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Preparation, characterization and non-linear optical properties of pristine *m*-nitroaniline (*m*-NA) and its recycled polystyrene (Re-PS) coated single crystals

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Abstract

Meta-nitroaniline (*m*-NA) is one of the organic single crystals extensively studied due to its high non-linear effect. *m*-NA is also known to exhibit comparable or even better non-linear optical (NLO) properties than known inorganic materials. In this paper, we report development of *m*-NA single crystals by solution growth technique using different solvent systems. The size of the single crystal varies depending on solvent. The highest average crystal size acquired was 10 mm × 5 mm × 5 mm using methyl ethyl ketone and acetone as solvent. These single crystals were characterized using various physico-chemical techniques such as XRD and scanning electron microscopy (SEM). The developed crystals were subsequently coated with recycled polystyrene (Re-PS) (1, 2, 5 and 10 wt% concentrations) to study the effect of polymer coating on the second harmonic generation (SHG) properties of the single crystals. The purpose of polymer coating on *m*-NA single crystal is to improve surface morphology of crystal (i.e. it makes surface smooth) and to enhance power handling capacity for pulse laser of a crystal which, in turn, improves the SHG intensity. The optimum percentage of coating was determined for the *m*-NA single crystals obtained from different solvent systems. Furthermore, the polymer coating also plays key role in preventing the degradation of the *m*-NA crystal (well-known as highly sublime material) and ultimately increasing the shelf life of the crystal for its device application.

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1. Introduction

In recent years, non-linear second-order cascading effects in organic crystals have drawn much attention in the context of not only basic understanding of non-linear optical (NLO) optical process which occurs in organic crystals but also in the context of potential end-applications related optical devices [1,2]. Organic crystals with large second-order non-linear susceptibilities are of great interest because of their potential use as an optical parametric amplifier and an optical parametric oscillator in infrared region [3,4].

Meta-nitroaniline (*m*-NA) is an important material in the research field of non-linear optics, which exhibits enhanced non-linear and electro optic effects [5,6]. It may be noted that the effect of second harmonic generation (SHG) of *m*-NA is higher by one order magnitude than that of $LiNbO_3$ [7].

Development of organic single crystals is one of the important emerging areas of optoelectronics and molecular

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engineering for advanced high tech devices. There are various methods by which organic single crystals can be grown. For example, *m*-NA single crystal is grown either by chemical vapor deposition or by Bridgman method [8]. Huang et al. reported [9] growth of *m*-NA single crystal using solution growth technique. However, these methods produce only smaller size crystals. Therefore, by considering the difficulty in growing large size organic single crystals and importance of knowledge of intrinsic properties acquirable in very pure and perfect crystals, we have worked out a program to grow single crystals of high purity and crystalline perfection. In order to preserve the single crystals for repeated use, the single crystals require an appropriate polymer coating for a prolonged life and protection of the surface for reproducible results. In continuation with our previous work on *m*-NA single crystals and *m*-NA doped nanocomposite films [10–13], we herein report the growth of *m*-NA single crystals in different solvent systems like acetone, ethanol, methanol and methyl ethyl ketone (MEK). Besides, the surface of the crystal is coated with thin coating of recycled polystyrene [Re-PS] using dip coating technique. We have specifically used Re-PS due to its low price and optical transparency. Pristine crystals and polymer-coated crystals were characterized by different techniques. The effect of polymer coating on the optical properties of *m*-NA single crystals is studied using second harmonic generation properties. The polymer coating plays key role in preventing the degradation of the *m*-NA crystal (well-known as highly sublime material) and ultimately increasing the shelf life of the crystal for its device application. The preliminary account of this work is furnished in this paper.

2. Experimental procedure

Commercial grade *m*-NA powder (Loba Chemicals, India) was recrystallized 3 times in AR grade acetone for better purity. The recrystallized powder was again purified with utmost care by vacuum sublimation technique before its usage. Single crystals of *m*-NA were developed by solution growth technique in various solvent systems such as methanol, ethanol, acetone and MEK. For making the crystals, the saturated solution of *m*-NA in respective solvent was kept for few days in order to evaporate the solvent slowly (about three to four weeks, depending on the boiling point of solvent). Transparent crystals were obtained by evaporating the solvent at room temperature. To speed up the crystal formation process, seed crystals of *m*-NA were introduced in the solution. For minimizing the rate of evaporation, the beaker was kept tightly closed.

Subsequently, these single crystals were coated with Re-PS (1, 2, 5 and 10 wt% in benzene). Coating of Re-PS was done uniformly by dip coating method. After coating, the crystals were dried in an oven at 80 °C for 24 h.

Since the resultant single crystals were too large for the single crystal X-ray diffractometry, we relied upon powdered X-ray diffractometry of *m*-NA. Nevertheless, we selected the smallest crystal from the sample lot for single crystal X-ray analysis. The powdered diffractograms were recorded on a Philips PW 1710 diffractometer using Cu Kα ($\lambda = 1.541$) radiation and Ni filter. Single crystal X-ray analysis was done using single crystal X-ray CCD diffractometer (Bruker-AXS, SMART APEX). Scanning electron microscopy (SEM) image was obtained by means of Philips 30 XL instrument, which was operated at 10 kV in the secondary electron imaging mode.

3. Results and discussion

It is well-known that *m*-NA sublimes very readily which is one of the major problems in its potential use as a NLO material. To overcome this difficulty, we coated the *m*-NA single crystal with Re-PS. The polymer-coated single crystals are found to be environmentally more stable than the uncoated crystals.

Preliminary studies shown that the rate of evaporation of solvent plays important role in deciding the size and nature of single crystals. Moreover, the dielectric constant of a solvent also plays a key role in development of crystal and additionally governs the optical properties of the resultant crystal. It is worthwhile to note that slow evaporating solvent like MEK takes several days while relatively fast evaporating solvents like ethanol require few days for growing single crystals. Table 1 summarizes the effect of solvents on size and the nature of the crystals.

The powdered X-ray diffraction pattern is presented in (Fig. 1). The *hkl* and *d* values reasonably match with the reported values [14]. The single crystal XRD data (recorded in case of the smallest possible single crystalline *m*-NA) reveals that the crystals belong to the orthorhombic system with unit cell parameters ($a = 6.507$ Å, $b = 19.529$ Å and $c = 5.087$ Å). This is in gross agreement with the reported work [8].

Morphology of single crystal was examined by SEM. SEM images show (i) rough morphological features for pristine samples (Fig. 2a) while (ii) smooth morphology for Re-PS coated samples (Fig. 2b). The rough morphology might have been intrinsically originated at the time of crystal formation. However, Re-PS coating might render the surface smooth and, in turn, may favorably reduce the scattering of laser light. This ultimately reflects in the

Table 1
Effect of solvent on crystal nature

Solvents	Dielectric constant	Boiling point (°C)	Size/shape of the single crystals
Acetone	2.88	56.2	$10 \times 5 \times 5\,mm^3$
Methanol	1.70	65.0	$5 \times 2 \times 2\,mm^3$
Ethanol	1.69	78.5	Needle shaped single crystals of assorted size
Methyl ethyl ketone	2.78	79.6	$10 \times 5 \times 5\,mm^3$