Effect of Amino acid doping on the Growth and Properties of Potassium Chloride Crystal

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Abstract — Semi-organic nonlinear optical crystal of Glycine Potassium Chloride (GPC) and L-Histidine Potassium Chloride (HPC) has been grown by slow evaporation solution growth technique. The grown crystals have been investigated through various techniques. The X-ray diffraction (XRD) studies confirm the crystalline nature and purity of the grown crystals. FTIR analyses were used to estimate qualitatively the presence of the functional groups in the grown crystal. UV-Visible spectrum shows that optical quality of the as grown crystals. The emission spectra of the crystals were recorded using Spectrofluorometer. The emission peaks of GPC and HPC were absorbed at 452 nm and 530 nm respectively. The optical band gap energy was estimated as 2.7468 eV and 2.3425 eV. Thermo gravimetric and Differential Thermal Analysis (TGA-DTA) measurements indicate the thermal stability of the grown crystal. Scanning electron microscope (SEM) and energy dispersive X-ray analysis (EDAX) are presented and discussed. Nonlinear optical properties of GPC were 1.33 times that of KDP and HPC was not NLO active.

Index Terms — Amino acids, EDAX, GPC, HPC, Fluorescence, FTIR, NLO, SEM, TG-DTA, UV-Vis, XRD

1 INTRODUCTION

Potassium chloride (KCl) is an inorganic salt that belongs to cubic crystal. It is used in medicine in treatment of hypokalemia and food processing. KCl single crystal is widely used in the production of optical windows with wide band gap (~8eV) [1]. Moreover, there is application for optical components in wide spectrum band from the ultraviolet to the infrared, because of its transparency over the entire range of wavelengths. Though potassium chloride has a low refractive index, its damage threshold is high [2].Amino acid family crystals are the famous organic materials playing an important role in the field of non-linear optics due to the fact that almost all the amino acids have chiral symmetry and crystallize in non-centrosymmetric space groups such as L-histidine nitrate, L-arginine triflurocetate . An amino acid consists of a free NH_2 (amino) and a free COOH (carboxyl) group. Both are attached to the same carbon atom. Recently several new complexes incorporating the amino acid L-Alanine have been crystallized and their structural, optical and thermal properties have been investigated [3-6]. Semi organic materials possess the advantage of both inorganic and organic materials in terms of high thermal and mechanical stability as well as broad optical frequency range, higher second harmonic generation and high damage threshold [7-9]. Glycine ($C_2H_5NO_2$) is a non essential, simplest of the 20 protein amino acids which function as a neurotransmitter and one of the principle components of structural proteins, enzymes and hormones. It is the only protein forming amino acid without a center of chirality. L-Histidine ($C_6H_9N_3O_2$) is an essential amino acid, optically active, polar aromatic and is used to develop and maintain a healthy tissue in all parts of the body. From this motivation we select amino acids as dopant to this research work. We have grown doped KCl crystals by solution growth technique and subjected to different types of characterizations Fourier Transform Infrared Spectroscopy (FTIR), UV-Vis Spectroscopy, X-ray Diffraction (XRD), Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDAX), Fluorescence Spectroscopy, Nonlinear optic measurement (NLO), Thermo gravimetric and differential thermal analysis (TGA-DTA).

2 MATERIALS AND METHODS

2.1 GROWTH TECHNIQUE

Potassium chloride of AR (Merck) grade powder was selected as source material. This Powder was initially added with double distilled water and stirred well using magnetic stirrer for 2 hours continuously. Then the prepared super saturated potassium chloride solution was filtered with micro filter paper with 0.1 μm porosity. This mother solution was poured into two 100 ml beakers. Out of these two beakers one beaker containing the 50 ml of pure KCl solution was doped with 0 .1 mol percent of Glycine was added and other beaker containing 50 ml of KCl solution was doped with 0.1 mol percent of Histidine. Doped solutions were separately again stirred well using magnetic stirrer and filtered again using the filter paper then covered with separate perforated paper and each were placed in the dust free atmosphere in separate places and allowed to evaporation of solution, the seed crystals were grown from the respective solutions after two days. The seed crystals were harvested. Each one seed crystals were again placed in the same respective mother solutions and allowed for even growth until to attain the considerable sizes. These crystals were attained considerable size at 12 days. Fig.1. and Fig.2. shows the photograph of as grown GPC and HPC crystals with an average size of 5x5x3mm and 3x3x3mm respectively.

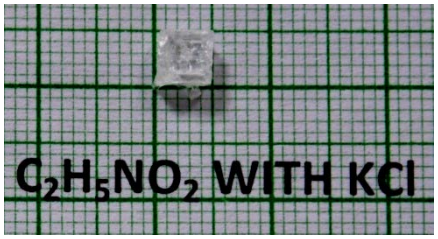

Fig.1.Photograph of as grown GPC crystal.

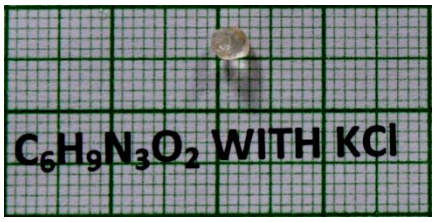

Fig.2.Photograph of as grown HPC crystal.

2.2 CHARACTERIZATION

The harvested single crystals have been analyzed by different instrumentation methods in order to check its suitability for device fabrication. The Powder X-ray diffraction (XRD) analysis has been carried out for the as grown crystals of GPC and HPC using SHIMADZU Model XRD-6000 made in Japan.The powdered samples were scanned in the range 10-90° at a scan rate of 2°/min. The Fourier transform infrared spectrums were recorded by SHIMADZU Model IR Perstege - 21 made in Japan. The presences of functional groups were identified from this spectral analysis in the range 4000- 400 cm^{-1}. The UV-Vis spectrums were recorded in the range 200-800 nm using JASCO - Vis NIR Model V-670 spectrometer. The emission spectra of GPC and HPC crystals were recorded in the range 250-700 nm using PERKIN ELMER Model LS-45 Spectrofluorometer. The Thermal stability of the samples were tested using thermo gravimetric analysis (TGA) and Differential thermo gram analysis (DTA) using SIINT Model TG/DTA 6200 made in Japan. The analyses were carried out between 30°C and 800°C in the nitrogen atmosphere at a heating rate of 20°C min^{-1}. The Scanning electron microscopy (SEM) and Energy dispersive X-ray analysis (EDAX) were performed using the JEOL Model JSM – 6390 made in Japan. Non linear optic measurements were carried out by using Kurtz powder technique. A Q-switched Nd: YAG laser beam of 1064nm wavelength with 1.9 mJ/pulse input power, 8ns pulse width and repetition rate 10Hz was used to estimate SHG efficiency of the as grown crystals.

3 RESULTS AND DISCUSSION

3.1 X-RAY DIFFRACTION ANALYSIS

Fig.3. Shows the X-ray powder diffraction pattern of the grown crystals of GPC and HPC. The sharp and well defined Bragg's peaks at specific 2θ angles confirm the crystalline nature and purity of the crystal. The lattice parameter values were calculated (Table1). Both the crystals are formed in cubic structure with space group Fm3m. The obtained lattice parameter values confirmed that the addition of amino acids did not change the structure of KCl.

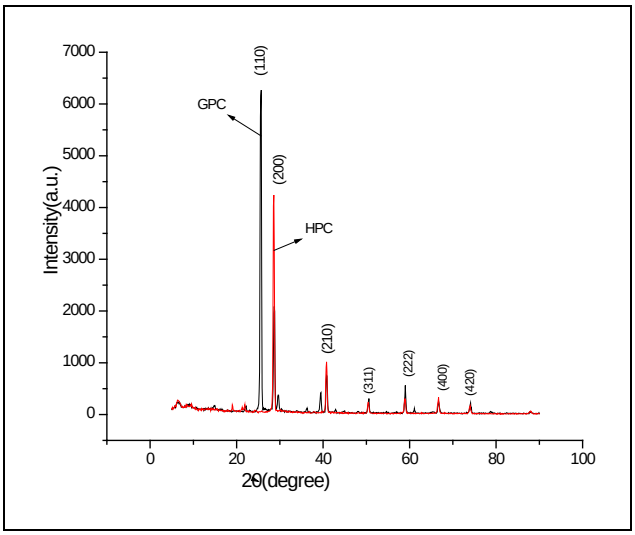

Fig.3. Powder XRD pattern of GPC and HPC crystals

TABLE 1
LATTICE PARAMETERS OF GPC AND HPC CRYSTALS.

S.No	Lattice parameter In Å units	GPC calculated Value	HPC calculated value
1	a	6.3227	6.3243
2	Volume(Å)	252.7596	252.9515

3.2 UV-Vis ANALYSIS

The recorded UV- Vis-NIR transmission spectrum of the grown GPC and HPC crystals are shown in the Fig.4. From the spectrum, it is noted that the UV transparency cut off is 240 nm and there are no significant absorptions observed in the entire region of the spectrum. . The transmission extends nearly from 250nm to 800nm, makes it valuable for those applications requiring blue/green light. It is an important requirement for NLO materials having nonlinear optical applications [10], [11].

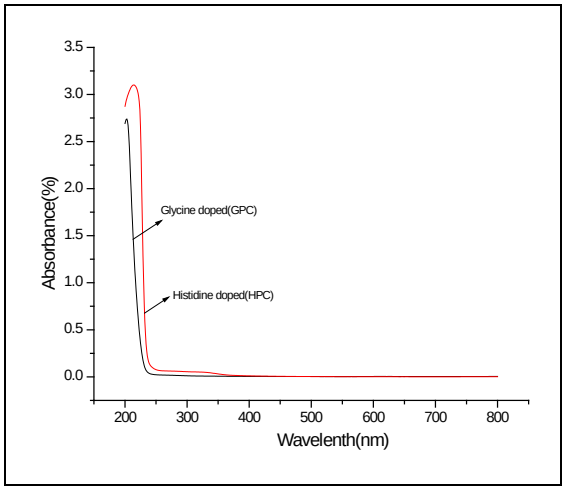

Fig. 4. UV- Vis spectrum of GPC and HPC crystals.

3.3 FTIR STUDIES

The Fourier transform infrared spectral analysis is a technique in which almost all functional groups in a molecule absorb characteristic frequencies. The functional groups of GPC and HPC crystals involved in vibration frequency have been identified using FTIR spectroscopy. The FTIR spectrum was recorded in the range 400-4000 cm^{-1}. The FTIR spectrum of GPC and HPC crystals are shown in Fig.5. The absorption peaks correspond to the molecular group vibrations are also shown in table 2. The relations of molecular group vibrations and the characteristics absorption bands were assigned according to the theories of infrared spectra [12]. The functional groups NH_3^+, CH, CN and COOH were identified and assigned for GPC and HPC crystal. The strong peak at 1327 and 1342 $cm^{-1}$is assigned to C-O stretching of GPC and HPC crystals. The peak at 1126and 1145 cm^{-1} is assigned to C-C stretching. The peaks appearing at 624 and 682 cm^{-1} are due to COO^- wagging and COO^- in plane deformation. CH_2wagging vibrational modes are observed at 1247 cm^{-1} . CH_2 sym-metric stretching is appeared at 3000cm^{-1}. The assignments confirm the presence of functional group present in Absorption peak at 2360 cm^{-1} 2314cm^{-1}could be the evidence for amino acid doping into as grown crystals.

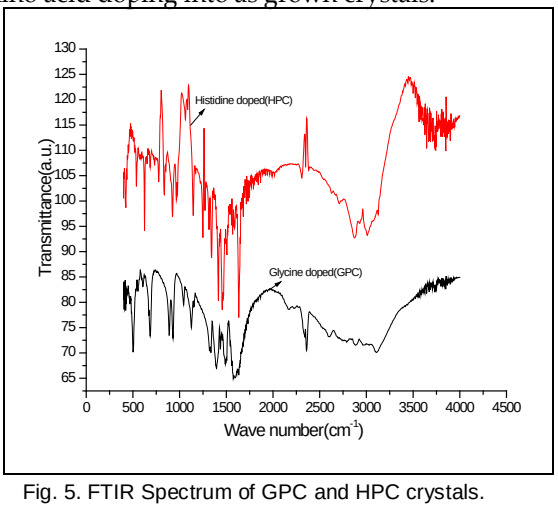

Fig. 5. FTIR Spectrum of GPC and HPC crystals.

TABLE 2
VIBRATIONAL BAND ASSIGNMENTS OF GPC & HPC CRYSTALS.

S. No	Observed FTIR Frequencies (cm^{-1}) for GPC	Observed FTIR Frequencies (cm^{-1}) for HPC	Vibrational Assignments
1	503	----	COO rocking
2	----	540	COO rocking
3	603	624	COO wagging
4	682	----	COO in plane deformation
5	887	835	C-C Stretching
6	927	923	NH_3^+roking
7	----	970	CH_2 rocking
8	1039	----	C-N Stretching
9	1126	1145	C=C Stretching
10	----	1247	CH_2 Wagging
11	1327	1342	C-O Stretching
12	1394	----	C-O Stretching
13	----	1462	CH_2 bending
14	1492	----	NH_3+ symmetric deformation
15	----	1633	Carboxylate group/ C=O asymmetric stretching
16	2360	2314	Absorption of dopant
17	2600	----	NH_3 Stretching
18	----	3000	CH_2 symmetric stretching

3.4 FLUORESCENCE STUDIES

The spectrum recorded by the emission of photo generated minority carriers is a direct way to measure the band gap energy [13]. Fig.6. shows the emission spectrum of GPC and HPC. The peaks at 452 nm and 530nm were observed in the

emission spectrum as shown in Fig.5. Band gap energy of GPC and HPC crystals were calculated using the formula $E_g = hc/\lambda e$. Where h, c and e are constant λ is the wavelength of fluorescence. The calculated band gap energy of GPC crystal is 2.7468 eV and HPC is 2.3425 eV.

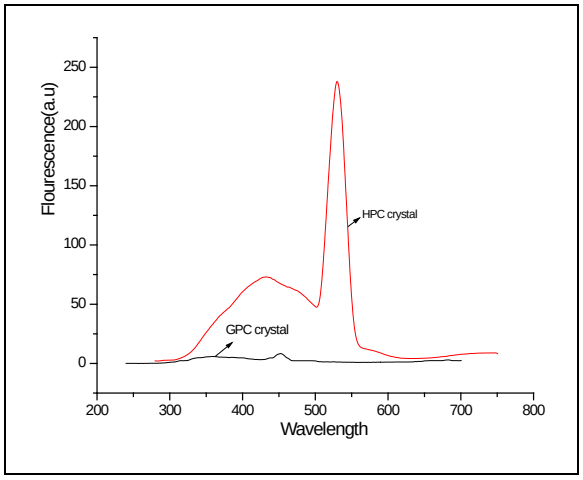

Fig.6.Emission spectrum of GPC and HPC crystals

3.5 THERMO-GRAVIMETRIC & DIFFERENTIAL THERMAL ANALYSIS

Thermo gravimetric and differential thermal analyses give information regarding phase transition, water of crystallization and different stages of decomposition of the crystal system. The TGA and DTA curves obtained for GPC and HPC are shown in figures 7 and 8. The weight loss starts at 80°C and 200°C for GPC and HPC crystal. At 250°C to 700°C the weight loss is more for GPC than the HPC crystal. The sudden decomposition takes place at 250°C observed in GPC.

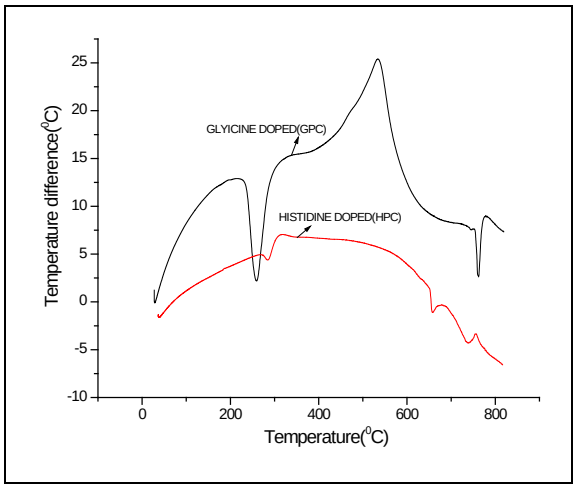

Fig.7.TGA curves of GPC and HPC crystals.

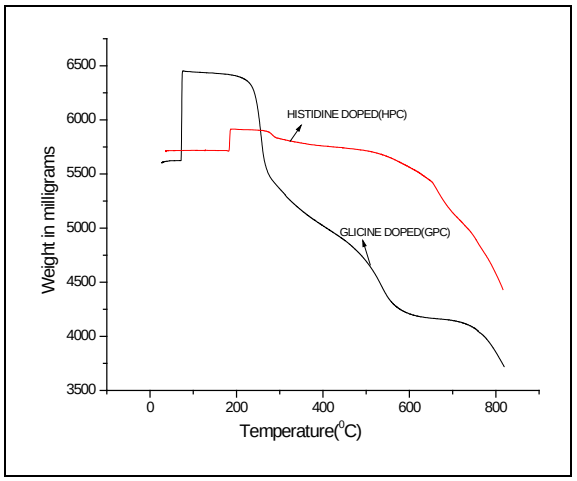

Fig.8.DTA curves of GPC and HPC crystals.

3.6 SCANNING ELECTRON MICROSCOPE (SEM) ANALYSIS

Scanning the surface with a high energy beam of electrons in a raster scan pattern is called Electron microscope. The shape and size of the particles making up the object can be viewed and studied. Fig.9and Fig.10 shows the SEM images of the as grown GPC and HPC crystals. The SEM micrographs show the purity and crystalline nature of the grown crystals. It is seen from the SEM pictures that the surface of the as grown crystal is smooth in the case of GPC and rough in case of HPC crystals[14].It is also seen that the addition of Histidine into the KCl which destroy the clarity of the crystal. It could be the evidence for higher NLO efficiency.

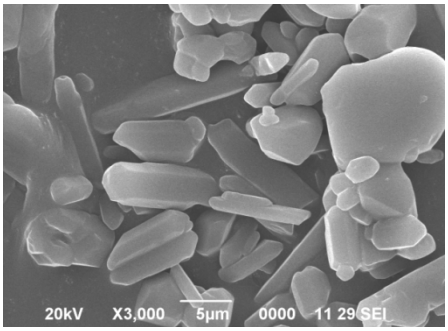

Fig.9.SEM image of GPC crystal.

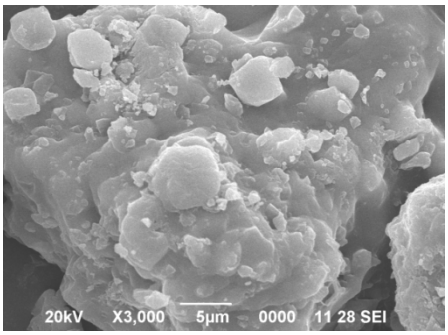

Fig.10. SEM image of HPC crystal.

3.7 ENERGY DISPERSIVE X-RAY DIFFRACTION (EDAX) ANALYSIS

The EDAX spectra for GPC and HPC crystals are shown in figure11 and 12. It is observed that the introduction of defects by partial cationic substitution in the host framework influences the physical properties. The elements were identified and presented. From EDAX spectrum the chemical composition weight has been calculated. The estimated % of N, O, Cl, K, C in HPC and N, O, K, Cl in GPC crystals are shown in table 3.

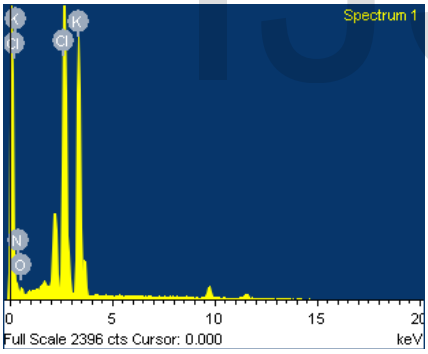

Fig.11.EDAX spectrum of GPC crystal.

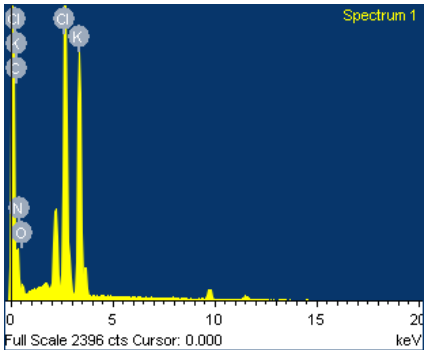

Fig.12. EDAX spectrum of HPC crystal.

TABLE 3
ESTIMATED WEIGHT PERCENTAGE OF GPC & HPC CRYSTALS

S. No	Element	GPC		HPC	
		Weight %	Atomic %	Weight %	Atomic %
1	N K	21.38	37.82	16.25	18.55
2	O K	10.97	16.99	6.75	6.75
3	Cl K	35.59	24.88	16.70	7.53
4	K K	32.06	20.32	14.22	5.82
5	C K	-	-	46.08	61.35
6	Total	100	100	100	100

3.8 KURTZ AND PERRY POWDER SHG TEST

The grown crystals of GPC and HPC were grounded into a fine powder and then packed in a micro-capillary of uniform bore and exposed to laser radiation. The fundamental input radiation (1064nm) was separated or filtered by a monochromator and the output was measured. Second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube (Hamamatsu R5 109). SHG was confirmed by the emission of green light. Using the Potassium dihydrogen phosphate (KDP) crystalline powder as reference material, the output of SHG signal were compared and found that the SHG conversion efficiency of GPC is 1.33 times that of KDP and HPC is zero.

4 CONCLUSIONS

KCl and organic impurities doped GPC and HPC crystals were grown using slow evaporation technique at room temperature. The X-ray diffraction analysis confirms the as grown crystal were cubic structure. FTIR analysis confirms the presence of organic additives Glycine and Histidine in KCl. The Fluorescence behavior of the crystals was determined and the SHG efficiency was also calculated. The decomposition of these crystals has been studied by Thermal Analysis. SEM reveals that the structural nature of GPC and HPC crystals. The presence of chemical composition has been identified by Energy Dispersive X-ray Spectroscopy and its weight percentage has been calculated. It can be considered that the GPC crystal is better candidate for fluorescence and NLO applications.

REFERENCES

[1] F.Samavat, E.H.Ali, S.Solgi, P.Taravati Ahmad , "KCl Single Crystals Growth with Mn, Ag and In Impurities by Czochralski Method and Study of Impurities Influence on Their Properties", Open Journal of Physical Chemistry, vol. 2, pp.185-188, 2012.

[2] J. Joseph, V. Mathew, and K. E. Abraham, "optical and structural properties of Mn doped potassium chloride crystals prepared by a mini melt growth setup", Journal of Physics, vol. 35, pp. 198–212, 2008.

[3] J.D. Bernal, Z. Kristallogr, "The Crystal Structure of the Natural Amino Acids and Related Compounds", Vol. 78, pp. 363-369, 1931.

[4] H.J.Simpson, R.E.Marsh, "The crystal structure of L-alanine", Acta Crystallographica, vol.20, p.550-555, 1966.

[5] R. Destro, R. E. Marsh and R. Bianchi, "A Low Temperature (23K) Study of L-alanine", The Journal of Physical Chemistry, Vol. 92, pp. 966-973,1988.

[6] L.Misoguti, A.T.Varela,F.D.Nunes,V.S.Bagnato,F.E.A.Melo,J.Mendes Filho, S.C.Zilio, "Optical Properties of L-Alanine Organic Crystals," Optical Matter, 6, p.147, 1996.

[7] L.F.Warren,R.E.Allred,R.J.Martinez,W.D.Wischmann,"NewDevelop ment in Semiorganic Non linear crystal",Electronic Materials, Vol.4, pp.388-396,1990.

[8] J.F.Nicoud ,R.J. Twieg ,D.S. Chemla , J. Zyss , Nonlinear Optical Properties of Organic Molecules and Crystals, Academic, Orlando, vol.1,1986.

[9] A.Jayarama,S.M.Dharmaprakash , "Structural distortion in thiourea-mixed ADP crystals", Applied Surface Science, 253,pp.944-949, 2006.

[10] R.Sankar ,C.M. Raghavan ,M. Balaji ,R. Mohan kumar , R.Jeyavel, "Synthesis and Growth of Triaquaglycinesulfatozinc(II) ,[Zn(SO4)(C2H5NO2)(H2O)3], A New Semiorganic Nonlinear Optical Crystal",R. Cryst. Growth & Design, vol.7, pp. 348-355, 2007.

[11] N.Vijayan, R.Ramesh Babu , M.Gunasekaran , R.Gopalakrishnan ,P. Ramasymy ,R. Kumaresan ,C.W. Lan, "Studies on the growth and characterization of p297 hydroxyacetophenone single crystals", J.Cryst. Growth, vol.249, pp.309-315, 2003.

[12] L.J.Bellamy, The Infrared Spectra of Complex Molecules, New York, 1958.

[13] N.C. Deshpande, A.A. Sagade, Y.G. Gudage, C.D. Lokhande, R. Sharma, "Growth and characterization of tin disulfide (SnS2) thin film deposited by successive ionic layer adsorption and reaction (SILAR) technique", J. Alloy Comp, vol.436,pp. 421-426,2007.

[14] S.Anie Roshan, Cyriac Joseph, M.A.Ittyachen, "Growth and characterization of a new metal-organic crystal: potassium thiourea bromide", Mat. Lett, vol.49, pp.299-304, 2001.

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