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Influence of Lanthanum (La^{3+}) on Structural, Spectral and Thermal Properties of Meta Nitro Aniline (mNa) Single crystals.

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ABSTRACT

Organic Nonlinear Optical single crystals of Pure and Lanthanam(La^{3+}) doped meta nitroaniline (mNa) were grown successfully by slow evaporation technique. Powder XRD analysis of pure and doped crystals confirm the crystalline nature of the grown crystals. It was found that doping has not altered the orthorhombic structure of crystals. Optical absorptions of the samples were analyzed using UV-Vis spectroscopic studies. Doped crystals exhibit low absorption in the visible region of the spectrum than the pure crystals. FT-IR and FT-Raman spectral analysis of the grown crystals confirm the presence of various functional groups in pure and doped samples. TG - DTA studies showed that doping had altered the decomposition temperature of the crystal. Second Harmonic Generating (SHG) efficiency of pure and doped crystals was found as 30.4 times and 32.6 times respectively as KDP.

Keywords: SHG, Lanthanum, mNA, FT-IR.

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INTRODUCTION

In recent decades, more attention had been paid towards organic nonlinear optical materials because of their wide transparency in UV and visible region, high nonlinear susceptibility, high laser damage threshold and fast response than the commercially available inorganic materials. By molecular engineering, one can develop many organic crystals displaying better nonlinear optical properties than the inorganic materials, in particular for Second Harmonic Generation (SHG) [1]. The basic structure of organic nonlinear optical (NLO) materials is based on the π bond system. Due to the over-lap of π orbital, delocalization of electronic charge distribution leads to a high mobility of the electron density [2]. Functionalization of both ends of the π bond system with appropriate electron donor and acceptor groups can increase the asymmetric electronic distribution in either or both ground and excited states, leading to an increased optical nonlinearity [3]. In this paper, we report for the first time optimization conditions for the growth of pure and La^{3+} doped good quality single crystal of mNA by slow evaporation method using acetone as solvent. The grown pure and doped single crystals of mNA were subjected to X-ray powder diffraction, UV-Vis spectroscopy, FT-IR, FT-Raman, TG-DTA and SHG studies.

GROWTH OF MNA SINGLE CRYSTALS

The saturated solution of pure and doped mNA in acetone was prepared at 40°C. The purified mNA materials were used for solubility studies and to grow bulk single crystals. Since mNA is less soluble in water acetone was chosen as the solvent. The solutions were filtered at the same temperature to avoid any insoluble impurities. Then, the solvent was allowed to evaporate, in order to obtain the maximum purification. The yielded materials were further recrystallized twice before the growth is initiated. The purified salts were used to grow good optical quality bulk single crystals of pure and La^{3+} doped meta-nitroaniline. Figure.1 and 2 shows the photograph of as grown pure and doped mNA single crystals respectively.

Figure 1: Photograph of pure mNA crystal

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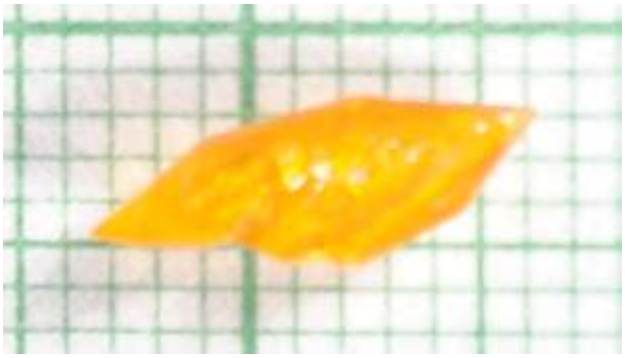

Figure 2: Photograp of La^{3+} doped mNA crystal

POWDER X-RAY DIFFRACTION TECHNIQUE

The grown mNA sample was crushed as fine powder for X-ray diffraction studies. The recorded X-ray diffraction pattern for pure and doped mNA sample is depicted in Figure 3 and 4. The recorded spectrum of the sample was taken at room temperature in a 2θ range of 10 to 50° using CuKα radiation of wavelength 1.5418 Å. Using the orthorhombic crystallographic equation, the lattice parameter values of mNA were calculated. . It is confirmed that mNA belongs to orthorhombic crystal system, the unit cell parameters were found to be a = 6.501 Å, b = 19.330 Å and c = 5.082 Å with point group mm2, space group $Pbc2_1$ and Z=4. There are slight variations in the lattice parameters and cell volume of the pure and doped crystals. These variations are due to the incorporation of La in the mNa crystal lattice.

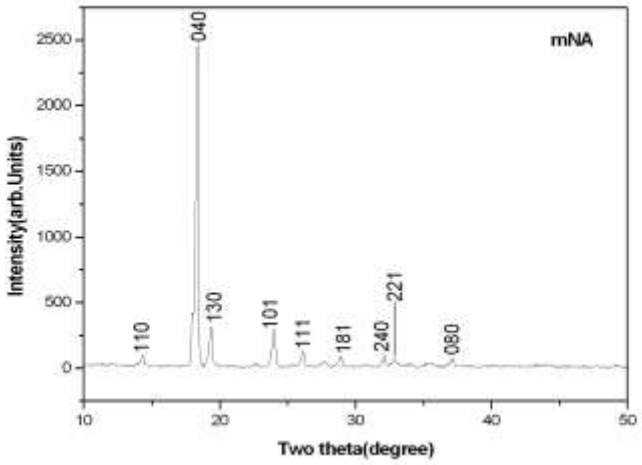

Figure 3: XRD pattern of pure mNA single crystal

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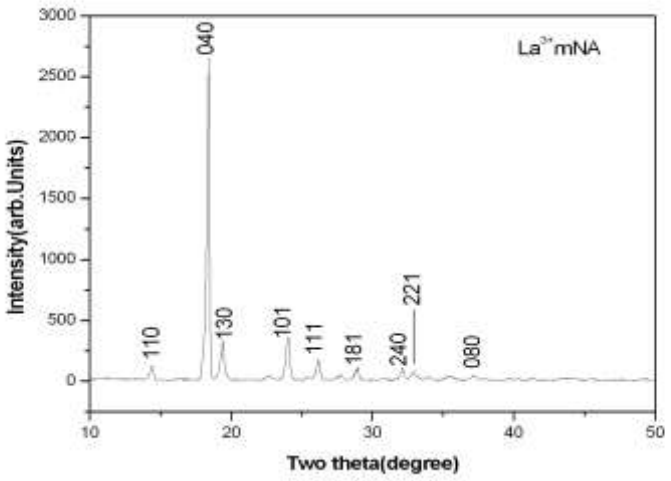

Figure 4: XRD pattern of La^{3+} doped mNA single crystal

UV-Vis STUDIES

Optical window width is an important characteristic of an NLO material. Hence, it is necessary that the transmission of electromagnetic waves of the UV–Vis range is measured [4]. The optical absorption spectra of pure and La^{3+} doped mNA crystals have been recorded in the region 200-2000 nm using Varian Cary 5E Model spectrophotometer. The UV-Vis transmission spectra of pure, and La^{3+} doped mNA single crystals are shown in Fig5. The lower UV cut-off for both the crystals is around 300 nm. It is seen that La^{3+} dopant has decreased the percentage of absorption in mNA.

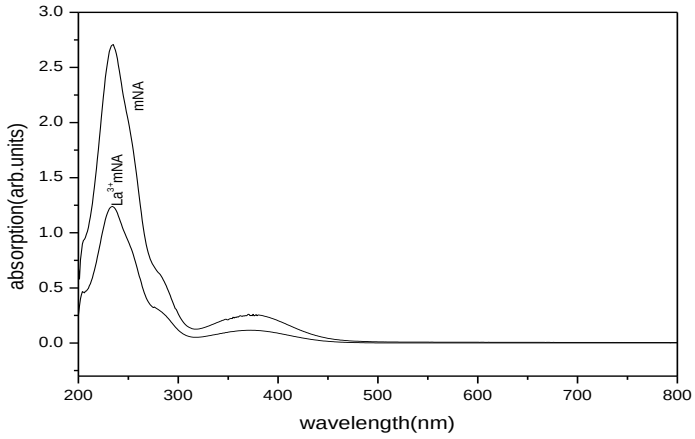

Figure 5: UV-Vis Spectrum of pure and La^{3+} doped mNA single crystal

RAMAN ANALYSIS

In order to qualitatively analyze the presence of functional groups in mNA, Fourier Transform Raman (FT-Raman) spectra were recorded for the pure and doped mNA, in the range 50 cm^{-1} – 4000 cm^{-1}. The recorded spectra of the pure and doped mNA are shown in Figure 6 and 7. The NH_3^+ stretching frequencies are found for both the pure and La^{3+} doped

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mNA compounds at 3074 cm^{-1}. For this compound a small peak observed in the measured Raman spectrum at 1522 cm^{-1} is assigned to NO_2 asymmetric stretching mode. A peak at 1477 cm^{-1} is due to CH_3 bending vibrations. A peak at 1265 cm^{-1} is CH_3 rocking mode.

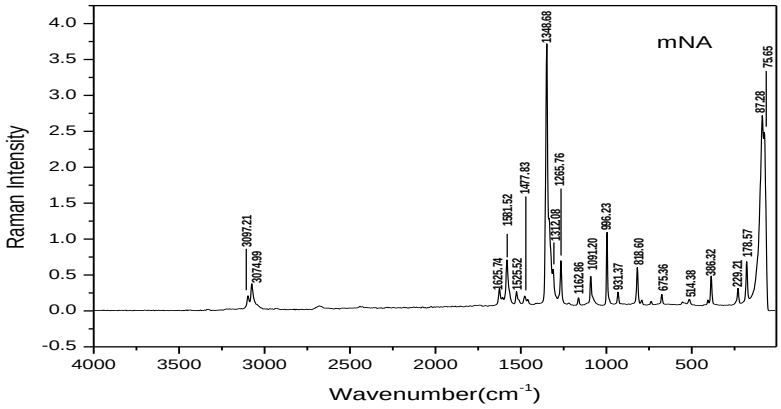

Figure 6: FT-Raman Spectrum of mNA single crystal

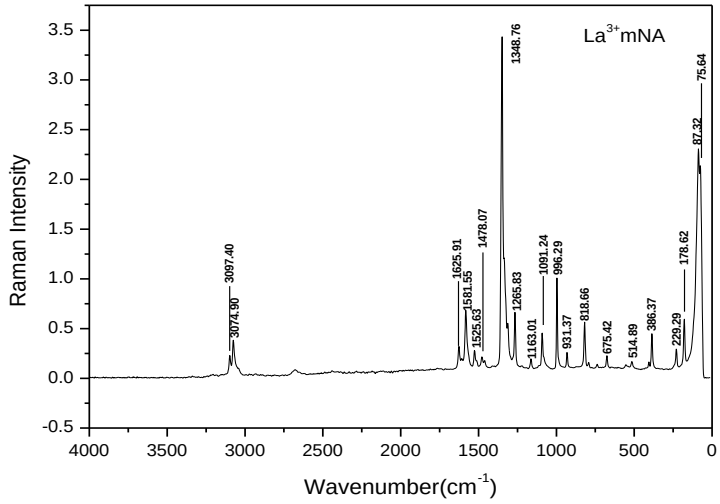

Figure 7: FT-Raman Spectrum of La^{3+} doped mNA single crystal

FT-IR STUDIES

To understand the presence of functional groups in mNA, FT-IR spectra of the pure and metal doped mNA crystals were recorded in the range 400 cm^{-1} to 4000 cm^{-1}, using KBr pellet on BRUKKER IFS FT-IR Spectrometer. The FT-IR Spectra of both the pure and doped mNA crystals are shown in Figure 8 and 9. The NH stretching bands are observed at 3201 cm^{-1},

3198 cm^{-1}, in the spectrum. A vibrational peak at 1522 cm^{-1} is due to NO_2 stretching vibrations. In general, the bands around1650–1300 cm^{-1} [5, 6] in benzene derivatives are assigned to skeletal stretching C–C bands. The bands for C – C stretching vibrations are observed at 1488 and 1465 in the pure and doped samples.

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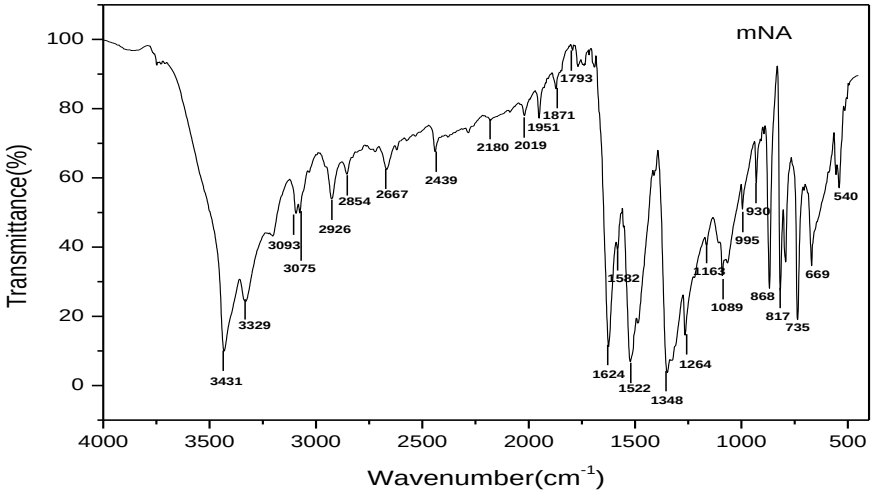

Figure 8: FT-IR Spectrum of pure mNA single crystal

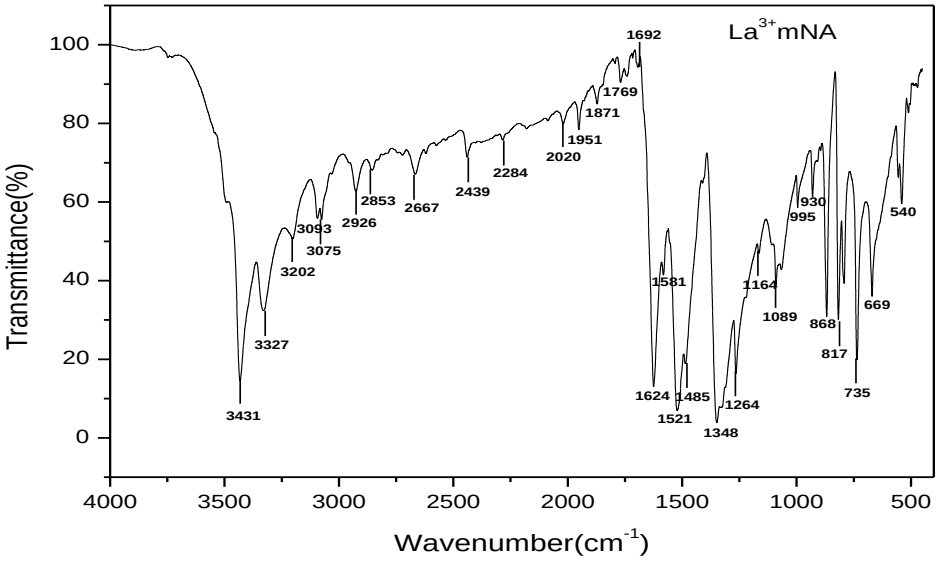

Figure 9: FT-IR Spectrum of La^{3+} doped mNA single crystal

THERMAL STUDIES

Thermo gravimetric and differential thermo gram analyses on pure and La^{3+} doped mNA were carried out at a heating rate of 20°C /min in nitrogen atmosphere. Fig. 10 & 11 shows the Differential Thermal Analysis (DTA) and Thermo-gravimetric Analysis (TGA) curves for pure and doped mNA sample. In the DTA curve the exothermic peak corresponds to its melting point at 118.2°C. Due to doping exothermic peak has changed to 114.0°C and the same can be seen in the above figure. The TGA curve of this sample coincides well with the DTA trace. The sharpness of the peak shows good degree of crystalline of the grown crystal.

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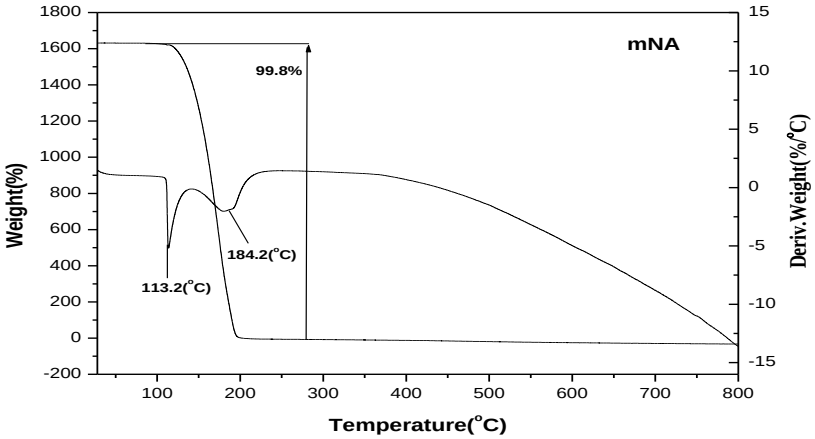

Figure 10: TG-DTA Cure of pure mNA single crystal

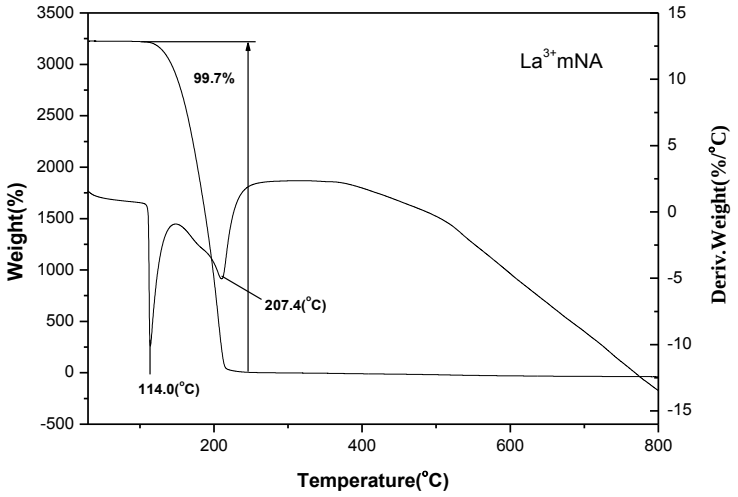

Figure 11: TG-DTA Cure of La^{3+} doped mNA single crystal

NLO STUDIES

The nonlinear optical property of the grown pure and doped mNA single crystal was tested by passing the output of Nd: YAG Quanta ray laser with pulse energy emitting 1064 nm, generating about 6 mJ / pulse. The SHG efficiency of pure and doped mNA was determined by Kurtz and Perry [5] powder technique. Microcrystalline material of KDP was used as a reference for comparison with mNA for Second Harmonic Generation experiments. For a laser input pulse of 6.2 mJ, the second harmonic signal (532 nm) of 92 mW, 2.8 W and 3.0 W, respectively were obtained for KDP, pure and La^{3+} doped mNA samples. Thus, the SHG efficiency of pure and La^{3+} doped mNA are 30.4 times and 32.6 times higher than KDP.

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CONCLUSIONS

Single crystal of pure and La^{3+} doped meta Nitroaniline (mNA) was grown by slow evaporation technique using acetone as a solvent. Powder X-ray diffraction studies were carried out to calculate the lattice parameters of the grown crystals. UV-Vis spectral analysis is carried out for grown crystals. The highest percentage of optical transmission makes the material suitable for second harmonic generation. Experimental Raman and IR spectroscopic analyses were carried out for both pure and doped samples and the presence of functional groups in mNA molecule was qualitatively analyzed. The TG curve of the sample indicates that pure sample is stable up to 118.2°C and doped is stable upto 114.0°C. The sharpness of the endothermic peak shows good degree of crystallinity of the grown crystals. Second harmonic generation was observed for the grown mNA crystal using a Q-switched Nd: YAG laser and the SHG efficiency of pure and doped mNA is 30.4 and 32.6times higher than that of KDP.

REFERENCES

[1] Madhavan J, Aruna S, Anuradha A, Prem Anand D, Vetha Potheher I, Thamizharasan K, Sagayaraj P. Optical Mater 2007; 29: 1211-1216.
[2] P Praveen Kumar, V Manivannan, S Tamilselvan, S Senthil, Victor Antony Raj, P Sagayaraj, J Madhavan. Opt Comm 2008; 281: 2989–2995.
[3] Senthil S, S Pari, R John Xavier and J Madhavan. Optik 2012; 123: 104–108.
[4] J Madhavan, S Aruna, K Prabha, J Packium Julius, Ginson P Joseph, S Selvakumar, P Sagayaraj. J. Crystal Growth 2006; 293: 409–414.
[5] G Socrates. Infrared Characteristics Group Frequencies, John Wiley, GB, 1980.
[6] S Ahmad, PK Verma. Ind J Phys 1990; 64: 50–55.
[7] Kurtz SK, Perry TT. J Appl Phys 1968; 39: 3798.