit cell parameters of KDP crystal

Molecular formula	KH_2PO_4
Cell Parameters	a = 7.448 Å b = 7.448 Å c = 6.977 Å
System	Tetragonal

Table 2: FTIR assignments of KDP crystal

Wave number (cm^{-1})	Assignments
1299.51	P = O stretching
1100.28	P-O stretching
3500 – 2400	O-H stretching
2443 –2773	O-H stretching
541.73	$(PO_4)^{3-}$ symmetric bending
114.61	P-O and $(PO_4)_3$ plane bending
1683.02 – 906.56	P-O-H stretching

UV-Vis studies

The UV-Vis absorption spectrum was recorded using a Shimadzu UV-106 UV-Vis spectrophotometer in the range 200-1100 nm covering the infrared region to find the transmission range to know the suitability for optical applications. An optically polished 5 x 5 x 2 mm^3 single crystal was used for this study. A strong absorption was observed at 200 nm. The transparency of < 50% in the lower region reflects the incorporation of impurities that may be potentially coming from the water that is only partially purified and the slow dissolution of the borosilicate glass by the growth solution. The grown crystal has no absorption in the visible region. The recorded spectrum is shown in Fig. 5. This illustrates the optical quality of the SR- grown KDP crystal.

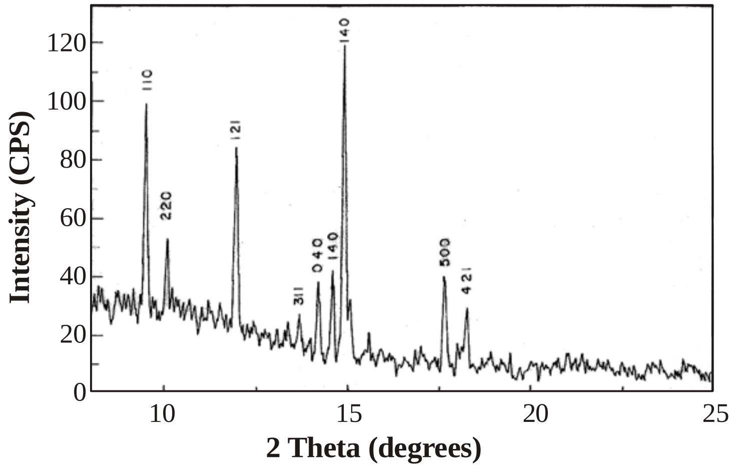

Fig. 3: Powder XRD spectrum of KDP Crystal

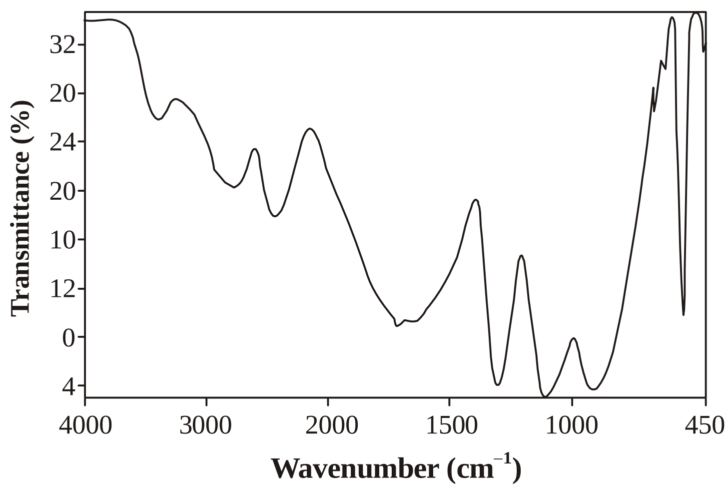

Fig. 4: FTIR spectrum of KDP crystal

The second harmonic generation efficiency of the grown crystal has been verified using the Kurtz powder technique[9]. The fundamental beam 1064 nm from Q switched Nd:YAG laser is used. The emission of intense green light confirms the second harmonic efficiency of the Potassium dihydrogen phosphate crystal.

Laser raman studies

Fig. 6 shows the typical Raman spectrum of the KDP sample recorded at room temperature in the frequency range of 200-2000 cm^{-1}. Compared to the Raman spectrum[10] of aqueous solution of the $H_2PO_4^-$ anion, it is easy to assign the internal vibration modes of the $H_2PO_4^-$ anion in KH_2PO_4 as an asymmetrical P $(OH)_2$ stretching vibration at 916 cm^{-1} and a PO_2 bending vibration at 515 cm^{-1} respectively. No deformation or distortion of $H_2PO_4^-$ cluster due to the constraint growth into the vessel is found because the wave number of all Raman peak remain unchanged for the SR method experiment does not affect the crystalline perfection.

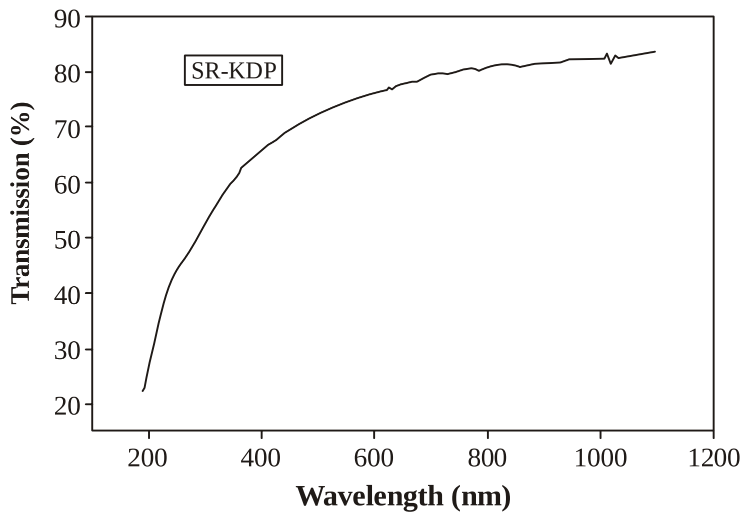

Fig. 5: UV-Vis absorption spectrum of KDP Crystal

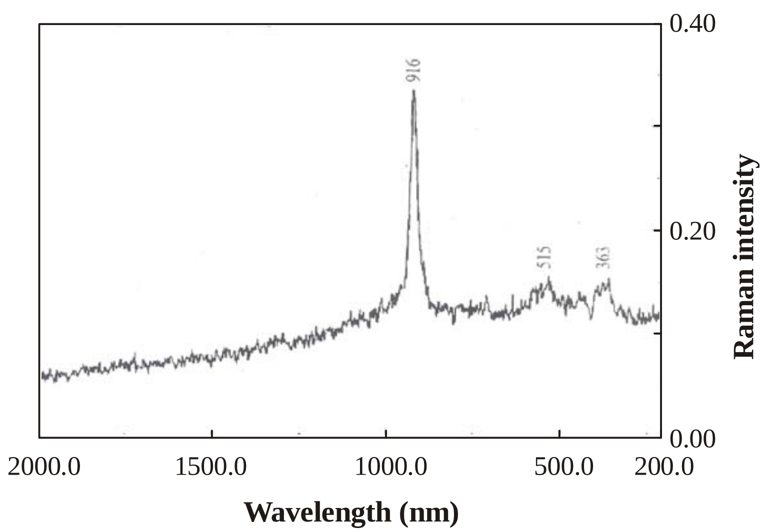

Fig. 6: Laser raman spectrum of KDP crystal

CONCLUSION

The single crystal of KDP has been grown by Sankaranarayanan-Ramasamy method. The next task of this work is to develop a reproducible technique for obtaining KDP crystals as big in size as possible which have high optical quality, including perhaps the most important parameter. The lattice parameters of grown crystals were confirmed by X-ray diffraction analysis. The presence of functional groups in the grown crystal was confirmed using FTIR studies. The optical transparency of the grown crystal was measured. The Laser Raman study was also carried out.

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