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Research Article

CRYSTAL GROWTH, XRD, MECHANICAL, FTIR, DIELECTRIC AND NONLINEAR OPTICAL PROPERTIES OF L-LYSINE OXALIC ACID CRYSTALS

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ABSTRACT

An organic nonlinear optical (NLO) crystal viz. L-lysine oxalic acid (LLOA) has been synthesized and grown in the form of single crystal by solution method with slow evaporation technique. Single crystal X-ray technique was used to find the crystal lattice parameters and structure. The FT-IR spectrum was recorded to identify the functional groups of the prepared sample. The fluorescence spectrum was recorded for the grown LLOA crystal and colour of emission and region are reported. The micro hardness was measured at different applied loads and work hardening coefficient was evaluated. Dielectric studies were carried out for the grown crystal LLOA and electrical properties were studied. The EDAX spectrum of the sample was recorded to identify the various elements in the crystal. LLOA crystal was powdered and the SHG efficiency was found by Kurtz-Perry technique.

Keywords: L-lysine complex; single crystal; XRD; FTIR; Dielectrics; Microhardness; NLO; Fluorescence; SHG

1. INTRODUCTION

Nonlinear optical (NLO) crystals are used for optical frequency conversion, electro-optic phase modulation and other NLO phenomena and these phenomena are useful in generating UV laser light, visible laser light and infrared laser light. The generated laser light from NLO crystals could be used in fibre optics, optical communication and optical computing, optical signal processing devices etc [1-3]. Amino acid family crystals exhibit excellent electro-optic and nonlinear optical properties. Review of literature shows that many technologically important NLO crystals are the complexes of amino acids. Amino acids like L-arginine, L-lysine, L-alanine, L-histidine are used to prepare important NLO crystals [4-6]. It is reported that many L-lysine based NLO crystals have been synthesized by adding organic acids [7-10]. Srinivasan *et al.* have grown and studied L-lysine lysinium dichloro nitrate [11] and its vibrational spectral analysis was done by Briget Mary *et al.* [12]. In this work, L-lysine was added with oxalic acid to form L-lysine oxalic acid crystal by taking the reactants in 1:1 molar ratio. Solution method was adopted to grow the single crystals of L-lysine oxalic acid (LLOA) and various characterizations like XRD, FTIR, fluorescence, SHG, dielectric, EDAX and microhardness studies were carried out for the grown crystals of LLOA.

2. Experimental

2.1. Growth of LLOA crystal

Good quality commercially available L-lysine and oxalic acid were taken in 1:1 molar ratio and the reactants were dissolved in double distilled water to prepare the saturated solution. The solution was continuously stirred using a magnetic stirrer for about 4 hours and at the same time, it was heated at 50°C for synthesis of the sample. Then solution was cooled to room temperature and it was filtered using the good quality Whatman filter papers.

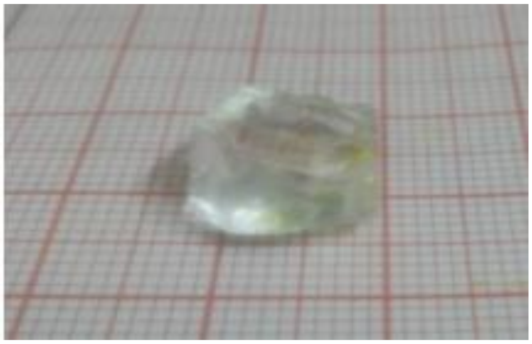

Fig.1: The photograph of grown LLOA crystal

The filtered solution was taken in the growth vessel covered with a perforated sheet. Due to slow evaporation, initially small-sized crystals were formed in the solution and after a period of 30-35 days, big-sized crystals of LLOA crystals grown. Fig.1 shows one of the harvested crystals of LLOA.

2.2. Characterization methods

Single crystal XRD data have been obtained using an ENRAF NONIUS CAD4-MV31 single crystal X-ray diffractometer with MoK_α (λ=0.71073 Å). The presence of functional groups, absorption peaks and the bond assignments, nature of the bonds present in the title materials were assessed by the FTIR spectral analysis using PERKIN ELMER FTIR spectrophotometer. Fluorescence spectrometer using analysis PERKIN ELMER LS45 evaluated the spectrum range 250-800 nm. Dielectric analysis for LLOA crystal was carried out using an LCR meter at different frequencies and temperatures. Vickers microhardness measurement for the grown crystal of LLOA was performed using SHIMADZO HMV hardness tester fitted with a diamond indenter. The second harmonic generation (SHG) efficiency of LLOA crystal was tested by an AQ switched high energy Nd: YAG laser (λ=1064 nm) (QUANTA RAY MODEL LAB-170-10).

3. RESULTS AND DISCUSSION

3.1. Structural studies

The grown crystal of LLOA was subjected to single crystal X-ray diffraction (XRD) studies to find the crystal structure. In this method, when monochromatic X-rays from the molybdenum target fall on a small piece of crystal, X-rays are diffracted and this is known as the XRD and this is the principle of single crystal X-ray diffractometer [13]. Using the single crystal X-ray diffractometer, XRD data were collected. This method is used to check the single crystallinity of the sample and if the sample is a polycrystal, it cannot be used to collect the data here. It is to be noted here that a small piece of a single crystal is sufficient to fine the lattice parameters. The crystal parameters of LLOA crystal are obtained to be a= 6.125(3) Å, b = 12.648 (2) Å, c= 8.329 (3) Å, α =90°, β = 90°, γ= 90° and V= 645.24(2) Å^3. From the data, it is confirmed that the grown LLOA crystal has the orthorhombic structure.

3.2. FTIR studies for finding functional groups

The FTIR spectrum was recorded using Perkin Elmer spectrometer with KBr pellet technique in the region 400-4000 cm^{-1}. When infrared radiation falls on KBr mixed LLOA sample, a part of radiation is absorbed and the remaining part of the radiation is transmitted from the sample. The transmitted radiation was measured at various values of wave number and the FTIR spectrum was recorded using the FTIR spectrometer [14]. The recorded FTIR spectrum of LLOA sample is presented in the figure 2. The values of absorption frequencies and their assignments are provided in the table 1.

Table 1: FTIR absorption frequencies and their assignments for LLOA crystal

Absorption frequencies (cm^{-1})	FTIR assignments
3100-3400	NH_3^+ asymmetrical stretching and OH stretching
2937	NH_3^+ symmetrical stretching
2126	CH_2 stretching
1584	NH_3^+ asymmetrical bending
1512	NH_3^+ symmetrical bending
1406	COO^- stretching
1323	CN stretching
1149	CH_2 scissoring
865	NH_3^+ rocking
766	CH_2 wagging
705	CH_2 rocking
770	C-C stretching
668	O-C=O deformation
548	Torsional oscillation
437	COO^- wagging

The peak observed at 438 cm^{-1} is due to COO^- wagging and the peak observed at 548 cm^{-1} is assigned to torsional oscillation. The peak at 668 cm^{-1} indicates the group O-C=0 deformation. The C-C stretching occurs at 766 cm^{-1}. The rocking of CH_2 is indicated by 865 cm^{-1}. The absorption peak at 1019 cm^{-1} represents CH_2 wagging. The peak at 1119 cm^{-1} represents the rocking NH_3 group. The 1323 cm^{-1} peak is due to C-N stretching. The peak at 1406 cm^{-} corresponds to COO^- stretching. Twisting and CH_2 scissoring vibrations are revealed at 1339 cm^{-1}. The absorption peaks at 1512 cm^{-1} and 1584 cm^{-1} are due to symmetrical asymmetrical bending vibrations. The absorption peak at 2126 cm^{-1} is corresponding to CH_2 stretching vibration. NH_3^+ symmetric stretching vibration is observed at 2937 cm^{-1}. The OH stretching and NH_3^+ asymmetric stretching vibrations are due to the broad absorption band 3100-3400 cm^{-1}.

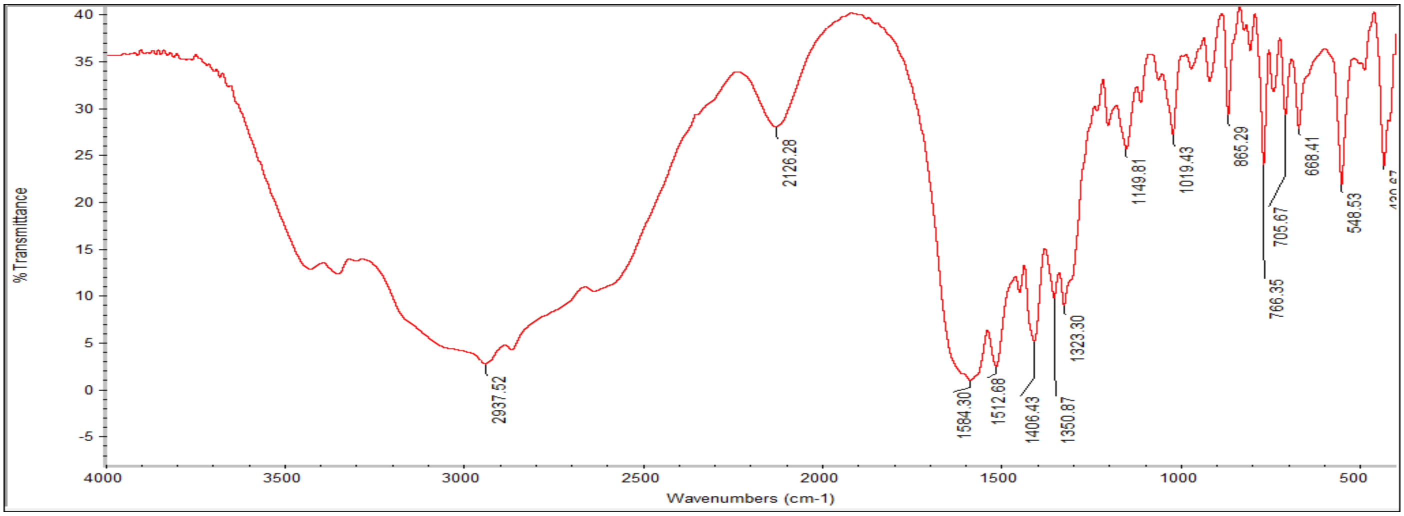

Fig.2: The recorded FTIR spectrum of LLOA crystal

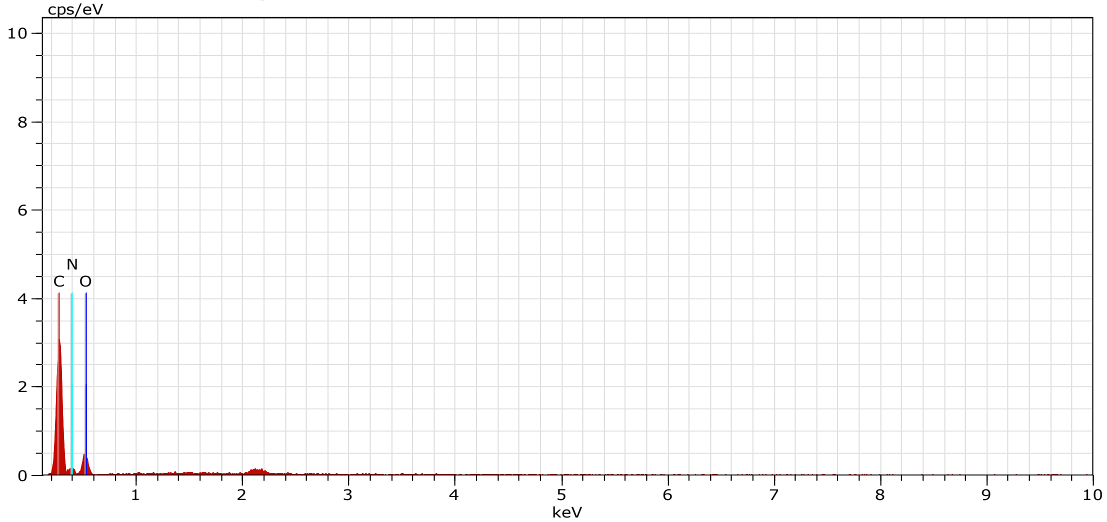

Fig.3: EDAX spectrum of LLOA crystal

3.3. EDAX and CHN studies

Energy dispersive analysis by X-rays (EDAX) is a technique used for identifying the elements in a sample. The EDAX analysis system works as an integrated feature of a Scanning Electron Microscope (SEM) and here the sample is bombarded with an electron beam inside the scanning electron microscope. The bombarding electrons collide with the the atoms of the sample, knocking some of them off in the process. A position vacated by an ejected inner shell electron is eventually occupied by a higher energy electron from an outer shell and X-rays are emitted. By measuring the amount of energy present in the X-rays being released by the sample during electron beam bombardment, the elemental composition of the sample can be found. The recorded EDAX spectrum of LLOA crystal is shown in the figure 3. The spectrum indicates that LLOA crystal has the elements like carbon, oxygen and nitrogen. The element hydrogen was identified in LLOA crystal using CHN analysis. The elemental composition of the grown LLOA crystal is provided in table 2.

Table 2: Elemental composition of LLOA crystal

Element	Wt.%
Carbon	40.673
Hydrogen	6.826
Oxygen	40.610
Nitrogen	11.851

3.4. Fluorescence studies

Photoluminescence or fluorescence spectroscopy is a non-destructive method of probing the electronic structure of materials. Light is directed onto a sample, where it is absorbed and imparts excess energy into the material in a process called photo-excitation. This excess energy will be dissipated by the sample through the emission of light, or luminescence. Fluorescence spectrometer (Model: Perkin Elmer LS45) was used to record the emission spectrum and here the measurement was carried out for the excitation wavelength of 240 nm. The emission spectrum was measured in the range 250 - 800 nm (Fig. 4). The strong luminescence peak at 488 nm was observed in the emission spectrum and this peak corresponds to bluish green emission from LLOA crystal. This spectrum contains also small-intensity peaks at 347 nm, 536 nm and 737 nm. The peak at 347 nm is due to emission of UV light, the peak at 536 nm corresponds to green light and the peak at 737 nm is due to infrared radiation from LLOA crystal.

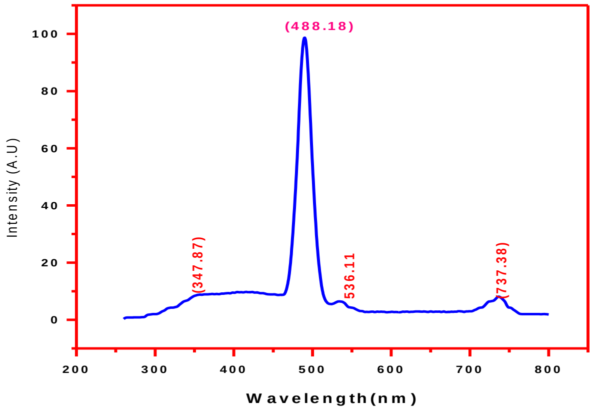

Fig.4: Fluorescence emission spectrum of LLOA crystal

3.5. Microhardness studies

The microhardness values were measured at different applied loads using HMV SHIMADZU microhardness tester. Molecular binding, yield strength, hardness and elastic constant are some of the mechanical properties and these properties are important as far as mechanical strength is concerned. The hardness of a material was determined by heat formation, Debye temperature, lattice energy, and inter atomic spacing. Here Vickers microhardness method was adopted to carry out the study. The Vickers microhardness number (H_V) was calculated using the relation

$$H_V = 1.8544\ (P/d^2)\ \text{kg/mm}^2$$

where P is the load applied and d is the average diagonal length of impression. The variation of hardness with applied load for LLOA crystal is shown in the figure 5. The result indicates that the hardness increases with increase of the applied load up to 75 g and then it decreases. The increasing trend is due to reverse indentation size effect and the decreasing behavior is due to direct indentation size effect. Meyer's law can be used to find the value of work hardening coefficient (n) and this law is given by $P = a\ d^n$ where 'a' is a constant depending on the material of the crystal. A plot (Fig. 6) is drawn between log P versus log d for LLOA crystal and the slope of best fitted straight line gives the value of work hardening coefficient (n) and the obtained value for LLOA crystal is 4.357. Since this value is greater than 1.6, the grown crystal of LLOA is considered to be a soft material [15].

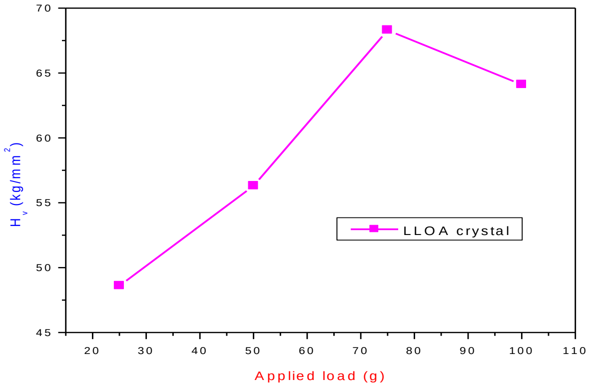

Fig. 5: Plot of Vickers microhardness number versus applied load for LLOA crystal

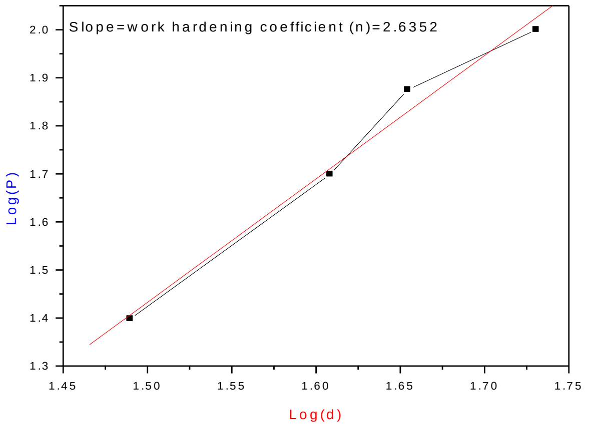

Fig. 6: Plot of log (P) versus log (d) for LLOA crystal

3.6. Dielectrics studies

Dielectric analysis was carried out for the grown crystal of LLOA to understand the electrical properties. The dielectric constant and loss factor of the sample crystal were measured using an LCR meter in a frequency range 10^2 Hz-10^6 Hz at room temperature. The grown crystal of LLOA was polished and coated on either side with silver paste to make a parallel plate capacitor. The values of capacitance with sample and without sample were measured and dielectric constant was calculated. The dielectric loss of LLOA crystal was measured directly from the LCR meter. The plots of dielectric constant and dielectric loss versus frequency (log f) at different temperatures for LLOA crystal are shown in the figures 7 and 8.

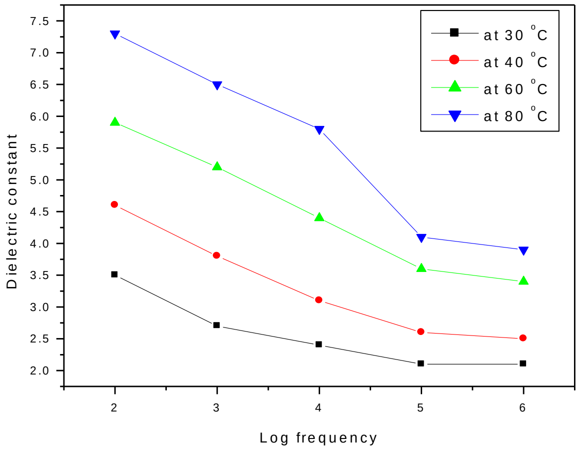

Fig. 7: Plots of dielectric constant versus frequency at various temperatures for LLOA crystal

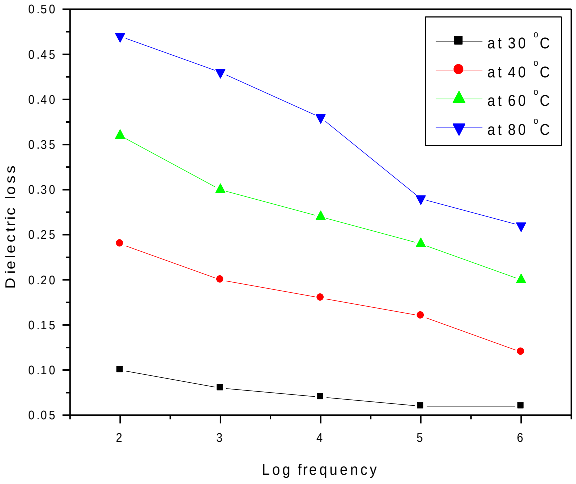

Fig. 8: Plots of dielectric loss versus frequency at various temperatures for LLOA crystal

From the results, it is found that both dielectric constant and loss factor of LLOA crystal are high in the low frequency region and these values decrease with increase of frequency. The higher values of dielectric constant in the low frequency region are due to space charge polarization [16]. Generally, the dielectric loss of the material denotes dissipation of the electrical energy due to electrical conduction, dielectric relaxation, dielectric resonance etc. Here dielectric loss of LLOA crystal is highly dependent on the frequency of the applied field and this behavior is similar to an ionic crystal. When the temperature of LLOA crystal increases, polarization increases hence dielectric constant also increases. Defects will be introduced in the crystal as the temperature increases and hence the dielectric loss increases. From the results, it is observed that the dielectric constant values for LLOA crystal are low at higher frequencies and according to Miller's rule low value of dielectric constant is a suitable parameter for the enhancement of SHG coefficient of the sample. The low dielectric loss of the sample at room temperature indicates that LLOA crystal is of good quality crystal.

3.7. SHG measurement

Second harmonic generation (SHG) measurement was carried out using Kurtz and Perry experimental set-up [17]. A Q-switched Nd: YAG laser (quanta RAY model LAB-170-10) was used in the experiment. The laser operates at 1064 nm and 8 ns pulse with the repetition rate of 10 Hz. The green emission of wavelength 532 nm from the powder sample confirms the NLO activity of LLOA crystal. Here KDP crystal was used as the reference sample. From the data, it is observed that the relative SHG efficiency of LLOA crystal is 1.26 times that of KDP sample.

4. CONCLUSIONS

Slow evaporation technique was used to grow the single crystals of L-lysine oxalic acid (LLOA). From XRD studies, it is concluded that LLOA crystal crystallizes in orthorhombic crystal system. The functional groups like NH_3^+, OH, COO^-, CH, CN, CH_2 etc of LLOA crystal were identified by FTIR technique. Fluorescence spectrum of LLOA crystal was recorded and the emission peaks have been identified. The Vickers microhardness of the grown LLOA crystal measured and work hardening coefficient of the sample was calculated. The dielectric measurement was carried out for LLOA crystal at various frequencies and temperatures and the frequency response has been analysed. SHG efficiency of LLOA sample was found to be 1.26 times that of KDP crystal. The elemental composition of the grown crystal of LLOA was found by EDAX and CHN analyses.

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6. REFERENCES

1. Ramesh Kumar G, Gokul Raj S, Shankar R, Mohan R, Pandi S P, Jayavel R et al. *Journal of Crystal Growth*, 2004; **267:** 213-217.
2. Chemla DS, Zyss J, et.al. Nonlinear Optical Properties of Organic Molecule and Crystal, Academic Press, New York, 1987; **1(2)**.
3. Suresh kumar MR, Ravindra HJ, Jayarama A, Dharamaprakash SM, et.al. *Journal of crystal Growth*, 2006; **286:**451-456.
4. Razzetti C, Ardoino M, Zanotti L, Zha M, et.al. *Cryst. Res. Technol*, 2002; **37:**456-465.
5. Narayan Bhat M, Dharmaprakash SM, et.al. *J. Cryst. Growth*, 2002; **236:**376-380.
6. Meera K, Muralidharan R, Tripathi AK, et.al, *J. Cryst. Growth,* 2004; **263:**524-531.
7. Marchewka MK, Debrus S, Ratajczak H et.al, *Cryst. Growth Des,* 2003; **3:**587.
8. Ramesh Babu R, Vijayan N, Gopalakrishnan R, Ramasamy P, et.al, *Cryst. Res. Technol*, 2006; **41:**405.
9. Lefur Y, Bagieu M, Beucher, Masse R, Nicoud JE,et.al, Chem.Mater,1995;**8:**68.
10. Krishnakumar V, Nagalakshmi R, Manohar S et.al, *Spectrochimica Acta Part A*, 2008; **71:**471-479.
11. Srinivasan N, Sridhar B and Rajaram R K 2001 Acta Crystallogr. E57 888.
12. Briget Mary M, Umadevi M and Ramakrishnan V 2005 Spectrochim Acta A 61 3124.
13. Pickworth Glusker J., Trueblood K. N,Crystal structure analysis, A premier, Oxford University press, New York, 1985
14. Skoog DA, Priciples of Instrumental Analysis 3rd. Ed. Saunders College Publishing 1985.
15. Neil, H.O, Hardness measurements of metals and alloys, Chapman and Hall, London, 1967.
16. Krishnan P, Selvarajan TH, Freeda CK. et al, *Mahadevan, Physica B*, 2009; **404:**289.
17. Kurtz SK, Perry TT, *J. App. Phys*, 1968; **39:**3798.