GROWTH AND CHARACTERIZATION OF HEXAMINE SINGLE CRYSTAL

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ABSTRACT

A nonlinear optical crystal of hexamine single crystal was grown by slow evaporation solution growth technique by using deionized water at room temperature. The functional groups and vibrational frequencies were identified using FTIR spectrum. The cell parameters were determined from single crystal X-ray diffraction analysis. Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were used to study its thermal properties. The optical transmittance window and lower cutoff wavelength have been identified by double beam UV-absorption spectrum analysis. Second harmonic generation (SHG) efficiency measurement was carried out by X-ray powder diffraction analysis.

Key words: Nonlinear optical crystal, Solution growth technique, Characterization technique, Second harmonic generated.

INTRODUCTION

Recent research is focused on search for suitable material displaying excellent second order nonlinear optical (SONLO) properties for potential applications in optoelectronics, telecommunication (Large transmission range) and optical storage device(F) deionized water are interesting materials for NLO application Among all the deionized water, Hexamine is the simplest one and is observed that the hexamine crystal belongs to cubic crystal system and are having a unit cell dimensions of, a = 7.201 g.

In the present study, we have reported the growth and characterization of hexamine single crystals from slow evaporation solution growth technique by using deionized water at room temperature.
EXPERIMENTAL

Crystal growth

The single crystal of hexamine was successfully grown from slow solvent evaporation solution growth technique at room temperature using water as solvent. The commercially available hexamine was purified by successive repeated recrystallization process. The repeated recrystallization material has been used for the growth as charge material; the growth process and the quality of crystal significantly depend on super saturation. The saturated solution of hexamine was obtained by dissolving the charge material into the solvent. This prepared super saturated solution was filtered with borosil filter paper and taken in different clean glass vessels. These vessels were closed with thick filter paper which was controlled by the rate of evaporation and kept at dust free atmosphere with in 50 hrs. The nucleation was absorbed in the solution, then, they were allowed to grow for another few days in order to get the appreciable size of single crystals were depicted in Fig. 1.

![Grown single crystal of Hexamine](image)

RESULTS AND DISCUSSION

Characterization

Single crystal XRD analysis

To confirm the identity of the hexamine single crystal, unit cell parameters were calculated from single crystal XRD analysis\(^6\),\(^7\). RICH seifert diffractometer was used to collect free intensity data using \(c_0k_\lambda (\lambda = 1.5418 \text{ Å})\) radiation. The reflections on the powder
douple are recorded with a moving pen arrangement and whose reflections are approximately proportions to the intensity of reflection. The rate of scanning is 20 per minute. The recorded X-ray diffraction spectrum for hexamine is shown from the Fig. 2. 20 values are found and \( d \) spacing values are calculated using Bragg’s equation. The reported lattice parameter values of hexamine hkl and \( d \) values are tabulated along with experimental a values in Table 1. Using crystallographic equation, the unit are dimensions \( a = 7.201 \, \text{Å} \). This values are very good agreement with the reported values.

**Table 1: X-ray powder data for hexamine crystal**

<table>
<thead>
<tr>
<th>S. No.</th>
<th>2 Theta</th>
<th>( d ) values (Å)</th>
<th>hkl</th>
<th>I/Io</th>
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<tbody>
<tr>
<td></td>
<td></td>
<td>Calculated</td>
<td>Standard</td>
<td></td>
</tr>
<tr>
<td>1</td>
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<td>5.3982</td>
<td>4.9680</td>
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<tr>
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</tr>
<tr>
<td>3</td>
<td>31.13</td>
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<td>2.8700</td>
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</tr>
<tr>
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<td>2.3493</td>
<td>2.2240</td>
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<tr>
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<td>2.0291</td>
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<tr>
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<td>1.8784</td>
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</tr>
<tr>
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<tr>
<td>8</td>
<td>58.70</td>
<td>1.4839</td>
<td>1.5713</td>
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</tr>
</tbody>
</table>

**Fig. 2: Powder XRD pattern of Hexamine single crystal**
FTIR Spectral analysis

The FTIR analysis of hexamine single crystal was carried out in the middle IR region, ranges between 1400 cm\(^{-1}\) and 400 cm\(^{-1}\) by BROKER 66v FT-IR spectrometer (KBr) pellet technique. The recorded spectrum was shown in Fig. 3. The intense sharp peak at 3325 cm\(^{-1}\) in the higher energy region assigned to N-H asymmetric stretching mode and peak at around 3100 cm\(^{-1}\) is due to the N-H symmetric mode of vibration\(^8\).

![Fig. 3: FTIR spectrum of Hexamine single crystal](image)

The N-H, the plane bending mode of vibration was observed at 1625 cm\(^{-1}\). The intense sharp peak at 1529 cm\(^{-1}\) was assigned NH\(^3+\) asymmetric bending mode of vibration. The E-N stretching mode of vibration was observed at 1237 cm\(^{-1}\). There are kindly resolved bends below 1000 cm\(^{-1}\), due to CH and O-H bending modes of vibration.

Thermal analysis

The thermo gravimetric analysis (TGA) and differential thermal analysis (DTA) were carried are (using NETZSCH STA) between 30 and 600°C thermal analyzer at a heating rate of 10°C/min\(^9\). In the nitrogen atmosphere, thermal stability of the crystal was determined and shown in Fig. 4. The DTA curve shows a major endothermic peak, which corresponds to the melting points of the material at 220°C. Another Important observation is that, there is no phase transition until the material melts and twist enhances the temperature range of utility of crystal for NLO Applications. The absence of water of crystallization in the molecular structure was indicated by the absence of weight log around 100°C. From the TGA curve, it was observed that the material is stable upto 150°C and it shows a sharp single weight loss after 190°C which ends at 190-220°C. At elevated temperature, this
decomposition process continuous up to 600°C. Hence, it is concluded that the thermal behavior of hexamine is more stable.

![Thermal analysis of Hexamine single crystal](image)

**Fig. 4: Thermal analysis of Hexamine single crystal**

### UV-Visible NIR spectral study

The UV-Visible NIR absorption spectrum of the hexamine crystal was carried out between 300 and 1200 nm using double beam UV spectrophotometer\(^\text{10}\). The recorded UV-absorption spectrum is shown in Fig. 5. The absorption spectra were taken at room temperature. In present Investigation, the absorption spectrum of hexamine single crystal was taken in the range of 200 nm to 1200 nm, is shown in Fig. 6.

![Absorption spectrum of Hexamine single crystal](image)

**Fig. 5: Absorption spectrum of Hexamine single crystal**
Fig. 6: Transmission spectrum of Hexamine single crystal

The range of transmission for hexamine was determined between 200 nm to 1200 nm. Absence of absorption region between 300 and 1200 nm is advantageous as it is the key requirement for material having NLO properties\textsuperscript{11}. Hence, the title compound may be used for the NLO applications.

CONCLUSION

The Hexamine single crystals have been grown by solvent evaporation method at room temperature. Its lattice parameters have been determined from single crystal X-ray diffraction analysis. The presence of functional groups has been identified from the FTIR analysis. From the thermal measurements, we found that the compound is more stable. From optical assessment, we concluded that it has a large transmission range and it may be used for frequency doubling and other optical applications. It is observed that the hexamine crystal belongs to cubic crystal and unit all dimension, \( a = 7.201 \text{ Å} \).

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