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Gel Growth and Characterization of New $PbHNSO_3$ Crystals

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Abstract - *Gel growth technique is another method of solution growth method to grow crystals. It is found that the structure of $PbHNSO_3$ consists of the NSO3 pseudo-tetrahedra, the PbO9N3 polyhedra, and the NSO3-Pb-NSO3 frameworks [1]. New $PbHNSO_3$ crystals have been grown from employing a double diffusion gel technique. Agar gel is used as the growth medium. Dark brown colour crystals of dimension 0.25x0.30x0.40mm were harvested after 20 days. The crystallinity and structural parameters were found from powder and single crystal XRD. FTIR spectra confirmed the functional groups present in the crystal. The thermal decomposition and phase transformation were evaluated from TG-DSC spectra. The emission spectrum of PbHNSO3 was recorded using photoluminescence spectrophotometer.*

Key Words: $PbHNSO_3$, Single crystal XRD, Thermal decomposition, PL Spectra.

1.INTRODUCTION

Crystal growth in gel media is very effective and has attracted much attention in recent years, due to its unique characteristic of suppression of nucleation centres. The use of gel in the growth of crystals was explained by H.K. Henisch [1]. Simplicity of the process [2, 3] and its unique advantage in terms of crystal product [4, 5] makes this technique more popular. Crystals having low solubility [6] can also be grown using this technique. Due to gelled medium properties, gel growth allows one to obtain nearly defect free crystals useful in optical applications [7,8].

New $PbHNSO_3$ crystals belong to an orthorhombic system and the space group is determined to be Pnma. This new crystal is found to consist of NSO_3 pseudo-tetrahedra, PbO_9N_3 polyhedra and NSO_3-Pb-NSO_3 frameworks very close to that of $PbSO_4$. Growing bulk size $PbSO_4$ crystal commercially is still a novel problem for researchers. Lead sulphate also crystallizes in the orthorhombic system with the space group of Pnma. The interest behind the present work is to grow $PbHNSO_3$ crystals by employing double diffusion gel growth technique and to compare its optical and thermal behaviour with $PbSO_4$. The molecular weight of the $PbHNSO_3$ is calculated as 302.27. This crystal has no phase transition in the range of 100-960K.

2. MATERIALS AND METHODS

Agar-agar powder was purchased from M/S.Sisco Research Laboratories Pvt Ltd, Mumbai and used for preparing the gel for growth medium. Agar gel is prepared by dissolving 1% of agar powder in double distilled water. The agar-agar powder gets dissolved at the boiling point of the water. The gel is about to set in a U-tube of 165mm length and 20mm diameter columns. The gel sets after gentle cooling to room temperature. The growth of the crystal was achieved by allowing 1M Pb $(NO_3)_2$ and H_3NSO_3 of 10ml solution through the gel on each column separately. Both the chemicals were purchased from M/S.Himedia Laboratories PVT LTD, Mumbai. The chemical reaction involved during the synthesis of $PbHNSO_3$ may be as follows:

$$Pb(NO_3)_2 + H_3NSO_3 \Rightarrow PbHNSO_3 + 2HNO_3$$

Crystals of visible size were grown after 20 days. The well grown crystals had been separated using distilled water. The crystals were washed repeatedly several times. The micrographs of the harvested crystal were shown in fig 2. These crystals were characterized with powder and single crystal XRD, FTIR spectra, PL spectroscopy and TG-DTA analysis.

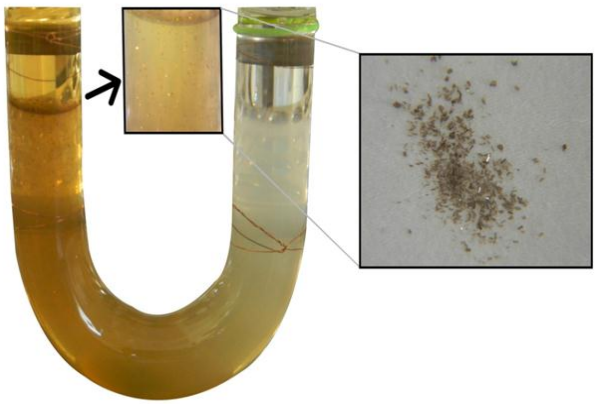

Fig -1: PbHNSO3 crystals grown from Agar gel in U-tube

3. CHARACTERIZATION

The phase composition of the prepared samples was studied from the powder X-ray diffraction (XRD) patterns of the samples observed by an XPERT-PRO diffractometer fitted

with CuKα radiation (λ=1.5406Å) of 30mA and 40kV at room temperature. The intensity data was recorded by continuous scan in θ/θ mode from 10° to 80°. The single crystal X-ray diffraction analysis of $PbHNSO_3$ crystal is carried out using Enraf (Bruker) Nonius CAD4-MV31 with MoKα of wavelength 0.71073Å. Fourier transformed Infrared (FTIR) spectroscopy was recorded using a Perkin Elmer spectrometer in the region of 4000 – 400 cm^{-1} under room condition using KBr pellet technique. Photoluminescence (PL) spectra were recorded using Cary Eclipse spectrometer model WinFLR EL08083851 with a photomultiplier tube and xenon lamp of 450W at room temperature covering a wavelength range from 265 nm to 475 nm with an excitation wavelength of 245 nm. TGA and DSC studies of $PbHNSO_3$ were carried out at NETZSCH Technologies India Pvt Ltd, Chennai. The heating rate was 10K/min with flowing N2 gas using Al_2O_3 crucible.

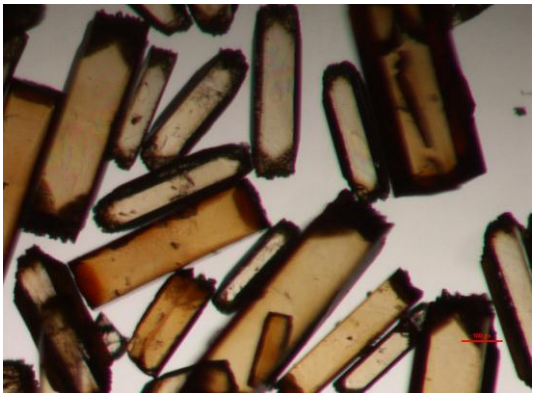

Fig -2: Micrograph of as grown PbHNSO3 Crystals

4. RESULTS & DISCUSSIONS

4.1 Powder X-Ray Diffraction Analysis

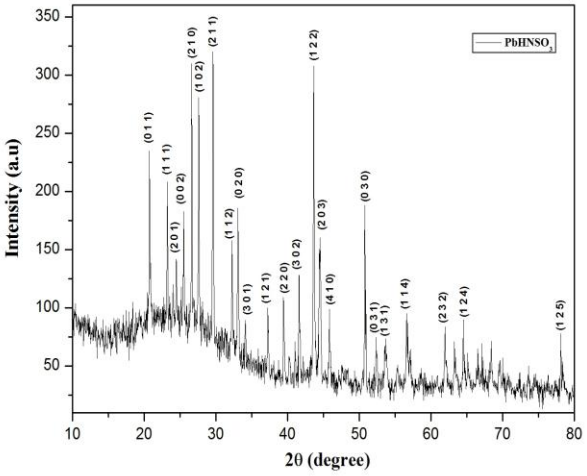

Fig -3: XRD pattern of as grown PbHNSO3 crystal

Fig 3 shows powder X-Ray diffraction patterns of as grown $PbHNSO_3$ crystals. From the XRD pattern, it is observed that each peak is extremely sharp which confirms the crystalline nature of the crystals. The (h k l) values have been indexed from the single crystal XRD report.

4.2 Single Crystal XRD

The lattice parameters obtained from the single crystal X-ray data are shown in Table 1.

It is observed from the study that the crystal belongs to orthorhombic system with the space group P*nma*. The cell parameters obtained were very well in agreement with the literature [9]. The molecular weight and density of the crystal were found to be 302.27 g mol^{-1} and 6.331 mg m^{-3} respectively. The crystal structure was shown in fig 4.

Table -1: Cell parameter values of $PbHNSO_3$ Crystal

Cell Parameters	Reported Value	Observed Value
a (Å)	8.469	8.472
b (Å)	5.393	5.389
c (Å)	6.953	6.947
V ($Å^3$)	317.59	317.14

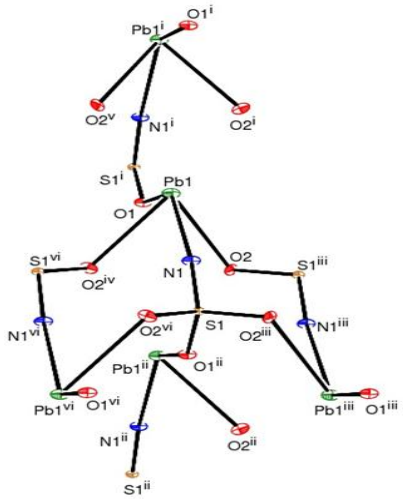

Fig -4: Projection view of Crystal Structure of $PbHNSO_3$

4.3 FTIR Analysis

Fig 5 shows the FTIR spectrum of $PbHNSO_3$ crystals.
Pb-O stretching vibrations may be responsible for the doublet peak at 592cm^{-1}. Generally, S-O stretching vibration occurs at

700-600cm^{-1}[10] which takes place near 621cm^{-1}. The peaks at 1250-1140cm^{-1} and 1070-1030cm^{-1} will be assigned to R-SO_3- with =S=O stretching vibrations. The absorption band near 1129cm^{-1} represents υ_3 symmetrical stretching vibration of the SO_2^{-3} ion [11]. The absorption near 1588cm^{-1} is assigned to N-H bending vibration which may occur at 1650-1580cm^{-1}[10, 12]. The broad peak at 3404 cm^{-1} may be attributed to =N—H and =N—H with N—H stretching, which normally occurred at 3500-3300 cm^{-1} [10].

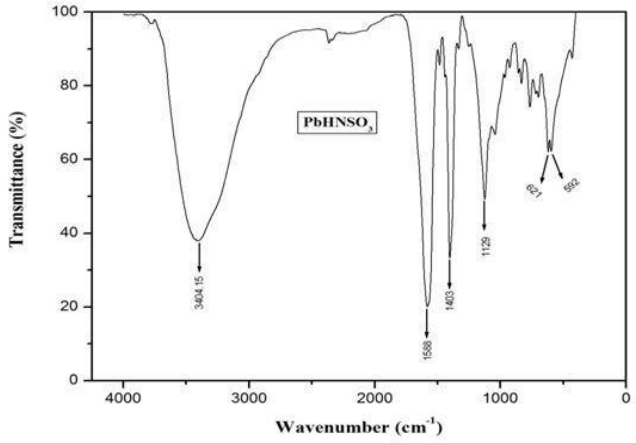

Fig -5: FTIR Spectra of as grown $PbHNSO_3$ Crystals

4.4 PL Spectroscopy

$PbHNSO_3$ crystals are brown in colour, which may be produced by the absorption of blue wavelengths of light. The excitation wavelength of $PbHNSO_3$ crystals was found to be 290 nm. The $PbHNSO_3$ crystals give very weak emission at 317nm. The emission peak at 332nm is much intensified than 317nm peak. Two strong emission peaks are obtained at 417nm and 477nm shown in fig 6.

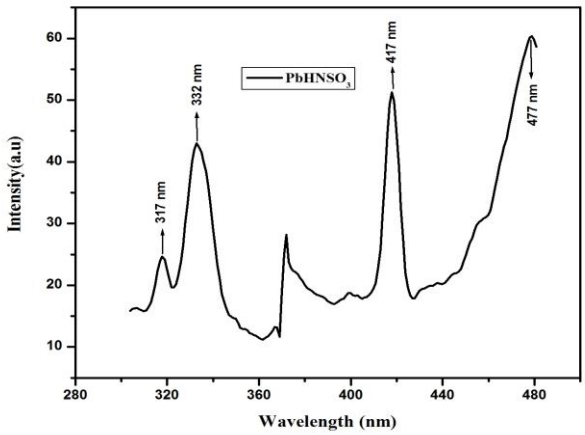

Fig -6: PL Emission Spectra of $PbHNSO_3$ Crystal

Lamellar $PbSO_4$ Nanocrystals gave two emission bands centred at 340 and 360 nm (UV band) using an excitation wavelength of 270 nm[13]. Similarly $PbHNSO_3$ also gives two emission peaks at UV band region. The peak at 332 nm (UV region) is well in agreement with the nano $PbSO_4$ crystals reported previously which was attributed to radiative dissociation of an anion exciton [14, 15].

The peak at 417 nm may be observed due to the presence of sulphur vacancies or extrinsic defects [16]. An emission peak located at 477 nm was observed, which is similar to that measured at low temperature for large single crystals of $PbSO_4$ need to be investigated further [17, 18].

4.5 Thermal Analysis

In the TG analysis of $PbHNSO_3$ which is shown in fig 7, the curve slightly increases with increasing the temperature, up to 862°C which may be due to the presence of any residues.

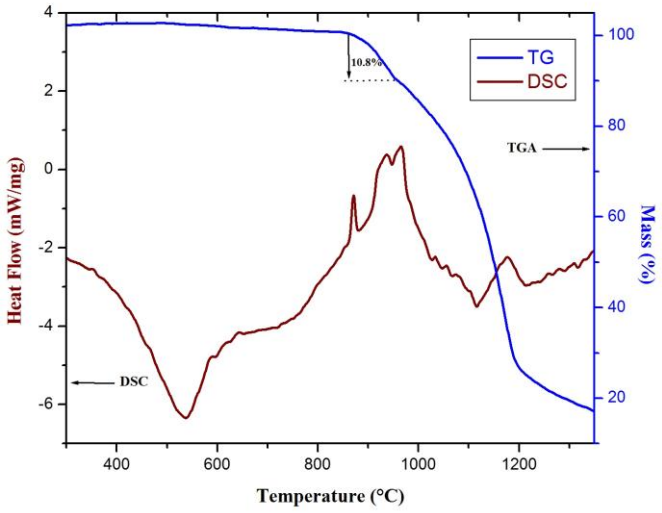

Fig -7: TG-DSC Curve obtained for $PbHNSO_3$ Crystal

The DSC curve implies that there is some change at 537°C. After 537°C, the DSC curve increases further up to 862°C. There should be no solid to liquid phase change which was confirmed by the TG curve. The curve in the DSC spectrum was expected due to some structural change as in $PbSO_4$ crystals. $PbSO_4$ has melting point of 1170°C [19]. It decomposes at 900°C and has a solid-solid phase transition at 856°C from monoclinic to orthorhombic [20].

The weight loss of about 10.8% is observed in the temperature range of 862-952°C. At 862°C, assuming the decomposition is accompanied by the evolution of O_2 composed of two oxygen atoms; the theoretical weight loss is calculated to be 10.59%. Evolutions of SO and SO_2 may be

responsible for the drastic weight loss which is noticed above 952°C.

5. CONCLUSIONS

The $PbHNSO_3$ crystals were characterized by structural, functional, optical and thermal studies. These new crystals have been grown from agar gel medium. Single crystal XRD revealed that $PbHNSO_3$ crystallizes in orthorhombic system with Pnma space group. The presence of functional groups was confirmed from FTIR studies. The optical studies have the maximum emission peak at the wavelength of 477nm. Thus the brown colour of the crystal is due to the absorption of blue wavelength of light. From the thermal studies, it is found that the crystal starts decomposition after 863°C. But there is no phase change from room temperature to 863°C. The phase change occurs only at 863°C.

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