

# Growth, spectral and thermal characterization of 8-hydroxyquinoline

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**Abstract** A novel nonlinear optical organic crystal 8-hydroxyquinoline has been grown by slow evaporation technique at room temperature (RT) using chloroform as the solvent. The solubility of 8-hydroxyquinoline in chloroform has been determined at various temperatures. The grown crystals were found to be transparent in the visible region. The grown crystals were characterized employing several techniques such as UV, FT-IR,  $^1\text{H}$  NMR spectral analysis and TG–DTA studies. Preliminary measurements indicate that the second-harmonic generation efficiency at a fundamental wavelength of 1064 nm is roughly 4.28 times that of KDP crystal.

**Keywords** 8-Hydroxyquinoline · TG–DTA · UV · FT-IR ·  $^1\text{H}$  NMR · SHG

## Introduction

Organic nonlinear optical (NLO) materials have been intensively investigated due to their potentially high nonlinearities and rapid response in electro-optic effect compared to inorganic NLO materials. These molecular organic

compounds with one or more aromatic systems in conjugated positions, leading to charge transfer systems have been intensely studied for the past two decades. These compounds must crystallize in a non-centrosymmetric class in view of application making use of quadratic optically nonlinear effects.

The organic NLO materials play an important role in second-harmonic generation (SHG), frequency mixing, electro-optic modulation, optical parametric oscillation, optical bistability, etc. However, their practical applications are limited by poor chemical stability, poor phase matching properties caused by large birefringence and difficulties still remain in crystal growth. Thermal analysis and spectral analyses are very useful methods for materials characterization. Therefore, many authors have used these techniques for various materials characterization [1–20]. In this paper, we report the studies on growth and characterization of 8-hydroxyquinoline, a promising material for NLO applications.

## Experimental

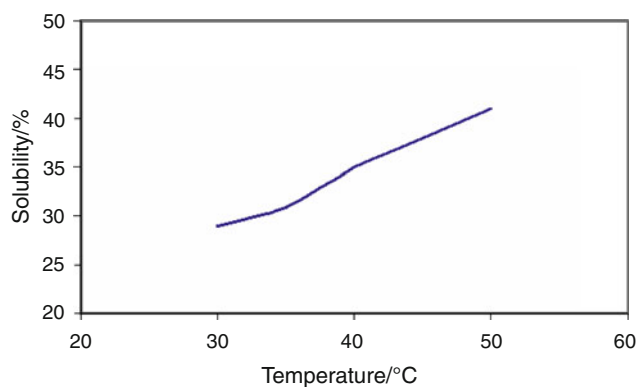
### Crystal growth

The 8-hydroxyquinoline has a molecular mass of 145.16 g with a melting point of 74–76 °C. The starting material (AR grade) was recrystallized several times from chloroform to ensure low absorption and scattering good quality transparent crystals should be grown. The solubility curve of 8-hydroxyquinoline in chloroform is shown in Fig. 1. The positive slope of the curve shows that crystals of better size can be grown by slow cooling technique. Since chloroform was used as solvent, slow evaporation method was found to be more convenient for crystal growth.

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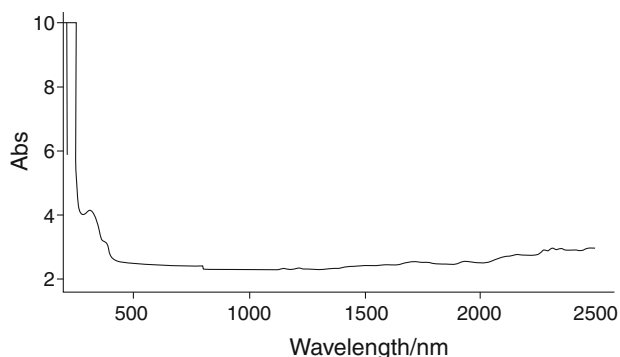
**Fig. 1** Solubility diagram of 8-hydroxyquinoline

A saturated solution of 8-hydroxyquinoline was taken in a beaker covered with thick polythene cover for controlled evaporation. Good transparent, needle shaped crystals were obtained within 2 days.

## Results and discussion

### UV–visible spectral analysis

A good optical transmittance is very desirable in an NLO crystal since the absorptions, if any, near the fundamental or the second harmonic of a Nd:YAG laser, 1064 and 532 nm, respectively will lead to a loss of conversion efficiency of SHG and this has been a specific drawback in many organic crystals. To determine the optical absorbance range and hence to know the suitability of 8-hydroxyquinoline single crystals for optical applications the UV–Vis–NIR absorbance spectrum (Fig. 2) was recorded with a Cary 5E UV–Vis–NIR spectrophotometer in the range 200–2500 nm. The spectrum shows the characteristic absorption below 400 nm and is assigned to aromatic ring [21]. The lower cut off below 400 nm combined with the very good transparency, attests the usefulness of this material for optoelectronic application, the generations of



**Fig. 2** UV–visible spectrum of 8-hydroxyquinoline

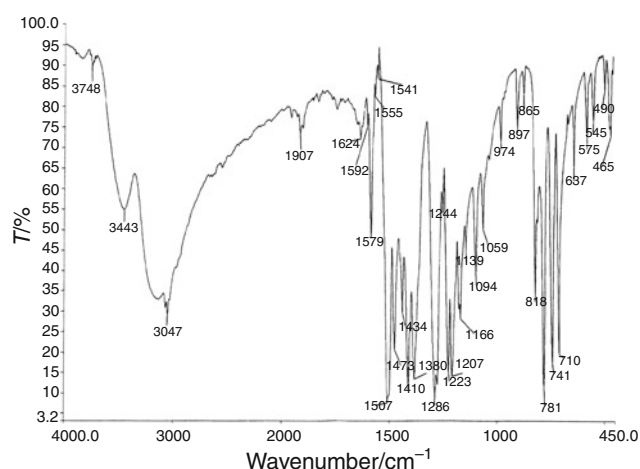
the second harmonic and for the generation of sum and difference frequencies.

### FT-IR spectral analysis

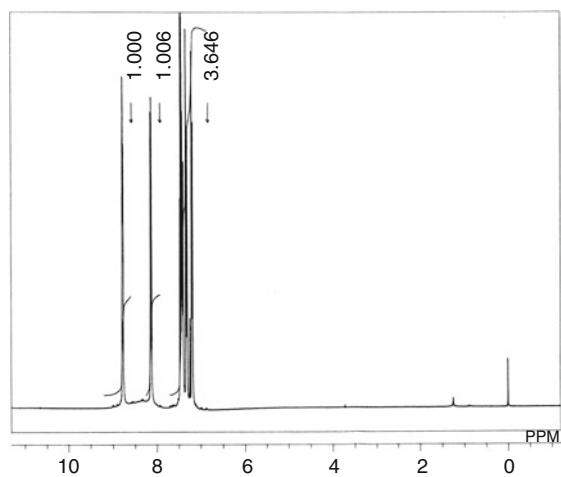
The infrared spectral analysis has been carried out to understand the chemical bonding and it provides useful information regarding the molecular structure of the compound. The infrared spectrum of 8-hydroxyquinoline (Fig. 3) was recorded with a Bruker IFS 66 VFT-IR spectrometer equipped with a cooled MCT detector at a resolution of  $\pm 1 \text{ cm}^{-1}$  in the range 450–4000  $\text{cm}^{-1}$ . To analyze the FT-IR spectrum, the molecular structure of this compound has been taken into account. The presence of a sharp peak in the IR between 3590 and 3400  $\text{cm}^{-1}$  is due to hydroxyl group vibrations of the system which possess intra molecular hydrogen bonding [21].

Accordingly, in 8-hydroxyquinoline the –OH absorption band is found at 3443  $\text{cm}^{-1}$  in the measured FT-IR spectrum.

The C–O stretching frequency was observed between 1600 and 1700  $\text{cm}^{-1}$  in the compounds where the C–O group is intra molecularly hydrogen bonded to the OH group. In 8-hydroxyquinoline the FT-IR bond observed at 1579  $\text{cm}^{-1}$  is due to C–O stretching mode. The infrared band found at 1380  $\text{cm}^{-1}$  is assigned to ring stretching vibration of 8-hydroxyquinoline. The characteristic absorption of broad band near 3047  $\text{cm}^{-1}$  is assigned to C–H stretching vibration of 8-hydroxyquinoline. The very strong absorption band of C=C stretching is observed at 1507  $\text{cm}^{-1}$  and C–O stretching is found at 1223  $\text{cm}^{-1}$ . The out-of-plane bending of C=C in the ring is at 710  $\text{cm}^{-1}$ . The most characteristic absorption of poly nuclear aromatic compounds results form C–H out-of-plane bending at 781  $\text{cm}^{-1}$ . The C=N stretching vibration is observed at



**Fig. 3** FT-IR spectrum of 8-hydroxyquinoline



**Fig. 4**  $^1\text{H}$  NMR spectrum of solution grown 8-hydroxyquinoline

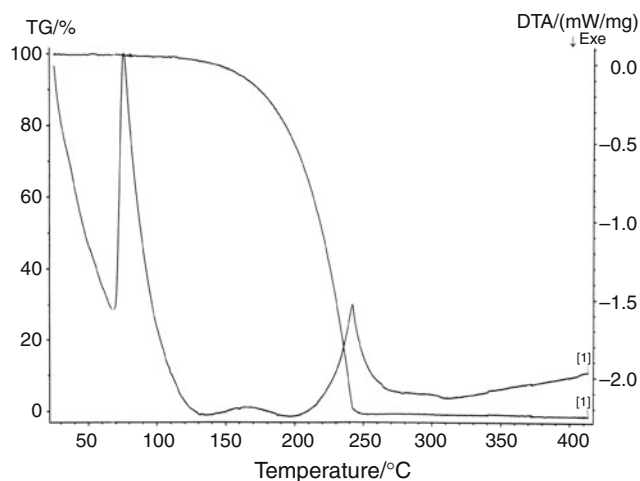
$1624\text{ cm}^{-1}$ . The different modes of vibration of 8-hydroxyquinoline were well found in the vibrational spectrum in their respective characteristic regions.

#### FT-NMR spectral analysis

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra of 8-hydroxyquinoline were recorded using JEOL GSX 400 NMR spectrometer 400 MHz with a resolution of 0.49 for  $^1\text{H}$  NMR to confirm the molecular structures. The observed spectra are shown in Fig. 4. In  $^1\text{H}$  NMR spectrum, a doublet observed at 8.78 is assigned to H-2 proton. At 7.20 a doublet of doublet is observed for H-3 proton. A doublet observed at 8.13 is assigned for H-4 proton. A doublet of doublet is observed for H-6 proton at 7.40. A multiplet is observed for H-5 and H-7 protons between 7.43 and 7.46 [21]. Due to hydrogen bonding,  $\tau$  values may be lowered to about one and chelated OH absorb at negative  $\tau$  (off the scale) [21].

#### Thermal analysis

The thermogravimetric (TG) analysis and differential thermal analysis (DTA) curves for 8-hydroxyquinoline obtained to assess the thermal ability of the grown crystals using simultaneous thermogravimetric analyzer (STA 409C thermal analyzer) up to 400 °C are shown in Fig. 5. The TG curve shows that there is a mass loss of about 98% in the temperature range 150–240 °C. The mass loss in this range is due to the decomposition of 8-hydroxyquinoline. The reported melting point range of 8-hydroxyquinoline is 74–76 °C which is in accordance with the exothermic peak observed in DTA at 75.80 °C. The melting point of 8-hydroxyquinoline was also determined using melting point apparatus and found to be 76 °C. This supports the purity of the grown crystals.



**Fig. 5** TG and DTA curves of solution grown 8-hydroxyquinoline

#### SGH study

A preliminary study of the powder SHG measurements were performed using a modified Kurtz technique [22] with 1064 nm laser radiations. An Nd:YAG laser producing pulses with a width of 8 ns and a repetition rate of 10 Hz was used. The crystalline sample was powdered to particle sizes in the range 125–150  $\mu\text{m}$ . To make relevant comparisons with known SHG materials, KDP was also grinded and sieved into the same particle size range. The powdered samples were filled air-tight in separate micro-capillary tubes of uniform bore of about 1.5 mm diameter. The SHG output (532 nm) was emitted and collected by a photo multiplier tube. The optical signal incident on the photo multiplier tube was converted into voltage output at the CRO. The SHG output in each case was measured as the average of a few pulses to eliminate slight variations of input power. The input laser energy incident on the capillary tube was chosen to be 4.8 mJ, an energy level optimized not to cause any chemical decomposition of the sample. The results obtained for 8-hydroxyquinoline show a powder SHG efficiency of about 4.28 times that of KDP.

#### Conclusions

A potential organic material, 8-hydroxyquinoline for NLO applications is grown by slow evaporation solution growth technique using chloroform as solvent. The solubility study was performed at various temperatures. The FT-IR and FT-NMR spectroscopic analysis confirms the molecular structure of the compound. The melting point of the crystal is found to be 75.8 °C, using DTA. The material has no absorption in the range 400–2500 nm, thus confirms the

suitability of this material for NLO application. The powder SHG efficiency is about 4.28 times of that of KDP.

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