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Optical and Biological investigations of semi-organic L-Serine Zinc Acetate single crystal grown by solution growth technique

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Abstract

A semi organic nonlinear optical, L-Serine Zinc Acetate (LSZA) single crystals have been grown by slow evaporation technique. Bulk size single crystal was obtained in 47 days. Using single crystal X-Ray diffractometer to find inter atomic distance values are a = 14.31Å, b =5.28Å and c = 10.84Å, α=90˚, β=100˚, γ=90, and volume 807 $Å^3$ with Non - Centro symmetric monoclinic space group C. The UV-Vis graph of the grown L-Serine Zinc Acetate crystal shows good transmittance in the entire visible region. The cut of wavelength is 245 nm. The band gap energy was found to be 5.06 eV. The dielectric constant measurements of the crystal at different temperatures and frequencies of the applied field are measured and calculated. The anti-bacterial and anti-fungal activities of the developed materials were performed by Agar well diffusion method against the standard bacteria Escherichia coli, Staphylococcus aureus, Salmonella typhi, Shigella flexneri (S. flexneri) and against the fungus Aspergillus Niger, Candida albicans and Aspergillus clavatus. Scanning Electron Microscope (SEM) results were carried out to study the surface morphology of the grown crystal. The second harmonic generation efficiency of the developed materials was calculated using Nd: YAG Q-switched laser and found that LSZA is 1.9 times higher than that of KDP crystal.

Keywords: Semi organic crystal; Optical Properties; Dielectric Studies; SEM Studies; Antimicrobial activity.

1. INTRODUCTION

Now a day nonlinear optical bulk size single crystal is playing main role in the field of science and technology. Second harmonic generation is the major role of high-speed information processing, optical communications and optical data storage [1-3]. Comparing organic and inorganic materials have different characterisation. Inorganic material possesses high melting point, high mechanical strength. But their optical nonlinearity is very lower value. Whereas, organic compounds are having high nonlinearity due to the weak Vander Waals and hydrogen bonds and possess high degree of delocalization. Organic materials L-Serine having good nonlinear optical property but mechanical strength, chemical stability and low temperature [4, 5].

In order to overcome all these difficulties, a new semi organic L-Serine Zinc Acetate (LSZA) single crystal was grown. Semi-organic materials have the potential for combining high optical nonlinearity and chemical flexibility of organics with the physical roughness of inorganic. In this present work Zinc Acetate is doped with L-Serine to prepare a new semi organic nonlinear optical material. The present report is the crystal growth and characterization studies of L-Serine Zinc Acetate (LSZA) single crystal grown by solution growth method. The developed materials is subjected to X-ray diffraction, NLO studies, thermal analysis, Micro hardness, Dielectric studies, SEM Analysis and Antimicrobial activity are presented and discussed.

2. EXPERIMENTAL PROCEDURE

2.1 Material Synthesis

The new semi organic material L-Serine Zinc Acetate (LSZA) was synthesized by mixing an aqueous solution of L-Serine with Zinc Acetate in the stoichiometric ratio of 1:1.

The correct amount of Zinc Acetate and L-Serine was dissolved in pure distilled water. The solution was mixed with a magnetic stirrer and filtered after complete dissolution of the starting materials. The prepared solution was left stand by for several days at room temperature thereby good quality transparent crystal were obtained in 47 days shown in Fig.1.

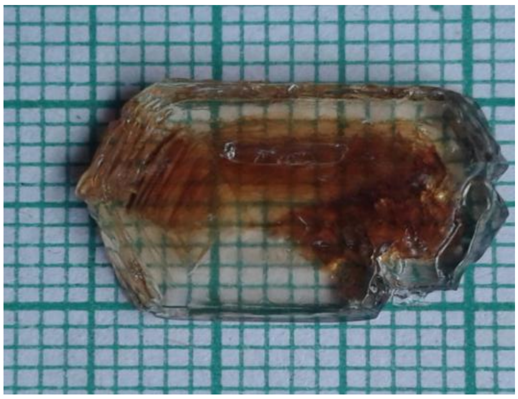

Fig.1. L-Serine Zinc Acetate (LSZA) single Crystal

2.2. Solubility

The solubility study was carried out in a constant temperature bath with temperature controller of accuracy ±0.01◦C. Solubility of L-Serine Zinc Acetate (LSZA) was determined at four different temperatures 30, 35, 40 and 45°C. The solution was stirred continuously or several hours to achieve homogenization using a magnetic stirrer. After attaining saturation, the equilibrium concentration of the solute was estimated gravimetrically. The solubility curve of L-Serine Zinc Acetate (LSZA) is shown in Fig.2.

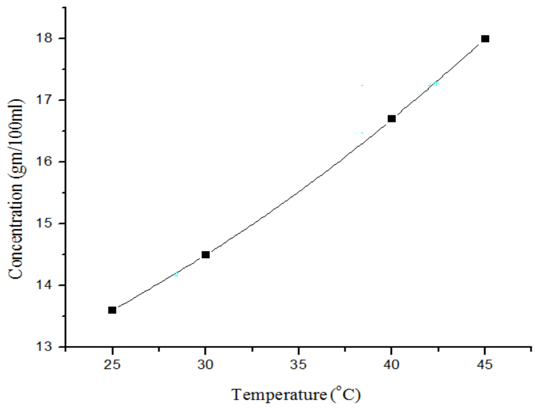

Fig.2 Solubility curve of L-Serine Zinc Acetate (LSZA)

3. CHARACTERIZATION TECHNIQUES

Single crystal XRD was recorded by Enraf Nonius CAD/MACH3 single crystal X-ray diffractometer to find the molecular structure, atomic coordinates, bond lengths, bond angles and molecular orientation. Mechanical properties of the grown LSZA crystal were studied using M H – 5 hardness testers. The Antimicrobial activity (antibacterial and antifungal activity) of the grown crystal was calculated by agar well diffusion method. To know the surface morphology of the crystal Scanning Electron Microscopy (SEM) was carried out.

4. RESULTS AND EXPLANATION.

4.1. Single crystal X-Ray Diffraction Analysis

LSZA was subjected to Single crystal X-ray diffraction study. The X-ray data were collected using an Enraf Nonius CAD/MACH3 single crystal diffractometer instrument for grown L-Serine Zinc Acetate crystal. The calculated lattice parameter values are a = 14.31Å, b =5.28Å and c = 10.84Å, α=90˚, β=100˚, γ=90, and volume 807 $Å^3$ with Non - Centro symmetric monoclinic space group C. The XRD results are in good agreement with the reported values and thus confirm the growth of grown LSZA crystal.

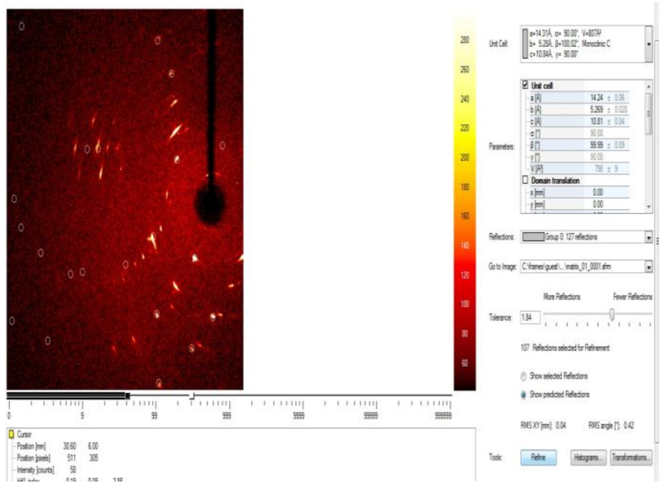

Fig. 3. X-Ray Diffraction Pattern L-Serine Zinc Acetate crystal

4.2 Optical Absorption Analysis

UV-Vis study is to find the absorption and transmission of the developed materials. Optical absorption and transmission property is an important role of a NLO material. Fig. 4show the UV Absorption spectrum of the materials scanned between the wavelengths of 190 to 1100 nm. There is no absorption band in the region between 250 to 1100nm. This shows that the absence of absorbance due to electronic transitions above 245nm. Hence the crystal of LSZA is expected to be transparent to all the UV-Visible radiation between these two wavelengths [6]. Using the relation

$$E_g = 1240/\lambda$$

The band gap energy was found to be 5.06 eV.

Transmission spectra are very important for any NLO material. The transmission spectra obtained is shown in the graph Fig. 5. The transmittance window in the visible region and IR region enables good optical transmission of the second harmonic frequencies of Nd: YAG lasers.

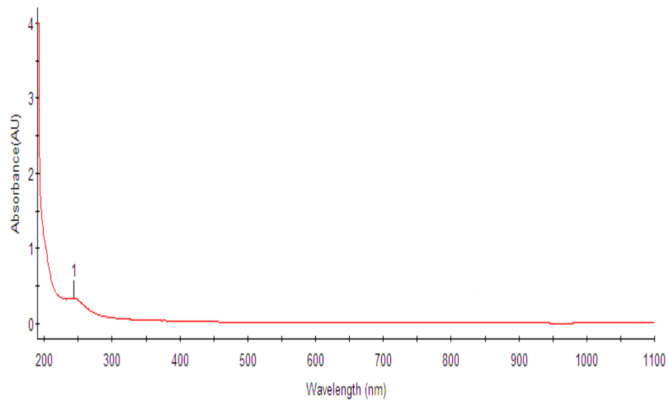

Fig. 4. Absorption spectra for L-Serine Zinc Acetate (LSZA) Crystal

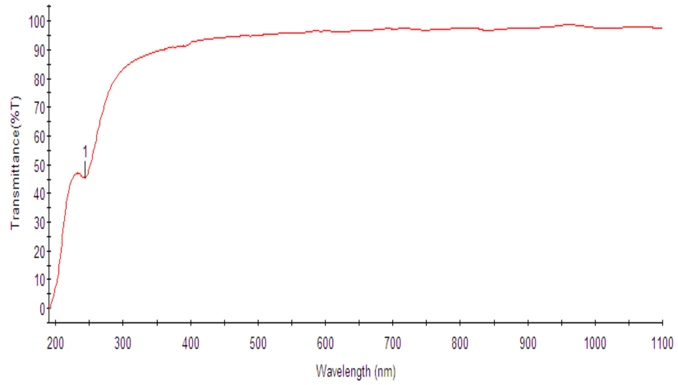

Fig. 5. Absorption spectra for L-Serine Zinc Acetate (LSZA) Crystal

4.3 Mechanical Studies

The stability of the materials is very important role for device fabrication. Vickers micro hardness is used to find the mechanical strength of the developed materials. It is related with elastic constants, yield strength, brittleness index and temperature of cracking [7]. The punching marks were made on the surface of the materials at normal temperature by applying loads of 25, 50 and 100 grams. The load increases Hv value also increases from 25 to 100 g and crack occurs at higher loads. The MH–5 hardness tester is used to find the mechanical strength of the materials. The Vickers micro hardness values were calculated from the standard formula [8]

$$Hv = 1.8544 (P/d^2) \text{ kg/mm}^2 \qquad \text{------- > Eq}$$

The micro hardness value was taken as the average of the several impressions made [9].

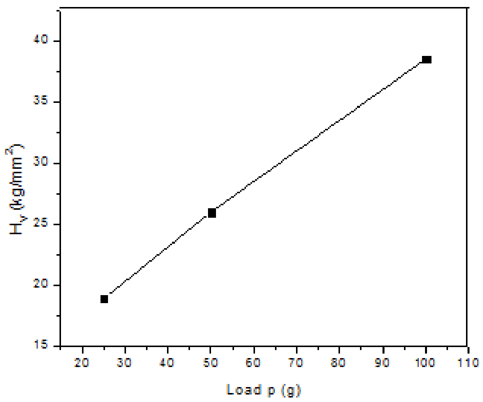

Fig.6 Variation of hardness with load P.

4.4. Thermal analysis

The thermal stability of the developed materials is to find using Differential scanning calorimeter (DSC). The instrument NETZSCH STA 409C in the temperature range 50- 400ºC at the heating rate of 10ºC/min in nitrogen atmosphere. For the observation of thermal absorption of the materials is usually kept in an alumina crucible. In the scanning graph (Fig.7), the exothermic peak of the materials is at 110ºC is indicate to melting point of the crystal. After that there is no phase transition involved in the materials. This indicates that the material has a large temperature range that is attractive functional for NLO function. Based on the melting point the crystal can be adopted for laser production at high temperature. From the graph, at the temperature 250ºC the crystal is totally decomposed. The sharp peaks in the graph are shows that the grown crystal has pure crystalline materials.

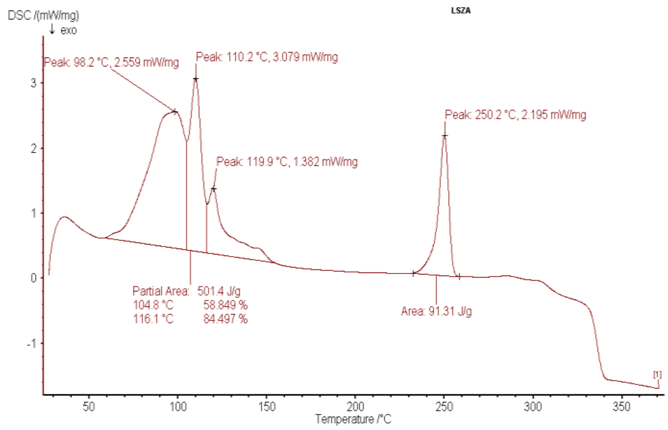

Fig.7. Differential scanning calorimeter (DSC) studies

4.5 Dielectric Studies

The dielectric constant and dielectric loss were carried out using TH 2816 A Digital LCRZ Meter in the frequency from 50 Hz to 2 MHz. For the dielectric measurement we can make a capacitor with the crystal as a dielectric medium. Both opposite faces of the crystal is coated by silver paste and the thickness of the crystal is 0.83mm. The sample was placed between two cooper electrodes, which act as a parallel plate capacitor. Dielectric studies give useful information about charge transport mechanism inside the crystal. The observed readings of dielectric constant and log frequency are used to draw a graph is shown in Fig. 8. From the graph the applied frequencies increases the value of dielectric constant is decreases. Same in reverse, if the frequency decreases the dielectric constant increases. The dielectric constant is depends on the four polarizations namely, space charge, orientation, electronic and ionic polarization and its low value at higher frequencies may be due to the loss of significance of these four polarizations gradually [10]. The especially low value of dielectric constant at higher frequencies are vital for these materials in the production of photonic and NLO devices.

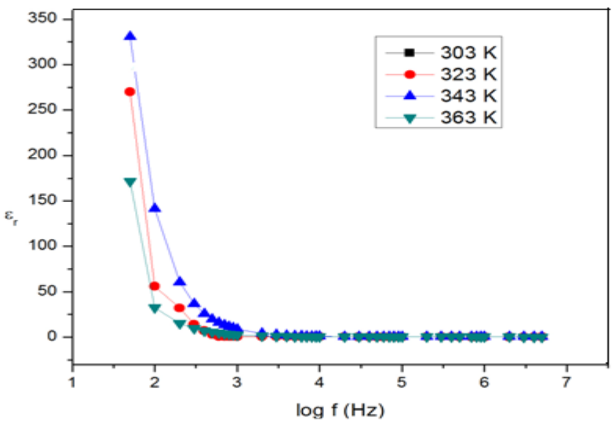

Fig. 8. The variation of dielectric constant with log frequency

4.6 Antibacterial studies

The variation in the effectiveness of the different compounds against different organisms depends on their impermeability of the microbial cells or on the difference in the ribosome of the microbial cells [11]. Antibacterial activities were investigated by using agar well diffusion method, against the Staphylococcus aureus (RCMB 010010) {as Gram-positive bacteria} and Salmonella typhi (RCMB 010043) and Escherichia coli (RCMB 0100052) and Shigella flexneri {as Gram-negative bacteria}. Different concentrations of Samples (250, 500, 700, 1000µg/well) were used in this study. Nutrient Agar (NA) plates were inoculated with test organisms. The plates were evenly spread out. Then wells were prepared in the plates with a cork borer. Each well was loaded with 0.1ml of corresponding concentration of sample and 10 µg of Tetracycline dissolved in 1 mL of DMSO was used as a Positive control for antibacterial activity. The plates were incubated for 24h at 37°C. Tetracycline was used as a standard drug for the comparison bacterial results. The diameter of zone of inhibition in millimeters for the grown crystal is shown in table 2 the photograph of antibacterial activity of the bacteria's are shown in Figs. 9 (a), (b), (c), (d) respectively. From the data it is observed that the LSZA crystal has good inhibitory action against gram positive and gram negative bacteria's [12,13]. Moreover the antibacterial action of the LSZA crystal towards E. coli, Staphylococcus aureus, Salmonella typhi is stronger than that towards Shigella flexneri. Hence this result provides a strong platform for further researchers to probe and develop organism specific antibiotic.

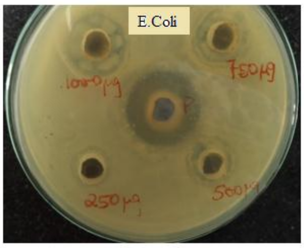

Fig.9 (a) Zone of Inhibition of LSZA in E.coli

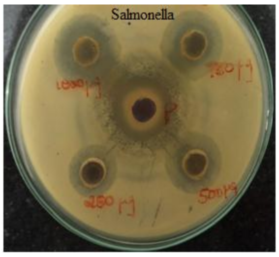

Fig. 9 (b) Zone of inhibition of LSZA in Salmonella

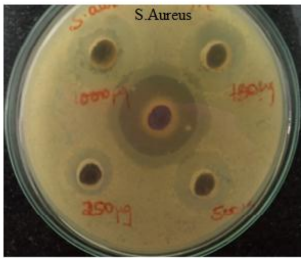

Fig. 9 (c) Zone of inhibition of in S. Aureus

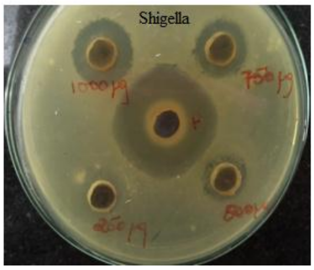

Fig. 9 (d) Zone of inhibition of in Shigella

4.7 Antifungal studies

The synthesized compounds LSZA were tested for antifungal activity by using Ketoconazole as standard drug against three fungal strains including Aspergillus Niger, candida albicans and Aspergillus clavatus using agar well diffusion method. Antifungal activity was carried out using well diffusion method. Petri plates were prepared with 20 ml of sterile DA (Hi- media, Mumbai). The test culture was swabbed on the top of the solidified media and allowed to dry for 10 min. Wells were made on the media using a well borer. Different concentrations of the sample (250, 500, 750& 1000 µg/per well) were loaded on the wells. Ketoconazole (10µg/1ml) was used as a positive control. These plates were incubated for 48hr sat 28°C. Zone of inhibition was recorded in millimeters (mm). The filamentous fungi were grown on Sabouraud dextrose agar (SDA) slants at 28ºC for 10 days. The spores were collected using sterile double distilled water and stored in refrigerator. The grown crystals were found to be moderate active compared to the standard [14]. The activity of the

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LSZA crystal was found to increase with the concentrations of the samples. The diameter of zone of inhibition in millimeters for the grown crystal is shown in table 3 the photograph of antifungal activity of the Aspergillus niger, candida albicans and Aspergillus clavatus are shown in Figs. 10 (a), (b), (c) respectively.

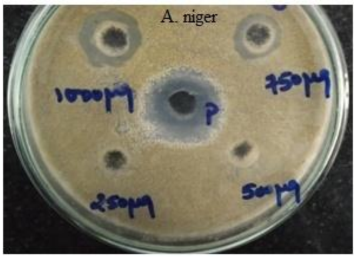

Fig. 10 (a) Zone of Inhibition of LSZA in A. nigerin

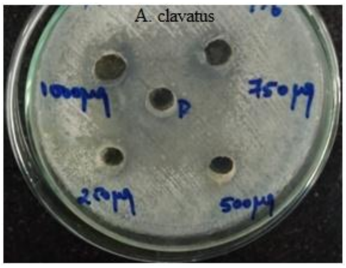

Fig. 10 (b) Zone of Inhibition of LSZA A. clavatus

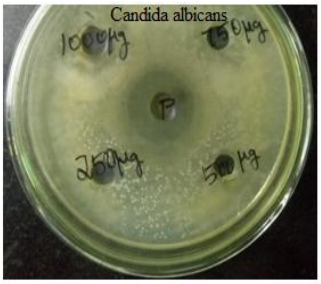

Fig. 10 (c) Zone of Inhibition of LSZA in candida albicans

4.8 SEM studies

The Scanning Electron Microscopy (SEM) image of the grown crystal was recorded using FEI Quanta FEG 200 - High resolution Scanning Electron Microscope to study the surface morphology of LSZA crystal. A two dimensional image was generated over a selected area of the sample. Since LSZA is a semi organic crystal, which is poor conducing in nature, the sample was subjected to gold/carbon coating.

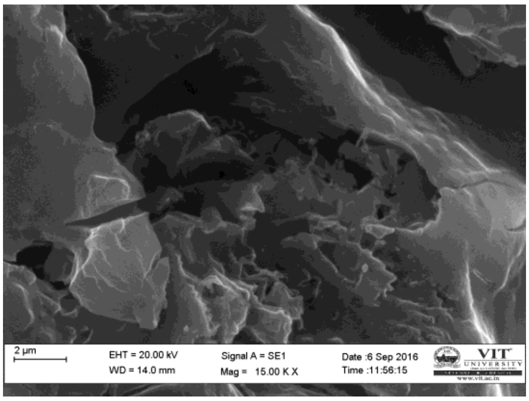

Fig. 11. Scanning Electron Microscopy (SEM) image

From the figure.11, it is clear that the surface of the grown crystal appears very smooth though it has pots and microcrystal on the surface. The grain boundaries are clearly seen which shows the perfect growth of the crystal.

4.9. Nonlinear optical studies

For finding the second harmonic generation, Kurtz and Perry powder method is an important tool for researchers searching for organic/semi organic/inorganic NLO material. The materials were grinding into fine powder and filled inside the micro capillary tube. The input energy of 3.2 mJ/pulse and pulse width 8ns was incident on the fine crystalline powder using Nd: YAG laser (1064 nm). When the laser light is fall on the sample, the absorption takes place. Due to emission the Second Harmonic Generation signal at 532 nm is detected using a photomultiplier tube (PMT). The emission wavelength of green radiation is confirmed that the materials have second harmonic generation. It is observed that the measured second harmonic generation efficiency of LSZA crystal was 1.9 times higher than that of KDP crystal.

5. CONCLUSION

L-Serine Zinc Acetate (LSZA) single crystal has been grown by solution growth slow evaporation technique. The Single crystal X-ray diffraction studies confirm the grown crystal belongs to Triclinic (P) system. The band gap energy was found to be 5.06 eV. Vickers micro hardness reveals that the hardness number Hv increases with increasing load exhibiting Reverse Indentation Size Effect and Meyer's index, n, Yield strength, and elastic stiffness constant have been carried out by indentation method. The dielectric constant and dielectric loss measurements of the crystal at different temperatures and frequencies of the applied field are measured and calculated.

The antibacterial results revealed that newly synthesized crystal show higher activity than the ligand but markedly lower than the standard drug. The SHG measurement has confirmed the NLO property of the grown crystal.

REFERENCES:

[1] P.N. Prasad and D.J. Williams. Introduction to Nonlinear Optical Effects in Molecules and Polymers; Wiley: New York, 1991.

[2] N.J.Long, Organo metallic compounds for nonlinear optics the search for enlightenment, Angew. Chem. Int. Ed.34 (1995)21–38.

[3] T. Pal, T. Kar, X.Q. Wang, G.Y. Zhou, D. Wang, X.-F. Cheng, Z.-H. Yang, Growth and characterization of nonlinear optical material, LAHClBr – a new member of L-arginine halide family, J. Cryst. Growth 235 (2002) 523–528.

[4] R. Hierle, J. Badan, J. Zyss, Growth and characterization of a new material for nonlinear optics: methyl-3-nitro-4-pyridine-1-oxide (POM), J. Cryst. Growth69 (1984) 545–554.

[5] J. Williams, Nonlinear Optical Properties of Organic and Polymeric materials, Am. Chem. Soc. Symp. Ser. 233, American Chemical Society, Washington D.C., 1983., 216 - 218.

[6] R.M. Silverstein, G.C. Bassler, T.C. Morrill, Spectroscopic Identification ofOrganic Compounds, 4th Ed., John Wiley and Sons, New York, 1991.

[7] C.N.R.Rao, Ultra violet and visible spectroscopy of organic compound, Prentice-Hall of India Pvt. Ltd., New Delhi, 1984.

[8] R.Shankar, C.M.Raghavan, R.MohanKumar, R. Jayaval, Growth and characterization of a new semi organic nonlinear optical thiosemicarbazide cadmium chloride monohydrate single crystal, J.Cryst. Growth 305(2007)156–161.

[9] J.P.Cahoon,W.H.Bhoughton, A.R.Katzuk, Metallurgical and Metal Transactions 2(1971)1979.

[10] W.A.Wooster, Reports in Progress in Physics 16(1953)62.

[11] CharlesKittle,in: Introduction to Solid State Physics, Wiley Eastern Limited, New Delhi,1993.

[12] Prabhakaran R, Geetha A, Thilagavathi M, Karvembu R, Krishnan V, Bertagnolli H, et al. Synthesis, characterization, EXAFS investigation and antibacterial activities of new ruthenium (III) complexes containing tetradentate Schiff base. J InorgBiochem 2004, 98(12):2131–40.

[13] Malibari AA: Isolation and screening of antibiotics producing Streptomycetes from western region soils of Saudi Arabia. J King Abdulaziz Univ Sci 1991; 3:31-42.

[14] Zhou J, McClean S, Thompson A, Zhang Y, Shaw C, Rao P, Bjourson AJ: Purification and characterization of novel antimicrobial peptides from the skin secretion of Hylaranaguentheri. Peptides 2006; 27:3077-3084.