

Synthesis, Growth and Characterization of Bis p- Nitrophenol Magnesium Chloride (BPNPMC) Single Crystal for NLO Applications

V.Revathi Ambika, D.Shalini, R.Usha, N.Hema and D. Jayalakshmi*

PG and Research Department of Physics, Queen Mary's College, Chennai -600 004, India.

ARTICLE INFO

Article history:

Received: 23 July 2016;

Received in revised form:

11 September 2016;

Accepted: 21 September 2016;

Keywords

Crystal Growth,
Slow Evaporation Process,
Structural Studies,
Optical Studies,
Dielectric Studies,
Micro hardness.

ABSTRACT

Good quality single crystals of a new semi organic Bis p- Nitrophenol Magnesium chloride (BPNPMC) were grown from solution by slow evaporation technique at room temperature. The grown crystal have been confirmed by single crystal X-Ray Diffraction Method. UV -Vis transmission and absorption studies reveals that the grown crystal were optically transparent through the visible range. The vibrational frequencies of various functional groups in the crystals have been derived from Fourier transform infrared spectrum (FTIR). In the dielectric studies, the dielectric constant and dielectric loss of the crystal were measured as a function of frequency and various temperatures. The optical studies indicate the sample, optical transparency window is quite wide, making it suitable for NLO applications. Micro hardness studies were carried out to confirm the mechanical behavior of the crystal. The second harmonic generation (SHG) test has been confirmed by the Kurtz powder test and its efficiency 1.73 times higher than that of KDP.

© 2016 Elixir All rights reserved.

1. Introduction

In recent years, many significant achievements have been occurred in the field of nonlinear optics because of the development of new nonlinear optical (NLO) crystals of both organic and inorganic types. Single crystals made from the organic and inorganic compounds play an important role in nonlinear optical device fabrication due to their versatile property such as second harmonic generation efficiency, fast response and high mechanical strength over the organic crystals. Organic NLO materials exhibiting large optical nonlinearity have wide range of application in telecommunication, optical information processing and high optical disk data storage [1,2]. The materials possessing large second order nonlinear susceptibility with favourable in thermal and mechanical stability are intensively used in many device applications [3]. Hence, there is a great demand to synthesize and grow new organic NLO materials and their single crystals. The advantages of organic materials over inorganic compounds comprise high second order nonlinear optical susceptibility through high molecular Polarizability, fast response time, low dielectric constant and refractive index.

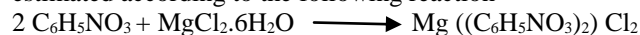
In the last decades, many researchers have tried to find varieties of new NLO materials for laser applications [4]. The main drawback in organic nonlinear optical materials is low mechanical strength and poor physico-chemical stability. To overcome these drawbacks an attempt has been made to grow semi-organic nonlinear optical crystals which makes the material have large damage threshold, wide transparency range, excellent nonlinear optical coefficient, low angular sensitivity and exceptional mechanical properties [5,6]. Sodium p-nitrophenolate p-nitro phenol dehydrate as a semi-organic non-linear optical material in which the nitrophenoyl ions are ionically bonded to the metal ion was reported [7-14]. It has an efficient NLO co-efficient (d_{eff}) 1.2 times larger than that of KTP. Many device applications of NLO require single

crystals in the bulk form. This is achieved only with the semi organic crystals, which exhibits wide transparency and bulk crystal morphologies. Sodium p-nitrophenolate p-nitrophenol dihydrate is a semi organic NLO material possessing large values of hyper polarizability due to the presence of an organic p-nitrophenol [15]. In the present investigation, attempts have been made to grow single crystal of Bis p- Nitrophenol Magnesium chloride (BPNPMC) for the first time and characterize by single crystal X-ray diffraction (XRD), Fourier transform infrared (FTIR) analysis, optical transmission and absorption, dielectric studies, Micro Hardness studies and SHG efficiency studies.

2. Experimental Procedure

2.1. Material Synthesis

BPNPMC salt was synthesized using Magnesium Chloride Hexahydrate (AR grade) and p-Nitrophenol (AR grade) in the stoichmetric ratio 1:2. The required quantity of magnesium chloride hexahydrate and p-Nitrophenol was estimated according to the following reaction



The calculated amount of Magnesium chloride hexahydrate was first dissolved in the deionized water. Then p-Nitrophenol was added to the solution slowly with stirring. The prepared solution was led to dryness at room temperature. The purity of the synthesized salt was improved by repeated successive recrystallization. The careful observation was taken for drying the prepared solution and the temperature was never allowed to exceed 30 °C so as to avoid decomposition of the solute molecules.

2.2. Growth of PNPMMC

In the present study, BPNPMC crystals were grown by using slow evaporation technique. Recrystallized salt of BPNPMC was taken as a raw material. Saturated BPNPMC solution was prepared at room temperature with deionized water as solvent. The prepared solution was filtered with a micro filter.

The solution was taken in vessels and closed with covers and kept in a dust-free atmosphere. The crystals were harvested within 10 weeks and they attained an optimal size and shape. The grown crystals are shown in Fig.1.

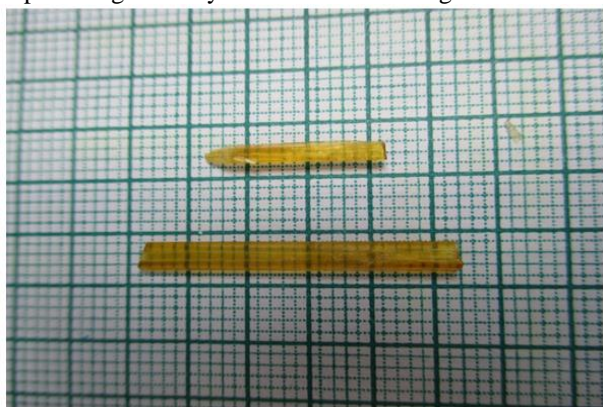


Figure 1. Photograph of Grown BPNPMC Crystal.

3. Results and discussion

3.1. Single crystal X-ray diffraction

The grown crystals were subjected to single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 X-ray diffractometer to determine the cell parameters and it reveals that the MPNP crystal crystallizes in monoclinic system. The lattice parameters were found to be $a = 3.80\text{\AA}$, $b = 11.21\text{\AA}$, $c = 14.86\text{\AA}$, $\beta = 92.92^\circ$ and $V = 632\text{\AA}^3$.

3.2. FTIR analysis

FTIR spectroscopy finds application in determining the size of the coordination, the nature of organic ligand bonding as well as in the elucidation of structures of coordination compounds. The FTIR spectrum was recorded in the spectral range $400\text{--}4000\text{ cm}^{-1}$ using Perkin-Elmer Lambda-35 FTIR spectrometer, where the B4NPMC crystalline sample was in Pellet form in KBr phase. The vibration observed between 846 and 694 cm^{-1} are usually associated with the presence of benzene rings. The peak between 755 and 846 cm^{-1} shows the meta position of the substituted. The minor peaks appearing in wavenumber region 755 cm^{-1} corresponds to the out of plane N-H wagging. The peak at 846 cm^{-1} is assigned to C-N vibration. The peaks at 1340 cm^{-1} are due to the vibration of NO_2 stretching modes. As either the N-H stretching modes or NO_2 stretching modes are not much broad, their interaction with the neighbouring molecule is recognized to be weak bonds. The -OH peak is broadened owing to hydrogen bonding present in phenols. These confirm that the compound consists a phenol group. If a nitro group is attached to an aromatic ring, the N-O stretching bands shift to down to slightly lower wave numbers from $1550\text{--}1475\text{ cm}^{-1}$ and $1360\text{--}1290\text{ cm}^{-1}$. Hence these peaks observed at the region of 1493 cm^{-1} and 1340 cm^{-1} as symmetric and asymmetric stretching vibrations respectively were assigned to N=O group [16]. Compounds that do not have a C=C bond show C-H stretches only below 3000 cm^{-1} . But the C-H stretch observed at 3087 cm^{-1} shows the presence of aromatic ring. The important infrared modes for nitro compounds (-C- NO_2) were usually observed in the finger print region between $1300\text{--}1100\text{ cm}^{-1}$. The peak at 1187 cm^{-1} confirms the presence of C- NO_2 bonding. The peak at 3087 cm^{-1} is due to aromatic C-H vibration. The absorption peak at 2822 cm^{-1} is due to H-C=O stretching and the aldehydic C-H stretching absorption peak at 2701 cm^{-1} is to confirm the presence of aldehydic group (silverstein1991). The aromatic skeletal ring is observed at 1599 cm^{-1} . Peak at 1286 cm^{-1} is due to N-H bending and C-N stretching vibrations [17].

The peak at 3363 cm^{-1} corresponds to NH_2 stretching. The peak at 3596 cm^{-1} corresponds to OH stretching due hydrogen bonding. 694 cm^{-1} which are assigned to C=C bending.

Table 1. Peak assignments of BPNPMC.

Wave Number cm^{-1}	Assignments
3596	OH Stretching
3363	NH_2 Stretching
3087	Aromatic CH
1599	C=C
1493	N=O Asymmetric stretch
1340	N=O Asymmetric stretch
755	Out of plane N-H wagging
694	C=C bending

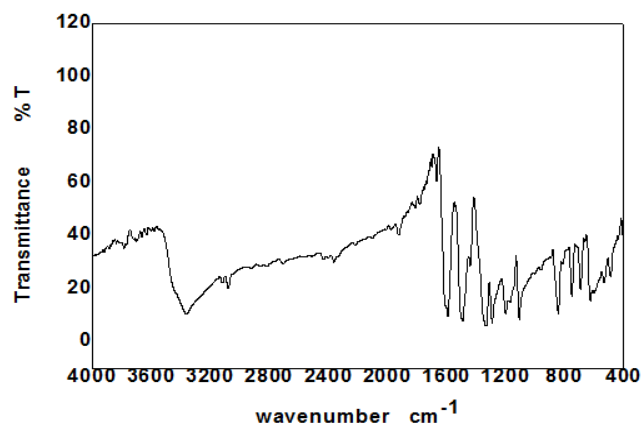


Figure 2. FTIR spectrum of BPNPMC of single crystal.

3.3. UV-VIS Spectral analysis.

Good optical transmittance and lower cut off wavelength are very important properties for NLO crystals. The spectrum has been recorded in the wavelength range from 190 nm to 900 nm and is shown in the fig.3. The lower cut off wavelength is around 300 nm . The π electron dislocation is responsible for absorption in near UV region (Ushasree *et al*, 1999). Thus the grown crystal has got good transmission in UV as well as invisible region $300\text{ nm--}900\text{ nm}$. The wide range of transparency of grown crystal is an added advantage in the field of optoelectric application (Bairava Ganesh *et al*, 2007). Energy band gap has been calculated from the UV-Vis absorbance data. Using the formula $E_g = hc / \lambda$, the band gap energy was found to be 4.133 eV .

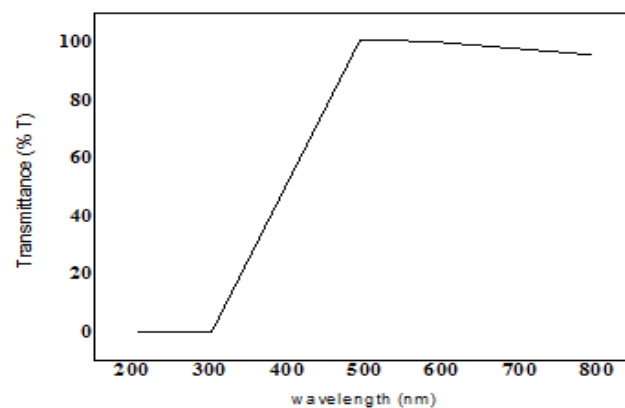


Figure 3. UV Transmission spectrum of BPNPMC.

3.4. Dielectric studies

The study of dielectric properties of solid gives information about the electric field distribution within the solid. The frequency dependence of dielectric property gives the insight into the materials applications.

Dielectric measurements were performed on BPNPMC crystal (dimensions: 1.59mm thickness and area 16.45mm²) using HIOKI-LCR HiTester 3535 in the frequency range 50Hz to 5MHz at room temperature... The conventional parallel plate capacitor method was employed by coating the silver paste on the opposite faces of the crystal to get contact between crystal and electrodes. The variation of dielectric constant (ϵ_r), dielectric loss ($\tan\delta$) and AC conductivity (σ_{ac}) were measured at room temperature as a function of frequency. Dielectric constant has been calculated using the relation

$$\epsilon_r = Ct / \epsilon_0 A, \quad (1)$$

where C is capacitance, t is thickness of the sample, $\epsilon_0 = 8.854 \times 10^{-12} \text{Fm}^{-1}$ is permittivity of free space and A is the area of cross section. The variation of ϵ_r and $\tan\delta$ with applied frequency are shown in Figs.4 and 5 respectively. It is seen that dielectric constant value is high at low frequencies because, the electronic, ionic, dipolar and space charge or interfacial polarization are predominant. Further, as the frequency increases, the dielectric constant decreases and for high frequency region, it is almost constant. This can be explained based on polarization phenomenon. The electronic exchange between ions in the crystal gives local displacement of electrons in the direction of applied field, which causes the polarization.

As the frequency of applied field increases a point will be reached where the space charge polarization cannot sustain and comply with variation of the external field and hence polarization decreases. The lower value of dielectric constant at higher frequency for a given crystal is a suitable parameter for the enhancement of SHG coefficient [18]. Fig.5, it is observed that the dielectric loss is high at lower frequency and the loss becomes less at higher frequencies. The characteristic of low dielectric loss at higher frequency indicates that the grown crystal has good optical quality with lesser defect and this parameter is of vital importance for nonlinear optical materials in their applications.

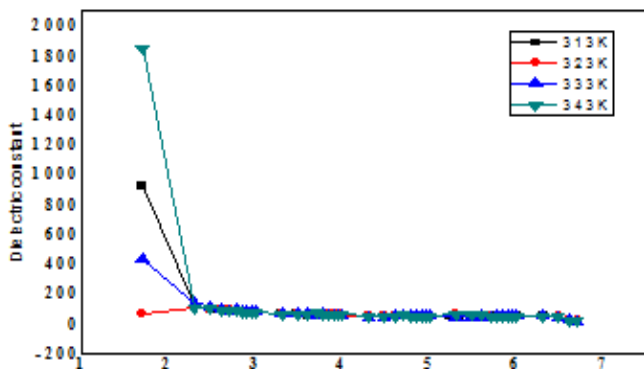


Figure 4. Dielectric Constant Vs Log f.

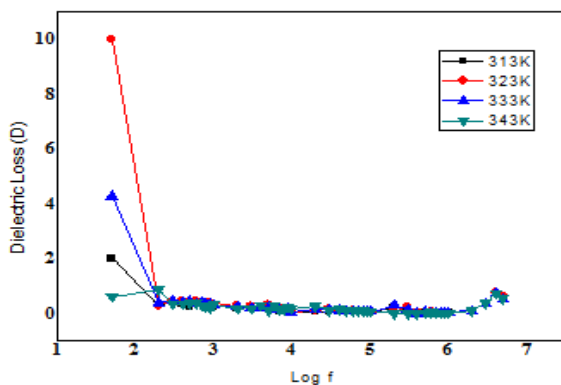


Figure 5. Dielectric Loss Vs Log f.

The nature of decrease of dielectric constant and dielectric loss with frequency suggests that the grown crystal seems to contain dipoles of continuously varying relaxation times. As the dipoles of larger relaxation times are not able to respond to the high frequencies, dielectric constant and dielectric loss are low at high frequencies [19].

3.5. Microhardness Study

Measurement of hardness is an useful non-destructive testing method to determine the bond strength. The microhardness value correlates with other mechanical properties such as elastic constants and yield strength. The hardness of a material depends on different parameters such as lattice energy, Debye temperature, heat of formation and interatomic spacing[20–22]. According to Gong[23], during an indentation process, the external work applied by the indenter is converted into a strain energy component which is proportional to the volume of the resultant impression and a surface energy component is found to be proportional to the area of the resultant impression. Microhardness studies of any system has direct correlation with the crystal structure and is very sensitive to the presence of other phases or phase transition prevalent in the system. Microhardness studies were carried out on BPNPMC single crystals using Vickers hardness tester fitted with pyramidal indenter. The diagonal length of the indentation in mm for various applied loads in kg are measured for a constant indentation time of 15 s. The Vickers hardness number is calculated using the relation

$$Hv = 1.8544 p/d^2 \text{ kg/mm}^2 \quad (2)$$

The value of Hv increases as the load increases and finally decreases for higher loads in the range of 200g for the crystals. The variation of Hv with applied load for BPNPMC crystals is shown in Fig.6. Work hardening coefficient n, a measure of the strength of the crystal, is computed from the logp-logd plot (Fig.7). It brings forth the fact that the BPNPMC crystals are found to have been improved in mechanical strength. The plot of logp-logd yields a straight line and its slope, and the work hardening index, n are found to 1.33. The value of the work hardening co-efficient n was estimated from the plot of Log p versus log d drawn by the least square fit method. It is observed that the Vicker's hardness number and work hardening coefficients of the crystal increase with increasing load. According to Onistich, $1.0 \leq n \leq 1.6$ for hard materials and $n \geq 1.6$ for soft materials [16]. n is found to 1.33 which lie lesser than 1.6 for the BPNPMC crystal. Hence it is concluded that BPNPMC belongs to hard materials.

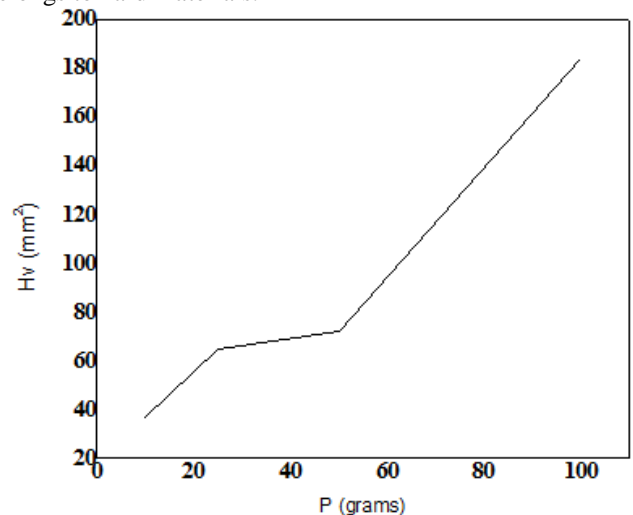


Figure 6. Hardness Number Vs Applies Load.

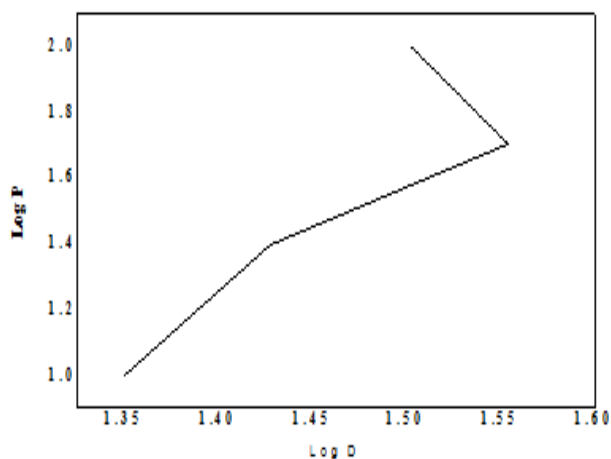


Figure 7. Log P Vs Log D.

3.6. Second Harmonic Generation

The SHG of the crystal was checked using the powder SHG technique developed by Kurtz and Perry [24]. A Q-switched Nd:YAG laser beam of wavelength 1064 nm, with beam energy of 4.5 mJ/pulse, and pulse width of 8 ns with a repetition rate of 10 Hz were used. The grown single crystal was crushed to fine powder and then packed in a micro capillary of uniform bore and exposed to laser radiations. The 532 nm radiation was collected by a monochromator after separating the 1064 nm pump beam with an infra-red blocking filter. The second harmonic radiation generated by randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube (Hamamatsu R2059). The second harmonic generation is confirmed by the emission of green light and its efficiency is found to be 0.73 times greater than that of KDP crystal.

4. Conclusions

Optically transparent single crystals of BPNPMC were grown from aqueous solution using slow evaporation technique. Single crystal X-ray diffraction analysis confirms that the grown crystals crystallize in monoclinic system. FTIR analysis confirms the presence of functional groups in the BPNPMC. The UV cut-off wavelength is found to be at 300nm. Dielectric constant decreases with increase in frequency and very low values of dielectric loss infer very high purity of the crystal. Microhardness test shows that hard nature of the crystal. NLO property is confirmed by Kurtz powder test. The NLO efficiency is 1.73 times greater than that of KDP. All these studies indicate that the PNPMP crystal can be considered as a potential candidate for the fabrication of optoelectronic devices.

5. Acknowledgement

One of the authors (D.JAYALAKSHMI) is grateful to the university grants commission for financial support under minor research project scheme.

References

- [1] P.N. Prasad, D.J. Williams, Introduction to Nonlinear Optical Effects in Molecules and Polymers, Wiley-Interscience, New York, 1991.
- [2] D.S. Chemla, J. Zyss, Nonlinear Optical Properties of Organic Molecules and Crystals, vols. 1 and 2, Academic Press, New York, 1987.
- [3] T. Pal, T. Kar, G. Bocelli, L. Rigi, Cryst. Growth Des. 3 (2003) 13e16.
- [4] M.H. Jiang, Q. Fang, Adv. Mater. 11 (1999) 1147.
- [5] H.O. Marcy, M.J. Rosker, L.F. Warren, P.H. Cunningham, C.A. Thomas, L.A. Deloach, S.P. Velsko, L.A. Ebberts, J.H. Liao, M.G. Kanatzidis, Opt. Lett. 20 (1995) 252e254.
- [6] M.D. Agarwal, J. Choi, W.S. Wang, K. Bhat, R.B. Lal, A.D. Shields, B.G. Penn, D.O. Frazier, J. Cryst. Growth 204 (1999) 179e182.
- [7] H. Mimento, Y. Ozaki, N. Sonoda, J. Appl. Phys., (1994), 76 (7), 3975.
- [8] H. Mimento, Y. Ozaki, N. Sonoda, Appl. Phys. Lett., (1993), 63 (26), 3565.
- [9] H. Mimento, N. Sonoda, K. Miki, Acta Crystallogr (1992) ,48 , 737.
- [10] H. Mimento, Y. Ozaki, K. Wakita, N. Sonoda, T. Sosaki, Jpn J. Appl. Phys (1995) ,34, 497
- [11] S. Brahadeeswaran, V. Venkataramanan, J.N. Sherwood, H.L. Bhat, J. Appl. Phys., (1995), 34, 497
- [12] R.P. Sharma, S. Kumar, K.K. Bhasin, E.K.T. Tiekink, Z. Kristallogr., (1997), 212, 548
- [13] B.L. Davydov, S.G. Kotovshchikov, V.A. Nefedov, sov. J. Quantum Electron (1997), 548
- [14] S. Brahadeeswaran, V. Venkataramanan, H.L. Bhat, J. Cryst. Growth, (1999), 205, 548
- [15] S. Dhanuskodi, A. Pricilla Jayakumar, S. Manivannan, Spectrochimica Acta (2007), 66, 318
- [16] R. Uthrakumar, C. Vesta, M. Jose, K. Sugandhi, S. Krishnan, S. Jerome Das, Physica B 405 (2010) 3371-3375
- [17] Agnieszka J. Abkowitz-Bieko, Zdzisław Latajka, Dariusz C. Bieko, Danuta Michalska, Chemica I Physics., 250, 123 (1999)
- [18] M. Meena, C.K. Mahadevan, Arch. Appl. Sci. Res., 2010, 2(6), 185.
- [19] P. Selvarajan, B.N. Das, H.B. Gon, K.V. Rao, J. Mater. Sci. Lett., 1992, 11, 1312.
- [20] P.H. Soni, C.F. Desai and S.R. Bhavsar: Indian J. Pure Appl. Phys., 2004, 42, 371.
- [21] C.J. Benet, K. Sivakumar and F.D. Gnanam: Cryst. Res. Technol., 1990, 25, 1259.
- [22] E. Chacko, J.M. Linet, S.M.N. Priya, C. Vesta, B.M. Boaz and S.
- [23] J.H. Gong: J. Mater. Sci. Lett., 2005, 19, 515.
- [24] S.K. Kurtz and T.T. Perry, J. Appl. Phys., 1968, 39, 3798.