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Research Paper

Growth and Characterization of 2, 4, 6 Triamino-1, 3, 5 Triazine – An Organic Single Crystal

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Single crystals of 2, 4, 6 triamino-1,3,5 triazine (melamine) have been grown successfully by slow evaporation solution growth technique at room temperature. Single crystal X-ray diffraction studies reveals that the crystal crystallizes in monoclinic system $P2_1/c$ with lattice parameters a = 7.29Å, b = 7.48Å, c = 10.33Å, $\alpha = 90^o$, $\beta = 108.52^o$, $\gamma = 90^o$ and V = 534(Å)^3. The functional groups have been identified by FTIR spectral analysis. The chemical structure of the compound was established by FT-NMR technique. The thermal stability and decomposition of the crystal were studied by thermo gravimetric analysis and it was found that the material was thermally stable up to 336^{o}C. The NLO property was confirmed by Kurtz and Perry powder technique.

Key Words: Powder X-Ray Diffraction; Fourier Infrared Spectroscopy; Organic Material; Thermal Analysis

1. Introduction

During the past 20 years, the search for new materials exhibiting non linear optical properties has never ceased in the endeavour to develop new laser sources and extend applications in the area of telecommunication and information storage materials. Non Linear Optical materials are mainly used in the field of Photonic and Opto electronic technologies. Progress in these areas would be greatly enhanced by the availability of materials compatible with various device embodiments and having sufficiently large NLO response. Melamine (2,4,6-triamino 1,3,5-triazine), a crystalline N-heterocyclic organic base is an industrial chemical intermediate product, mainly used to manufacture plastics, dyes, fertilizers and fabrics [1]. Melamine is actually a raw material for industrial use and used in the production of melamine-formaldehyde resins for surface coatings, laminates and adhesives and in the production of flame retardants [2]. Melamine boards, paper and dinnerware are made from thermoplastic melamine. It is also used to make pesticides and plant fertilizers. Melamine and its salts are widely used in the formulation of fire retardant additive systems for polymeric materials [3, 4]. Melamine molecule could be used as organic part of investigated crystals. This molecule and its polymers found application in a wide variety of technological fields [5]. The theoretical calculations of NLO properties and dipole moments of the molecule were already discussed [5]. Marchewka *et al*. [5-8] revealed the suitability of melamine family of crystals for their non linear optical properties and future applications. Also a lot of works were performed to explain the behaviour of melamine molecule in the

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solid state and few papers with assignments of internal vibrations of melamine molecule were already published [9-15]. In the present work, spectroscopic and thermal studies of grown crystals are discussed in detail.

2. Experimental

AR grade sample of melamine was taken and dissolved in doubled distilled water. Since the solubility is poor, 2 ml of dilute hydrochloric acid was added dropwise to adjust pH value as six and saturated solution was obtained. Then the solution was stirred well for 6 hours, filtered and allowed to cool at room temperature. After several days, tiny colourless crystals produced which is transparent while it is inside the solution. Once it taken out, transparency of the crystal is reduced because of its hygroscopic nature. Fig. 1 shows the photograph of the grown crystal.

2.1 Characterization

The grown crystals have been subjected to various characterization studies like Single crystal XRD, Powder XRD, FT-IR, FT-NMR, TG-DTA and SHG. The grown crystals of 2,4,6-triamino 1,3,5-triazine was subjected to single crystal XRD analysis using ENRAF Nonius AD4/MAC4 X-ray diffractometer with M_oK_α (λ = 0.71073Å) radiation. The grown crystals have been characterized by X-ray powder diffraction technique using Rich Seifert X-ray powder diffractometer with CuK_α radiation of λ = 1.5406Å. The 2θ range was analyzed from 10° to 70° by employing the reflection mode for scanning. The detector used was a scintillation counter. A Perkin Elmer Spectrum one FTIR spectrometer was employed to record the IR spectrum to analyze the functional groups present in the crystals. The sample for this measurement was finely grounded and mixed with KBr. Proton NMR and Carbon NMR spectra of melamine crystal were recorded using D_2O as solvent on a Bruker Avance III 500 MHz spectrometer at 22°C to confirm the molecular structure of the grown crystal. The thermal behaviour of the crystal was determined by thermo gravimetric analysis and differential thermal analysis using Universal V4.7A TA Instruments thermal analyzer at a heating rate of 20°C/min in the nitrogen atmosphere in the temperature range of 25-1200°C. The grown crystals of melamine was subjected to Kurtz second harmonic generation test by using Nd:YAG Q switched laser beam with input pulse of 5.2 mJ for the non linear optical property.

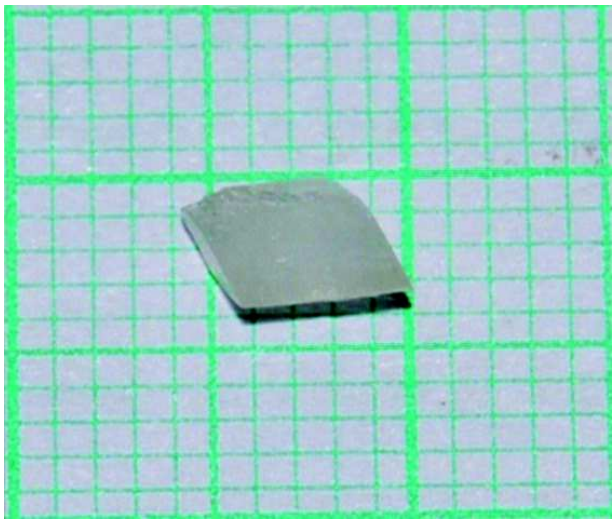

Fig. 1: Photograph of 2, 4, 6 triamino-1, 3, 5 triazine (melamine) crystal

3. Results and Discussion

3.1 Single Crystal XRD

The single crystal XRD data of the title crystal indicates that it crystallizes in the monoclinic system with space group $P2_1/c$. The obtained lattice parameters are a = 7.29Å, b = 7.48 Å, c = 10.33 Å, α = 90°, β = 108.52°, γ = 90° and Volume = 534 $(Å)^3$ and are given in Table 1. These values are in good agreement with the reported values [16] and thus confirm the grown crystal.

3.2 X-ray Powder Diffraction Analysis

Fig. 2 shows the X-ray Powder diffraction pattern for the grown title crystal. The crystal structure of the grown crystal has been already studied [16-18]. From the X-ray powder diffraction data, the lattice parameters and the cell volume have been calculated as a = 7.1530±0.0769Å, b = 7.4454±0.0623 Å, c = 10.3822±0.0433 Å, α = 90°, β = 113.41±0.52, γ = 90° and V = 507.424 $(Å)^3$ and are given in Table 1. These reveal a close agreement with the reported values

Table 1: Lattice parameters for the 2, 4, 6 triamino-1, 3, 5 triazine (melamine) single crystal

Crystallographic lattice parameters	Data of single crystal XRD	Data of powder XRD	Reported [16]
a(Å)	7.29	7.1530±0.0769	7.2454(6)
b(Å)	7.48	7.4454±0.0623	7.4595(7)
c(Å)	10.33	10.3822±0.0433	10.4733(12)
α(degree)	90	90	90
β (degree)	108.52	113.41±0.52	113.099(8)
γ (degree)	90	90	90
V (Å^3)	534	507.424	520.67

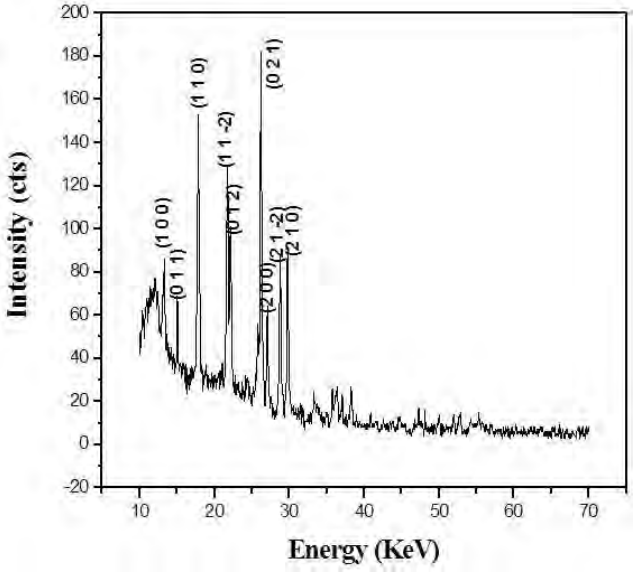

Fig. 2: Powder XRD pattern of 2,4,6 triamino-1,3,5 triazine (melamine) crystal

[16] and the values obtained from the single crystal X-ray diffraction. The prominent peaks have been indexed.

3.3 FTIR Analysis

The FTIR spectrum of 2,4,6-triamino 1,3,5-triazine is shown in Fig. 3, and the vibration band assignment is given in Table 2. The strong IR absorption peaks at 3469 cm^{-1} and 3419 cm^{-1} were attributed to NH_2 stretching of melamine and these peaks are absent in

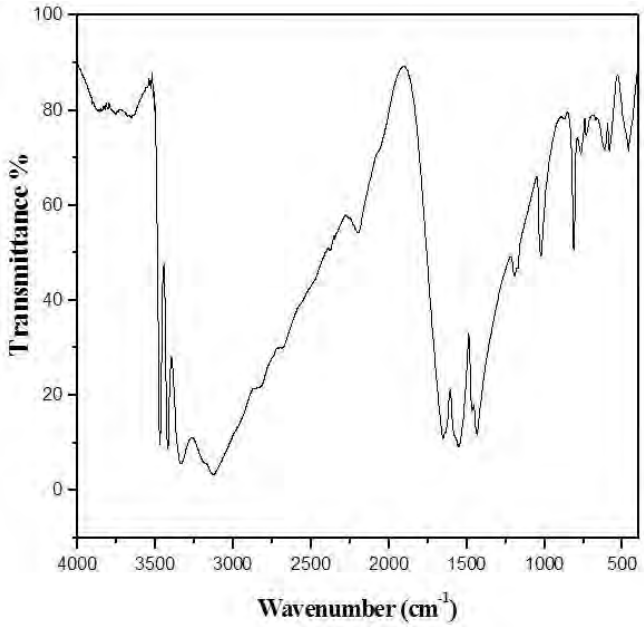

Fig. 3: FTIR spectrum of 2, 4, 6 triamino-1, 3, 5 triazine (melamine) crystal

salts of strong acids which clearly confirms the absence of hydrochloric acid. An intense sharp peak at 3334 cm^{-1} and 3128 cm^{-1} was due to asymmetric NH_2 stretching and symmetric NH_2 stretching respectively [20]. The medium IR band at 1024 cm^{-1} was assigned to C-N stretching [19]. A sharp peak at 1653 cm^{-1} was assigned to NH_2 deformation [19]. The strong absorption peaks at 1551 cm^{-1} and 1436 cm^{-1} and medium band at 813 cm^{-1} were assigned to 1,3,5 s-triazine ring quandrant stretching, semicircle stretching and out of plane ring bending sextant [19]

3.4 FT NMR Studies

In the present work, the ^{1}H NMR and ^{13}C NMR spectra of the grown melamine crystal have been recorded. The ^{1}H NMR and ^{13}C NMR spectral analysis are the two important analytical techniques used to study the structure of organic compounds. The spectra are presented in Figs. 4a and 4b respectively. An intense singlet peak observed at 4.514 δ (ppm) is due to the presence of undeuterated water in D_2O. Melamine peak at 5.93 ppm is not seen because of rapid proton exchange in the NH_2 groups with the solvent proton [21]. The upfield signals at 162 and 172 ppm in ^{13}C NMR spectrum may be attributed to triazine part of melamine [21]. The lack

Table 2: Vibration band assignment

Wave number (cm^{-1})	Description	References
3469	NH2 stretching of melamine and absent in salts of strong acids	19
3419	NH2 stretching of melamine and absent in salts of strong acids	19
3334	Asymmetric NH2 stretching	19,20
3128	Symmetric NH2 stretching	19
1653	NH2 deformation	19
1551	1,3,5 s-triazine quadratic stretching	19
1436	1,3,5 s-triazine semi circle stretching	19
1195	C-N stretching mode	19
1024	C-N stretching, primary amine	19
813	1,3,5 s-triazine out of plane ring bending by sextants	19

of signals pertaining to NH groups indicates that none of the nitrogen atoms of the constituents is protonated or deprotaned.

3.5 Thermo Gravimetric Analysis

The TGA and DTA traces are shown in Fig. 5a. The TGA curve gives useful information regarding the thermal stability and composition of the sample under investigation. The thermal behaviour of melamine was already published [22]. The TG curve exhibits mass loss in two stages which indicate that the decomposition takes place continuously. It is seen that the TG curve shows a plateau up to 238.39°C suggesting that the materials is thermally stable upto a temperature of 238.39°C. After this temperature, the curve describes a mass loss of 73.29 % in the temperature range of 238.39°C to 274.95°C, 57.05% upto 305.21°C. The curve shows multiple indistinguishable peaks between 233°C to 365°C. This indicates that the intermediate products undergo multiple oxidative decomposition process. The DTA curve of the sample show one sharp exothermic peak at 336.31°C which is assigned as the melting point crystal. DSC curve is shown in Fig. 5b. In the DSC study, one endothermic stage is observed. Area under a peak is 473.9 J/g. The DSC curve comprises of one step. The initial temperature is 250°C and

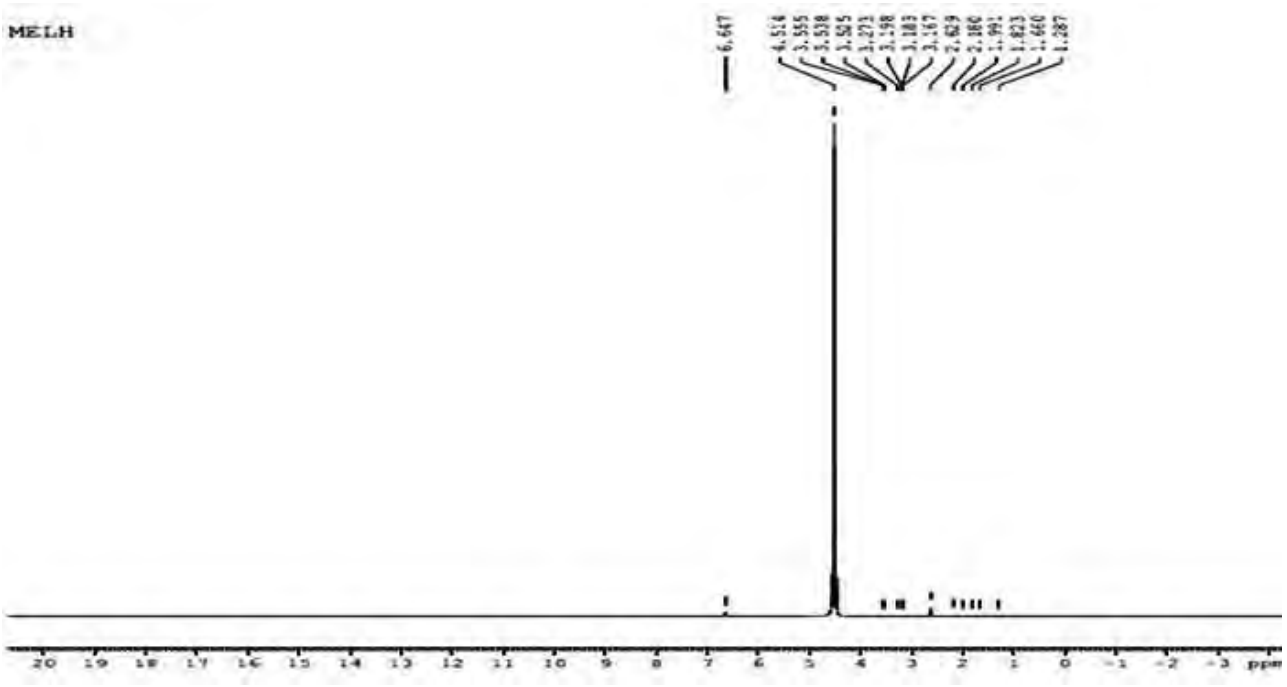

Fig. 4a: Proton NMR spectrum of 2, 4, 6 triamino-1, 3, 5 triazine (melamine) crystal

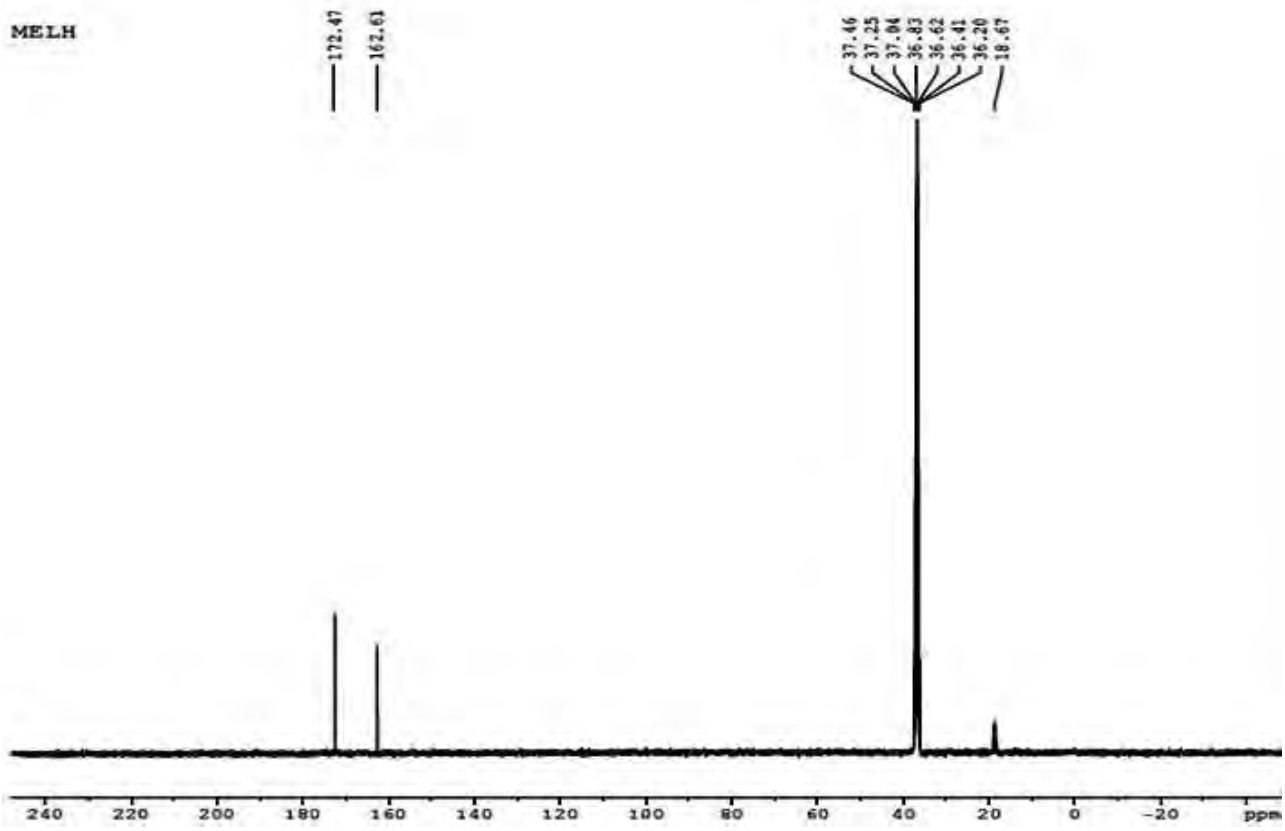

Fig. 4b: Carbon NMR spectrum of 2, 4, 6 triamino-1, 3, 5 triazine (melamine) crystal

equilibrium is 337.64ºC. At 250ºC, the initiation of phase change starts and completed at the peak exotherm temperature of 337.64ºC. The TG/DTA results obtained are fairly in agreement with those in the literature [22]. The presence of triazine ring in their structure provides improved thermal stability [23]. From this, it is identified that there is no phase transition up to its melting point and this enables the suitability of the crystal for NLO applications.

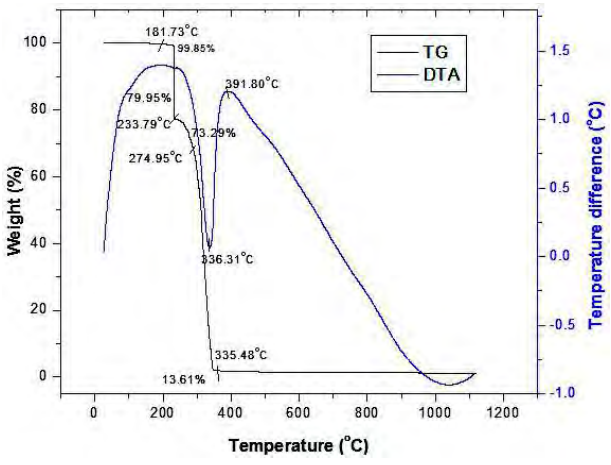

Fig. 5a: TG-DTA spectrum of 2, 4, 6 triamino-1, 3, 5 triazine (melamine) crystal

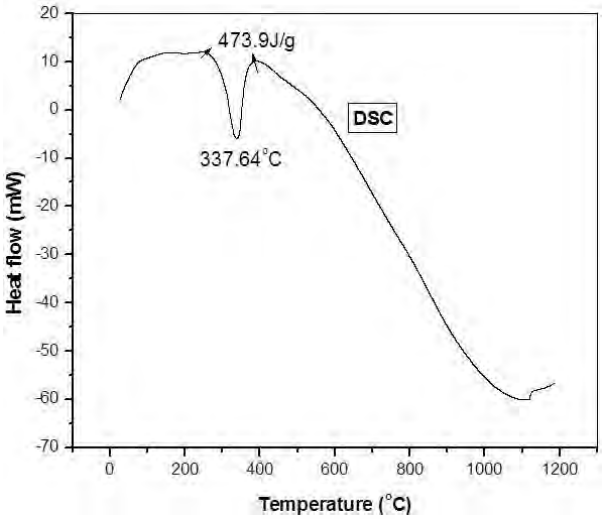

Fig. 5b: DSC spectrum of 2, 4, 6 triamino-1, 3, 5 triazine (melamine) crystal

3.6 Non Linear Optical Test

Kurtz second harmonic generation (SHG) test was performed to find the NLO property of the grown crystal. Nd:YAG laser using the first harmonics output of 1064 nm with pulse width of 8 ns and repletion rate 10 Hz was passed through the sample. The second harmonics signal, generated in the crystal was confirmed to form the emission of green radiation by the crystal. Usually SHG signal was not observed in the centrosymmetric crystals, but in the present case, the emission of green radiation may be due to the presence of surface defects or any other factor [24].

4. Conclusion

The single crystals of 2,4,6-triamino 1,3,5-triazine (melamine) have been grown by slow evaporation method with the addition of hydrochloric acid. From the XRD analysis the lattice parameters of the grown crystal were calculated. They are in good agreement with reported values. The functional groups were identified by FTIR analysis which confirms the absence of hydrochloric acid. FT-NMR spectroscopic analysis confirms the molecular structure of the grown compound. The thermal analysis reveals that the grown crystal is stable up to 336ºC. The SHG signal was confirmed by Kurtz Perry method.

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