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Growth, optical, Mechanical and Dielectric Properties of Promising NLO L-Serine Potassium Di hydrogen Phosphate Single Crystals

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ABSTRACT: *Optically good quality single crystals of L-Serine Potassium Di hydrogen Phosphate (LSKDP) were grown from aqueous solution employing slow evaporation technique. Structural characterization of the grown LSKDP crystals was carried out by single crystal X-ray diffraction. The functional groups present in the grown crystals were ascertained using FTIR spectroscopic analysis. The second harmonic generation efficiency (SHG) and the UV-Vis spectral studies justified the nonlinear optical property and the optical transparency of the grown LSKDP crystal. Thermal behavior of the grown crystal has been studied by TGA-DSC analysis. Mechanical strength and electrical property of the crystal was evaluated by Vickers micro hardness and dielectric analysis. Photo conductivity studies have been carried out and the material is found to possess negative conductivity.*
Keywords: *L-Serine, Solubility, Dielectric, Micro hardness, Photoconductivity*

I. INTRODUCTION

The fast development in the field of opto-electronics includes optical frequency conversion, optical data storage and optical switches in the initially confined laser fusion systems has stimulated the search for highly nonlinear optical crystals for efficient signal processing and many Opto-electronic devices. The nonlinear optical (NLO) materials possess a wide range of applications in the field of telecommunications, high density optical recording, color display, medical diagnostics, etc., [1-3)]. The overwhelming success of molecular engineering in controlling NLO properties has promoted the growth and characterization of a variety of new types of NLO materials [4]. The search for new frequency conversion materials over the past decades has concentrated primarily on organic and inorganic compounds. The organic crystals and inorganic crystals have inherent limitations in their technological properties. These limitations made scientists to focus alternate strategies which led to the discovery of a new class of semi organic nonlinear optical materials for device fabrication technology, owing to large nonlinearity, high resistance, too large induced damage, less deliquescence, low angular sensitivity and good mechanical hardness [5-7]. Semiorganic hybrid materials have received extensive attention in recent years owing to their great fundamental and practical interest in second order nonlinear optical (NLO) responses, magnetism, luminescence, photography and drug delivery systems [8]. Potassium Di hydrogen phosphate (KDP) and its isomorphs are representatives of hydrogen bonded materials that posses important piezoelectric, ferroelectric, electro-optic and nonlinear properties. Semiorganic crystals have attracted the interest of many experimental researchers probably because of their comparatively simple structure and very fascinating properties associated with a hydrogen bond system involving a large isotopic effect, broad transparency range, a high laser damage threshold and relatively low production cost [9]. The rapid growth of good quality crystals and various studies of organic and inorganic with KDP crystals have been reported by various investigators [10-13].

L-Serine is one of the naturally accruing and proteinogenic amino acid. Proteinogenic amino acids are amino acids that are precursors to proteins, and are produced by cellular machinery coded for in the genetic code [14]. By virtue of the hydroxyl group, serine is classified as a polar amino acid, and its hydrogen can easy to remove.

In the present investigation, of L-Serine Potassium Di hydrogen Phosphate (LSKDP) crystals were grown by slow solvent evaporation technique at room temperature. Solubility of the material was measured at different temperatures and solubility curve was drawn. The grown crystal is confirmed by single crystal XRD and FT-IR analysis. Characterization studies such as UV-Vis, Dielectric, thermal, hardness and photo conductivity of the crystal was carried out. The NLO property of the single crystal has been confirmed by SHG test.

II. SYNTHESIS AND GROWTH TECHNIQUE

Highly pure L-Serine and KDP are taken in stoichiometric1:1 ratio and dissolved in deionized water and aqueous solution was prepared. The reaction which is forms LSKDP is

$C_3H_7NO_3$+KH_2PO_4--------$C_3H_7NO_3.KH_2PO_4$

The prepared solution was allowed to evaporate for several days at room temperature. Color less and transparent crystals were obtained in 25 to 30 days. The quality of the synthesized crystal was improved by successive recrystallization processes. Photograph of the as grown L-Serine KDP crystal is shown in Figure 1.

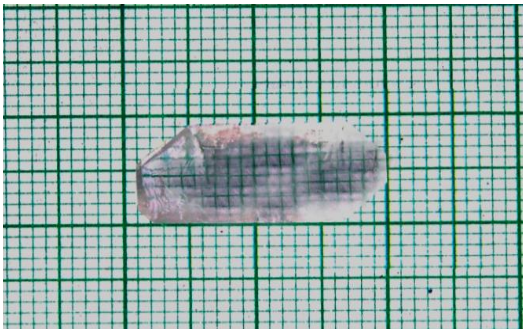

Figure 1- Photograph of as grown LSKDP crystal

2.1 Solubility studies

Solubility is one the most important parameter for the growth of good quality crystals in low temperature solution growth method. The solubility of LSKDP crystal was determined at different temperatures by dissolving it in millipore water in an airtight container maintained at a constant temperature with continuous stirring**.**

After saturation was attained, the equilibrium concentration of the solute was analyzed gravimetrically. The same procedure was repeated to estimate the solubility for different temperatures. Figure 2 shows the solubility curve of LSKDP in aqueous solution.

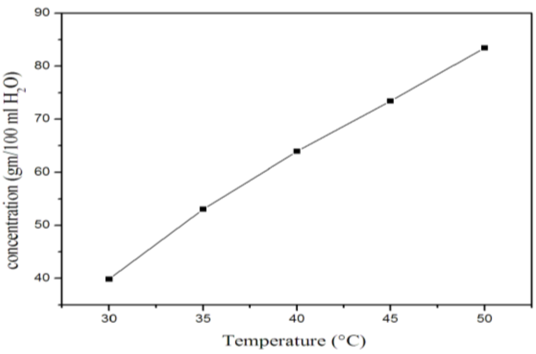

Figure 2 - Solubility curve of LS-KDP crystal

III. RESULTS AND DISCUSSION

3.1 Single crystal XRD analysis

The unit cell parameters of grown crystal were carried out using Enraf Nonius-CAD4 diffractometer with Mo Kα radiation at room temperature. The LSKDP crystallizes in orthorhombic crystal system with space group $P2_12_12_1$ and the lattice parameter values of the grown crystal are a = 7.7336 Å, b = 8.7143 Å, c = 11.013 Å. crystallographic data of LSKDP crystals are shown in the **table 1**.

Table 1: crystallographic data of LSKDP

Cell parameters	LSKDP
a	7.7336 Å
b	8.7143 Å
c	11.013 Å
Cell volume(V)	742.12 Å^3
Space group	$P2_12_12_1$
crystal system	Orthorhombic
α	90°
β	90°
γ	90°

3.2 FTIR spectroscopic analysis

In order to find the functional groups present in the LSKDP crystal the FTIR spectrum was recorded in the region 400 $cm^{-1}$and 4000 cm^{-1}.The recorded FTIR spectrum of the grown crystal is shown in Figure 3. On examining the FTIR spectrum the frequency absorption peak at 3454 $cm^{-1}$is assigned to –OH and N-H symmetrical starching. This confirms the presence of primary amines in the spectrum. The peaks at 3053 $cm^{-1}$and 3039 cm^{-1} attributed to the water OH stretching vibrations. The sharp peak at 2926 cm^{-1}indicates the CH_2 asymmetric stretching. The weak absorption peak at 2449 cm^{-1} is due to N-H frequencies. The sharp peak at 1604 cm^{-1} is corresponds to aromatic C-C stretching vibrations. COO- asymmetric stretching band is observed at 1481 cm^{-1}.

The OH deformation is observed at 1298cm^{-1}. The sharp absorption at 1107 cm^{-1} and 1037cm^{-1} is due to C-O symmetrical stretching of (PO_4). The hydroxyl stretching deformation modes of OH are confirms from the peak 902 cm^{-1}which confirms the presence of phosphate in the crystal spectrum [15]. The peaks between 485 to 902 $cm^{-1}$are due to the O-N=P and –ONO_2 bond vibration in LSKDP crystal.

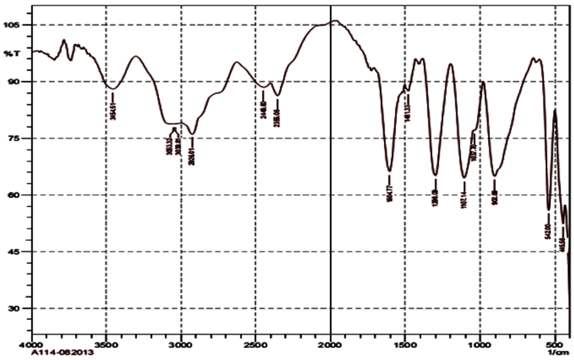

Figure 3 - FTIR Spectrum of LSKDP

3.3. Optical Studies

The optical absorbance spectrum of LSKDP single crystal was recorded in the wavelength region 190 nm– 500 nm. Figure 4 shows the optical absorbance spectrum of LS-KDP crystal. For optical fabrication, the crystal should be highly transparent in the visible region of wavelength [16]. Favorable transmittance of the crystal in the entire visible region suggests its suitability for second harmonic generation [17]. Figure 4 shows the UV-Vis-NIR Spectrum of LSKDP crystal. The UV absorption edge for the grown crystal was observed to be around 197.20 nm.

The dependence of optical absorption coefficient on photon energy helps to study the band structure and type of transition of electrons [18]. Optical absorption coefficient (α) was calculated from transmittance using the following relation

α= 2.3026log (1/T)/ t.

Where, T is the transmittance and t is the thickness of the crystal. As a direct band gap material, the crystal under study has an absorption coefficient (α) obeying the following relation for high photon energies ($h\nu$).

$\alpha h\nu = A (h\nu-E_g)^{½}$

Where E_g is the optical band gap of the crystal and A is a constant. A plot of variation of $(\alpha h\nu)^2$ versus photon energy is shown in Figure 5. $E_g$is evaluated using extrapolation of the linear part [19]. The energy absorption gap is of direct type and the band gap energy is found to be 6.25eV.

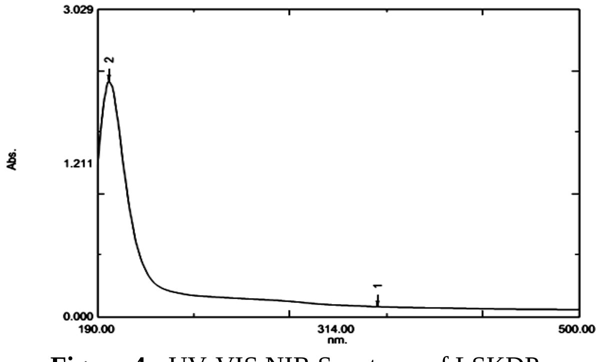

Figure 4 - UV-VIS NIR Spectrum of LSKDP

3.4 Dielectric analysis

The dielectric study of LSKDP single crystal was carried out using the HIOKI 3532-50 LCRHITESTER instrument. The capacitance values for grown LSKDP crystal are found for frequencies varyingfrom50Hz to 5MHz at different temperature range. The rectangular shaped crystal of thickness 6.44 mm area is used for dielectric studies. The dielectric constant is calculated using the formula

$$\varepsilon' = \frac{Ct}{\varepsilon_0 A}$$

Where C is the capacitance value, t is the thickness of the crystal, A is the area of the crystal, and ε_0 is the absolute permittivity in the free space.

The dependence of dielectric constant, dielectric loss on log frequency of the applied AC voltage was studied in different temperature range. Figure 6 and Figure 7 shows the variation of dielectric constant (ε') and dielectric loss with log frequency at different temperature ranges.The dielectric behavior of the material is described in two frequency intervals, first in lower frequency range and second in higher frequency range. Both dielectric constant and dielectric loss are decreasing with increasing frequency.

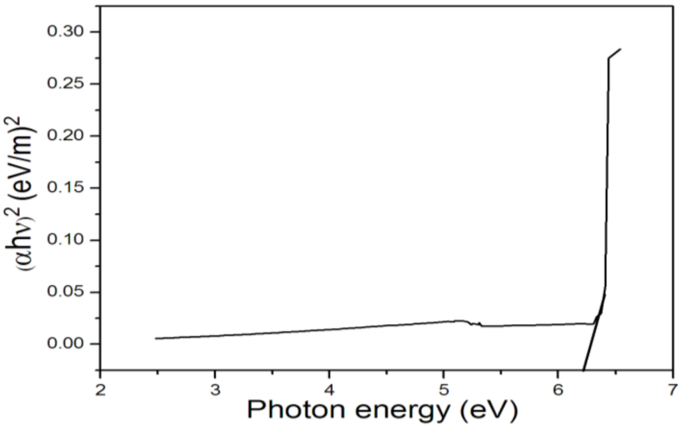

Figure 5 - Energy band gap plot of LSKDP

At low frequencies the dielectric constant and dielectric loss decreases with frequency. It is also found that the dielectric constant and dielectric loss changes with temperature at low frequencies. It shows that both dielectric constant and loss are dependent on temperature in lower frequency range [Bhat et al (1995)].

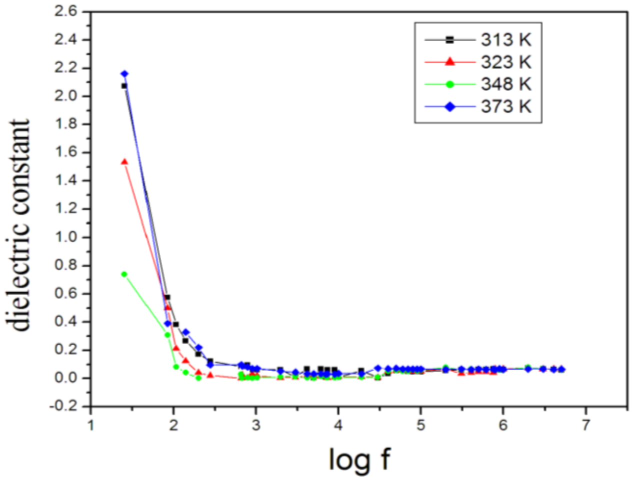

Figure 6 - log frequency verses dielectric constant

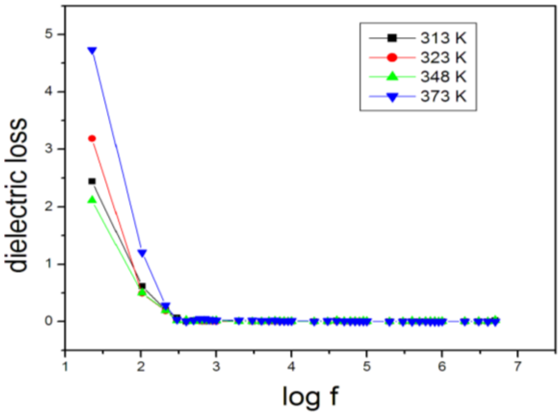

Figure 7 - log frequency verses dielectric loss

3.5 Thermal studies

Differential Scanning Calorimetric analysis (DSC) and thermo gravimetric analysis (TGA) give information regarding phase transition, crystallization and different stages of decomposition of the crystal system [21]. The thermo gravimetric analysis of LSKDP crystals were carried out between 23 °C and 500 °C using TGA Q500 instrument in the nitrogen atmosphere at a heating rate of 10 K/min. Figure 8 shows the TGA&DSC curve of LSKDP crystal.

The decomposition of the crystal is observed in three stages. In the first stage the material start to decompose and a weight loss of 7.77 percentages is observed. The sharp weight loss of the material starts around 219°C . The crystal is completely free of any water of crystallization or any physically adsorbed water on the surface. 3.71 percentage of weight loss is occurred in the second stage. Heating the crystal above 219 °C, resulting the liberation of volatile substances, probably carbon dioxide and ammonia. The sharp exothermic peak absorbed at 219°C matches with the decomposition point of the material**.**

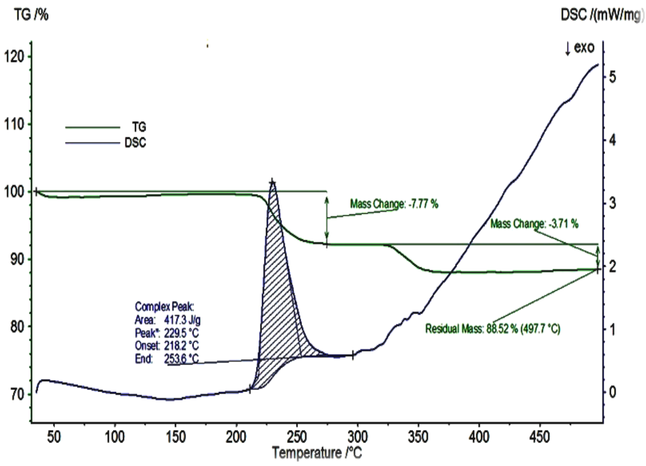

Figure 8 - TGA and DSC curve of LSKDP

3.6 Photoconductivity studies

Photoconductivity studies were carried out for the LSKDP crystal using keithley 485 Picoammeter at room temperature. The dark current (I_d) of the sample was measured using DC power supply and picoammeter. Photo current of the sample was measured using halogen lamp of 100 W, which contains iodine vapor.

The light from halogen lamp is focused on the material using convex and the photo current is measured. DC supply is increased step by step from 10 V to 100 V and the photo current (I_p) was measured. Figure 9 shows the variation of photocurrent and dark current as a function of applied field.

It is observed from the plot that dark current (I_d) and photo current (I_p) of the sample increase linearly with the applied field and the dark current is always higher than the photo current. This phenomenon is known as negative photoconductivity which in this case may be due to the reduction in the number of charge carriers or their lifetime in the presence of radiation. When the sample is kept under exposure to light, the recombination of electrons and holes takes place, resulting in decrease in the number of mobile charge carriers, giving rise to negative photoconductivity [22].

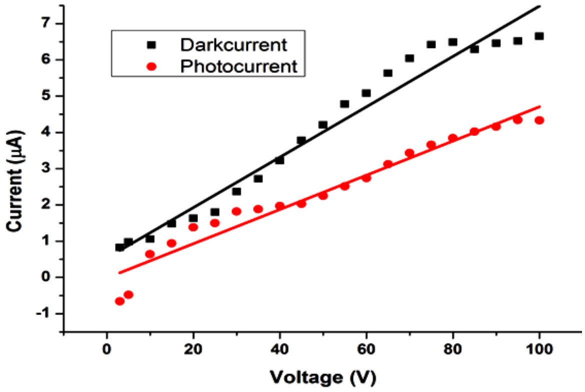

Figure 9 - Photoconductivity plot of LSKDP crystal

3.7 Vickers Micro hardness studies

Hardness of the crystal carries information about the mechanical strength, molecular binding between atoms, and yield strength and elastic constants of the materials [23]. In the present study, micro hardness measurements were carried out on LSKDP single crystals. Vickers micro hardness number was then evaluated from the relation

H_v= 1.8544 P/ d^2(kg/mm^2)

where, 'H_v' is the Vickers microhardness number, 'P' is the applied load and 'd' is the diagonal length of the indentation impression. To evaluate the Vickers micro hardness, several indentations were made on the face of the crystal. The diagonal length of the indentations was measured using a micrometer eyepiece. Dependence of the micro hardness on the load for LSKDP crystal has been evaluated. Load of different magnitude (25 g, 50 g, 75 g and 100 g) were applied on the crystal surface for the fixed interval of time.

Figure 10 shows the variation of load (P) with hardness number of LSKDP crystal. Hardness is found to increase gradually up to the load value of 75 g. At lower loads there is an increase in the hardness number which can be attributed to the electrostatic attraction between the zwitterions present in the molecule [24].

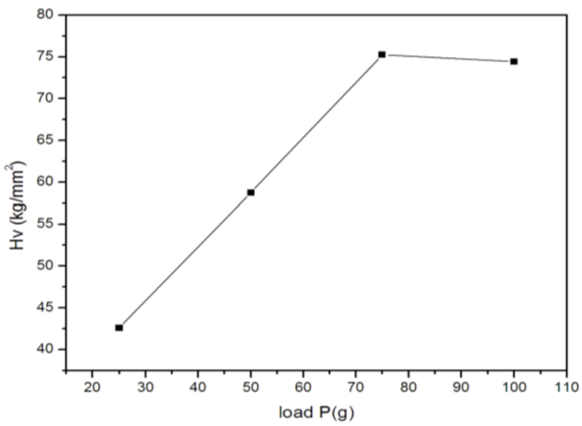

Figure10 - load versus hardness number plot of LSKDP

Above the load of 75g multiple cracks were developed on the crystal surface due to the release of internal stresses generated locally by indentation. The hardness coefficient 'n' of the material was calculated and it is found to be 2·55. According to Onitsch, n lies between 1 and 1.6 for hard materials and n is greater than 1.6 for soft materials [25]. Thus, LSKDP belongs to soft material category. This implies that LSKDP single crystal is a good engineering material for device fabrications**.**

3.8 NLO Studies

The Second Harmonic Generation efficiency of LSKDP has been found by Kurtz powder technique. The sample subjected to Nd:YAG laser beam(1064 nm, quanta ray) with a input pulse of 0.6 J. The SHG efficiency of the frequency conversion is confirmed by the emission of green light from the powder sample. Standard KDP crystal was used as reference material for the NLO test. The input pulse of 0.6 J was allowed through the same size pellet of LSKDP crystal and KDP crystal and the output was compared.

The SHG signal of 22.7 mV is obtained for LSKDP crystal, while the reference KDP crystal gives a SHG signal of 11.3 mV for the same input pulse. It shows that the NLO efficiency of the grown LSKDP is 2 times that of KDP.

IV. CONCLUSION

A potential and new semi organic nonlinear optical single crystal of LSKDP was grown by slow evaporation technique. Single crystal X-ray diffraction study confirmed that the grown crystal belongs to orthorhombic system with the space group $P2_1P2_1P2_1$. FTIR studies confirm the functional groups present in the crystal. The grown LSKDP has a wide transparency window in the entire visible region with a lower cutoff wavelength of 197 nm thus confirming the suitability of this material for optical fabrications. The hardness of the material indicates that the material having appreciable hardness values which can be useful for the high frequency conversion devices. Thermal studies reveal that LSKDP crystal thermally stable up to 219 °C. Photo conductivity studies shows that the material posses negative photo conductivity. The powder SHG efficiency of LSKDP is about 2 times that of KDP. It is concluded that LSKDP can be used as a suitable material for NLO applications with higher efficiency.

REFERENCES

[1] Singh N. B., Henningsen T., Hopkins R. H., Mazelsky R., Hamacher R. D., Supertzi E. P., Hopkins F. K., Zelmon D. E. and Singh O. P., "Nonlinear Optical Characteristics of Binary Organic System," Journal of Crystal Growth, 128, 1993, 976-980.

[2] Chemla D.S, Zyss .J (Eds), Nonlinear optical properties of organic molecules and Crystals, (Vol. 1, Academic Press, London, 1987),

[3] Badan J., Hierle R., Perigand A., Zyss J., Willaims D. J. (Ed), Nonlinear Optical Properties of Organic Molecules and Polymeric Materials 233 D.5,(American Chemical Society, Washington, DC 1993),.

[4] Aka G., Mougel F., Auge F., Harari A.K., Vivien D., Benitez J.M., Salin F., Pelene D., Balembois F., Georges P., Brun A., Zenain N., Jalquet M., Experimental and Computing Methods in High Resolution Diffraction Applied for Structure Characterization of Modern Materials HREDAMMJ. Alloys Compounds, 401, 2004, 303-304.

[5] Sonal D., Gupta Ranjith S., Pardhan A., Mareano O., Noureddine melkechi, Desai C.F, Laser damage studies in zinc (tris) thiourea sulfate: Nonlinear optical crystal, J.Appl. Phys. 91 (5), 2002, 3125-3128.

[6] Ittyachan R, Sagayaraj P, Growth and characterization of L-arginine diphosphate crystals', J. Cryst. Growth 243,2002, 356 – 360.

[7] Rajesh N.P., Kannan V., Ashok M., Sivaji K., Santhana Ragavan P., Ramasamy P., A new nonlinear optical semi-organic material: cadmium thiourea acetate, J. Cryst. Growth 262, 2004, 561- 566.

[8] Bringly J. F., Rajeshwaran M, organic-inorganic hybrid materials, Acta.Cryst., E62, 2006, m1304 – m1305.

[9] Shirsat v, Hussaini S.S, Dhumane N.R., and Dongre V.G., Influence of lithium ions on the NLO properties of KDP single crystals, Cryst .Res.Technol. 43, 2008, 756-761.

[10] Zaitseva N.P, Devoreo J.J, Dhehaven M.R, Vital R.L, Montgomery K.E, Richardson M., Rapid growth of large-scale (40–55 cm) KH2PO4 crystals, J. Cryst Growth 180, 1977, 255-262.

[11] Dixit V.K, Rodrigues B.V., and Bhat H.L, Experimental setup for rapid crystallization using favoured chemical potential and hydrodynamic conditions, Bull. Mater.Sci. 24, 2001, 455-459.

[12] Ananda Kumari R., and Chandramani R., Electrical conductivity and dielectric measurement on Au+ doped KDP crystal, Indian journal of Pure and applied Physics, 43, 2005,123-128.

[13] Priya M., Padma C.M, Freeda T.H, Mahadevan C.K., and Balasingh C., Electrical conductivity measurements on gel grown KDP crystals added with urea and thiourea, Bull.Mater. Sci, 24, 2001,511-514.

[14] Ambrogelly A, Palioura S, Söll D,. "Natural expansion of the genetic code", Nat. Chem. Biol, 3 (1), 2007, 29–35.

[15] Reddy, Jagannadha and Frost, Ray and Martens, Wayde, Characterisation of conichalcite by SEM, FTIR, Raman and electronic reflectance spectroscopy, Mineralogical Magazine, 69(2), 2005, 155-167.

[16] Kannan V., Bairava Ganesh R., Sathyalakshmi R., Rajesh N.P., and Ramasamy P, Influence of La3+ ions on growth and NLO properties of KDP single crystals, Cryst. Res. Technol., 41, 2002, 678–682.

[17] Zaitseva N.P, Rashkovich L.N., and Bogatyreva S.V., Stability of KH2PO4 and K(H,D)2PO4 solutions at fast crystal growth rates, J.Cryst Growth 48, 1995, 276- 282.

[18] Mark A.Rhodes, Woods B., De Yoreo J.J, Roberts D., Atherton L.J, Performance of large-aperture optical switches for high-energy inertial-confinement fusion lasers, J.Appl. Opt, 34, 1995, 5312-5325.

[19] Balamurugan S., Ramasamy P., Yutthapong Inkong, Prapun Manyum, Effect of KCl on the bulk growth KDP crystals by Sankaranarayanan-Ramasamy method, Mater.Chem. Phys.113, 2009, 622-625.

[20] Bhat.S, Khosa S. K., Kotru P. N., and Tandon R. P., Dielectric characteristics of neodymium heptamolybdate crystals grown by gel encapsulation technique, Crystal Research and Technology 30 (2), 1995, 267-273.

[21] Dhanaraj P.V., Mahadevan C.K., Bhagavannarayanan G., Ramasamy P., Rajesh N.P., Growth and Characterization of KDP crystal with potassium carbonate as additive, J. Cryst. Growth 310, 2008, 5341-5346.

[22] Bube R. H, Photoconductivity of solids, (Wiley, New York. 1981),

[23] Ducourant B., Fourcade R., Mascherpa G., structure of Ammonium Decafluoro Triantimonate (III) H4Sb3F10, Rev.Chim.Miner. 20, 1983, 314-320.

[24] Gokul Raj S., Ramesh Kumar G, structural And Hardness of Nonlinear Optical L-alanine Single Crystals, Adv. Mat. Lett. 2(3), 2011,176-182.

[25] Mukerji S. and Kar T., "Vicker's microhardness studies of L-arginine hydrobromide monohydrate crystals (LAHBr),"Crystal Research and Technology,34, 1999, 1323–1328.