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Growth And Physico Chemical Characterization Of L-Arginine Added Inorganic Single Crystals

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ABSTRACT

Amino acids are the organic compounds and they play a vital role in maintaining good health of our human body. L-arginine was added separately with potassium chloride, potassium nitrate and potassium bromide. The crystals were grown by slow evaporation method at room temperature The grown crystals L-arginine added with potassium chloride (LARPC), potassium nitrate (LARPN) and potassium bromide (LARPB), were analyzed with the help of various characterization techniques. Structural details of the grown crystals were identified using SXRD and PXRD analysis, Various functional groups present in the crystals were confirmed using FTIRstudies , UV –Vis spectra proves that the crystals are opticaly transparent, thermal stability of the grown crystals were determined with the help of TGA analysis and were found to be stable, mechanical hardness measurements were done using Vickers microhardness test and dielectric studies gives details about the dielectric constant and dielectric loss values of the grown crystals. The results proved that the developed materials are good crystal with their own crystal structure. They are optically transparent in nature.They found to be thermally stable.

KEYWORDS: Crystal Structure; X-ray Diffraction; Nonlinear optic materials; Dielectric Material;

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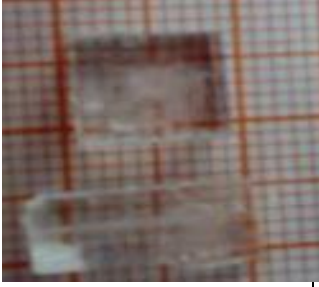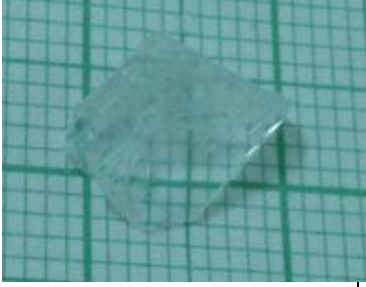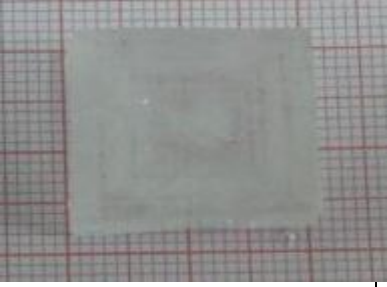
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INTRODUCTION

The immortal goal for the science and technology of crystal growth, namely the improvement of the microscopic and macroscopic homogeneities a necessity for any application. The ever-increasing application of semiconductor based electronics creates an enormous demand for high quality semiconducting ferroelectric and piezoelectric oxide single crystals. Continuous effort is on in growing organic, inorganic and semi organic materials with high damage threshold, wide transparency range and high nonlinear coefficient which make them suitable for device fabrication.[1-2] Most of the organic crystals usually have poor mechanical and thermal properties and are susceptible for damage during processing. Purely inorganic materials have excellent mechanical and thermal properties but possess relatively modest optical nonlinearity because of the lack of extended π-electron delocalization. Hence it may be useful to prepare crystals which combine the positive aspects of organic and inorganic materials with enhanced properties. The concrete form of all amino acids (except glycine) have centrosymmetric space group which is the major criteria for NLO applications.[3-4] Among all the amino acids, L-arginine crystal has excellent NLO properties. The amino acid L-Arginine contains anα-amino group and a terminal guanidyl group and is basic in nature.It is a polar amino acid with positive charge on the R group having more amino groups as compared to carboxyl groups with a molecular formula $C_6H_{14}N_4O_2$.[5]

MATERIALS AND METHODS

Saturated solutions of L-arginine, potassium chloride, potassium nitrate and potassium bromide were prepared at NTP separately. Doubly distilled water was used to prepare the saturated solutions. The materials selected were of analytical grade. The prepared saturated solution of L-arginine (organic) was mixed with potassium chloride, potassium nitrate and potassium bromide (inorganic) separately in the ratio of 1:3. To have a good homogeneous nature the prepared saturated solutions were stirred well for about 4 h using magnetic stirrer. The filtered solutions were taken in separate beakers and were placed in a vibration free and undisturbed environment to favour the slow evaporation at room temperature. The good quality single crystals of L-arginine added potassium chloride (LARPC), L-arginine added potassium nitrate (LARPN) and L-arginine added potassium bromide (LARPB)were harvested after a time span of 63, 45 and 97 days respectively. The photographs of the grown crystals are shown in the Table 1.

Table 1. Photographs of the L-arginine added crystals

Crystal	LARPC	LARPN	LARPB
Photo-graph			

3. RESULTS AND DISCUSSION

3.1. XRD analyses

Powder X-ray diffraction (PXRD) pattern was recorded using a Rich Seifert diffractometer with Cu Kα (λ = 1.5418 A°) radiation by crushing the grown crystals into fine powder. The samples were scanned over the range 10 ° - 90 ° at the rate of 1° per minute. The indexed PXRD (using X Powder software) patterns of the grown crystals LARPC, LARPN and LARPB are shown in Figure 1. Appearance of sharp and strong Bragg peaks at specific 2θ angles confirms the good crystallinity of the grown crystals.[6-7] The prominent peaks have been indexed.

Single crystal X-ray diffraction is a non-destructive analytical technique which provides information about the unit cell dimensions and packing of molecules in crystals.The grown crystals LARPC, LARPN and LARPB were also subjected to single crystal X-ray diffraction (SXRD) analysis. The unit cell parameters are given in Table 2.

The PXRD pattern of grown LARPC crystals consists of peaks correspond to both L-arginine and KCl. The SXRD result reveals that the crystal system belongs to triclinic.The PXRD pattern of grown LARPN crystal confirms the presence of peaks corresponding to both the parent materials. The SXRD studies identify the crystal system of LARPN as orthorhombic which corresponds to that of potassium nitrate.
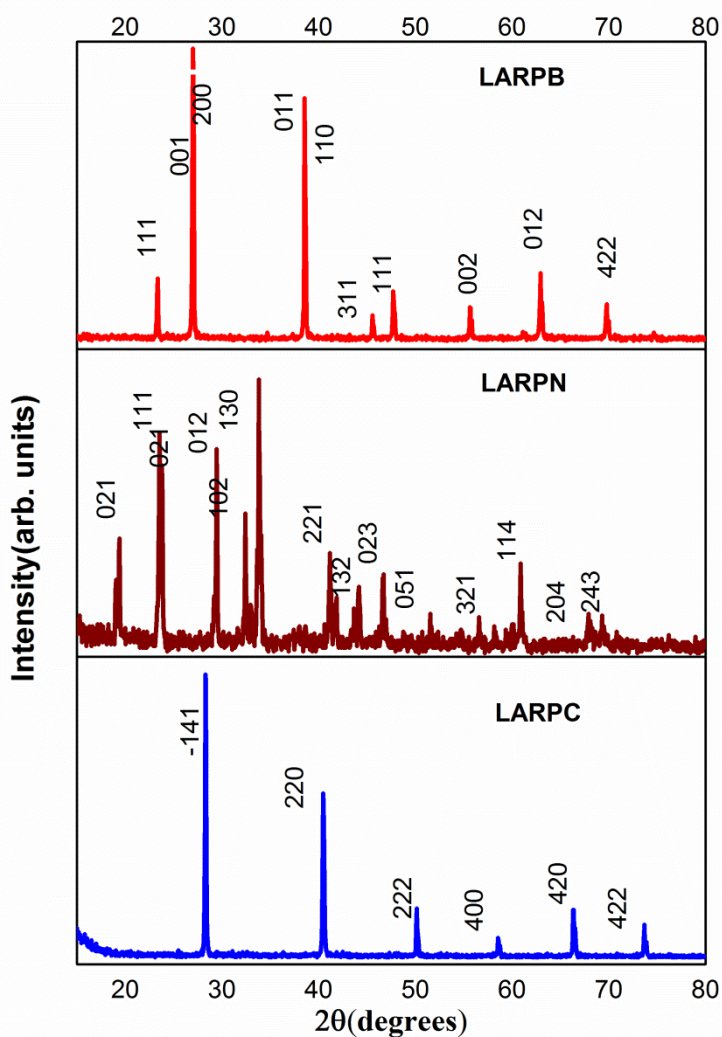
Figure 1. Powder XRD patterns of L-arginine added crystals

This proves that the addition of L-arginine with potassium nitrate did not alter the structure and a very mild change in the values of lattice parameters and unit cell volume of potassium nitrate was observed.

The presence of peaks representing both L-arginine and potassium bromide were attested from the PXRD pattern of LARPB crystals. The SXRD analysis proves crystal belongs to tetragonal system which is different from both of the parent materials. The addition of L-arginine with potassium bromide has also reduced the volume of LAPB crystal.

Table 2. Lattice parameters of L-arginine added single crystals

Crystal	Lattice parameters							Crystal system
	a (A^0)	b (A^0)	c (A^0)	α (^{0})	β (^{0})	γ (^{0})	Volume (A^{03})	
LARPC	3.24	3.32	3.35	91.58	90.21	91.65	36	Triclinic
LARPN	5.398	6.526	9.05	90	90	90	318.7	Orthorhombic
LARPB	3.24	3.24	3.34	90	90	90	35	Tetragonal

3.2. FT-IR analysis

FTIR spectra were recorded using Perkin Elmer spectrometer by KBr pellet technique in the region of 400-4000cm^{-1}. The recorded spectra are shown in Figure 2. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data.

From the FTIR spectra of the grown LARPC, LARPN and LARPB crystals the C-H groups produces the characteristic peaks at 2380 cm^{-1}, 2917 cm^{-1} and 2056, 2400, 2740 cm^{-1} respectively. Similarly, the COO$^-$ stretch of COOH seems to have some intense sharp peaks at 1557, 1132, 1010 cm^{-1}, 2090 cm^{-1} and 725 cm^{-1} respectively. The sharp peak at 1446 cm^{-1} is assigned to COO$^-$ symmetric stretching of L-Arginine. The broad band at 3450 cm^{-1}, for the grown LARPB crystal is attributed to O-H (-COOH) vibration. The involvement of NH$_3^+$ in hydrogen bonding is evident by the fine structure of the band in the lower-energy region. For the grown LARPC, LARPN and LARPB crystals the peaks at 1670, 1620 and 1756 cm^{-1} are due to asymmetrical NH$_3^+$ bending modes respectively. [8] The CH$_2$ bending modes are observed at 1430, 1350, 1480 cm^{-1} and 966 respectively for above crystals. Since the stretching vibrations of the O–H bonds in the COOH group fall into the same region as the stretching vibrations of the OH bonds in water molecules and the deformation vibrations of the water molecules fall into the region of the deformation vibrations of NH$_2^+$ and NH$_3^+$ groups, it is difficult to determine with certainty the presence or absence of water molecules on the basis of the IR spectrum alone.[9]
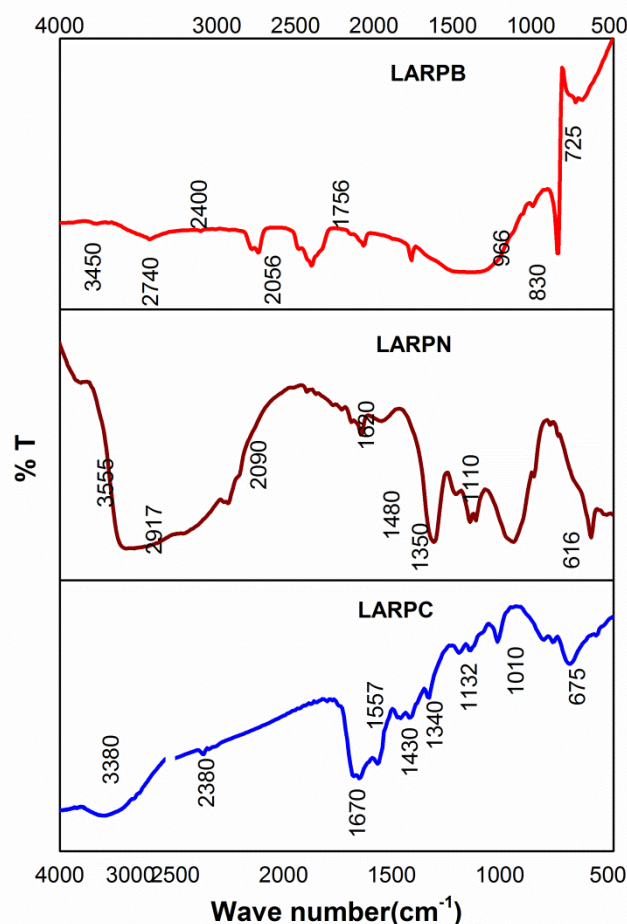
Figure 2. FT-IR spectra of L-arginine added crystals.

3.3. Optical studies

Transmission spectra are very important for any NLO material because, an NLO material can be of practical use only if it has a wide transparency window. The determination of UV transparency and cutoff wavelength is very important since these crystals are mainly used in optical application. Ultraviolet and visible light are energetic enough to promote outer electrons to higher energy levels. This transparent nature of the crystals in the visible region is the property which makes the material important for NLO applications.[10]
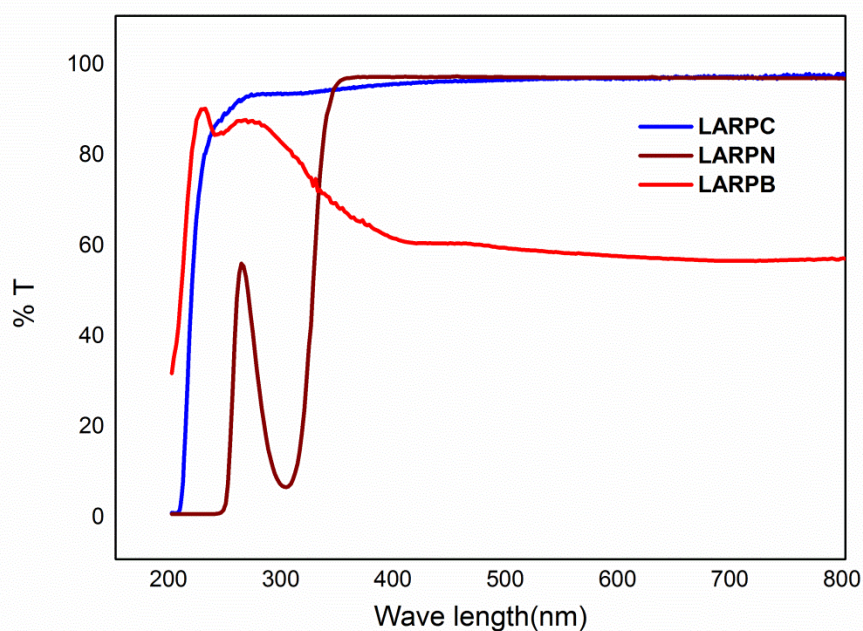
Figure 3. UV- visible spectra of L-arginine added crystals

The optical transmission spectra of the grown crystals were recorded using Shimadzu UV-Vis spectrophotometer in the wavelength range of 200 and 800 nm. The recorded spectrum is shown in Figure 3. The lower cutoff wavelength of the crystals LARPC, LARPN and LARPB were found to be 228, 336 and 221 nm respectively. The percentage of transmission of the grown LARPC, LARPN and LARPB crystals were 94.2, 97 and 60.2 respectively.

The grown LARPN crystals shows a strange character in the optical spectrum that it shows more than 50% of transparency around 275 nm and the transparency falls to the minimum around 300 nm. Hence it suggests the presence of potassium nitrate in the grown GPN crystals. Between 400 and 800 nm, there is no absorption of wavelength which clearly indicates that grown crystals can be used as window material in optical instruments.[11-12] The transparency window of all the three grown crystals lie in the UV and visible region. The band gap energy of the above crystals was calculated using the formula,

$$E_g = \frac{hc}{\lambda_{min}}$$

and it attains the values of 5.43, 3.6 and 5.6 respectively for the above crystals.The wide range of transparency suggests that the crystals are good candidates for nonlinear optical applications.[13-14]

3. 4. Vicker's micro hardness test

Hardness is a complex property related to the extent to which solids resist both elastic and plastic deformations. Experimentally, its value is measured by the indentation size after a hard

indenter has deformed a material. At the microscopic level, the hardness of an ideal solid depends on the nature of its chemical bonding.

The micro hardness of the grown crystals was measured using a Shimadzu Micro hardness tester with a diamond indenter. The polished surface of the crystals LARPC, LARPN and LARPB were indented at different sites for the loads 25, 50 and 100 g for 10 seconds and the average values of the hardness were found. The diagonal lengths of the indented impression were measured using calibrated micrometer attached to the eyepiece of the microscope. The impression was measured using calibrated micrometer attached to the eyepiece of the microscope. The micro hardness is calculated using the formula

$$H_V = \frac{1.8544\,P}{d^2}\ Kg/mm^2$$

where P is the applied load in grams and d is the average diagonal length of the Vicker's impression in mm after loading.
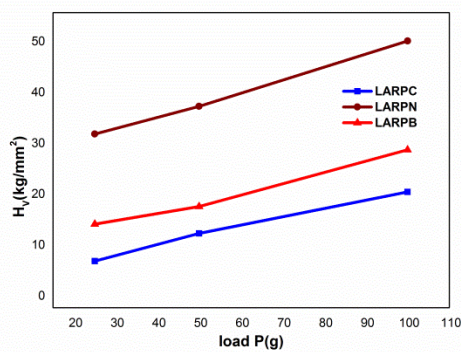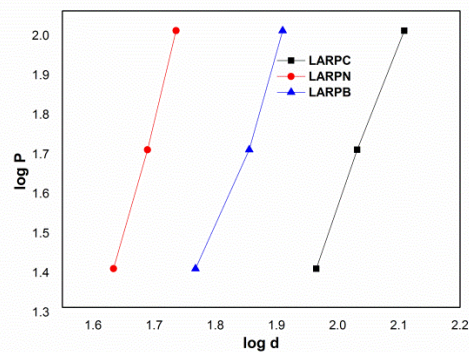

Figure 4 (a) Plot between load p and H_v **Figure 4 (b) Plot between log d and log P**

Plot of H_v versus load P for the investigated samples are shown in figure 4(a). The nonlinear variation of H_v with load implies the presence of imperfection and voids. The imperfections aremainly impurity, dislocation or grain boundary diffusion. The Meyer's index number n gives the value of work hardening index. Materials are normally characterized by Meyer's index or work hardening index. According to Onitsch and Hanneman, n should lie between 1 and 1.6 for hard materials and should be above 1.6 for soft materials.[14-15] The lower the value of the work hardening index better will be the hardness of the material. The log-log plot between d and P yields almost straight-line graph and is shown in figure 4b. The slope of the line gives the work hardening indexn. The value of work hardening index of the grown crystals LARPC, LARPN and LARPB was found to be 4.5, 5.2 and 3.5 respectively. Hence the grown crystals are characterized as soft materials. The elastic stiffness constant C_{11} were determined from Wooster's empirical relation $C_{11} = H_V^{7/4}$ and are presented in Table 3.

Table 3. The elastic stiffness constants for L-arginine added crystals

Load	LARPC		Crystal			
			LARPN		LARPB	
	H_v	C_{11}	H_v	C_{11}	H_v	C_{11}
25	6.17	24.15	31.15	410.72	13.45	94.46
50	11.6	72.91	36.60	544.62	16.90	140.86
100	19.75	185.03	49.45	922.12	28.05	341.89

3.5. Thermal analyses

Thermo gravimetric analyses (TGA) gives information regarding water of crystallization and different stages of decomposition of the crystal system[16]. The thermogravimetric analysis of the grown crystals was carried out between 20 °C and 800 °C in the nitrogen atmosphere at a heating rate of 20 °C min^{-1} using Perkin-Elmer thermal analyzer (STA 409 PC). The obtained spectrum is shown in figure 5.

From the TGA curve, the grown LARPC crystal proves to be stable up to the temperature of 220 °C and it starts to decompose in the temperature range of 220-700°C. During this process only 2% of the sample was found to be lost which indicates the presence of a small portion of L- arginine in the lattice sites of the grown crystal. After a very slow process of weight loss, around 98.3% of the crystal was left as residue. The absence of water of crystallization in the molecular structure is indicated by the absence of the weight loss around 100 °C.[16-18] This ensures the suitability of the material for possible application in lasers, where the crystals are required to withstand high temperatures.
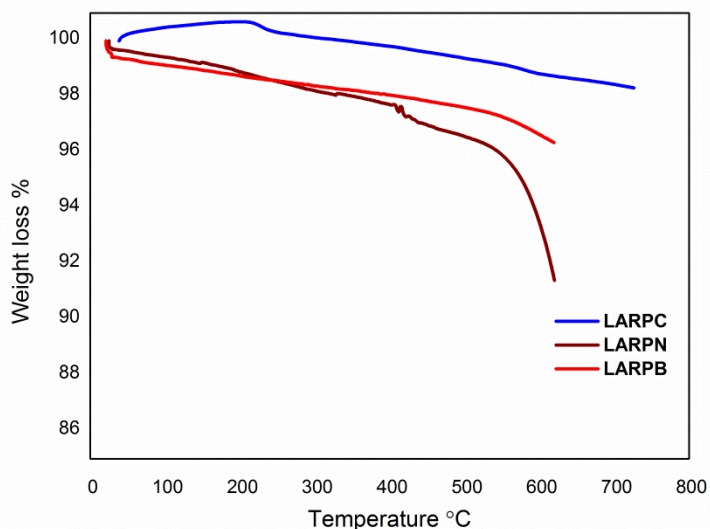
Figure 5. Thermograms of L-arginine added crystals

The TGA curve of the grown LARPN crystal shows its stable nature where a very gradual decomposition occurred up to 415°C causing a little amount of weight loss, which is only 2.5% of the initial mass of the sample. In the second stage of decomposition in the temperature range of 415-548°C, another 1.2% of the sample was lost. From 548-621°C a weight loss of 4% of the sample was noticed. Around 91% of mass of the sample retained in the anhydrous form of the crystal. This analysis concludes the enhancement of the melting point of potassium nitrate (334°C) when added with L-arginine and this also enhances the temperature range for the utility of the crystal for NLO applications.

From the TGA curve of LARPB crystal, quite interesting and important to be noticed is the very good thermal stability of the material. Only 0.6% of the sample was lost by decomposition at the temperature of 32°C. During the second stage of decomposition up to 553°C around 2% mass of the sample was lost. A gradual and slow weight loss occured leaving 96% of the sample undisturbed. This thermal behavior of the grown LARPB crystal proves the thermal stability of the grown crystal and their utility in the high temperature region.[19-20]

3.6   *Dielectric studies*

Dielectric measurement is one of the useful characterizations of the electrical response of solids. A study of the dielectric properties of solids gives information about the electric field distribution within the solid. The frequency dependence of these properties gives a great insight into the materials applications. The conventional parallel plate capacitor method was employed for measuring the dielectric properties. The variation of dielectric constant (εr) and dielectric loss (tan δ)

were measured for the grown crystals at room temperature as a function of frequency ranging from 100 Hz to 5 MHz (Figures 6 a and b).

The dielectric constant has high values in the lower frequency region and then it decreases with the increase in frequency. The very high value of ε_r at low frequencies may be due to the presence of all the four polarizations, namely, space charge, orientational, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these polarizations gradually.[21-23]
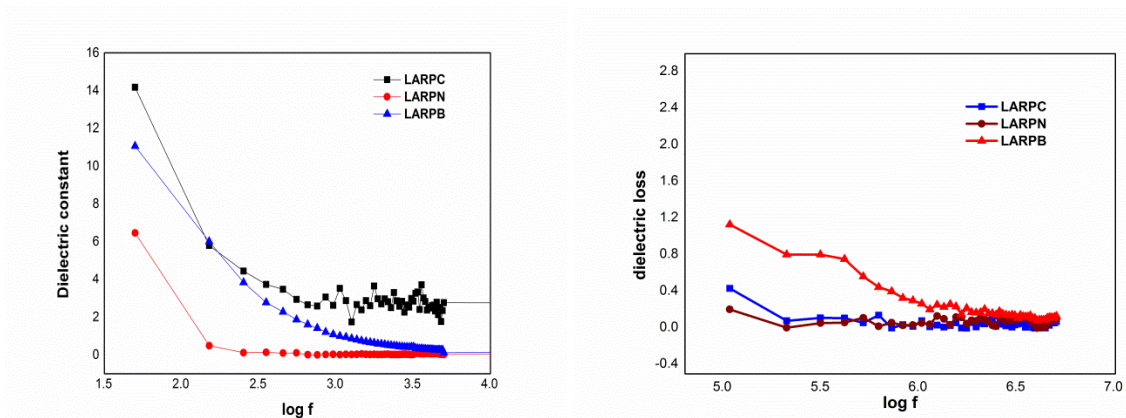

Figure 6. Plot between (a) log f and dielectric constant (b) log f and dielectric loss

The dielectric loss is a measure of the energy absorbed by dielectric. It is known that in a capacitor, the dielectric usually has a resistance R and reactance $1/\omega C$. Which arerelated to the phase angle $\tan\delta = 1/\omega CR$. Here $\tan\delta$ is referred to as the dielectric loss. The dielectric loss is also studied as a function of frequency at room temperature, as shown in Figure 6b. These curves suggest that the dielectric loss strongly depends on the frequency of the applied field, similar to dielectric constant. The variation of loss tangent with frequency can be assigned to the dipole alignment when the field is applied. At low frequencies, the dipoles easily switch alignment with the changing field. The characteristic of low dielectric loss with high frequency suggests that the crystals possess good optical quality with lesser defects and this parameter is of vital importance for nonlinear optical materials in their application.[24-25]

CONCLUSION

L-arginine added Single crystals of salts of potassium (LARPC, LARPN and LARPB) were grown using slow evaporation method. Crystalline nature was verified with PXRD analysis for each of the successfully developed crystals and the prominent peaks were duly indexed. From the single crystal XRD analysis the lattice parameters of the grown crystals were determined. The LARPC and LARPN crystals possesses monoclinic crystal system whereas the LARPB crystalized in cubic form.Various functional groups present in the grown crystals were identified by FTIR analysis and they are in line with the findings of XRD. This analysis proved the presence of both the parent

materials in the grown crystals. UV-Vis-NIR study reveals the suitability of the crystal for NLO applications and the lower cut off wavelengths of LARPC, LARPN and LARPB are found to be 228, 336 and 221 nm respectively. There is no absorption of wavelength in the entire visible region.The bandgap energy values of the grown crystals were calculated and they are 5.43, 3.6 and 5.6 eV respectively. The optical study reveals that the developed crystals had lower cut-off wavelength and relatively higher transparency range. Careful inspection strongly suggests that LARPC, LARPN and LARPB single crystals have bandgap energy of 5.43, 3.6 and 5.6 eV respectively. The grown crystals, therefore, can be used in the optoelectronics and photonics device fabrication fields. Vicker's micro hardness analysis recognizes the grown crystals as soft materials based on indentation analysis since their n values are greater than 1.6. The elastic stiffness constant C_{11} for grown L-arginine added crystals were also determined. Thermal analysis proves the thermal stability of the grown crystals LARPC, LARPN and LARPB as 220, 415 and 553 °C respectively. Hence the grown crystals can be recommended for their application in high temperature region. From the dielectric study, it is found that both dielectric constant and dielectric loss of the crystal decrease with increase in frequency. The low value of dielectric constant (ε_r) at high frequencies are important for these materials in the construction of photonic and NLO devices which suggests that the sample possesses enhanced optical quality with low level defects.

REFERENCES

1. Alexandar A, Surendran P, Sakthypriya S, Lakshmanan A, Rameshkumar P. Growth and characterizations of Lemethioninium picrate single crystal for nonlinear optical applications. J. Nonlinear Opt. Phys. Mater. 2016; 25: 1650052.

2. Alex AV, Philip J. Elastic properties of zinc tris (thiourea) sulphate single crystals. J. Appl. Phys. 2001; 90: 720-723.

3. Wang X, Wang D, Gao H, Yang Z, Cao H, Yang H, He W, Wang H, Gu J, Hu H. Third-order nonlinear optical properties of a novel series of D- p-A pyrene-aldehyde derivatives. J. Nonlinear Opt. Phys. Mater. 2016; 25: 1650014.

4. Ozga K, Krishnakumar V. L-lysine monohydrochloride dehydrate as novel elasto and electro-optical materials. Mater. Lett. 2008; 62: 4597-4600.

5. Vasudevan P, Sankar S, Gokul Raj S. Studies on second harmonic generation efficiency of organic material L-arginine maleate dehydrate. Optik. 2013; 124: 4155–4158.

6. Mohd Shkir, Haider Abbas. Physico chemical properties of L-asparagine L-tartaric acid single crystals: A new nonlinear optical material. Spectrochem. Acta A. 2014; 118: 172-176.

7. Mohd Anis, Ramteke SP, Shirsat MD, Muley GG, Baig MI. Novel report on γ -glycine crystal yielding high second harmonic generation efficiency. Optical Materials. 2017; 72: 590-595.

8. Zulifiqar Ali Ahamed S, Dillip GR, Raghavaiah P, Mallikarjuna K, Deva Prasad Raju B. Spectroscopic and thermal studies of γ-glycine crystal grown from potassium bromide for optoelectronic applications. Arab. J. Chem. 2013; 6: 429-434.

9. Tanusri Pal, TanusreeKar, Gabriele Bocelli, Lara Rigi. Synthesis, Growth, and Characterization of L-Arginine Acetate Crystal: A Potential NLO Material.Crystal growth & Design. 2003; 3 (1): 13-16.

10. Dillip GR, Raghavaiah P, Mallikarjuna K, Madhukar Reddy C, Bhagavannarayana G, Ramesh Kumar V, Deva Prasad Raju B. Crystal growth and characterization of γ-glycine grown from potassium fluoride for photonic applications.Spectrochim. Acta A. 2011; 79: 1123–1127.

11. Baig MI, Anis M, Muley GG. Comprehensive study on crystal growth, optical and dielectric properties of potassium dihydrogen orthophosphate crystal influenced by organic additive salicylic acid.Optik. 2017; 131: 165–170.

12. Shejwal NN, Anis M, Hussaini SS. Ab-initio UV-vis, SHG efficiency, photoluminescence, dielectric, thermal and mechanical studies of pure and l-glutamine doped ZTS crystal for optoelectronics device applications.Optik. 2015; 127: 6525–6531.

13. Ramajothi J, Dhanuskodi S, Nagarajan K. Crystal growth, thermal, optical and microhardness studies of tris (thiourea) zinc sulphate - a semiorganic NLO material. Cryst. Res. Technol. 2004; 39: 414-420.

14. Subhadra KG, Kishan Rao K, Sirdeshmukh DB. Systematic hardness studies on lithium niobate crystals. Bull. Mater. Sci. 2000; 23: 147-150.

15. Mukerji S, Kar T. Vicker's Microhardness Studies of L-arginine Hydrobromide Monohydrate Crystals (LAHBr). Cryst. Res. Technol. 1999; 34: 1323-1328.

16. Andrew Knox Galwey, Michael E Brown. Thermal decomposition of ionic solids, Elsevier: Netherlands. 1999.

17. Wiberg Egon, Nils Wiberg. Arnold Frederick HollemanInorganic chemistry, Academic Press: Germany, 2001.

18. Kyungho Park, James MB, Evans Allan S. Myerson.Determination of solubility of polymorphs using differential scanning calorimetry. Cryst. Growth Des. 2003; 3: 991-995.

19. Perlovich GL, Hansen LK, Bauer-Brandl A. The Polymorphism of Glycine. Thermochemical and structural aspects. J. Thermal Anal. Calorim. 2001; 66: 699-715.

20. Anis M, Hussaini SS, Shirsat MD. Analysis of the X-ray diffraction, etching, luminescence, photoconductivity, thermal and dielectric properties of an ADP crystal influenced by the bimetallic additive sodium metasilicate ($Na_2 SiO_3$). Mater Res Express. 2016; 3: 106204–106210.

21. Rak M, Eremin NN, Eremina TA, Kuznetsov VA, Ohkrimenko TM, Furmanova NG, Efremova E.P. On the mechanism of impurity influence on growth kinetics and surface morphology of KDP crystals-I: defect centres formed by bivalent and trivalent impurity ions incorporated in KDP structure-theoretical study. J. Cryst. Growth. 2005; 273: 577-585.

22. Debrus S, Ratajczak H, Venturini J, Pincon N, Baran J, Barycki J, Glowiak T, Pietraszko A. Novel nonlinear optical crystals of non-centrosymmetric structure based on hydrogen bonds interactions between organic and inorganic molecules. Synthetic Met. 2002; 127: 99-104.

23. Anis M, Baig MI, Muley GG, Hussain SS, Shirsat MD. Monocrystal growth, X-ray diffraction, photoluminescence, thermal and dielectric studies of cadmium thiourea acetate complex doped with l-cysteine. Optik. 2016; 127: 12043-12047.

24. Senthil Pandian M, Boopathi K, Ramasamy P, Bhagavannarayana G. The growth of benzophenone crystals by Sankaranarayanan–Ramasamy (SR) method and slow evaporation solution technique (SEST): a comparative investigation. Mater. Res. Bull. 2012; 47: 826-835.

25. Arivuselvi R, Ruban Kumar A. Crystallization of inorganic nonlinear optical zinc di-magnesium chloro sulphate (ZDMCS) single crystal. Optics & Laser Tech. 2017; 88: 147–151.