Available online at www.elixirpublishers.com (Elixir International Journal)

Crystal Research Technology

Elixir Crystal Research Tech. 41 (2011) 5689-5692

ISSN: 2229-712X

Growth and characterization of MPHB nonlinear optical single crystal

J. Felicita Vimala[1], M.Lawrence[2] and J.Thomas Joseph Prakash[3]

[1]Department of Physics, DIET, Mayanur, Karur(DT).

[2]Department of Physics, Kurinji College of Arts and Science, Trichy, Tamilnadu, India.

[3]Department of Physics, H.H.The Rajah's Government Arts College, Pudukkottai -1.

ARTICLE INFO

Article history:

Received: 11 September 2011;
Received in revised form:
16 November 2011;
Accepted: 27 November 2011;

Keywords

Characterization x-ray diffraction;
Single crystal growth;
Organic compounds;
Nonlinear optical materials.

ABSTRACT

Single crystals of methyl para hydroxyl benzoate a nonlinear optical (NLO) material were grown by slow solvent evaporation technique at room temperature. Acetone was used as solvent. The MPHB crystals obtained by the above technique were subjected to different characterization analysis. Unit cell parameters were evaluated by single crystal X-ray diffraction technique. The lattice dimensions were determined from the powder x-ray diffraction analysis. The functional groups and optical behaviour of the crystals were identified from FTIR and UV-vis analysis. Micro hardness, thermal and etching studies were also carried out on the sample respectively. The SHG efficiency of the grown crystal was measured through NLO studies.

Introduction

Organic crystals have been shown to have potential applications in nonlinear optics. In recent years, organic crystals are given much importance compared to inorganic in view of their large electro-optic effects with low frequency dispersion, low cost, fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility and intrinsic tailorability [1,2]. High quality face-matched second harmonic generation (SHG) single crystal is the current interest in the field of organic NLO materials. High quality organic NLO crystals posses sufficiently large NLO coefficient, transparent in uv region, high laser damage threshold power and easy growth with large dimensions [3-6].

Nonlinear optics (NLO) is at the forefront of current research because of its importance in providing the key functions of frequency shifting optical modulation, optical switching, optical logic, and optical memory for the emerging techniques in areas such as telecommunications, signal processing, and optical interconnections [7-9].

Organic materials have been of particular interest because the nonlinear optical response in this broad class of materials is microscopic in origin, offering an opportunity to use theoretical modeling coupled with synthetic flexibility to design and produce novel materials [10-12] organic NLO materials have a very large nonlinear susceptibility, which is in many cases several orders of magnitude higher than that of inorganic crystals such as LiNbo3, KNbo3 and potassium titanyl phosphate (KDP) [13,14].

Methyl-para-hydroxy benzoate (MPHB) is a recently discovered organic NLO material. It is reported that the second harmonic generation (SHG) efficiency of MPHB crystal was 40 times that of urea [15]. 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) [16, 17]. In the present paper, we report the growth and characterization of good quality single crystal of MPHB by slow evaporation method using acetone as solvent.

Experimental

Cystal growth

The slow evaporation technique is widely used for the growth of organic crystals to get more transparent single crystals. The single crystals of MPHB were successfully grown by slow evaporation solution growth technique at room temperature using acetone as solvent.

The commercially available methyl 4-hydroxy benzoate was purified by repeated recrystallization process and the repeated recrystallized materials were used for growth as charge material. Since MPHB is insoluble in water, acetone was chosen as the solvent for our growth. The saturated solution of MPHB was obtained by dissolving the charge material into the acetone solvent with continuous stirring of the solution using a Magnetic stirrer at room temperature. After reaching saturation the beaker containing the solution was optimally closed for controlled evaporation. Transparent single crystals were obtained from mother solution after 30 days (Fig.1).

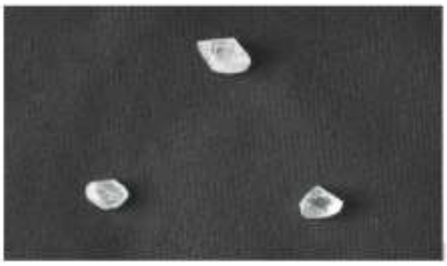

Fig. 1 MPHB single crystals

Molecular structure

The molecular formula of methyl para hydroxyl benzoate (MPHB) is $C_8H_8O_3$. This is a nonlinear optical crystal which is an isomer of vanillin, another well known NLO organic material. The ester carbonyl group ($COOCH_3$) is a strong electron absorber and the hydroxyl group (OH) is an electron donor.

Tele:
E-mail addresses: vimalafelicita@gmail.com

Hence, a charge transfer interaction can be established which will increase the molecular hyper-polarizability. Moreover, the para position of the substituents, relative to the carbonyl group enhanced the possibility of the compound to crystallize with a non-centric unit cell. It has also been reported that the compound crystallizes in the monoclinic system with space group Cc. The structure is shown in Fig. 2.

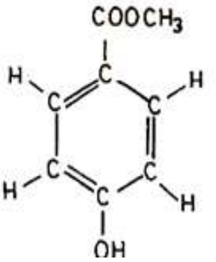

Fig. 2 Molecular structure of MPHB

Characterization

The Grown single crystals of MPHB have been analyzed by different characterization techniques. The crystals were confirmed by single crystal and powder X-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. The functional groups were identified by using PERKIN ELMER RX1 Fourier Transform Infrared spectrophotometer in the range of 400-4000 cm^{-1}. The optical properties of the crystals were examined between 200 and 1200 nm using LAMBDA-35 UV-Vis spectrometer. The mechanical and thermal property of the grown crystals have been analysed. The NLO efficiency of the grown crystal was measured was also subjected to etching studies.

X-ray diffraction

The unit cell dimensions were measured using ENRAF-NONIUS CAD-4 single crystal x-ray diffractometer. The crystal system was found to be monoclinic with space group Cc and unit cell dimensions are a = 13.977Å, b = 15.774 Å, c = 12.684 Å, $\alpha = \gamma = 90°$, $\beta = 131.77°$ which coincide with the reported values [18]. The stability of the molecular conformation is reached with a balance between intermolecular hydrogen bonds of the hydroxyl groups with carbonyl oxygen (C=O…H). In both the intermolecular H-bonds, one hydroxyl oxygen atom acts as a donor to the adjacent carboxyl oxygen.

This has been confirmed by powder XRD diffraction analysis by using a Rich Seifert diffractometer with $C_uK_\alpha(\lambda=1.5417A°)$ radiation. The powder XRD pattern of MPHB crystal is shown in fig 3, Which seems to confirm the monoclinic structure of the grown crystals. The well-defined peaks at specific 2θ values show high crystalline of the grown crystals. This work was indexed using the TREOR software package following the procedure of Lipson and Steeple[19]. Also UNIT CELL software package was used to confirm the indexing.

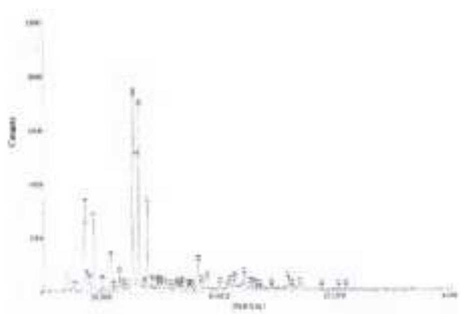

Fig.3 –Powder XRD Patterns of MPHB crystal

FTIR

The FTIR spectrum of MPHB crystal is shown in fig.4. An examination of the spectrum is indicative of the following points. The frequency corresponding to 3302.30 cm^{-1} may be due to the presence of OH group which may be hydrogen bonded since hydrogen bonded OH group has a frequency range between 3550-3300cm^{-1}.

The peak at 2961.79 cm^{-1} is due to CH stretch of methyl and CH stretch of phenyl, respectively. The hyperfine peak in the lower energy side of OH stretch envelope clearly indicates varying degree of interaction in the crystal lattice. The peak at 1917.88 cm^{-1} is assigned to overtone or combination bond.

The frequencies pertaining to 1680.61 and 1594.26 cm^{-1} show the presence of carboxyl group since the carboxyl group absorbs around 1670cm^{-1}.

The maximum percentage of absorption occurs at 1594.26 cm^{-1}. Its intensity and broadness also support the importance of ester group contribution through hydrogen bonding in the packing of methyl p-hydroxy benzoate molecules in the crystal lattice. It is also supported by finely resolved intense and broad peaks between 1000 and 1400 cm^{-1}. The peaks at 1434.56 and 1512.77 cm^{-1} are due to aromatic ring skeletal vibrations. The sharp peaks below 1000 cm^{-1} illustrates the aromatic rings of methyl 4-hydroxybenzoate not providing much cohesive force in the crystal lattice. The peaks at 779.37 cm^{-1} show the meta position of the substituted molecules in the benzene ring of MPHB crystals [20].

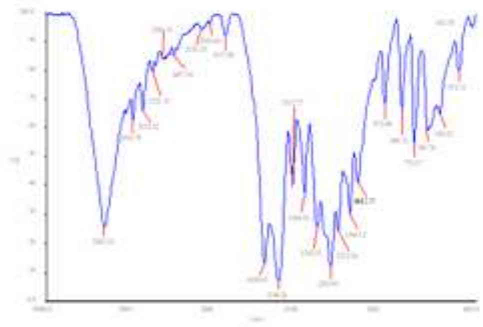

Fig.4 FTIR spectrum of MPHB crystal

UV-Visible transmittance study

The UV-Vis-NIR transmission spectrum MPHB crystal is shown in the Fig.5. which gives information about the structure of the molecule, because the absorption of UV and visible light involves promotion of the electron in the s and p orbital from the ground state to higher states[21]

The instrument used was LAMBDA-35 UV-Vis spectrophotometer. From the spectrum, it is seen that the crystal has a lower cut-off wavelength of 470 nm. The spectrum further indicates that the crystal has wide optical window from 400 nm to 1100 nm. The crystal is transparent in the yellowish red and near infrared spectral regions.

Optical transmittance of MPHB crystal is 65% .This was observed for 3 mm plates of MPHB crystals. The MPHB crystal has good optical transmission in the visible region.

The transparency in the visible region and the lower cutoff at 470 nm attest the usefulness of this material for optoelectronic applications and the second harmonic generation of the Nd:YAG laser and for the generation of the higher harmonics of the laser diodes.

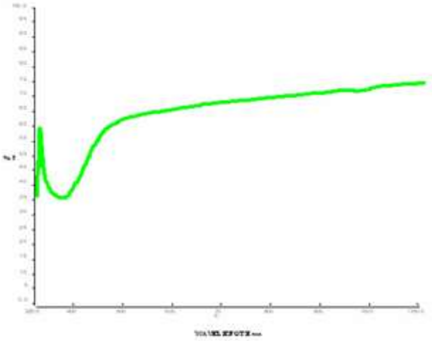

Fig. 5 UV-Vis spectrum of MPHB crystal

Thermal Analysis

The simultaneously recorded DTA and TG curves of the sample is shown in fig(6). The thermal analysis (TGA) was carried out by using TAQ-500 analyser at a heating rate 250 / min for temperature range 50 to 900^o in nitrogen inert atmosphere to study the weight loss and thermal stability. The thermogram shown in the figure reveals that the major weight loss takes place in the region 128.53^o C and 268.75^o C. This loss of weight may be due to the liberation of volatile substances from the sample. From the figure it is clear that the grown MPHB crystals are stable upto the temperature of 128.53^oC. There is no weight loss upto 100^o C, ensuring the absence of water in the crystal structure. Thus the grown crystal is a best suitable material for NLO application.

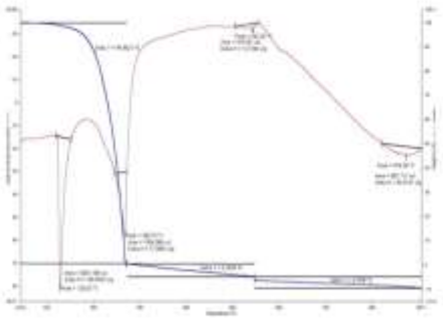

Fig.6. DTA and TG curves of MPHB crystal.

Vickers hardness test

The MPHB crystal grown was subjected to Vickers microhardness testing. Vickers microhardness indentation test is used to characterize the hardness of the material. Measurement of hardness is a non-destructive testing method to determine the mechanical behavior of the materials. The Vicker's hardness value is calculated from the formula Hv = 1.8544 * (P/d2) kg/mm2. Where P is the applied load in kg and d is the average diagonal length in millimeters of the indented impressions. In the present study, hardness was measured using Leitz-Wetzler hardness tester. Different loads were applied at a time of 10 seconds. Plot of load (P) against Vicker's hardness (Hv) is shown in the fig.7. It was observed that the micro hardness number decreases with the increase of load in the given planes. It is noted that the hardness decreases as the load increases, which is in agreement with the normal indentation size effect (ISE) observed for other NLO crystals. . At higher loads above 50 gm cracks begin to occur which may be due to the release of internal stresses generated locally by indentation[22]. Hence it may be suggested that the material may be used for the device below the applied load of 50gm. The relation connecting the applied load(P) and diagonal length (d) of the indenter is given by the Meyer Law[23]. From Meyer's Law P=adn connecting the applied load (P) and diagonal length (d) of the indentation, the work hardening coefficient 'n' was calculated. Here 'a' is a constant for a given material From the observations on various materials [24,25], it is pointed out that 'n' lies between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials. Since the value of work hardening coefficient of the grown crystal is 2.3 it is considered to be a soft material.

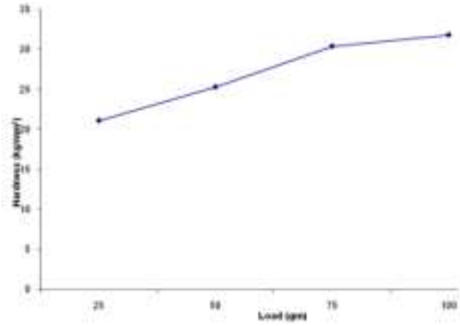

Fig.7 Plot of Load Vs Hardness of MPHB crystal

SHG efficiency measurement

The grown crystals were subjected to the NLO study to measure its conversion efficiency. The SHG property of a grown crystal was tested by the Kurtz and Perry powder method [26].The fundamental beam of wavelength 1064 nm from a Q-switched Nd:YAG laser with a pulse energy 3mJ/pulse, pulse width 8ns,and repeatition rate of 10 Hz was used.

The sample was powdered and was packed in a micro capillary of uniform bore and exposed to laser radiations. The optical signal generated from the sample was converted into an electrical signals and was measured using an oscilloscope.

The SHG conversion efficiency was found to be 297mV which very much higher than that of KDP. Hence it is a best suitable material for NLO applications.

Etching studies

Crystal defects may affect the properties of light absorption, scattering, refractive index, chemical homogeneity, electron mobility, mechanical strength and thermal stress. The defects were revealed using chemical etching. Chemical etching is able to develop some or all the features such as etch spirals, terraced, flat-bottomed pits, pits, etch hillocks, etc., on a crystal surface. The etch pits are the result of chemical attack at the strain field surrounding the dislocation line. The shape and orientation of the pits can be related to crystal symmetry. In the present study, acetone is used as an etchant. The surface of as-grown crystal is shown in Fig.8 for the etching on {100} face for 5,10 and 15 secs. The grown crystal has been completely immersed in the etchant for a given time and it was wiped out using a dry filter paper. Using a Magnus MLX microscope the surface nature has been analyzed. Small etch pits and striations were observed as shown in fig. 8(a) for 5 sec. When the crystal was etched for 10 sec, the kinks and more striations were observed as shown in figure 8(b). Minimum patterns were observed for 15 sec etching time, as shown in figure 8(c). This may be due to change in diffusion field around a dislocation site with increase of etching time. The minimum dislocations observed ensures the quality of the grown crystal.

Fig .8(a) 5 sec

Fig.8(b) 10sec

Fig.8(c) 15sec

Conclusion

Good optical quality single crystals of MPHB have been grown by solution growth method at room temperature. The lattice parameters have been found by single crystal X-ray diffraction technique. The FT-IR spectrum reveals the various functional groups present in the grown crystal. The optical absorption spectrum reveals that the crystal has wide optical window from 400nm to 1100 nm. The crystal is transparent in the visible and near infrared spectral regions. Optical transmittance of the crystal is high. From the thermogram it is evident that the crystal is stable upto the temperature of 128.53°C. The Vicker's microhardness was calculated in order to understand the mechanical stability of the grown crystals. Since the value of work hardening coefficient of the grown crystal is 2.3 it is considered to be a soft material. The SHG output voltage was measured using a photomultiplier and a digitalizing oscilloscope assembly. The output voltage was found to be 297mV which is very much higher than KDP. Thus the grown crystal is a best suitable material for NLO application.

References

[1] H.S. Nalva, S. Miyata, Nonlinear Optics of Organic Molecules and Polymers, CRC Press, Boca Raton, 1997

[2] P.N. Prasad, D.J. Williams introduction to Nonlinear Optical Effects in Organic Molecules and Polymers, Wiley, New York, 1991.

[3] D.S. Chemla, J.Zyss (Eds.), Nonlinear Optical Properties of Organic Molecules and Crystals, Academic Press, New York, 1987.

[4] S.R. Marder, B. Kippelen, A.K.-Y. Jen, N.Peyghambarian, Nature 388 (1997)845

[5] H. Ikeda, T.Sakai, K. Kawasaki, Chem. Phys. Lett. 179 (1991) 551.

[6] H.E. Katz, K.D. Singer, J.E. Sohn, C.W. Dirk, L.A. King, H.M. Gorden, J. Am. Chem. Soc. 109 (1987) 6561

[7] A.S. Haja Hameed, G.ravi, R. Dhanasekaran, P.Ramasamy, J. Crystal Growth 212 (2000) 227.

[8] J. Zaccaro, F. Lorut, A. Ibanez, J. Mater. Chem. 9 (1999) 1091.

[9] M.D. Aggarwal, J. Choi, W.S. Wang, K. Bhat, R.B. Lal, A.D. Shields, B.G.Penn, D.O. Frazier, J. Crystal Growth 204 (1999) 179.

[10] C.C. Frazier, M.P. Cockerham, J. Opt. Soc. Am. B 4 (1987)

[11] H.O. Marcy, M.J. Rosker, L.F. Warren, P.H. Cunning-ham, C.A. Thomas, L.A. Deloach, S.P. Velsko, C.A. Ebbers, J.H. Liao, M.G. Konatzidis, Opt. Lett. 20 (1995) 252.

[12] H.W. Zhang, A.K. Batra, R.B. Lai, J. Crystal Growth 137 (1994) 141.

[13] H.G. Gallagher, R.M. Vrceli, J.N. Sherwood, J. Crytal Growth 250 (2003) 486.

[14] D. Haarer, N. Kar, Chem. Phys. Lett. 21 (1973) 49.

[15] M. Arivanandham, K. Sangaranarayanan, K. Ramamoorthy, C. Sanjeeviraja, P. Ramasamy, Cryst. Res. Tech. 39 (2004) 692.

[16] J. Bleay, R.M. Hooper, R.S. Narang, J.N. Sherwood, J. Crystal Growth 4 (1978) 589.

[17] M. Arivanantham, K. Sankaranarayanan, C. Sanjeeviraja, A. Arulchakkaravarthi, P. Ramasamy J. Crystal Growth 281 (2005) 596.

[18] Li. Zhenhdong, Su. Genbo, Whu B. Chang, J. Cryst. Growth 121 (1992) 516.

[19].Shteinberg B.Y, Mushkiw Y.I, Finkelshtein A.I, Opt. Spectrosc. 33 (1972) 589.

[20].Szostak, M.M.,Raman. J.,Spec., 12 (1982) 228.

[21].R. Sankar, C.M. Raghavan, M. Balaji, R. Mohan Kumar, R. Jayavel, Cryst. Growth Des. 7 (2007) 348.

[22]. N. Vijayan, R. Ramesh Babu, M. Gunasekaran, R. Gopalakrishnan, P. Ramasamy, R Kumaresan, C.W. Lan, J. Cryst. Growth 249 (2003) 309.

[23].B.W.Mott ,Micro indentation Hardness Testing,Butterworth London(1956)

P.M.Ushasree, R.Jayavel, C.Subramanian, P.Ramasamy ,Bull.Electorchem.14 (1998) 407.

[24].M.A.Meyers, some aspects of the hardness of metals ,Ph.D.,Thesis,Dreft,(1951)

[25].E.M.Onitsch,Mikroscopia 2(1947) 131.

[26].S.K.Kurtz, T.T. Perry , J.Appl.Phys.39 (1968) 3798.