International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.10 No.7, pp 260-266, 2017

Crystal growth and characterization of phthalate based single crystals

Sivanantham M

Department of Physics, Centre for Research and Development, PRIST University, Vallam, Thanjavur 613 403, Tamilnadu, India

Abstract : We discuss the growth of two different phthalate based crystals such as potassium acid phthalate (KAP) and sodium acid phthalate (NaAP) by slow evaporation solution growth technique. We compare the physical properties of these crystals using several experimental techniques. The single crystal X-ray diffraction is used to find out the formation and type of crystalline structures of KAP and NaAP crystals. Based on the results of Fourier transform infrared spectroscopy, functional groups present in the crystals have been identified. Microhardness measurements on these crystals are used to evaluate the strength of the crystals. Thermal stability of the crystals is judged from the thermo gravimetric and differential thermal analyses.
Key words : Sodium acid phthalate; Single crystals; Optical transmittance; Microhardness; Thermal stability; Melting point.

Introduction

Semi-organic crystals possessing non-linear optical (NLO) properties, high stability upon laser irradiation and higher mechanical strength have received considerable attention because they have been used in many fields such as electronic, photonics industries and also in fiber optic communications [1]. Semi-organic crystals prepared from the phthalic acid derivatives are exhibiting above mentioned properties including NLO and electro-optic phenomena. Typical examples for the semi-organic crystals that belong to phthalic acid family are potassium acid phthalate (KAP) and sodium acid phthalate (NaAP). Synthesis, crystal growth and characterization of KAP have been extensively investigated [2-9] whereas those of NaAP have been scarcely reported [10-12].

Ramasamy et. al. [11] reported the crystal growth of NaAP single crystals by slow evaporation method. In that study, NaAP were obtained by solubilizing stoichiometric amounts of sodium bicarbonate and phthalic acid in water and then single crystals were grown from aqueous solution. X-ray diffraction (XRD) studies showed that crystals belong to an orthorhombic system. It was found that the second harmonic generation conversion efficiency of NaAP was found to be two times higher than that of KAP crystals. Gokul Raj et. al. [12] synthesized a new alkali metallo-organic single crystal of lithium sodium acid phthlate (LiNaAP) complex that crystallized in triclinic system. They have prepared the crystals from the aqueous mixture of lithium hydroxide, sodium hydroxide and phthalic acid in the molar ratio 3:1:2. These studies suggested that chemical constituents used in the crystals decide the final crystal structure of NaAP crystals. In view of this, we are interested to explore the effect of composition of chemicals used on the crystal growth and physical characteristics of NaAP crystals.

Herein, we report the synthesis and crystal growth of NaAP from the mixture of sodium hydroxide and phthlalic acid by slow evaporation technique. Further physical properties such of KAP and NaAP were compared. Various experimental techniques such as XRD, Fourier transform infrared spectroscopy, UV-Visible spectroscopy, micro hardness and thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were respectively used to examine the structural, optical, hardness and melting properties of the above mentioned crystals.

Experimental

Fabrication of phthalate based single crystals

Preparation of KAP

Fig. 1. As grown single crystals of KAP.

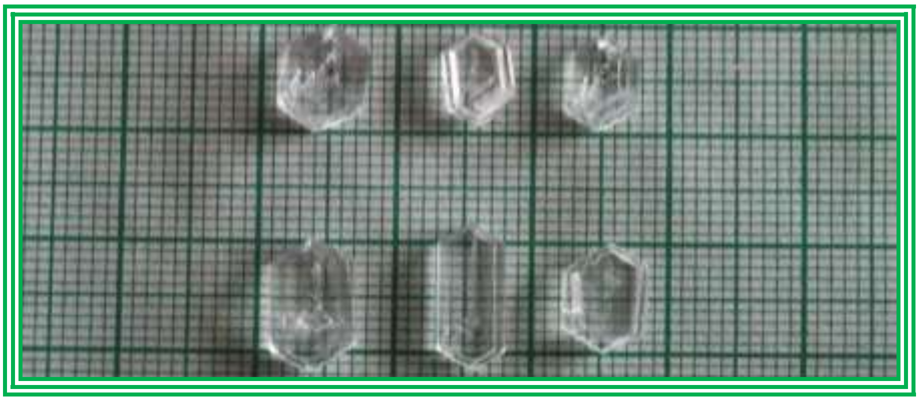


Fig. 2. As grown single crystals of NaAP.

One molar KAP solution was prepared by mixing KAP in the 100 ml distilled water and the mixture was subjected to stir well by the magnetic stirrer to obtain uniform concentration of the solution. Dust was removed by filtering the solution. The crystallization of the compound was performed by slowly evaporating the solution at room temperature. Optically transparent, uniform shaped, good quality single crystals were formed after one month and the photograph of grown KAP crystals are shown in Fig. 1.

Crystal growth of NaAP

NaAP single crystals were synthesized using sodium hydroxide (AR Grade) and pthalalic acid (AR Grade). Sodium hydroxide and phthlalic acid were dissolved in the distilled water in the molar ratio of 1:1. The mixture was thoroughly stirred using magnetic stirrer to get homogenous solution and subjected to react as mentioned in the following equation.

$$NaOH + C_8 H_6 O_4 \rightarrow NaHC_8H_4O_4 + H_2O$$

Crystallization of the solution was carried out at room temperature via slow evaporation methods. After two weeks the nucleation was observed in the solution. Good quality single crystals were obtained from the mother solution within the period of one month. Fig. 2 shows the photographs of grown NaAP crystals.

Characterization of phthalate based single crystals

The grown single crystals (KAP and NaAP) have been subjected to single crystal XRD measurements using ENRAF NONIOUS CAD-4 automatic X-ray diffractometer with M_oK_α radiations (λ = 0.717 Å) to determine crystal structure. FTIR spectra of KAP and NaAP were recorded using Perkin Elmer RXI spectrometer in the range of 400-4000 cm^{-1} using KBr pellet technique. UV-Visible transmittance spectra of KAP and NaAP single crystals of 2 mm thickness was recorded on a Lamda UV - Visible spectrophotometer in the range of 190 - 1100 nm. Vicker's microhardness measurements were conducted on KAP and NaAP crystals using Shimadzu HMV - 2 fitted with Vickers pyramidal indenter and attached to an incident light microscope. Microhardness measurements were performed for various loads from 2 to 50 grams. TGA and DTA were carried out on KAP and NaAP using SII Nanotechnology TGA/DTA 6200 in nitrogen atmosphere at a heating rate of 10°C/minute.

Results and Discussion

X-ray diffraction results

To find out the crystal structure of the grown single crystals (KAP and NaAP), single crystal XRD measurements have been conducted on these crystals. From the XRD data analysis we got the following information. For the case of KAP crystals, the values of cell parameters are found as follows: a = 6.67 Å, b = 9.97 Å and c = 13.74 Å and $\alpha = \beta = \gamma$ = 90° (Table 1). So the KAP crystal belongs to orthorhombic system.

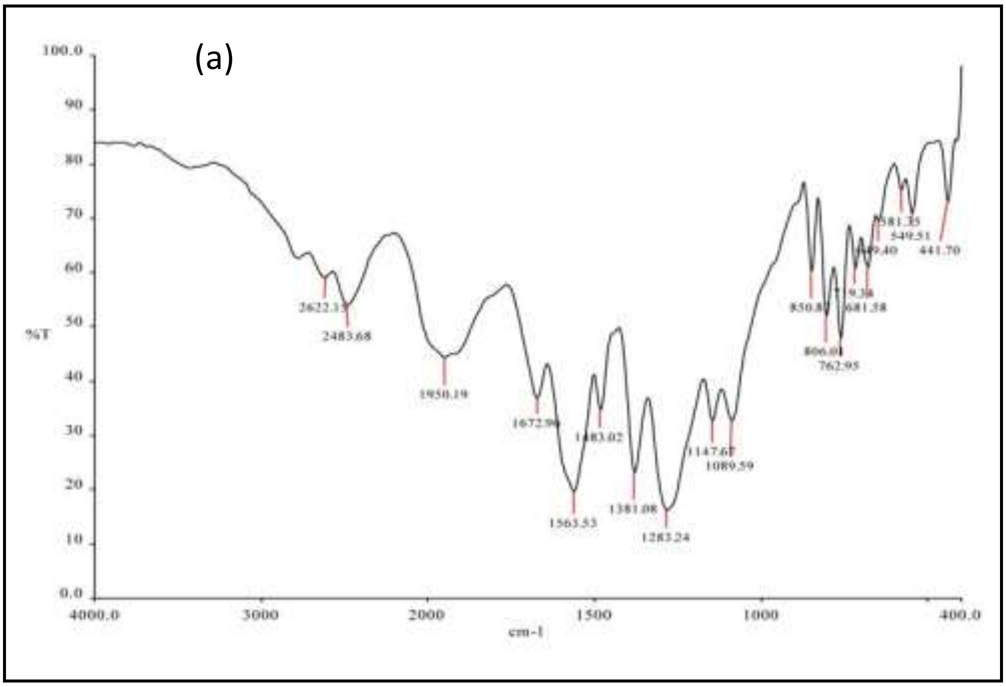
Table 1. Values of cell parameters of KAP and NaAP.

Sample name	Lattice parameter (Å)			Volume (Å^3)	α, β, γ	Crystal structure
	a	b	c			
KAP	6.67	9.97	13.74	913	$\alpha = \beta = \gamma$ = 90°	Orthorhombic
NaAP	6.92	9.51	13.84	884	$\alpha = \gamma$ = 90°, β = 104°	Monoclinic

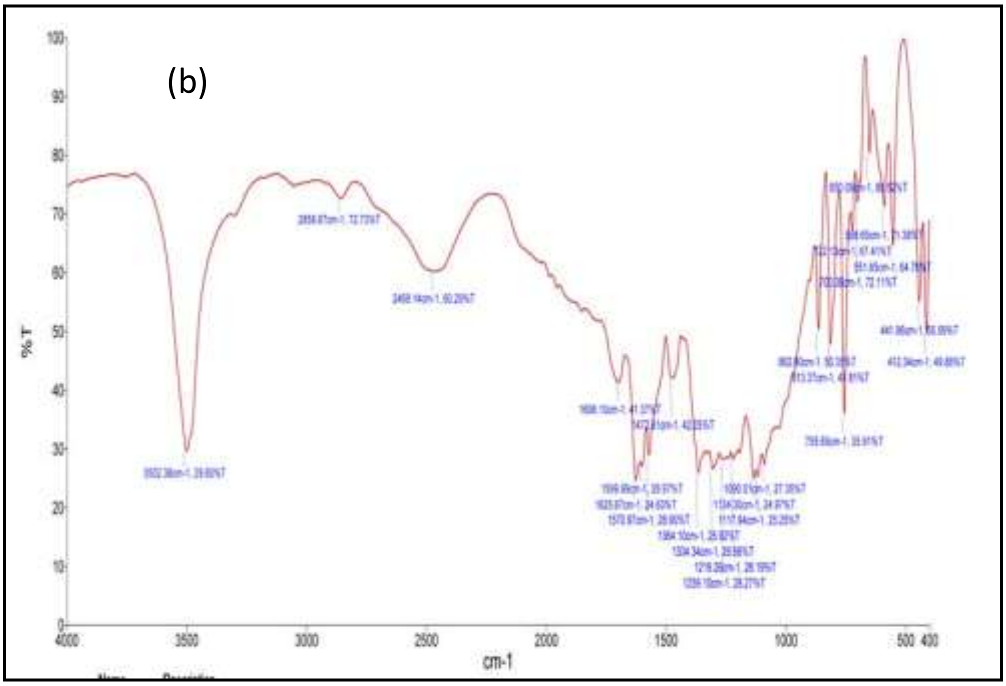
On the other hand, the values of cell parameters are determined as follows: a = 6.92 Å, b = 9.51 Å and c = 13.84 Å and $\alpha = \gamma$ = 90°, β = 104° in the case of NaAP crystal (Table 1). The lattice parameters suggested that NaAP crystal corresponds to monoclinic system. Ramasamy et. al. [11] found that NaAP crystals grown in their study belonged to an orthorhombic system. Gokul Raj and colleagues [12] observed that a new alkali metallo-organic single crystal of lithium sodium acid phthlate (LiNaP) complex crystallized in triclinic system. The difference in crystal structures of NaAP systems is attributed to the difference in chemical composition used in the crystals.

FTIR results

To confirm the functional groups that belong to KAP and NaAP structures, FTIR spectroscopic studies were performed on the crystals (KAP and NaAP). Fig. 3 shows the FTIR spectra of KAP and NaAP crystals and peak positions are assigned for both crystals as per previous reports [5, 7, 11, 12]. In the FTIR spectrum of KAP crystal, bands at 3469, 1563 and 1483cm^{-1} are respectively due to O–H stretching, C=O symmetrical stretching and O=C ring stretching. Further, peaks at 1381, 1090 and 719 cm^{-1} are appeared due to the C=C stretching, C–C=O stretching and O–H out of plane bending respectively. For the case of NaAP crystal, FTIR peaks at 3502 and 1698 cm^{-1} are because of O-H stretching and carboxyl (C=O) group vibrations. C=O stretching occurred at different peak position at 1626, 1599, 1571 and 1473 cm^{-1}. Peaks at 1364 and 1090 cm^{-1} are raised due to the presence of C=C stretching and C–C=O stretching. OH deformation out of plane is happened because of band at 756 cm^{-1}. So, it can be confirmed that formation of KAP and NaAP crystals because of presence of important FTIR peak positions that correspond to functional groups of KAP and NaAP crystals.



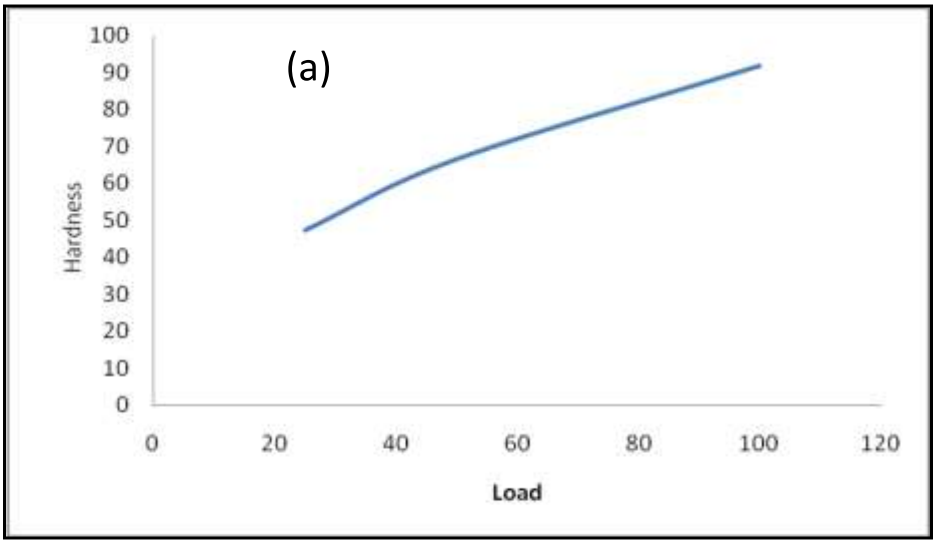
Wavenumber (cm^{-1})



Wavenumber (cm^{-1})

Fig. 3. FTIR spectra of (a) KAP and (b) NaAP crystals.

Microhardness results



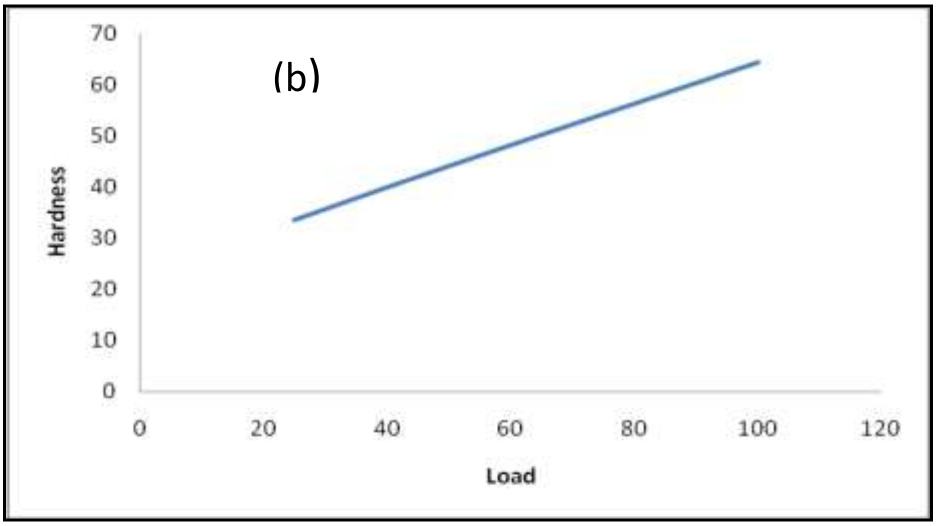


Fig. 4. Variation of hardness with load for (a) KAP and (b) NaAP.

To design the device from the crystals, used crystal must be strong and hence microhardness is an essential solid state property of the crystals. Thus Vicker's microhardness measurements were conducted on KAP and NaAP crystals using Shimadzu HMV - 2 fitted with Vickers pyramidal indenter and attached to an incident light microscope. Microhardness measurements were performed for various loads from 2 to 50 grams. The Vickers hardness number (kg/mm^2) was calculated using the expression;

$$H_V = 1.8544 P/d^2 \qquad (1)$$

where, P is the test load (Kg) and d is the average diagonal length (µm).

The grown crystal with well developed face was selected for microhardness study. A graph is plotted between the hardness number (H_V) and load (P) (Fig. 4). Hardness number increases with increase in load. From this study, it is found that hardness number of KAP is greater than that of NaAP at given load. This implies that KAP is stronger than NaAP.

Thermal properties of phthalate crystals

To get insights about thermal properties of crystals, thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried out on KAP & NaAP. Fig 5 (a) and (b) respectively show TGA/DTA curves of KAP and NaAP. The TGA curve of KAP shows that the KAP has very good thermal stability until

280°C as there is no weight loss below that temperature. Also the absence of weight loss around 100°C indicates that the absence of water in the KAP crystal. TGA studies showed that major weight loss about 45% is observed for KAP in the temperature range 281 – 300 °C. From the DTA studies, the melting point of KAP is found to be 281°C. It is noteworthy that absence of phase transition before the material melts and this aspect enhances the temperature range for the utility of the crystal for NLO applications. The sharpness of the melting curve suggests that well crystalline nature of the sample.

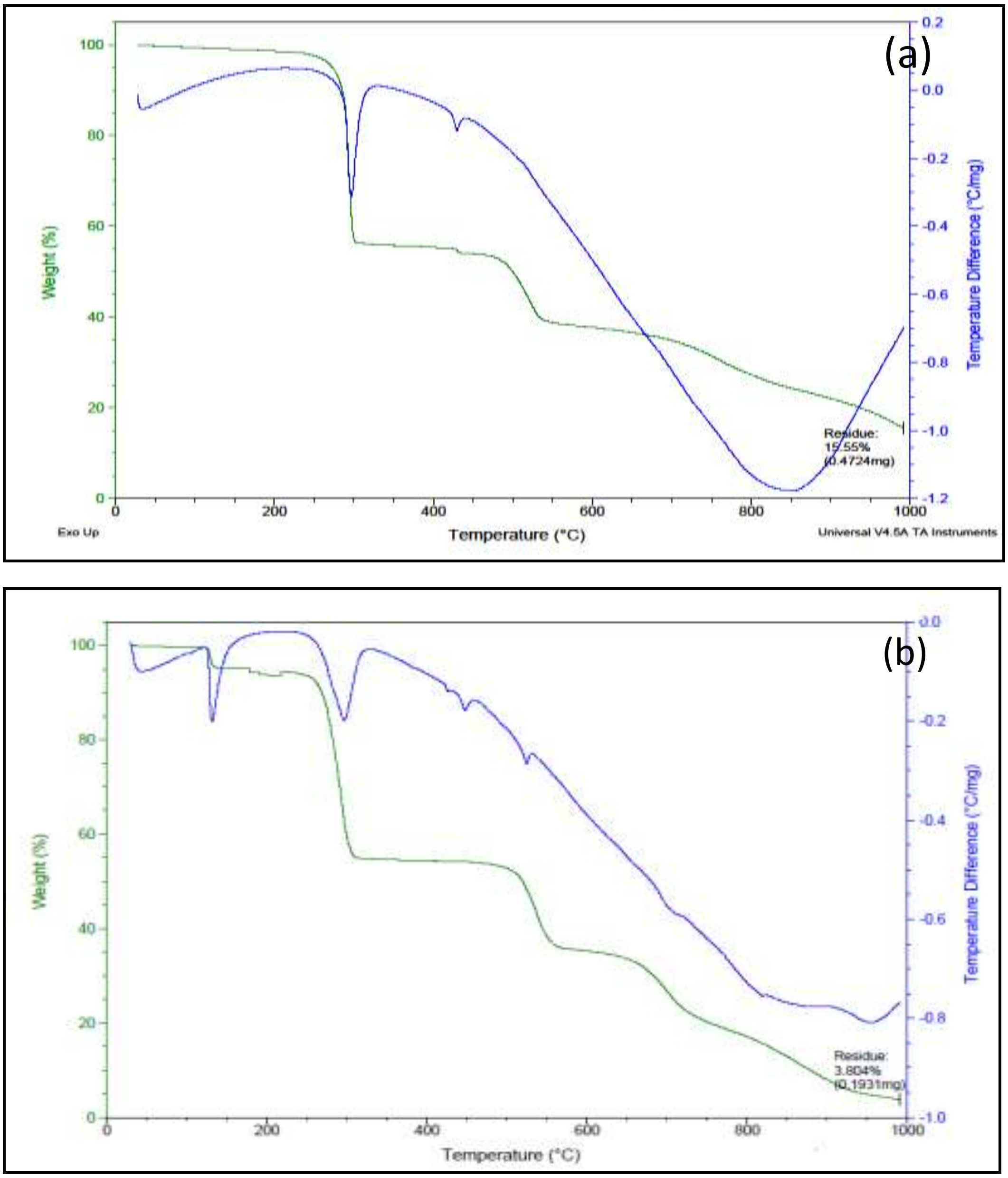


Fig. 5. TGA/DTA curves of a) KAP and b) NaAP crystals.

In contrast, the TGA curve of NaAP shows three stage weight loss patterns and the first weight loss about 4.5% in the temperature range of 120 - 133°C due to the liberation of water molecules. The second major weight loss occurred between the temperatures 244 - 306°C with 40% due to loss of sodium and carbon monoxide. The DTA curve of NaAP shows that the first endothermic transition at 243°C is due to the liberation of volatile substance like place at 364°C. DTA curve shows that the melting point of NaAP is 245 °C. Finally, TGA/DTA studies revealed that KAP crystals exhibited greater thermal stability as compared to NaAP crystals.

Conclusions

Two different phthalate based crystals such as KAP and NaAP crystals have been grown by slow evaporation solution growth technique at room temperature. The single crystal XRD analysis confirmed that KAP and NaAP crystals were respectively belongs to orthorhombic and monoclinic crystal structure. FTIR studies suggested the presence of functional groups that corresponds to KAP and NaAP. Microhardness measurements indicated KAP crystals have higher hardness number than NaAP crystals. This means that former is stronger than latter. It can be concluded from the TGA/DTA results that thermal stability of KAP crystals is relatively higher than that of NaAP crystals.

Acknowledgement

Author thanks K. Silambarasi and R. Muralidharan for preparation of crystals.

References:

1. Long NJ, Organometallic compound for nonlinear optics-The search for en-light-enment, Angew. Chem., 1995, 34, 21-38.
2. Manonmoni JV, Ramasamy G, Prasad AA, Meenakshisundaram SP, and Amutha M, Synthesis, growth, structure and characterization of potassium lithium hydrogen phthalate mixed crystals, RSC Adv., 2015, 5, 46282-46289.
3. Raju RK, Dharamaprakash SM, Jayanna HS, Effect of NaCl Doping on Growth, Characterization, Optical and Dielectric Properties of Potassium Hydrogen Phthalate (KHP) Crystals, Advances in Materials Physics and Chemistry, 2015, 5, 399-407.
4. Kejalakshmy N and Srinivasan K, Electro-optic properties of potassium hydrogen phthalate crystal and its application as modulators, J. Phys. D: Appl. Phys. 2003, 36, 1778–1782.
5. Ramasamy G, Parthiban S, Meenakshisundaram SP, Mojumdar SC, Influence of alkali metal sodium doping on the properties of potassium hydrogen phthalate (KHP) crystals, J Therm Anal Calorim 2010, 100, 861–865.
6. Sivakumar N, Geetha NK, Venkatamuthukumar J, and Jayakumar V, Mechanical Studies on Pure and Fe^{3+} DopedPotassium Hydrogen Phthalate Single Crystals for Device Fabrications, Indian Journal of Science and Technology, 2016, 9(36), DOI: 10.17485/ijst/2016/v9i36/100852.
7. Ramasamy G, Meenakshisundaram S, Synthesis and crystal structure of potassium hydrogen phthalate mixed crystal $K_{0.78}Na_{1.22}[C_6H_4(COO)_2].H_2O$, Journal of Crystal Growth 2013, 375, 26–31.
8. Muraleedharan R, Sathya U and Ramajothi J, Effect of Doping on the Morphology of KAP Nonlinear Optical Single Crystal, International Journal of ChemTech Research 2015, 7, 2691-2696.
9. Thilagavathy SR, Rajesh P, Ramasamy P, Ambujam K, Growth and characterization of pure and doped KHP NLO single crystals, Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 2014, 127, 248–255.
10. Smith RA, The crystal structures of a series of salts of phthalic acid. ii. the crystal structure of sodium acid phthalate hemihydrate, Acta Cryst. 1975, B31, 2345.
11. Bairava Ganesh R, Kannan V, Meera K, Rajesh NP, Ramasamy P, Synthesis, growth and characterization of a new nonlinear optical crystal sodium acid phthalate, Journal of Crystal Growth 2005, 282, 429–433.
12. Sivakumar B, Gokul Raj S, Ramesh Kumar G, Mohan R, Growth, crystal structure and characterization of a new single crystal: lithium sodium acid phthalate (LiNaP), for third order nonlinear optical applications, Journal of Crystallization Process and Technology, 2012, 2, 130-136.

*****