

# Effect of irradiation on dye doped 4-Methoxy Benzaldehyde-N-Methyl-4-Stilbazolium Tosylate (MBST) crystal

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The organic dye (Rhodamine B) is doped in 4-Methoxy Benzaldehyde-N-Methyl-4-StilbazoliumTosylate (MBST) crystal. Influences of super saturation and dye concentration in the solution, on the color and crystal habit of MBST, were observed. Rhodamine B in the solution at low super saturation and high dye concentration colored the pyramidal section (101) of the crystals. The highly super saturated solutions produce entirely colored crystals. The concentration of dopants in the mother solution was varied from 0.1 mole % to 10mole %. The studies on pure and doped MBST crystals clearly indicate the effect of dopants on the crystal structure, in the absorption of IR frequencies and the non-linear optical property. The frequencies with their relative intensities are obtained in FT-IR of pure and doped MBST. The very weak bands for dopants indicate its presence in low concentration. In view of the ever-growing importance of ion beams in optical material processing, this letter reports room temperature MeV Li<sup>+</sup> ion irradiation induced depletion of hydrogen from single crystalline MBST which has wide applications as a non linear optical material in optoelectronics technology. Irradiations have been performed using 25 MeV Li<sup>+</sup> ions up to a maximum dose of  $2.4 \times 10^{15}$  ions/cm<sup>2</sup>. Simultaneously, detecting the elastically recoiled Li atoms has done hydrogen profiling. A possible explanation of these phenomena is suggested.

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## 1. Introduction

One of the obvious requirements for a non-linear optical crystal is that it should have excellent optical quality. Crystallization is one of the basic processes in which a crystalline solid is formed out other phases, whether solid, liquid or gaseous. There is always an increasing demand to grow large size high quality crystals. They have innumerable potential applications including telecommunications, optical computing, optical data storage, etc. In this series, 4-Methoxy Benzaldehyde-N-Methyl-4-StilbazoliumTosylate (MBST) is one of the recently discovered potential organic NLO materials. MBST is a model system for non-linear optical device application. Optical quality MBST crystal can be grown by conventional solution growth methods as well as by fast growth techniques. MBST is an efficient angle tuned dielectric medium for optical harmonic generation in and near the visible region. This material offers high transmission throughout the visible spectrum and meets the requirement for optical birefringence, large enough to bracket its refractive index for even extreme wavelength range over which it is transparent. Among non-linear optical phenomena, frequency mixing and electro-optic are important in the field of optical image storage and optical communication [1-6]. The understanding of fundamental light-matter interaction has been a driving force in the several areas of optical technology. Non-linear optical materials utilize the non-linear dependence of the

refraction index on the applied electric field to produce other frequencies.

MBST finds widespread use as frequency doublers in laser applications and has been studied in great detail. Improvement in the quality of the MBST crystal and the performance of MBST based devices can be realized with suitable dopants. The effects of impurity atoms on the quality and performance of the material are analyzed. In the present investigation, the growth aspects of MBST and doped MBST have been studied. Bulk crystals of MBST and doped MBST were grown by slow evaporation and also by slow cooling techniques. The structural, chemical, optical, mechanical and non-linear optical properties of the doped crystals were studied with the characterization studies such as powder XRD, FT-IR, and SHG measurements respectively. The results for doped MBST are compared with the results of the pure MBST crystals and as well as the results available in [7-10] the literature. In the recent years, 25 MeV Li<sup>+</sup> ion implantation (up to dose of  $10^{16}$  ions/cm<sup>2</sup>) has been used to produce optical wave-guides in a large number of materials like oxides (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>), phosphate (KTiOPO<sub>4</sub>), niobates (LiNbO<sub>3</sub>, KNbO<sub>3</sub>) etc., for use in the optoelectronic technology. The desired changes [11] in optical properties are brought about by several process, viz., changes in stoichiometry properties of new phases, structural changes, defects produced by the electronic and nuclear energy loss, volume expansion in the nuclear damage region, stress effects etc. occurring during implantation.

## 2. Experimental Procedure

### 2.1 Crystal Growth

Pure MBST crystals were grown from aqueous solution by slow evaporation and also by slow cooling method (0.5 °/day). The same method was followed for doped MBST crystals (0.1 mole % Rhodamine B). The solubility of doped MBST in the solvent was determined for each dopant for temperature 35 °C by dissolving the MBST salt in deionised water in an air-tight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The solubility of doped MBST was measured for each dopant and was found to be 32.75 grams/100 ml at 40 °C for Rhodamine B. The seed crystals were prepared at low temperature by spontaneous nucleation. Seed crystals with perfect shape and free from macro defects were used for growth experiments. Single crystal of MBST and doped MBST were grown using a constant temperature bath (CTB), controlled by the Indtherm temperature programmer/controller. The mother solution was saturated using the initial pH value 4.5 for Rhodamine B dopant. The growth was carried out for more than 20 days by keeping the bath at a temperature of 40 °C.

A few nuclei of doped MBST had appeared at the bottom of the beaker and grew for a few days. The change of super saturation was greater than 15% of the critical super saturation during the growth of doped MBST crystals. Constant temperature bath were used for the bulk growth of dye doped MBST crystal. Transparent good quality crystals (Fig. 1) were obtained after 20 days.

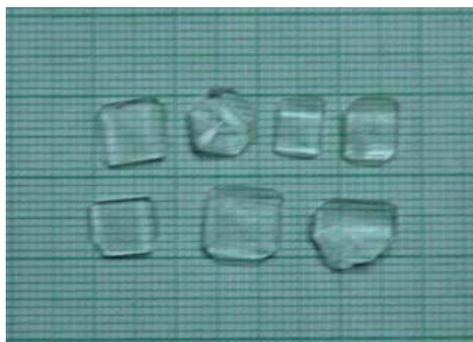


Fig.1 Seed crystals of Rhodamine B doped MBST crystal.

### 2.2 Characterization studies

Powder X-ray diffraction studies were carried out for the as grown crystals using a Rich Seifert X-ray diffractometer with  $\text{CuK}\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation. The FT-IR spectra of all the crystals were recorded from solid phase samples on Shimadzu-800, FTIR spectrometer using 1064nm output of a cw diode pumped Nd:YAG laser as a source of excitation in the region 400 – 4000  $\text{cm}^{-1}$  operating at 200 mW power at the samples with a spectral resolution of 2  $\text{cm}^{-1}$ .

The frequency for all sharp bands is accurate to  $\pm 1 \text{ cm}^{-1}$ . Kurtz SHG test was performed to find the non-linear optical property of MBST (doped with Rhodamine B). The crystal was illuminated using Spectra – Physics Quanta-Ray DHS2 Nd-YAG laser, using the first harmonics output of 1064 nm with a pulse width of 8 ns.

#### 2.2.1 X-Ray diffraction

Powder X-ray diffraction spectra (Fig.2) of the grown crystals were recorded on an automated Philips PW1050 powder diffractometer using the  $\text{CuK}\alpha$  radiation. The digitalized spectra were recorded by step scanning between 10° and 80° in  $2\theta$  with step size 0.05° by counting 2s/step. Throughout the experimental procedure the ambient temperature was maintained at 297K. The values of the lattice parameters were calculated by a local least-squares refinement programme.

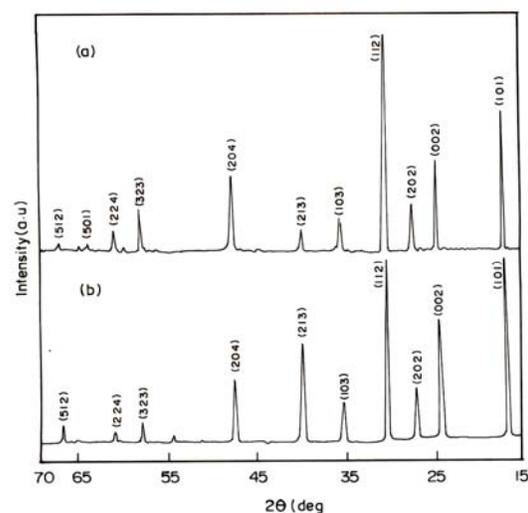


Fig. 2. XRD spectra of (a) Pure, (b) Rhodamine B doped MBST crystal.

#### 2.2.2 FTIR Studies

FT-IR spectra for the pure and doped MBST crystals are as shown in Fig.3. The frequencies with their relative intensities obtained in FTIR of pure and doped MBST. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data. The values of bond length and bond angles were taken from Sutton's table. Internal co-ordinates for the out of plane torsional vibrations [12] are defined as recommended by IUPAC. The general quadratic valence force was adopted for both in plane and out of plane vibrations. The normal co-ordinate calculations were performed using the program given by Schacht Schneider. The initial sets of force constants were taken from the literature for the derivatives of allied molecules. The calculated frequencies agree favorably with the observed frequencies.

With Rhodamine B and at  $3255\text{ cm}^{-1}$  in MBST doped with Rhodamine B indicated clearly the interaction of dopants with P–O–H group of MBST and in weakening the strength of the bond between oxygen and hydrogen. This leads to the decrease in the frequency of O–H stretching and confirmed the non-linear optical property of pure and doped MBST crystals at these sites in the crystal lattice.

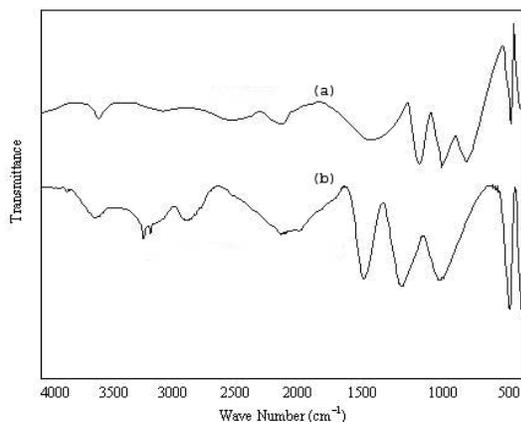


Fig. 3. FTIR spectra of (a) pure and (b) dye (Rhodamine B) doped MBST

The present IR study on pure and doped MBST clearly indicates the effect of dopants on the crystal structure of pure MBST, which leads to the change in the absorption of IR frequencies and the non-linear optical property of both the crystals. Its deviation from pure MBST to lower frequency at  $3100\text{ cm}^{-1}$  in MBST doped with amaranth and at  $3350\text{ cm}^{-1}$  in MBST doped with Amaranth indicated clearly the interaction of dopants with P–O–H group of MBST and in weakening the strength of the bond between oxygen and hydrogen. The study also confirmed that the dopants had entered the lattice sites of MBST.

### 2.2.3 Irradiation Studies on dye doped MBST

Well polished, transparent, single crystalline MBST sample, procured from the Applied Research Centre, Adhiparasakthi Engineering College, Melmaruvathur, Tamil Nadu, India, were used for  $\text{Li}^+$  irradiation at room temperature. The samples were irradiated with 20 MeV Li ions by using a 15 UD Pelletron Accelerator. These studies were performed at room temperature in an experimental chamber under vacuum better than  $10^{-7}$  Torr. The beam was scanned a  $10\text{ mm} \times 10\text{ mm}$  area on the sample using a magnetic beam scanner. The dose of charge accumulated in the sample was measured separately in terms of the fluences and the following fluences were used:  $1 \times 10^{11}$ ,  $1 \times 10^{12}$ ,  $1 \times 10^{13}$  and  $1 \times 10^{14}$  ions  $\text{cm}^{-2}$ . According to the calculation of stopping and ranges of ions in matter (SRIM) [13], the projected range ( $R_p$ ) of the 20 MeV Li ions in DAST is  $7.5\text{ }\mu\text{m}$ . Also the corresponding end of range lateral distribution of straggling is

$4.567\text{ MeV (mg cm}^{-2}\text{)}^{-1}$  and the longitudinal distribution of straggling is  $7.5\text{ MeV (mg cm}^{-2}\text{)}^{-1}$ . The atomic force microscopy (AFM) image was acquired using the Veeco Digital Nanoscope III AFM in the show mode. A Rich Seifert X-ray diffractometer with a monochromatic wavelength of  $1.5405\text{ (CuK}\alpha\text{)}$  was used to record the diffraction pattern.

### 2.2.4 NLO Studies

Schematic representation of the SHG setup is shown in the figure. Approximately 50 mg of material was loaded in to the sample cell, which was formed between two Pyrex  $25 \times 75 \times 1\text{ mm}$  microscope slides (Can lab). Two stripes of masking tape with a 2-cm diameter hole cut through the center were placed 3 cm from the end of one of the slides. The circular window was filled with a thin layer of sample (0.3 mm thick). The second microscope slide was clipped on to the first, sandwiching the sample between slides. The 1064 nm fundamental output from a Q-switched Nd-YAG laser (Quanta Ray) was divided [14-15] by a beam splitter, where one portion of the light was directed on to a reference cell containing urea.

The efficiency of doped MBST crystal was compared with pure MBST and also show that Rhodamin B doped MBST crystal has higher efficiency. A sample of MBST, also powdered was used for the same experiment as a reference material in the SHG measurement (Fig.3). It is found that the frequency doubling efficiency of the doped MBST is better than pure MBST. A comparison of NLO property of doped MBST crystal with a few well-known NLO crystals is presented in Table 1.

Table 1. SHG of pure and dye Rhodamine B doped DAST Crystal

S.No.	Compound	NLO efficiency
1.	KDP	1.00
2.	Rhodamine B doped MBST	1.72

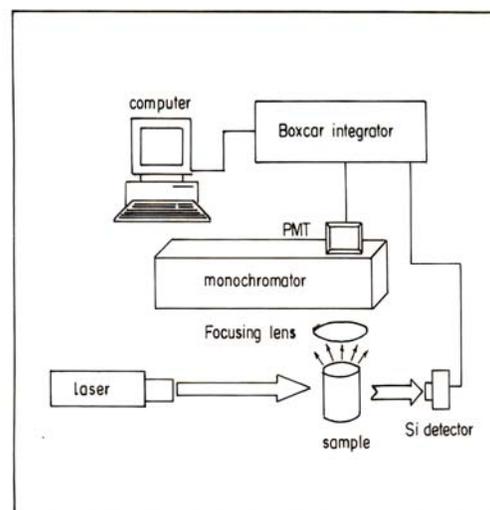


Fig. 3. SHG set up.

### 3. Results and discussion

The dopant Rhodamine B is expected to substitute in the MBST lattice due to their valency as well as their similarity of ionic radius. X – Ray diffraction pattern of the irradiated samples with the ion fluencies of  $1 \times 10^{11} \text{cm}^{-2}$ . It is observed that the prominent peak intensity at an angle ( $2\theta$ ) of  $39.3^\circ$ , which corresponds to bulk MBST, decreases as a function of the incidence ion fluence. Further, the full width half maximum (FWHM) values of the samples increased with the fluence. Since the X – ray-probing depth depends upon the angle of incidence, we have selected the angle of incidents in a wide range. Therefore, in our case, the X – ray penetrates more than 7 micrometers in the sample. This might be due also to creation of an extra plane of interstitials by the irradiation.

The functional groups present in the grown crystals have been confirmed by FTIR spectral analysis. The observed frequencies were assigned on the basis of symmetry operation on the molecule and normal coordinate analysis. The crystallinity of the grown sample was confirmed by single crystal X-ray diffraction analysis. Various functional groups present in the grown crystal were identified by FTIR spectroscopy.

$\text{Li}^+$  irradiations lead to the development [17-18] of a well-defined surface H peak. The depletion of hydrogen from the MBST sample in terms of the possible bond-breaking mechanism. Due to beam interaction, electron moves to the conduction band leaving behind the free hole, which can get self –trapped and configurationally changes occurring in the neighbouring structural units. Irradiation effects diffuse the dyes uniformly in the crystal.

### 4. Conclusion

The doped crystals show good second harmonic generation efficiency. There is a different class of non-linear optical materials, which possess important optoelectronic properties. However, to fabricate optical devices using these materials, a detailed and study of ion induced stoichiometric and structural changes occurring in them are necessary. Most irradiation studies in the hydrogen bonded ferroelectrics have been concentrated on the transient defects induced by ionising radiations such as X-ray and UV light, where the defects are closely related to the optical properties. On the other hand, heavy ion beam irradiation effects have rarely been studied. In this paper, it has been shown that irradiation modifies the optical properties of doped MBST crystal.

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