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GROWTH AND CHARACTERIZATION OF SEMI-ORGANIC NLO MATERIAL: GLYCINE BARIUM CHLORIDE (GBC)

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ABSTRACT

Single crystals of Glycine Barium Chloride (GBC), a semi organic nonlinear optical material has been grown from solution by slow evaporation at ambient temperature. The growth of crystals has been carried out at various pH values and the growth was confirmed at pH 6. The chemical composition of the grown crystals was determined by the FTIR spectra. The crystalline nature and its various planes of reflections were observed by the powder XRD. The structure is built from alternate layers of Glycine organic molecules and inorganic layers consisting of Ba^+ ions and Cl^- ions. The grain size is found to be 5 microns using SEM. The SHG was confirmed using the Kurtz powder technique.

Keywords: semi organic; nonlinear optical; slow evaporation; inorganic layers; grain size; SHG

INTRODUCTION

In recent years, organo-inorganic hybrid materials have attracted considerable attention. In particular, the inorganic derivatives of protein amino acids are often attributed to symmetric groups without an inversion centre mostly to polar symmetry groups. Their crystals have properties whose symmetry is described by odd -rank tensors such as pyro-electric effect, spontaneous electric polarization, piezoelectric effect, generation of second optical harmonics, etc. Moreover crystals that belong to the eleven enantiomorphic point groups, having no mirror reflection planes exhibit optical activity, which is described in terms of the axial generation tensors. While the structures of most amino acids are well defined, the structures of the derivatives of the protein amino acids with inorganic components are not. This paper defines the crystal structure of glycine barium chloride [GBC]. This has been investigated by the FTIR studies, its crystalline nature is studied by the powder XRD, and its grain size is 5 microns is confirmed by SEM studies.

EXPERIMENTAL

Synthesis and crystal growth

GBC was synthesized from analytic grade of Glycine and Barium Chloride (Merck) in equimolar ratio and dissolved in triple distilled water. The pH of the solution at super-saturation is kept at 6.0. The solution is filtered and transferred to a Petri dish for crystallization. This compound is re-crystallized 2 times for purity. Then the pure samples of seed crystals are taken and characterized.

Characterization

The crystals were characterized by FTIR spectroscopy, powder XRD, UV-Visible spectroscopy and SEM.FTIR spectra were recorded on Shimadzu IFS 66V FTIR. Powder XRD was obtained on a PHILIPS X'PERT MPD system. The absorption spectrum for the title crystal was recorded using JASCO corp., V-570, and Rev.1.00 UV-VIS spectrometer in the region 190-2500nm .Surface analysis of glycine barium chloride is carried out through JSM 6360 JEOL/EO make. The crystals were evaluated by the Krutz and Perry (1968) powder technique using a Q-switched, mode locked Nd: YAG laser. A micro-

crystalline material of KDP available at the Indian Institute of Science was used for comparison in the SHG measurements.

FT-IR ANALYSIS (Figure 1)
The grown crystals were subjected to FT-IR analysis with sample prepared with KBr in the palletized form. The FT-IR spectrum of glycine barium chloride was recorded in the region 4000-400cm^{-1} employing Shimadzu IFS 66V spectrometer. The broad envelope in the high energy region between 3487cm^{-1} and 2592 cm^{-1} is due to NH_3^+ stretching vibrations. The region of absorption bands extends to about 2015cm^{-1} due to multiple combination and overtone bands. The prominent band near 2713cm^{-1} and 2239 cm^{-1} may be assigned to a combination of the asymmetrical NH_2^+ stretching vibrations and torsional oscillation of the NH_3^+ group[3]. The NH_3^+ stretching region shows broad bands characteristics of hydrogen bonding. The frequencies of the vibrational mode of the crystal and their assignments are given in the Table 1. The absorption peaks characterizing the various functional groups are in very good agreement with those reported in the literature[1,2].

Table-1: Frequencies of the fundamental vibrations of GBC

Frequency in wave number (cm^{-1})	Assignment of vibration
3487	N-H – Symmetric Stretching
3068	NH_3^+ Stretching – amino acids
2987	CH_2 - Asymmetric stretching
2926	CH_2- symmetric stretching
2713 to 2239	NH_2^+ – Symmetric Stretching
1577(s)	NH_3^+ asymmetric bending- primary amine
1336(s)	C-N stretching –Aryle secondary amine
1300 (s)	O-H bonding - in solid state
1122(s)	NH_3^+ asymmetric bending- Amino acid
669	C-Cl - stretching

Powder XRD Analysis (Figure 2)
The powder XRD of glycine potassium chloride (GBC) is shown in the Figure 2. The peaks in the fig show the crystalline nature of GBC. Further the peaks are indexed. The intensity and 2θ values are in the Table 2.

Crystal Surface Analysis by SEM (Figures 3, 4 and 5)
Surface analysis of GBC is carried out through JSM 6360 JEOL/EO make. The maximum magnification possible in the equipment is 3, 00, 000 times with a resolution of 3 nm. The surface of the crystal was coated with a thin of carbon to make the sample conducting. From the fig. it is clear that the size of the crystals is 5 microns thick. Further the surface is very smooth without any defects.

NLO Studies
The NLO property of the crystal was confirmed by Kurtz powder technique. The determination of SHG intensity of the crystals using powder technique was developed by Kurtz and Perry[5] .The crystals are ground to powder and packed between two transparent glass slides. The first harmonic output of 1064 nm from a Nd:YAG laser was made to fall normally on the prepared sample with a pulse width of 8 ns. The second harmonic signal generated in the crystal was confirmed from the emission of green radiation by the sample. It is found that the SHG efficiency of the crystal is one and a half times higher than that in the case of KDP, which is in agreement with literature[1,4,6].

Table-2

# Strongest 3 peaks							
no.	peak no.	2Theta (deg)	d (A)	I/I1	FWHM (deg)	Intensity (Counts)	Integrated (Counts)
1	1	12.0468	7.34076	100	0.07050	1381	6294
2	25	38.5549	2.33323	25	0.07330	346	1539
3	26	40.7917	2.21030	24	0.07720	336	1855

| # Peak Data List						
peak no.	2Theta (deg)	d (A)	I/I1	FWHM (deg)	Intensity (Counts)	Integrated (Counts)
1	12.0468	7.34076	100	0.07050	1381	6294
2	12.3717	7.14870	14	0.13010	189	1543
3	15.6811	5.64667	3	0.06630	42	322
4	16.3402	5.42036	3	0.17050	48	447
5	19.2171	4.61490	11	0.09200	156	956
6	21.0589	4.21526	14	0.10180	200	1235
7	22.0191	4.03356	3	0.14390	41	347
8	22.6200	3.92775	3	0.07200	44	292
9	22.8352	3.89122	21	0.13850	286	2240
10	23.1669	3.83625	3	0.07210	45	222
11	24.1243	3.68613	15	0.06940	213	915
12	24.7537	3.59381	6	0.13680	81	590
13	28.1549	3.16692	24	0.07420	330	1521
14	29.0119	3.07529	4	0.10160	60	409
15	30.9105	2.89059	6	0.13180	87	715
16	31.4516	2.84208	17	0.09960	232	1377
17	32.1732	2.77996	12	0.08010	167	798
18	33.1399	2.70105	3	0.12350	43	399
19	33.5888	2.66597	12	0.09990	162	858
20	33.9800	2.63616	8	0.07760	108	954
21	36.4428	2.46346	17	0.06390	240	842
22	37.4455	2.39977	3	0.09110	45	247
23	37.7130	2.38336	7	0.10400	102	607
24	37.9740	2.36758	4	0.13470	54	400
25	38.5549	2.33323	25	0.07330	346	1539
26	40.7917	2.21030	24	0.07720	336	1855
27	42.3488	2.13257	4	0.11990	57	440
28	43.7232	2.06866	4	0.14360	57	832
29	45.3256	1.99919	3	0.08880	47	261
30	51.8760	1.76110	5	0.07080	63	276
31	52.3324	1.74681	7	0.07360	94	429
32	57.9639	1.58977	5	0.07980	70	357
33	66.9535	1.39649	24	0.07240	328	1397
34	76.4254	1.24527	3	0.07970	48	242
35	78.1627	1.22188	3	0.06860	46	212
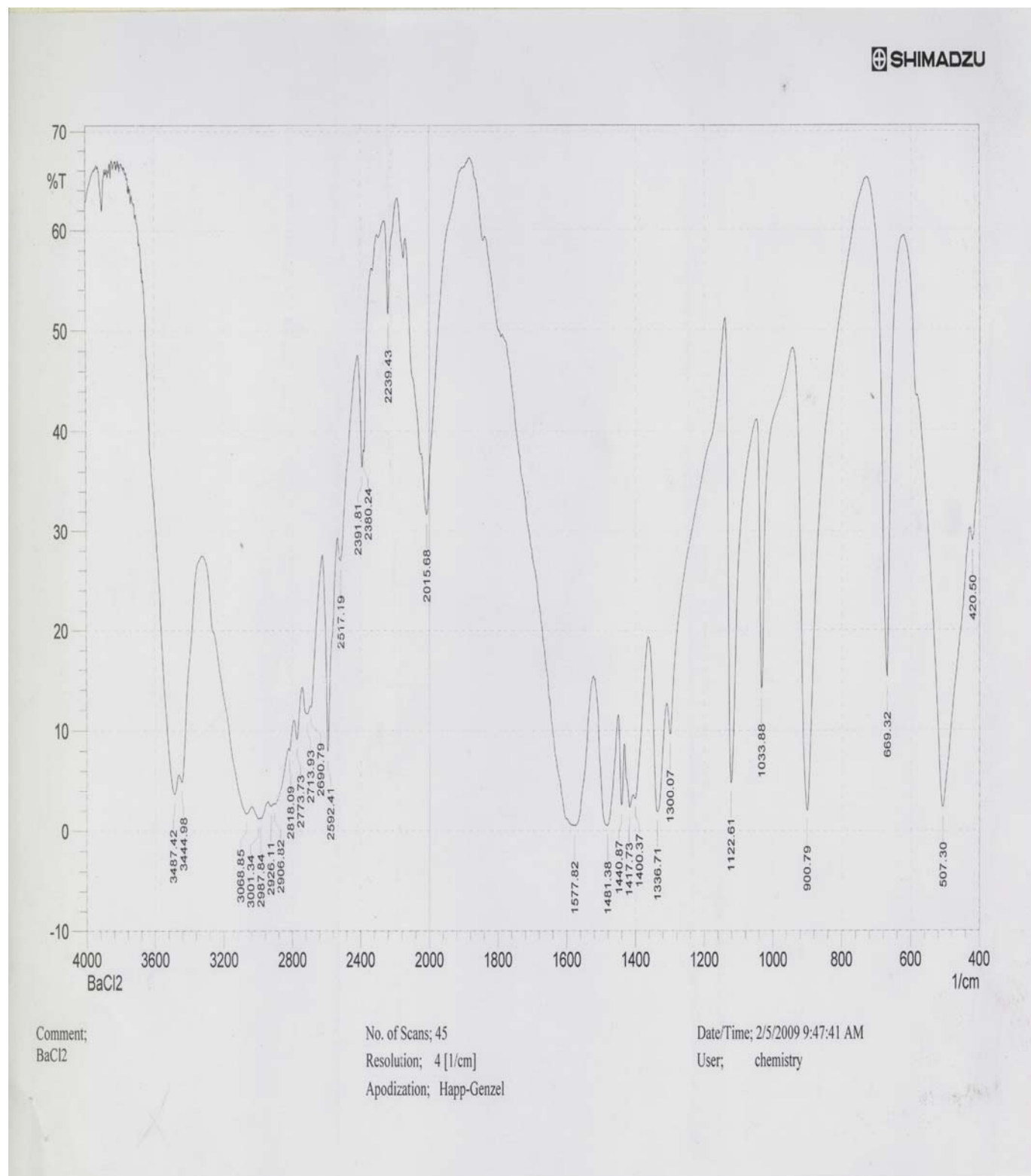
Fig.-1
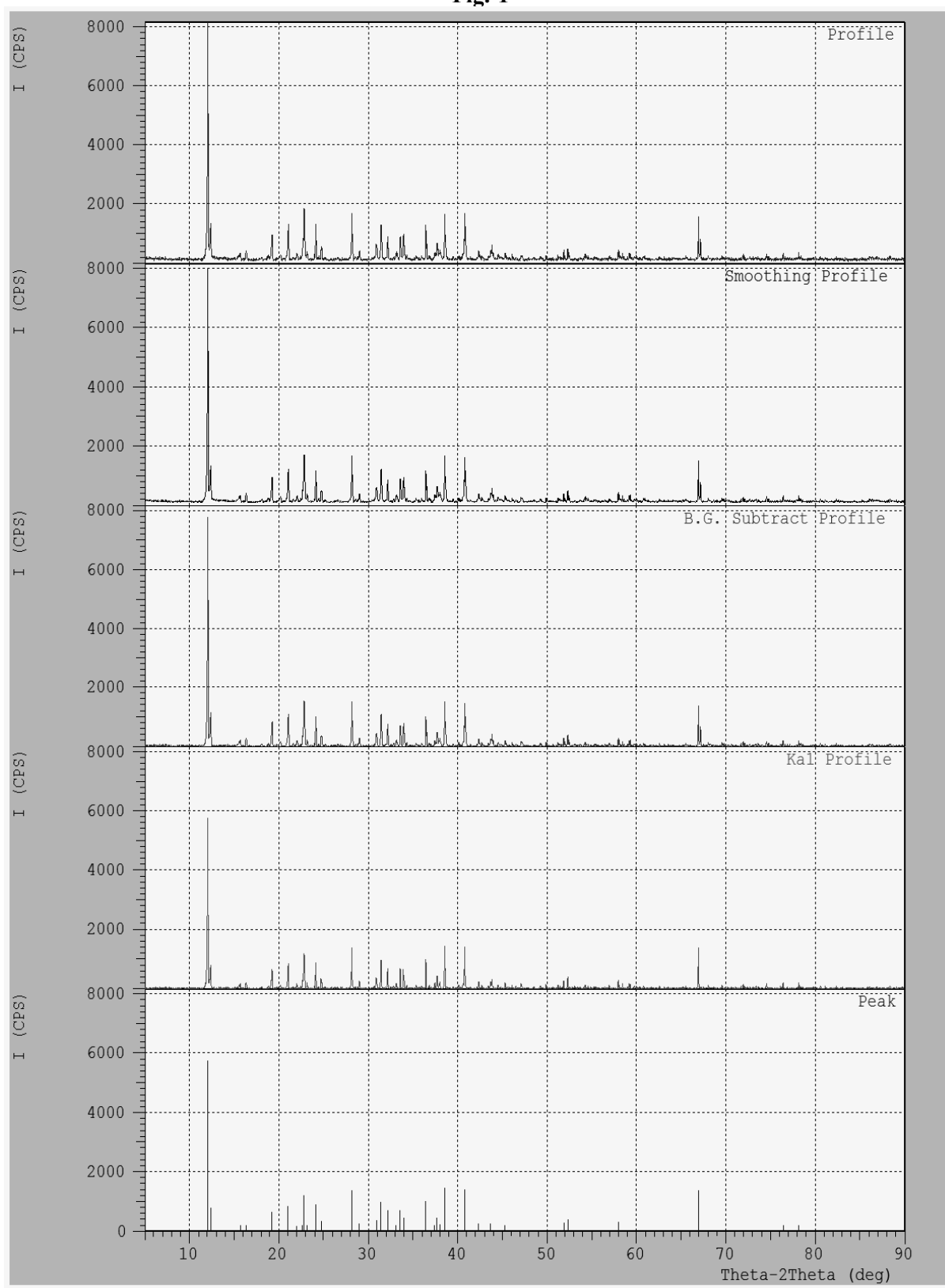
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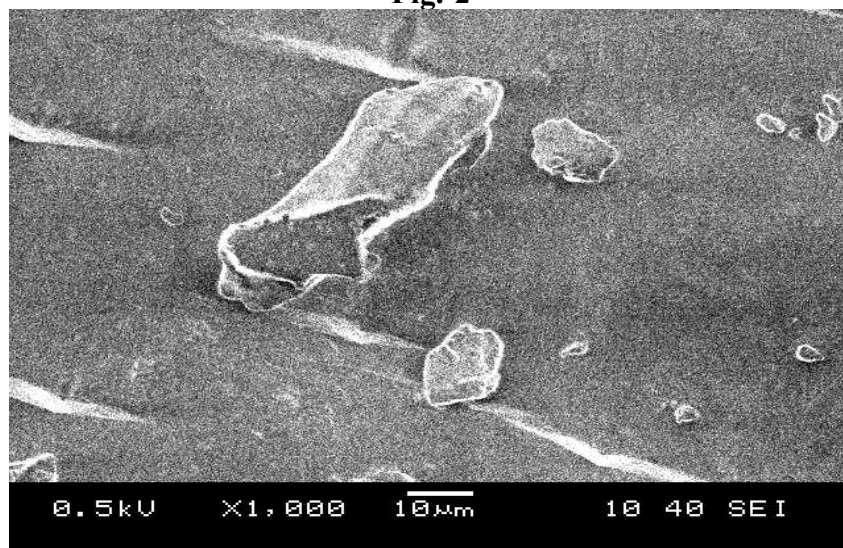
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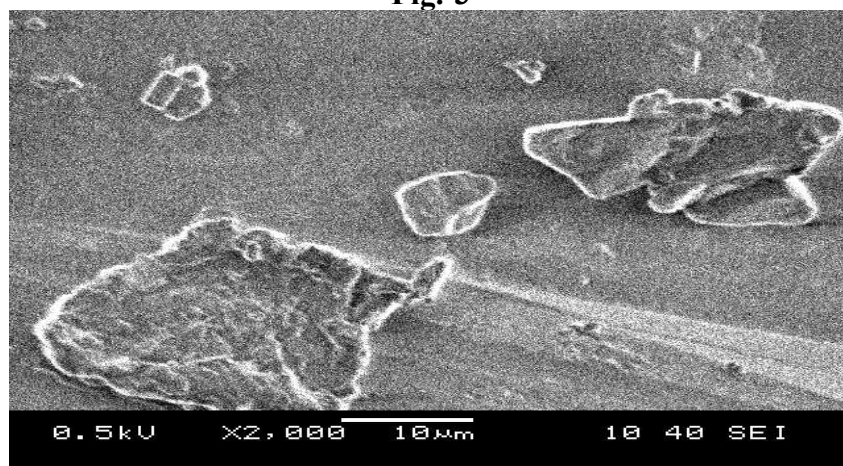
Fig.-4

Fig.-5

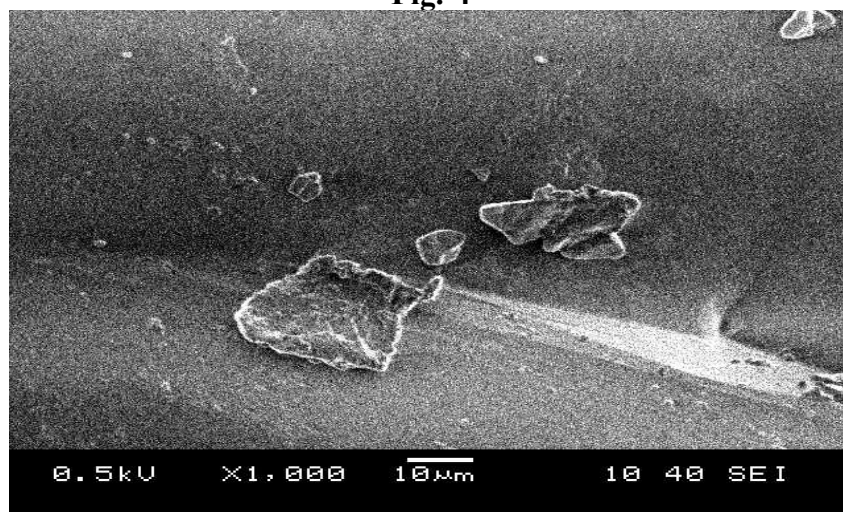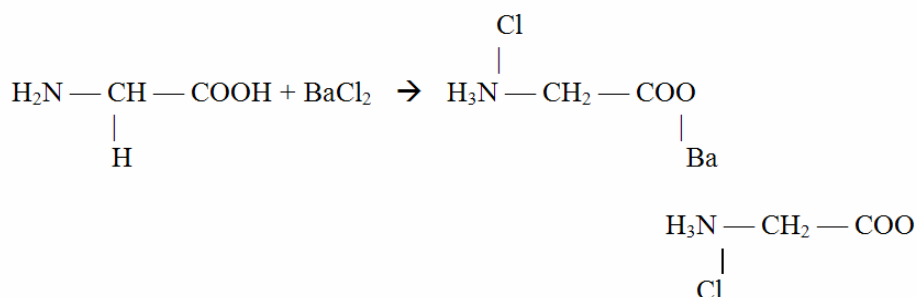## CONCLUSION

The crystal is grown at ambient temperature and the following are the points that are evolved from this research:

1. The crystal Glycine Barium Chloride is confirmed to be a non-linear optical crystal.
2. From FTIR studies, the formula of this crystal is confirmed to be

$$H_2N - CH - COOH + BaCl_2 \rightarrow H_3N \overset{\displaystyle Cl}{-} CH_2 - COO$$

$$\underset{H}{|} \qquad \qquad \underset{Ba}{|}$$

$$H_3N - CH_2 - COO$$
$$\underset{Cl}{|}$$

The crystal is found to be of the crystal system Monoclinic and the crystal parameters are found to be as follows:

Table-3: Crystal system of Glycine Barium Chloride is Monoclinic

a	b	c	α	β	γ	Cell Volume
6.73 A	10.92 A	7.14 A	90	90.92	90	524 A^3

REFERENCES

1. B.N. Moolya, A. Jayarama, M.R. Sureshkumar and S.M. Dharmaprakash, J. Cryst. Growth, **280**, 581 (2005).
2. R.K. Khanna and P.J. Miller, *Spectro Chem. Acta*, **26A**, 1667 (1970).
3. R. Silverstein, G.C. Bassler and T.C. Morrill, Spectrometric identification of organic compounds, John Wiley & Sons (1991).
4. N. Narayanan Bhat and S.M. Dharmaprakash, *J. Cryst.Growth*, **236**, 376 (2002).
5. S.K. Kurtz and T.T. Perry, *J.Appl.Phys.*, **39**, 3798 (1968).
6. S. Palaniswamy and O.N. Balasundaram *RASAYAN J. Chem*, **1**, 782 (2008).

Anyone who attempts to generate random numbers by deterministic means is, of course, living in a state of sin.

-John von Neumann