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Physical Properties of Morpholin-4-ium p-aminobenzoate: A Novel Organic NLO crystal from Benzoate Family

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ABSTRACT

Morpholin-4-ium p-aminobenzoate (MPABA) has been synthesized and crystallized for the first time. The crystal structure of MPABA was solved and found to crystallize in a monoclinic system with a space group Cc. The SHG efficiency was found to be about 11.45 times greater than that of standard KDP. The lower cut-off wavelength and band gap were found to be 327nm and 3.80eV respectively through UV-Vis-NIR spectrum. The dielectric constant and loss were found to be lower than that of important NLO and electro-optic crystals such as DAST, $LiNbO_3$ and $KNbO_3$. Vickers microhardness suggests that this material exhibits reverse indentation size effect. The studies reported suggest that MPABA could be a potential candidate for suitable NLO applications.

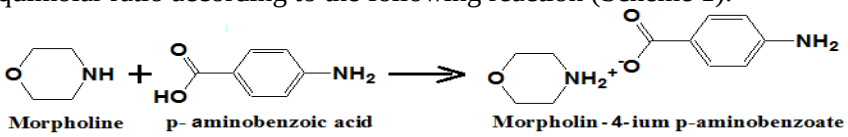
KEY WORDS: Organic compounds, Crystal growth, Crystal structure, Optical properties.

1. INTRODUCTION

In recent years much attention has been devoted to organic materials with high second order nonlinearities owing to their potential use in numerous modern research fields. 4-Aminobenzoic acid (PABA) has proved to be one of the most versatile reagents for structure extension by linear hydrogen bonding associations, through both the carboxylic acid and amine functional groups. This property of extension was recognized as a possible tool for promoting crystallization, with the aim of designing noncentrosymmetric organic materials. The addition of morpholine with PABA favorably modifies many of its physicochemical behavior and will be discussed in a detailed manner.

2. EXPERIMENTAL

2.1. Crystal growth: MPABA was synthesized by the slow addition of high purity morpholine (C_4H_9NO) (GR grade Merck, India) to a solution of p-aminobenzoic acid ($C_7H_7NO_2$) (GR grade Aldrich) in methanol (GR grade Merck, India), taking in the equimolar ratio according to the following reaction (Scheme 1).



Scheme.1.Synthesis of MPABA material

The prepared solution was then allowed to dry about 45°C and the final product was purified by recrystallization process several times. Seeded growth was carried out by slow cooling technique, in a controlled temperature bath equipped with a Programmable Eurotherm temperature controller.

2.2. Characterization techniques: The single crystal X-ray diffraction intensity data were collected using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å). The powder X-ray diffraction pattern was recorded using a microprocessor controlled X-ray diffractometer (XPERT-PRO) using Cu-Kα radiation (40 kV, 30 mA). Data were recorded over a 2θ range 10.03°–79.93° using step scan of 0.05° for a time interval of 10.14 s. The UV–Vis-NIR spectrum was recorded using JASCO V-650 spectrophotometer. For Kurtz powder technique a Q-switched Nd:YAG laser (6.05mJ/pulse at 1064nm) was used. Vickers hardness test on (020) was performed using Shimadzu Micro hardness tester whereas dielectric studies were carried out using HIOKI 3532–50 LCR HITESTER.

3. RESULTS AND DISCUSSIONS

The asymmetric unit contains one protanated morpholine ring and one benzoate ion as adduct. In this asymmetric unit, N_2—$H_3N\cdots O_1$ intramolecular hydrogen bond connects the two ions and this basis units are interconnected by another two N— H···O intermolecular hydrogen bonds and weak interactions, which stabilize the crystal structure. The solubility increases almost linearly with the temperature suggesting that slow cooling or slow evaporation solution growth could be a better method to grow good quality single crystals. It could also be understood from the nucleation curve that the metastable zone width (MSZW) of MPABA widens as the temperature decreases. This type wide MSZW is an essential parameter for the seeded growth of large-size single crystal from solutions because it can suppress any secondary nucleation and allow the use of a wide range of super saturation values for efficient growth. The morphology shows that the (020) and (0-20) planes were the most prominent planes over other planes.

From the powder X-ray data, various planes of reflections were indexed using Powder X software. The indexed powder X-ray diffraction pattern was compared with the XRD pattern simulated by the Mercury software and was found to agree with each other (Fig. 1).

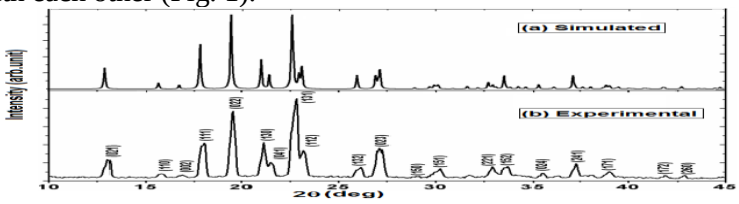


Fig.1. (a) Simulated and (b) Experimental Powder XRD patterns of MPABA

From the UV-Vis-NIR transmission curve it was understood that MPABA has a cutoff wavelength of 327 nm which was due to the n → π* transition and no other characteristic absorption was observed in the entire visible region. By taking the solitary linear behavior in Tauc's plot, as an evidence for the direct transition between valence and conduction bands, the band gap was estimated to be 3.80eV. As a consequence of this wide band gap, it is expected to have high damage threshold. By employing the Kurtz powder technique, SHG efficiency of MPABA powder was calculated as 1.49 and 11.45 times greater than that of urea and KDP respectively. This is relatively higher than the other reported PABA compounds such as Ethyl p-Aminobenzoate, 2-Amino 4-Picolinium 4-Aminobenzoate which exhibited the powder SHG efficiency of 6 and 3.74 times of KDP respectively. In addition, it was identified as a phase matchable material with an average coherence length of about 50 µm.

The hardness value of MPABA (Fig .2 (a)) increases up to a load of 50 g, above which cracks start developing due to the release of internal stress generated locally by indentation. The Vickers hardness values on (020) suggest that it follows the reverse indentation size effect in which the specimen does not offer resistance or undergo elastic recovery, but undergoes relaxation involving a release of the indentation stress away from the indentation site.

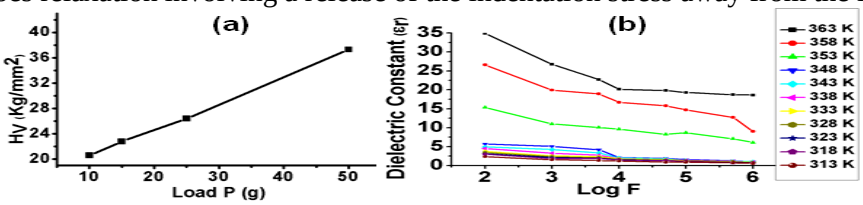


Figure.2.Variation of (a) Hardness number with load and (b) Dielectric constant with frequency

It essentially takes place in crystals which readily undergo plastic deformation. The work hardening coefficient or Meyer's index was found to be 3.1. For all temperatures up to 348 K, the dielectric constant were always lower than 5 (Fig 2(b)), which is comparatively lower than the high efficient organic NLO and electro optic crystal DAST ($\varepsilon_r \approx 5.2$) and some inorganic electro optic crystals $LiNbO_3$ ($\varepsilon_r \approx 85$) $KNbO_3$ ($\varepsilon_r \approx 154$). This property of low dielectric constant has wide spread applications since high dielectric constant materials tend to break down more easily when subject to intense electric fields than do materials with lower dielectric constant. It will also decrease the power requirement of electro optic modulators and enhance the velocity matching in THz generation which is necessary for the high efficiency. This kind of materials, due to their moderate flat response with frequency variation, are always recognized to minimize the phase distortion caused by the vast change of dielectric constant follow-on the variation of frequency. Therefore MPABA crystal could be an interesting candidate for high speed optoelectronic applications as interlayer dielectric and for high speed telecommunications as optical wave guide.

4. CONCLUSIONS

Good optical quality organic single crystals of MPABA were grown successfully by solution growth technique. The microhardness studies projected that they exhibited reverse indentation size effect for the applied loads. The numerical value of the work hardening coefficient suggested it as a soft material. The study of the dielectric behaviour of MPABA crystals shows the strong dependence of dielectric constant and loss on temperature. The values of dielectric constant, loss and activation energy of MPABA were found to be low and suitable for various NLO applications.

5. ACKNOWLEDGMENTS

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