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SECOND HARMONIC GENERATION IN KDP SINGLE CRYSTAL

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ABSTRACT
Potassium dihydrogen phosphate (KDP) is an excellent inorganic nonlinear optical material with different device applications. In the present work, single crystal of pure KDP crystal has been grown from the aqueous solution by slow evaporation technique. KDP crystal is a suitable nonlinear material for second Harmonic generation. UV- visible studies suggest that the crystal is suitable for nonlinear applications. During the growth it has been observed that the low evaporation rate gives good quality crystals, avoiding temperature fluctuation during stirring and for long time magnetic stirring gives good quality crystals with lesser defects. We synthesized KDP single crystal this crystal possess high optical and structural perfection that make it possible to produce elements for doubling and tripling of laser radiation frequency.

KEY WORDS: UV-Visible spectra, transparency, SHG efficiency and second harmonic generation, low evaporation rate and single crystal.

INTRODUCTION

Crystals are the pillars of modern technology. Without crystals, there would be no photonic industry, no fiber optic communications, which depend on materials crystals such as semiconductors, superconductors, transducers, radiation detectors, solid state lasers, nonlinear optics and crystalline films for microelectronics and computer industries. Crystal growth is an inter-disciplinary subject covering physics, chemistry, material science, chemical engineering, metallurgy, and crystallography *etc*. In the past few decades, there has been a growing interest on crystal growth processes, particularly in view of the increasing demand of materials for technological applications[1]. Atomic arrays that are periodic in three dimensions with repeated distances are called single crystals. It is clearly more difficult to prepare single crystal than poly crystalline material and extra efforts are justified because of the outstanding advantages of the single crystals[2]. The chief advantages of the single crystals are the anisotropy, uniformity of composition and the absence of boundaries between the grains, which are inevitably present in polycrystalline materials. Hence in order to achieve high performance from the device, good quality single crystals are needed. Growth of single crystals and their characterization towards device fabrication have assumed great impetus due to their importance for both academic as well as applied research. In order to see the second order effects that are atomic nonlinear polarization, which cause a doubling in the frequency of the incident light, the incident light must be an intense and coherent, like laser. KDP is a crystal that exhibits these nonlinear polarization properties and cheap to produce.

Nonlinear optical crystals are very important for laser frequency conversion[3], KDP (potassium dihydrogen phosphate) is suitable for higher harmonic generation to the huge laser systems for the fusion experiments because KDP crystals are good quality crystals, colorless transparent crystals having high value damage threshold. In present work the pure KDP single acrystal is grown in laboratory using slow evaporation technique and different characterizations are carried out. In order to study the second harmonic generation effect in a crystal, three steps are to be considered. The first is related to the characterization of the second order nonlinearity. The second consists in determination the direction of phase matching *i.e.* the orientation of crystal with respect to the fundamental beam and conversion efficiency, considering the experimental conditions (beam size and power of incoming beam).

We will consider here the second harmonic generation in KDP crystal for the conversion process 1064nm to 532nm. The crystal is a negative uniaxial. The KDP belongs to the symmetric group 42m, characterized by a $\chi^{(2)}$ tensor in which only three terms are non zero. Tensor is defined in the Cartesian frame of reference using the crystallographic axes.

Type I phase matching achievement in KDP crystal

In uniaxial crystal, the extraordinary refractive index varies with the angle Θ between the optical axis and the direction of wave vector (k^{-}). If the refractive index variation due to this birefringence is greater than the one due to dispersion, it is then possible to fulfill the phase matching condition.

Conversion efficiency

When the conversion efficiency becomes important, it is then false to assume that the fundamental wave will not be depleted through its propagation in the nonlinear crystal. In pump depletion regime, approximate expression for conversion efficiency is

$$\mathbf{I_{(2w)}/I_{(w)} = \tanh^2 (1.414\, \chi_{eff}^{(2)}\, L\, \sqrt{I_w}/\sqrt{\epsilon_0 c n_{2w} n^2_w . \lambda})}$$

This expression comes by solving the two coupled equations at ω and 2ω.

It clearly indicates that the efficiency directly proportional to the second order nonlinear coefficient and length of nonlinear crystal and inversely with the wave length of the pump wave.

Damage threshold of KDP single crystal

The laser induced breakdown in the crystals caused by various physical processes such as electron avalanche, multiphoton absorption, photo ionization for the transparent materials whereas in case of high absorbing materials, the damage threshold is mainly due to the temperature rise, which leads to strain- induced fracture[10, 11]. It also depends on the specific properties of material, pulse width and wavelength of laser used. LDT is perhaps most accurately specified in terms of pulse fluency for long pulse laser, this kind of laser have pulse durations in the nanoseconds to microseconds range, with repetition rates typically ranging from about 1 to 100HZ. Because the time between pulses is so large, (milliseconds), the irradiated material is able to thermally relax- as a result damage is generally not heat induced, but rather caused by nearly instantaneous optical field effects. Usually damage results from surface or volume imperfections in the material and the associated irregular optical filed properties near these sites, rather than catastrophic destruction of fundamental material structure[12].the different dopants like amino acids and alkali metals can increase the specific heat of KDP crystals and hence the damage threshold of crystals. Azarov et al.[13] reported that the damage threshold was influenced by the dislocation in the KDP crystal, and the crystal with many dislocations presented low damage threshold. On the other hand, Nwkirk et al.[14] showed no direct relation between the dislocation in KDP crystals and damage threshold. Nisshida et al.[15] used KDP samples with dislocations in which the organic impurities seemed to play the role in causing bulk laser damage. The mechanical hardness of the materials also plays a vital role in LDT of the crystals grown in different crystallographic orientations. Optical damage in dielectric materials (NLO materials) may severely affect the performance of high power laser systems as well as the efficiency of the optical devices. Hence, high damage threshold is a significant parameter for NLO crystals.

Growth of Pure KDP

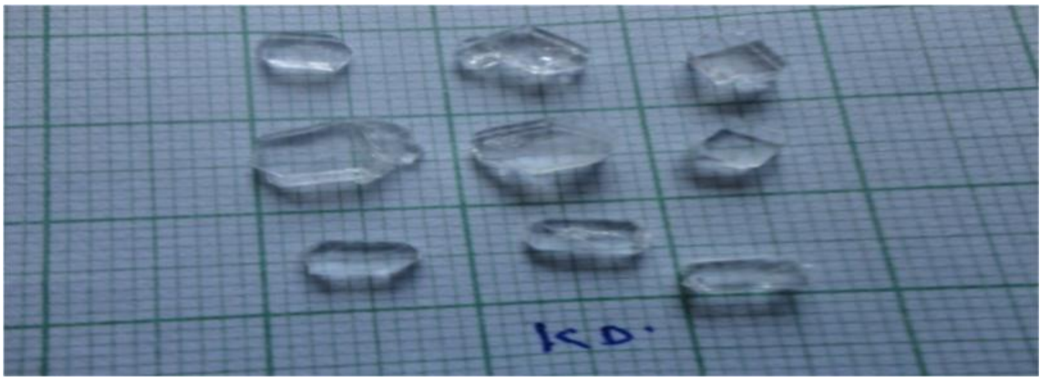

FIGURE 1: pure KDP single crystals

Single crystal of pure KDP was grown by slow evaporation of the saturated aqueous solution at room temperature. Analytical grade samples of Potassium dihydrogen phosphate with double distilled water was used for the growth of single crystals. A solution of potassium dihydrogen phosphate was preparing using water as solvent. The pH of the solution was 4. The solution is stirred for one hour at 40^0C using magnetic stirrer. The solution was then filtered and allowed to evaporate in a constant temperature bath at 32^0C temperature. After a period of fourteen days transparent colorless single crystals of pure KDP were harvested. The grown crystals are found to be transparent and they are of good optical quality. ADP and KDP crystals belong to the same family, and they have the same structure. KDP crystals could be changed into ADP crystal if K^+ is substituted by NH_4. A lot of data about the study on ADP crystal are piled up, and from them we know that with the change of P^H value and increasing super saturation, the growth rates along z and x axes accelerate rapidly. However the rate along x-axis is obviously slower than that along c-axis. When, the pH reaches 3.8, the rate along c-axis remains stable at a certain value, but the growth along x-axis stops. This phenomenon has been paid attention to for a long time. Mullin[7] believed that it resulted from the increase of H^+ in solution. Because H^+ appears around the prism faces in the form of H_3O^+, it brings a diluents effect to influence the diffusion of solute to prism faces and this will result in the slower growth of the prism faces. Zhong Weizhuo, YuXiling and Luo Haosu et al. also believed that hydration molecules can bring a diluents effect to tetragonal pyramid faces. When, the pH value is quite low, the tetragonal pyramid faces maintained the fast growth rate. Evidently it is not appropriate to interpret the diffusion of solute to interfaces with diluents effect. And it is easier for us to explain the differences in the growth rates of prism faces and pyramid faces in relation to pH value, because pH values in solution affect the bonding ability of $[H_2PO_4]^-$ unit to each face.

The combination of growth units to prism faces mainly depends on the hydrogen bonds. When pH value declines, H^+ ions concentrate around the interfaces and growth unit $[H_2PO_4]^-$ resulting a difficulty of combining to prism faces. However the situation changes to the pyramid faces. Because of O^{2-} at the vertex of tetrahedral $[H_2PO_4]^-$ is bound with K^+ and angle nearly normal to the pyramid faces $88^04^/$. The tetragonal pyramid faces can maintain certain growth rates if the concentration of H^+ is high enough. Only when the pH value declines does the rate decelerate. In solutions with different super saturation, growth units can assemble into different sizes of growth units, n $[H_2PO_4]^-$. In the boundary layers, the growth units have showed the characteristics of short range order as that in crystal. The stability of combination of growth units varies with their size and also varies with combining ability on crystal surfaces. In glycine doped KDP crystals that is the hydrogen bonded crystals, we observed the sufficient growth along x-axis and c-axis. Good quality, mechanical strong and optically good quality single crystals are obtained. The favorable structure of growth units varies with the conditions of crystal growth. So, the rates of combination of growth units varies with the crystal surfaces, and this is the reason why the morphologies are various for the same crystal under different growth conditions. Improved quality of crystals was obtained with the increasing the duration of stirring due the change of kinetics of the solution.

Characterizations

The grown crystals have been characterized for FTIR study. The FTIR spectra of the crystals have been recorded on Shimadzu spectrometer and SHG efficiency has been measured by Kurtz and Perry method [6]. The transparency of the crystals in the range 200 nm to 800 nm has been studied by using UV-1700 Shimadzu spectrometer. The powder XRD pattern of the grown crystal is recorded. The results have been discussed below.

4- Results and Discussion

UV-Visible Spectroscopy

Figure shows that the UV-Visible spectrum of pure crystal. For optical applications, the crystal should be highly transparent in the considerable region of wavelength[8]. The good transmission of the crystal in the entire visible region suggests its suitability for second harmonic generation devices[9]. The UV-visible spectral analysis shows that the crystals are transparent in the entire visible region. The absence of absorption and excellent transmission in entire visible region makes this crystal a good candidate of the opt-electronic applications [8-9]. Figures show the UV-Visible spectrum of pure KDP crystal.

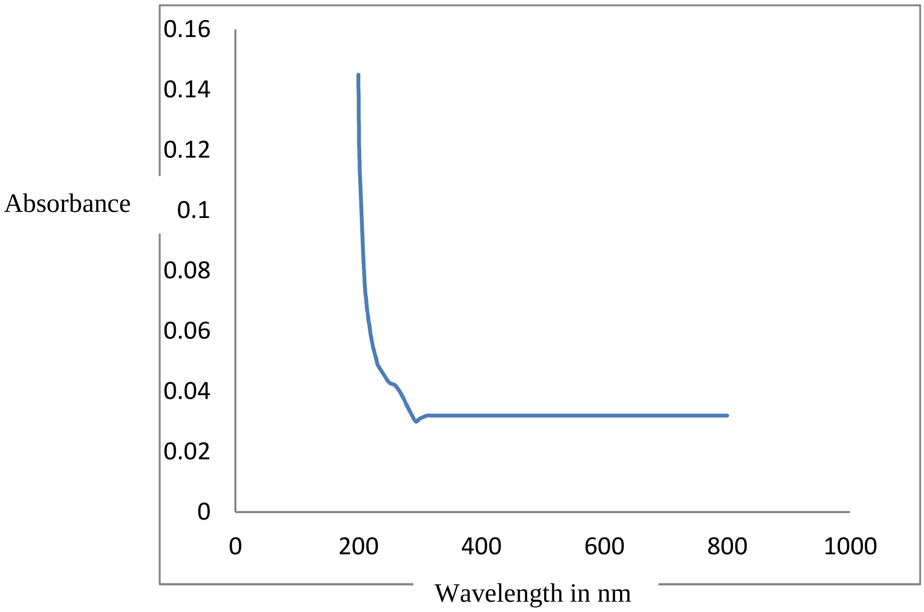

FIGURE 1: UV-Visible spectrum of kdp

SHG Measurements

The SHG intensity of the samples were tested by the modified version of the powder technique developed by Kurtz and Perry in 1968 using Quanta Ray Spectra Physics model: Prolab 170 Nd: YAG 10ns laser with a pulse repetition rate of 10HZ working at 1064nm at the department of Inorganic Physical Chemistry, Indian Institute of Science Bangalore. The energy per pulse is 4.4mj. The SHG was confirmed by the emission green radiation (λ = 532nm) which was finally detected by a photomultiplier tube and displayed on the oscilloscope. Measured powder SHG efficiency of pure ADP is 123mV and for KDP 71mV.

CONCLUSION

Transparent, colorless crystals of pure KDP single crystals were grown by slow evaporation technique at 32^0C. The absorption spectra reveals that grown crystals have better optical transparency and have sufficient transmission in UV- visible and IR regions. The lower cut-off wavelength is found to be 200nm. It has been observed that enhanced transparency is better for good NLO efficiency and also the indication of good quality crystal with good laser induced damage threshold.

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