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Growth of KDP crystal by automatic temperature controlled seed rotation method

Vikram[a], N Vijyayan[a], Ravindra[a], Sonia[a], Mahak[a], and Apurva[b]
[a]*CSIR- National Physical laboratory, New Delhi-110 012, India*
[b]*Jamia Millia Islamia, New Delhi-110 025, India*

In the recent past, nonlinear optical (NLO) materials are getting attention because of their excellent applications in the area of fiber optics communication and optical signal processing. The NLO crystals can be grown by different methods at a desired temperature. A variety of methods of crystallization from solutions can be classified in accordance with the conditions under which they are used. In this article, we describe the fabrication of a bidirectional seed rotation apparatus to grow bulk size single crystals. We have designed the automation circuit which will detect and control the temperature during seed rotation process. The aim of the present work is to grow the single crystal of KDP using seed rotation method. In order to study the properties of the crystal, the grown crystal is subjected to various studies. The PXRD study indicated that the grown crystal has good crystallinity and single phase nature. From the photoluminiscence spectrum it was found that the emission maximum occurs at 405 nm.

Keywords: NLO Materials, Seed rotation controller, Photoluminescence, Micro hardness. Etching study

1 Introduction

The nonlinear optical material (NLO) is different from the linear material in several aspects. In fascinating world, many researchers/scientists have been interested in the development of new nonlinear optical (NLO) materials because of their wide potential applications in the field of frequency conversion, optical data storage devices, optical switching, image processing, optical computing, second harmonic generation, and optical bistability etc. [1-3]. So, it's time demanding that many new methods should be developed for growing the bulk size NLO crystals. In NLO materials, the optical properties are dependent on the degree of charge separation and incident light intensity. Broadly, there are two types of NLO materials, organic NLO materials and inorganic NLO materials. For useful device application, the nonlinear materials have to meet the number of requirements. The materials must have high damage threshold to laser irradiation. In this respect, the organic materials are better than the inorganics. In inorganic materials, the NLO properties are induced by the charge transfer mechanism, whereas in organic materials, the NLO properties depend on the π- electron conjugated system [4]. Organic conjugated molecules are special candidates with nonlinear optical properties because of their high second and third order responses and larger optical nonlinearity. The phenomena of SHG in inorganic materials was first reported in 1961. Lithium niobate ($LiNbO_3$) is an example of this type of crystal. Lithium niobate ($LiNbO_3$) crystals are one of the most investigated materials for widespread and promising applications in nonlinear optics, e.g., for parametric amplification and second-harmonic generation, holographic data storage, optical information processing, phase conjugation, and wavelength filters [5]. Potassium dihydrogen phosphate (KH_2PO_4, KDP) is another nonlinear optical material of great interest because of its properties including transparency in a wide region of the optical spectrum,

Corresponding author :
e-mail: nvijayan@nplindia.org; vjnphy@yahoo.com (N Vijayan)

resistance to damage by laser radiation, good phase matching and relatively high nonlinear efficiency, in combination with reproducible growth of large size and easy finishing [6] . KDP crystal belongs to tetragonal crystal system with space group $I\bar{4}d2$ and efficient second harmonic generation was found [7,8]. As KDP crystal has many properties, like excellent piezoelectric, ferroelectric and electro-optic properties, they are highly demanded on the large scale. Currently, KDP and its analogues DKDP ($K(D_XH_{1-X})_2PO_4$) and ADP($NH_4H_2PO_4$) are the well known nonlinear crystals needed for laser radiation conversion in laser fusion system [9]. Laser fusion research needs large plates of nonlinear crystals for electro-optic switches and frequency converters. KDP crystal exhibits excellent electro-optical and nonlinear optical (NLO) properties and is commonly used in several applications such as frequency conversion, laser fusion and electro-optical modulation [10]. In this way, the aim of the present work is to grow the large size single crystal of KDP by seed rotation method for device purposes. In order to study the properties of the crystal, the grown crystal was subjected to various studies.

2 Design and fabrication of automatic temperature controlled seed rotation apparatus

To grow bulk size single crystal, we have designed and fabricated an automatic temperature controlled seed rotation solution growth apparatus. The complete setup of apparatus is shown in Fig 1. In this setup there is a seed rotation controller coupled with a stepper motor, which is controlled by using a microcontroller based drive. This controller is used to rotate the seed holder in the crystallizer. The seed crystal is mounted on the platform made up of non-reacting teflon material. The platform is fixed into the crystallizer. The seed mount platform stirs the solution very well and makes the solution more stable. The uniform rotation of the seed is required so as not to produce stagnant regions or re-circulating flows, otherwise inclusions in the crystals will be formed due to inhomogeneous supersaturation in the solution. To maintain the temperature throughout the saturated solution, we installed an Arduino based driver which is used to drive the relay circuit. Further, relay is used to drive the input of the heating element. For the automatic control of temperature Arduino is programmed for the certain value of temperature. Program for the temperature control is shown in Fig 2.

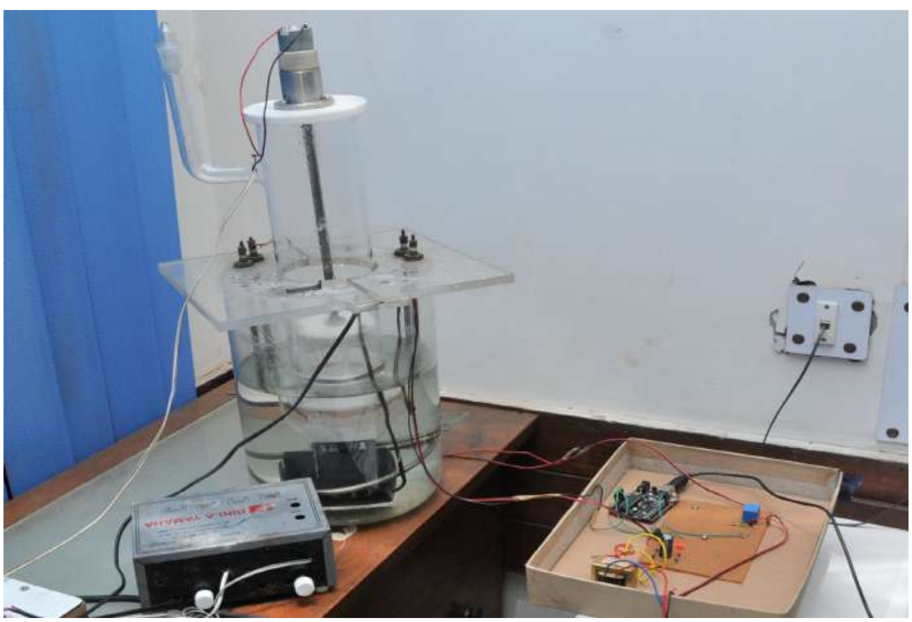

Fig 1. Full setup of seed rotation system

```
float temp1;
int tempPin1 = 0;



void setup()
{

  Serial.begin(9600);
  delay(100);

}

void loop()
{
  temp1 = analogRead(tempPin1);
  temp1 = temp1* 0.48828125;
  Serial.print("TEMP = ");
  Serial.print(temp1);
  Serial.print(".c");
  Serial.println();
  if(temp1>35.2)
  {

     digitalWrite(13, LOW);
     delay(1000);
  }
```

Fig 2. Arduino Code

The Arduino setup is the combination of three parts: input supply, Arduino circuit and relay circuit for output. For the input supply part, we are having step down transformer which converts 220V power supply into 12V supply. After that we have voltage regulator which converts 12V to 5V for Arduino board. Figure 3 shows the circuit diagram of second part of our Arduino board. With the help of available Arduino software we can code it according to our requirement. One temperature sensor (LM 35) is installed to measure the temperature of water. If the temperature is higher than the desired value then it automatically switches off the power supply to the heating element with the help of relay circuit and vice- versa. Third one is the relay part, the Relay is used for the switching operation of the heating element. It works in accordance with the Arduino output. Output of the relay is supplied to the heating element. When the temperature of the water is below the fixed temperature then it switches on the power supply and again when the temperature of the water is above the fixed temperature then it switches off the power supply. We also put a pump inside the container containing distilled water to maintain uniform temperature throughout the container.

3 Experimental detail

Before growing the bulk single crystal of KDP, first we produced a seed crystal using conventional slow evaporation solution technique (SEST). The concentrated solution was prepared and housed in a constant temperature bath at 40°C. After 20 days, a good quality single crystal was harvested from the saturated solution. The seed crystal that we obtained from the SEST was first lapped and polished to make it flat at bottom and oriented along (001) plane as shown in Fig 4.

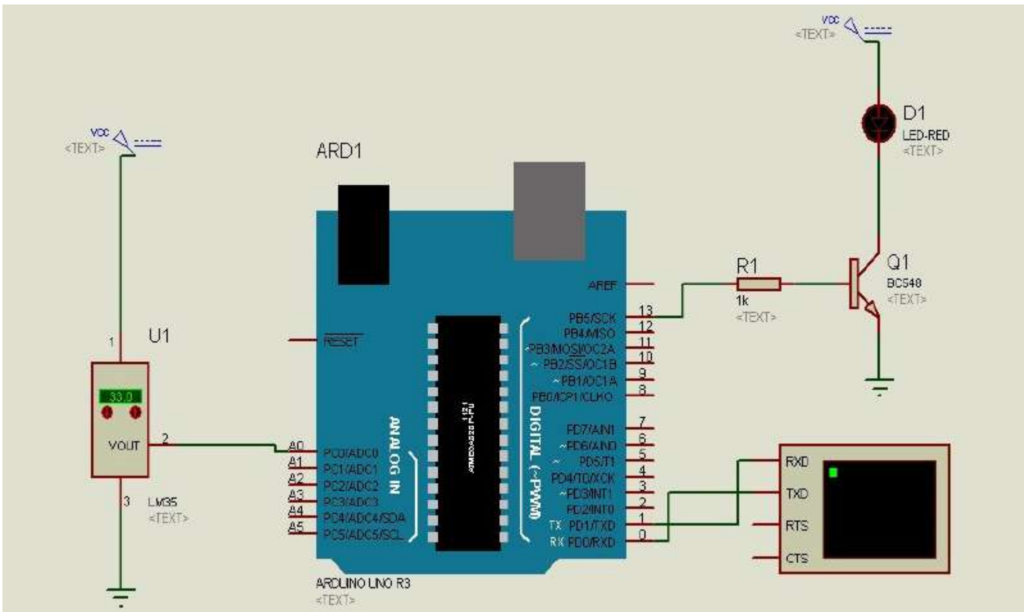

Fig 3. Circuit diagram of Arduino

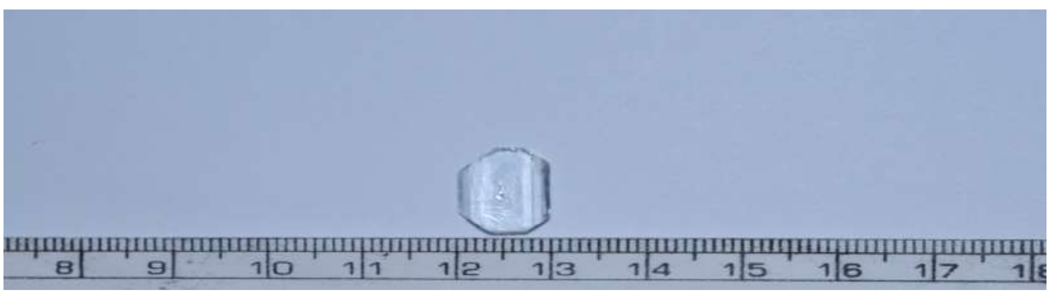

Fig 4. KDP seed crystal

The bulk crystal growth is carried out in a 5000 ml standard crystallizer used for conventional crystal growth method. By using an external water bath, crystallizer temperature is controlled, and the temperature fluctuations are less than 0.01°C. The saturation temperature was 37°C. First of all, the solution was filtered by Whatman filter paper of pore size 11 µm. After that, the filtered solution was overheated at 45°C for one day. Then the temperature was reduced to 3°C (at 1°C/h) higher than saturation point and again the temperature was decreased to saturation point at 1°C/day. After that the pure KDP crystal was fixed in the centre of the crystallizer and then it was kept inside a constant temperature bath (CTB), shown in Fig 5(a) and (b). The temperature was further decreased at the rate of 0.4°C/day and the crystallizer rotated at 40 rpm during the growth period. After 3 days of growth, the cooling rate was increased at the rate of 0.8°C/day. After 6 days of growth good quality KDP single crystal was harvested, Fig 6.

(a)

(b)

Fig 5. (a) Seed mount on the platform and (b) Dipped into solution

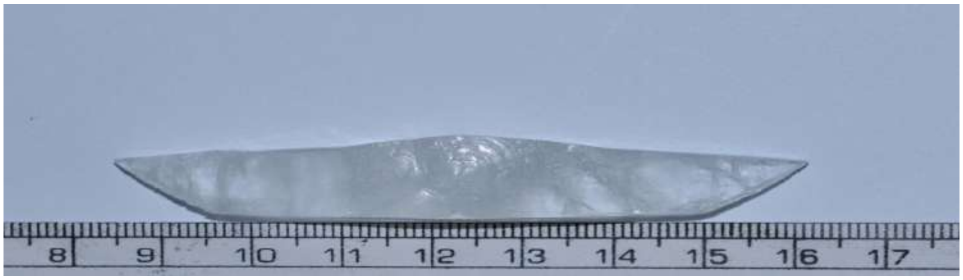

Fig 6. KDP crystal grown by seed rotation technique

4 Characterisation

Powder XRD

Powder X-ray diffraction (PXRD) technique is used to confirm the identity of a solid material and determining crystallinity and phase purity and for determining the crystallinity and phase purity of the material.

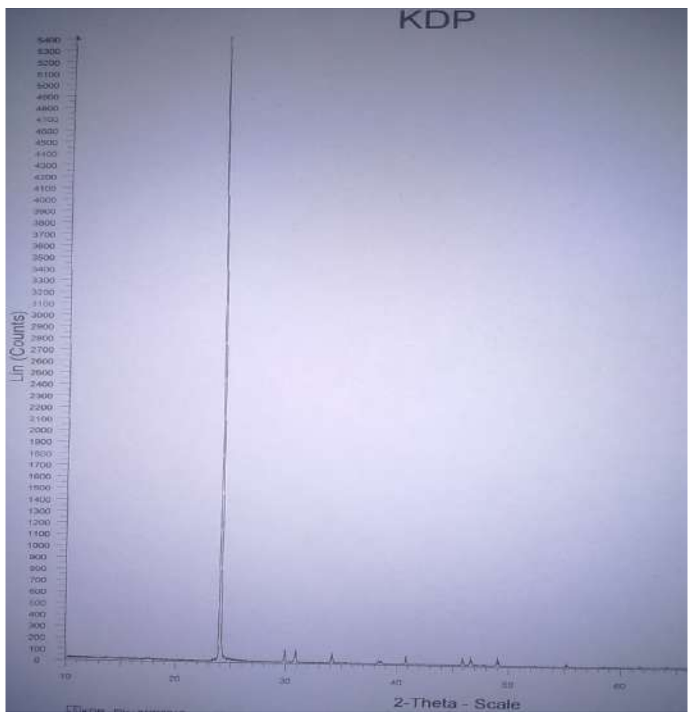

Fig 7. PXRD pattern of KDP crystal for determining the crystallinity and phase purity of the material.

In the present experimental study, we have characterized KDP powder by powder X-ray diffraction (PXRD) using Bruker D8 advance X-ray diffractometer. The recorded pattern of KDP is shown in Fig 7. Figure 7 shows that the grown material has good crystallinity and single-phase nature.

Photoluminescence

For examining the luminescence properties of the titled compound, Photoluminescence (PL) spectrum was recorded by using Fluorescence spectrometer (Edinburgh Instruments, UK: Model F900). The recorded PL spectrum of KDP is shown in Fig 8. From the figure we can observe emission peak at ~405 nm corresponding to excitation wavelength at ~240 nm. At about ~405 nm a broad band is observed which is the transition owing to the presence of defects in the KDP crystal. The sharp peak at ~405 nm indicates that the titled compound is a potential candidate for violet colour emission.

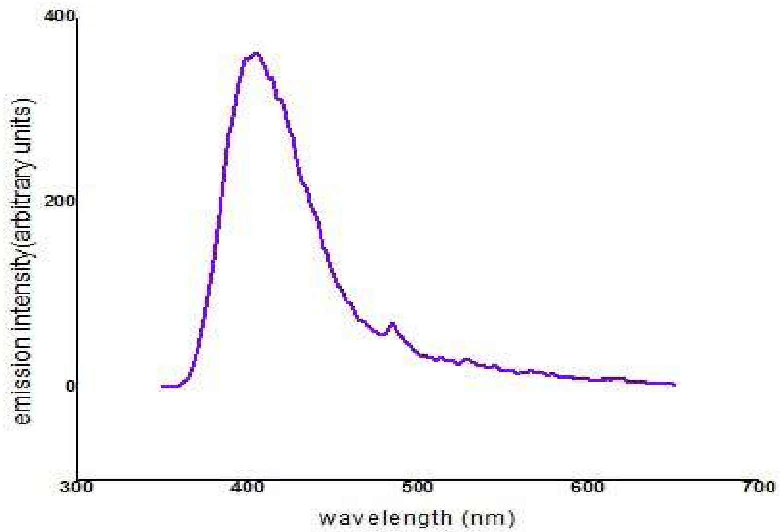

Fig 8. PL spectrum of the grown KDP crystal

Etching studies

For the investigation of surface morphology of the grown crystal, etch pit study is a well known method. The observed etch pits are used to give the details of structural defects present in the crystal and the growth pattern of the crystal. In the present work, the etching study of the grown KDP crystal was carried out using the optical microscope (model Omni Tech) of magnification of 100X. For etching analysis, the crystal was etched with water as the etchant at room temperature for 10 seconds, and then soaked with filter paper and examined under an optical microscope. Figure 9 (a, b, c, d, e and f) shows etched surface of the grown single KDP crystal. Figure 9 (b) shows the etch pattern of KDP single crystal for 10 s, and few etch pits can be observed. After that, this process was repeated up to 60 s having the same time interval of 10 s for studying its surface and we observed that the etch pits were reduced and surface became smooth as the etching time was increased.

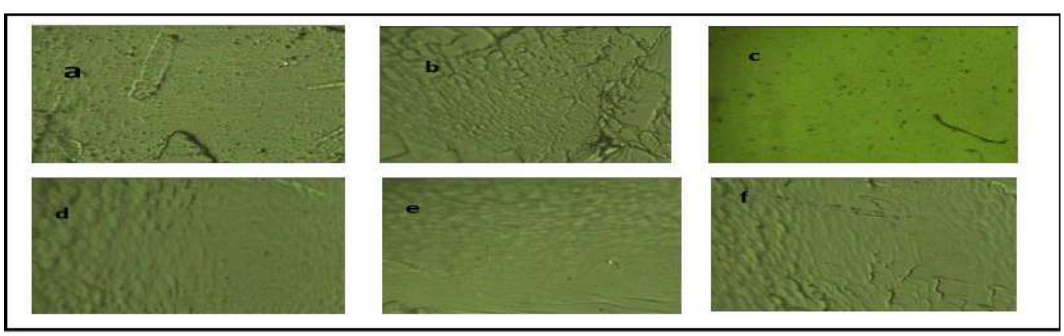

Fig 9. Surface (a) before etching, (b) after 10 s of etch, (c) after 20 s of etch, (d) after 30 s of etch, (e) after 40 s of etch, (f) after 50 s of etch

Vickers Micro hardness Measurement

This characterization technique is used for analysing the mechanical behavior of materials that are used for device fabrications. The smooth surface of pure KDP crystal was subjected to Vickers static indentation test at room temperature (303K) using a Shimadzu (Model HMV2) hardness tester. Load of different magnitudes (5, 10, 25, 50, 75, 100g) were applied on the specimen. The indentation time was kept as 10 s for all loads. Many parameters affect the hardness of the material, like interatomic spacing, lattice energy, and Debye temperature [11]. Figure 10 shows a graph of Vickers hardness (Hv) versus load (P) of the pure KDP crystal grown from the seed rotation technique. The hardness (Hv) of the material was calculated using the relation [12]: Hv = 1.8544P/d2, where *d* is the diagonal length of the indentation mark, and P is the load. From Fig 10 we observed that the value of the hardness increases upto applied load value of 27 g. After this load, the hardness number decreases because of formation of cracks in the crystal which results in release in energy [13,14].

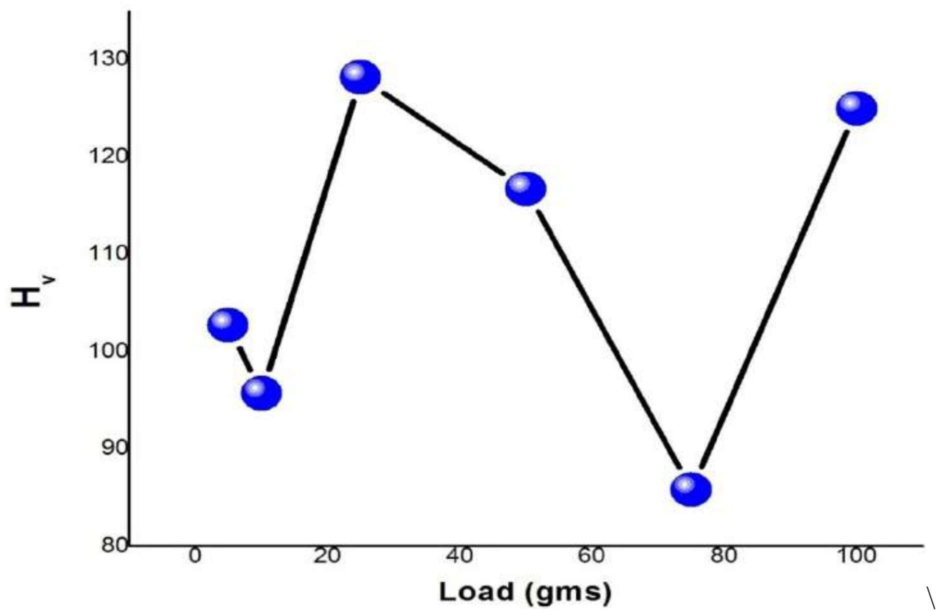

Fig 10. Plot offMicrohardness number Hv (kg/mm^2) vs load (g) of KDP

5 Conclusion

Bulk single crystal of KDP was grown using automatic temperature controlled seed rotation solution growth technique. During experimental process, temperature was controlled using Arduino device. The temperature was decreased step by step for the growth of KDP crystal. The PXRD study indicated that the grown crystal has good crystallinity and single phase nature. From the photoluminiscence spectrum we found that the emission maximum occurs at 405 nm, which lies in the visible region. Mechanical behaviour of the grown KDP crystal was identified by Vicker microhardness measurement. From overall results, we concluded that the grown material is good for NLO applications.

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Vikram brar did his B.tech from M.D.University, Rohtak, Haryana. He started his academic career in S.M.Hindu senior secondary school , Sonepat (Haryana).

Dr N Vijayan completed his doctorate degree from Anna University, Chennai. He has the recipient of BOYSCAST

Ravinder kumar did his B.Tech in ELECTRONICS & INSTRUMENTATION from Maharishi Dayanand university Rohtak ,Haryana. Presently he is pursuing Ph.D., in CSIR-National physical laboratory, New Delhi – 110 012 in the area of single crystal growth.

Apurva Gupta is a Ph. D student in Department of Physics, Jamia Millia Islamia, New Delhi. A research interest focuses on the Growth of technologically important NLO single crystals using different growth technique like slow evaporation solution technique (SEST), and unidirectional solution growth. She has done Master of Philosophy (M. Phil) 2013 in Physics from Bundelkhand University, Jhansi as well she has completed Master of Science (M.Sc.) 2012 in Physics from Bundelkhand University.

Sonia is a Ph.D Scholar under the supervision of Dr.N.Vijayan in CSIR-NPL, New-Delhi. Her research work concerns with growth and investigation of different physical properties of L- Arginine based single crystals. She has done MSc. (Physics) from M.D.U Rohtak in 2013. She has qualified the CSIR-JRF (Rank-30) and GATE Exam in 2014 (AIR- 449). She got best poster award in 22nd National Seminar on Crystal Growth And its Applications (NSCGA) -2018.