Synthesis, growth, structural, optical, mechanical and dielectric properties of an organic crystal: 1H-Benzimidazolium Hydrogen tartrate

S.Sivapriya[1], K.Balasubramanian[1],R.Subramaniyan @ Raja[2]

[1] Department of Physics, The MDT Hindu College, Tirunelveli-627006

[2]Department of Physics, SSN College of Engineering, Kalavakkam-603110

Abstract

1H-Benzimidazolium Hydrogen tartrate (BMZHT) were grown from mixture solvent (methanol and water) using slow evaporation solution growth technique. The solubility of BMZHT was found out. The lattice parameters of the grown crystal were found from single crystal XRD analysis. The Functional groups present in BMZHT single crystal were analysed using FTIR measurements. The cut off wavelength is identified from UV-Vis spectrum. The optical band gap value was evaluated from the transmission spectra and absorption coefficient by extrapolating technique. The dielectric behaviours of the grown crystals were investigated. The mechanical properties of the grown crystals were studied using Vickers microhardness tester.

Keywords: organic single crystal, slow evaporation technique.

Introduction

Organic nonlinear optical crystals play an important role in second- harmonic generation (SHG), frequency mixing, electro-optic modulation, and optical parametric oscillation, etc., [1]. The second harmonic generation (SHG) in crystals is influenced by molecular structure and crystalline arrangement. The second-order nonlinearity in organic compounds is enhanced due to the extension of conjugation, the presence of a low-lying electron and the spectroscopic charge transfer arising from electron-donating and electron-accepting substituent of an aromatic ring or a similar conjugated system [2]. Benzimidazolium tartrate is an organic compound synthesized using benzimidazole and L-tartaric acid. Benzimidazole is a very good proton acceptor and in the presence of a carboxylic acid, it always deprotonate that group. Hence it is widely used in the formation of organic molecular complex salt. L-Tartaric acid is one of the well-known carboxylic acids. In the present work, BMZHT is synthesized. Tartaric acid is promoting molecular self-assembly by means of strong hydrogen bonding through its carboxylic acid group and the ring substituted amino group of Benzimidazole [3]. BMZHT is grown as single crystal and it is subjected to various characterizations to find the physical properties.

Experimental details

Synthesis, Solubility and Crystal growth

The BMZHT was synthesized by taking Benzimidazole and L-Tartaric acid in an equimolar ratio 1:1. The solubility of BMZHT in various solvents and solvent combinations like ethanol, methanol, water, methanol+ water and ethanol+ water was carried out. BMZHT was found to be well dissolved in methanol + water combination. The solubility of BMZHT increases with increase in temperature. The curve shows the positive solubility temperature coefficient as shown in Fig.1.

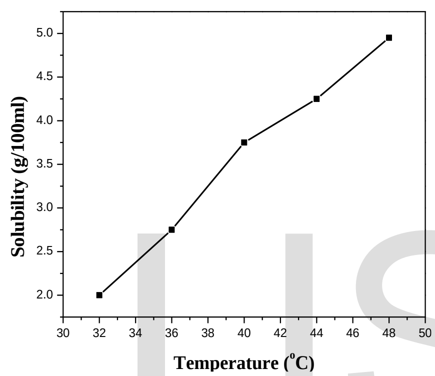


Fig.1 Solubility of BMZT

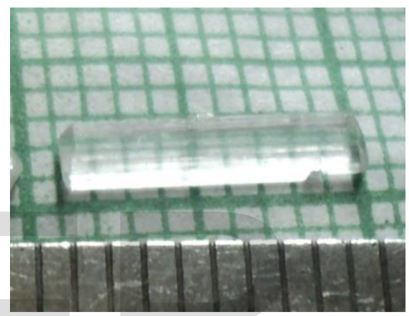


Fig.2 BMZT single crystal

The slow evaporation solution growth method was employed to grow BMZHT crystals using mixture solvent (methanol + water). The saturated solution is prepared and stirred well for 3hrs to attain the homogenous mixture. It is then filtered. The solution was kept in constant temperature bath at RT. The slow evaporation of the solvent yields good transparent bulk crystals within eighteen days.. A Crystal of size 9 ×2× 2 mm^3 was successfully grown as shown in Fig.2.

Result and discussions

Single crystal X-ray diffraction was carried out on grown BMZHT single crystal using a BRUKER AXS SMART APEXII to identify the lattice parameters. From the measurements, it was observed that BMZHT crystal belongs to monoclinic system with non-centrosymmetric space group $P2_1$. The lattice parameter values are a = 9.204 (2) Å, b = 7.240 (8) Å, c = 10.950 (10) Å and V = 689.3 (3) $Å^3$ which are in good agreement with the reported values [4]. Fig.3 shows the FTIR spectrum of BMZHT. The FTIR spectrum was recorded using SHIMADZU IR AFFINITY 1S Spectrometer in the range of 400cm^{-1} to 4000cm^{-1}. The peak at 3326cm^{-1} and 2981cm^{-1} is assigned to N-H and C-H stretching. The signal at 1741cm^{-1} is due to C=O vibration. The C-N stretch occurs at 1221cm^{-1}. The group of peaks below 1000cm^{-1} is due to C-H bending mode. The transmission spectrum of BMZHT was recorded using SHIMADZU SPECTROMETER UV-1800 in the range of 200nm-1100nm. The recorded transmission spectrum and inset band gap spectrum shows in Fig.5. From the optical transmission spectrum it is observed that the crystal has lower cut off wavelength at around 288 nm. The lower cut off wavelength and wide transparency is the important properties for NLO application. The optical band gap value of BMZHT was determined by using tauc plot. The band gap value of BMZHT is 4.28eV.

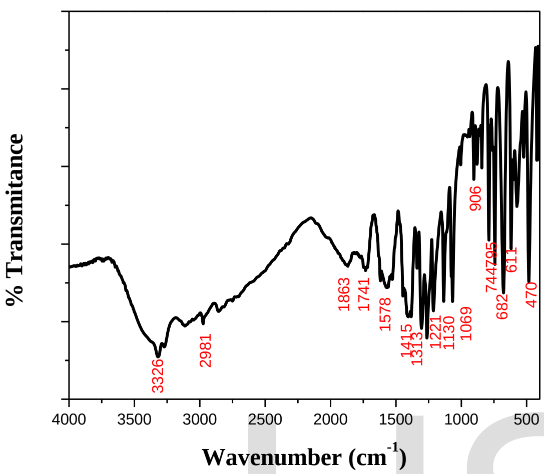


Fig.3 FTIR spectrum of BMZHT

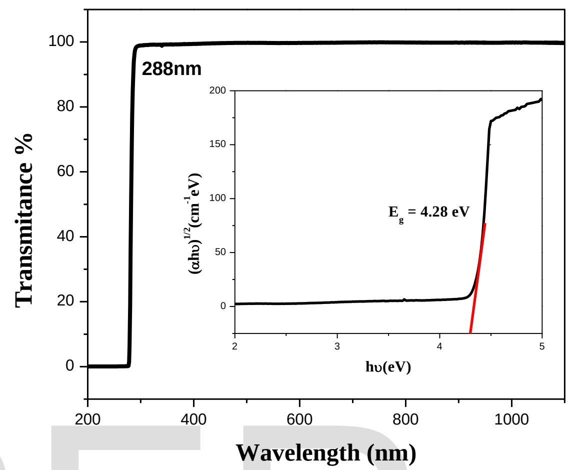
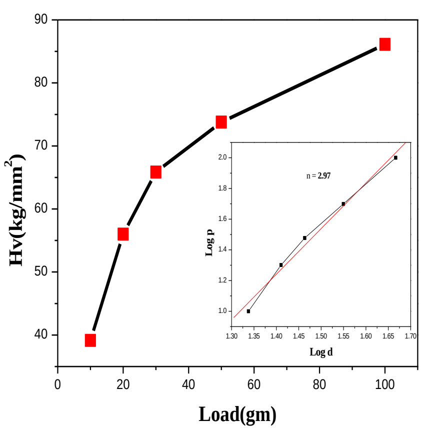
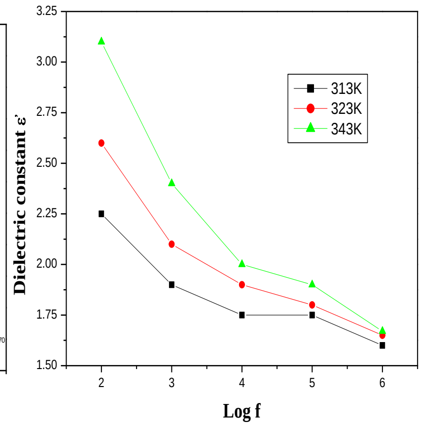


Fig.4 Transmission spectrum and inset Band gap spectrum of BMZHT

The microhardness for BMZHT crystal was carried out with the load in range between10gm and 100gm using Vickers hardness tester. The hardness number was calculated using the relation, Hv= 1.844P/d^2(kg/mm^2)Where P is the applied load and d is the diagonal length of the indentation.Fig.5shows that Hv increases with the increase of load, which indicates the reverse indentation size effect (RISE). The value of n for BMZHT is 2.97. Therefore BMZHT belongs to softer material category. The dielectric constant and the dielectric loss of BMZHT sample were measured. Fig.6 and 7 shows the variation of dielectric constant and dielectric loss with log frequency under different temperature. It is observed from plot (fig.6) that the dielectric constant decreases exponentially with increasing frequency and then attains almost constant in the high frequency region. It is also observed that the temperature increases the value of dielectric constant also increases. The same trend is observed in the case of dielectric loss versus frequency. The characteristic of low dielectric constant and dielectric loss with high frequency for a given sample suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is highly important for making this material suitable for various nonlinear optical applications.





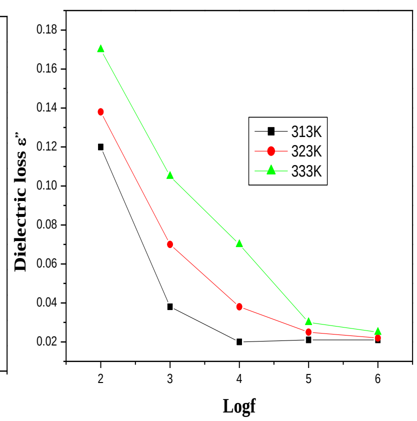


Fig.5 Hv Vs Load **Fig.6 Dielectric constant Vs Log f.** **Fig.7 Dielectricloss Vs Log f.**

Conclusion:

Crystalline substance of BMZHT has been synthesized. Single crystals of BMZHT were grown by using slow evaporation solution growth technique. The structure of BMZHT was confirmed by single crystal XRD. BMZHT belongs to monoclinic system with space group $P2_1$.The functional groups present in BMZT were confirmed by FTIR analysis. The cut off wavelength of BMZHT was found from transmission spectrum which is at around 288nm. Microhardness measurement reveals that the BMZHT belongs to soft material category. The dielectric constant and dielectric loss is found to be decreased with increase in frequency at different temperature.

References:

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