



Spectral and optical characterization of the new semi-organic crystal: 4-methylbenzylammonium chloride hemihydrate, to establish protonation and the effect of resultant hydrogen bonding

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Abstract. 4-Methylbenzylammonium chloride hemihydrate (4MLBACH) single crystals were obtained by slowly evaporating the solvent. The characterization of the title crystal was first carried out and reported in this article. The crystal system and space group of the title crystal are identified as monoclinic and $C2/c$, respectively. The lattice parameter values were also calculated. Using Fourier transform infrared spectroscopy the protonation of 4-methylbenzylamine by hydrochloric acid and the formation of the crystal 4MLBACH were confirmed. The transmission window of the grown crystal is between 261 and 1100 nm. The protonation of the amine group is confirmed by nuclear magnetic resonance spectral analysis. Z-Scan analysis was carried out to determine the nonlinear optical parameters. It reveals that the nonlinear susceptibility (χ^3) value is greater than some reported crystals. The title crystal exhibits saturable absorption and self-defocussing effects.

Keywords. 4-Methylbenzylammonium chloride hemihydrate; space group; protonation; molecular structure; third-order nonlinear susceptibility.

1. Introduction

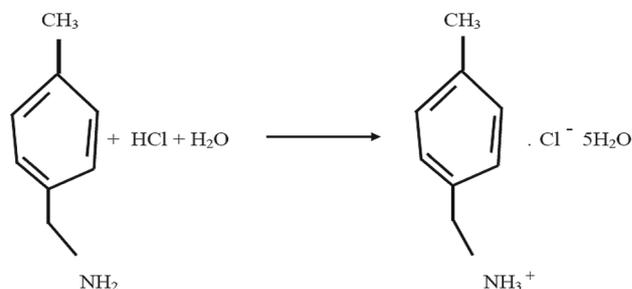
Single crystals play a vital role in the field of nonlinear optics. Efforts are being made throughout the world to identify better nonlinear optical (NLO) crystals [1,2]. Even though organic crystals are dominant in controlling the phase transitions, polarization and frequency of light have received very little attention in terms of their mechanical and thermal properties [3,4]. On the other hand, inorganic materials attracted interest because they exhibit good second-harmonic generation efficiency along with these superior mechanical and thermal properties. While these inorganic ionic bonded crystals have high-melting point and chemical inertness they possess low NLO properties [5,6]. Obviously, the semi-organic crystals exhibit the properties of both crystals. These hybrid compounds show potential applications in linear and nonlinear optics [7–10]. Attempts have been made by several researchers, to synthesize and grow semiorganic crystals which may exhibit the properties of both organic and inorganic crystals.

The authors have identified a new semiorganic crystal '4-methylbenzylammonium chloride hemihydrate' (4MLBACH) and its structure is reported by us [11]. This paper reports, the structural, spectral, linear and NLO properties of the title crystal. The structure of the crystal was dominated by the formation of a cationic hydrogen bond and anionic chloride interactions, which owes to a significant change in linear and nonlinear properties.

2. Experimental

2.1 Materials and methods

The crystal with the general formula $C_8H_{12}N^+ \cdot Cl^- \cdot 0.5H_2O$ was synthesized by crystallization in solution at $37^\circ C$ adopting a slow evaporation solution growth method. The chemical precursors 4-methylbenzylamine and hydrochloric acid are of 99.9% purity (Sigma Aldrich). The growth of the crystal has been reported by the authors [11]. Good quality crystals of dimension $1 \times 1 \times 1 \text{ mm}^3$ are obtained in a period of 15 days. The reaction scheme is given below.



3. Results and discussion

3.1 Single-crystal XRD analysis

This study was conducted using a BRUKER NONIUS CAD4 diffractometer and radiation used is $MoK\alpha$ with the

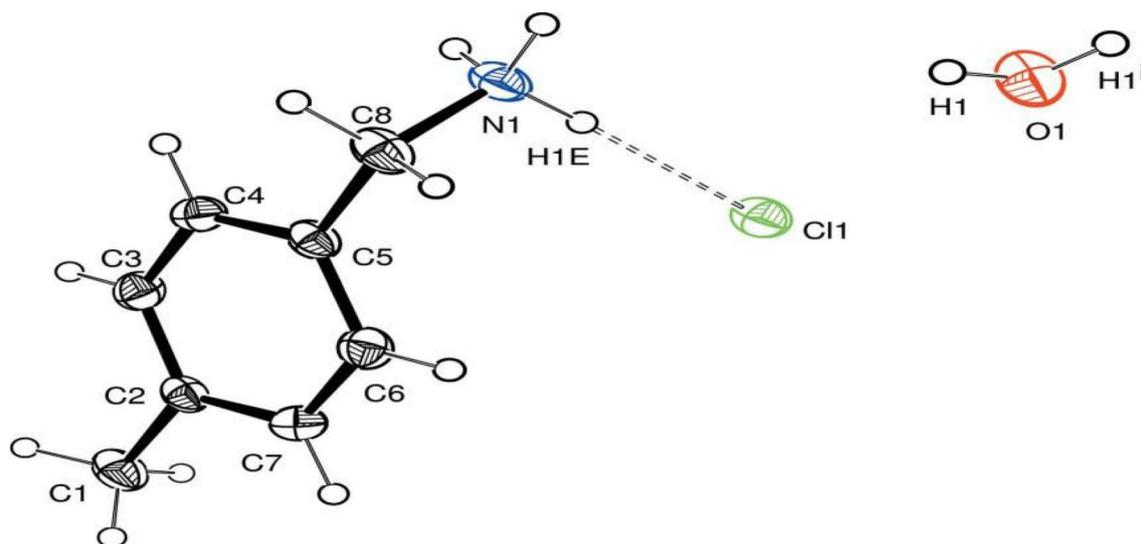


Figure 1. Molecular structure showing the protonated 4MLBACH [11].

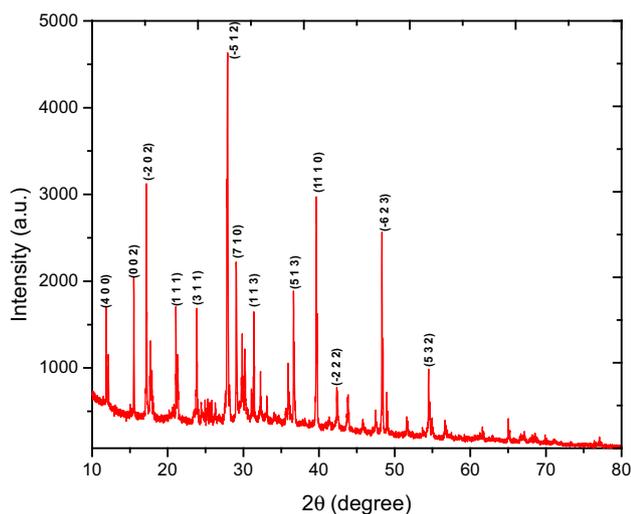


Figure 2. Powder XRD pattern of 4MLBACH crystals.

wavelength $\lambda = 0.71069 \text{ \AA}$. The structure of the title crystal is shown in figure 1. The X-ray diffraction (XRD) results reveal that 4MLBACH belongs to the monoclinic crystal system with the space group $C2/c$. The observed cell parameters are $a = 30.5325 (14) \text{ \AA}$, $b = 4.8966 (2) \text{ \AA}$, $c = 11.8973 (5) \text{ \AA}$, $\beta = 99^\circ 067'$ and volume = $1756.49 (13) \text{ \AA}^3$.

3.2 Powder XRD analysis

The powder XRD pattern and diffraction indices of the crystal are shown in figure 2. The crystallinity and cell parameters of 4MLBACH crystals have been studied from this analysis. The crushed powder sample was analysed using a Rich Seifert diffractometer with $\text{CuK}\alpha$ ($\lambda = 1.54060 \text{ \AA}$) radiation. The sample is scanned for 2θ values from 10° to 80° at a

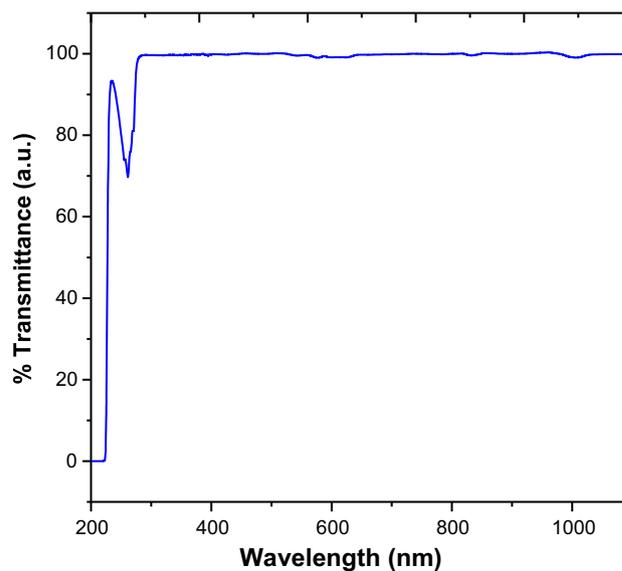


Figure 3. Optical transmission spectrum of 4MLBACH crystals.

rate of 2° min^{-1} . Sharp peaks reveal the good crystallinity of 4MLBACH. The diffraction pattern was indexed by the *indx* software package. The lattice parameter values were calculated by the Rietveld unit cell software package and were matched with single-crystal XRD data. The values, $a = 30.4915 \text{ \AA}$, $b = 4.9054 \text{ \AA}$, $c = 11.8255 \text{ \AA}$ and $\beta = 99^\circ 6337'$ obtained from powder XRD analysis match well with single-crystal XRD values [11].

3.3 Transmission spectral study

It is significant to find the optical transmittance window of the grown NLO crystals. The linear transmittance range of

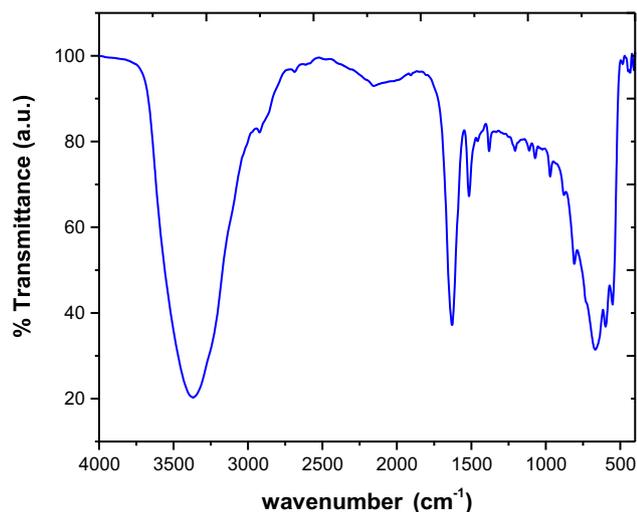


Figure 4. FTIR spectral pattern of 4MLBACH crystals.

4MLBACH crystals was measured in the range from 190 to 1100 nm using the Perkin-Elmer UV-Vis-NIR spectrophotometer. The 4MLBACH crystal sample is taken and mixed well with deionised water and kept in a cuvette. The transmission spectrum of 4MLBACH is presented in figure 3. The lower cut-off wavelength of the title crystal is 260 nm and it is transparent up to the region tested. This reveals that the crystal can be used in optoelectronic applications [12]. A crystal has to be transparent for all the interacting wavelengths in NLO applications. Since the crystal is transparent from 260 to 1100 nm it can be used to generate all these wavelengths by frequency mixing processes. As the crystal is transparent for a Nd:YAG laser with a fundamental wavelength of 1064 nm and its third harmonic at 355 nm, it can be used to generate the third harmonic generation [13].

3.4 FTIR spectral analysis

Fourier transform infrared (FTIR) spectroscopy is employed to find the presence of various functional groups present in the 4MLBACH crystal. A Perkin-Elmer FTIR spectrometer using a KBr pellet technique was used to record the spectrum in the range of 4000–400 cm^{-1} and the spectrum is shown in figure 4. KBr is used as a carrier for the sample in the IR spectrum and it is 100% optically transparent in the range of wavenumber (4000–400 cm^{-1}). The spectrum clearly depicts the formation of 4-methylbenzylamine with hydrochloric acid through the protonation of NH_2 . The broad band observed at 3368 cm^{-1} which is attributed to the symmetric stretching vibrations of NH_3^+ , C–H and O–H groups which is the confirmation for the protonation of NH_2 and also confirms the presence of CH and OH groups in the structure. The peak at 2922 cm^{-1} is due to the CH antisymmetric stretching vibration. For pure 4-methylbenzylamine the CH vibrations were observed between 2860 and 2921 cm^{-1} . A small peak observed at 2687 cm^{-1} was attributed to the H–Cl

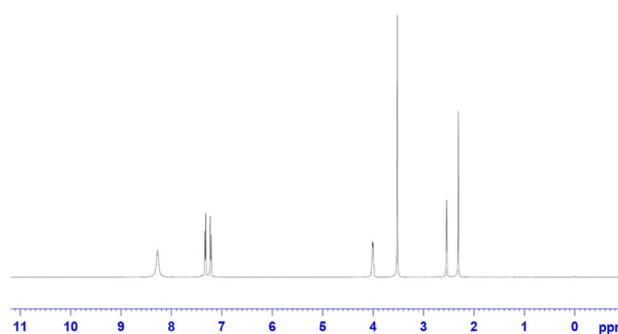


Figure 5. ^1H NMR chemical shifts (ppm) of 4MLBACH crystals.

vibration. A sharp peak at 1629 cm^{-1} is assigned to the NH_3^+ symmetric bending mode. An absorption peak at 1515 cm^{-1} shows the vibration of C=C aromatic stretching. The peak at 1457 cm^{-1} attributed to the CH_2 bending vibration. The CH_3 symmetric deformation mode of vibration is assigned to the peak at 1380 cm^{-1} . The absorption band at 1206 cm^{-1} is attributed to C–C bending vibrations. A peak observed at 1111 cm^{-1} is assigned to CH bending vibrations. A peak at 1071 cm^{-1} was attributed to the C–H in plane deformation vibrational mode. The peak at 970 cm^{-1} belongs to the C–C stretching mode of vibration. The CH_2 rocking vibration was observed at 808 cm^{-1} . A peak at 667 cm^{-1} owes to the C–H out-of-plane deformation mode. The peak with low intensity was observed at 551 cm^{-1} which could be assigned to the vibrations of the benzene ring. The assignments are made by comparing the 4MLBACH spectrum with the literature [14–18].

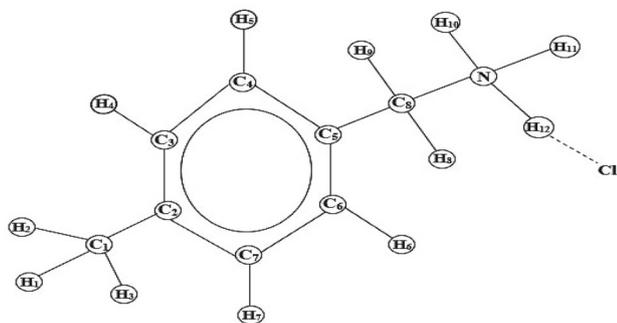
3.5 ^1H NMR spectral analysis

A Bruker AMX spectrometer at 300 MHz was used to record the ^1H nuclear magnetic resonance (NMR) spectrum of the title crystal using dimethyl sulphoxide as the solvent. The internal NMR reference is used as tetramethyl silane and the analysis was carried out at room temperature. Figure 5 shows the ^1H NMR profile of the title crystal. Table 1 shows its chemical shifts and assignments. The two observed peaks of the solvent clearly match well with the already reported value [19]. The spectrum showed that the 4MLBACH is coordinated with the chloride anion through the protonated NH_3^+ group. For pure 4-methylbenzylamine, NH_2 signals observed at 1.42 ppm [20]. The same is shifted downfield and observed at 8.278 ppm for the title crystal. The shift of the signal from lower ppm to higher ppm is due to the protonation of the NH_2 group to NH_3^+ [21]. The shifts for methylene protons bonded to nitrogen was observed at 4.015 and 4.002 ppm whereas, in the case of pure 4-methylbenzylamine the same was observed at 3.795 ppm. The difference observed in the chemical shift is $\Delta\delta = 0.22$ ppm indicating the formation of NH_3 . The signal at 2.311 ppm is attributed to the methyl group which established the presence of hydrogen in the aliphatic group.

Table 1. ^1H NMR chemical shift values and assignments of 4MLBACH crystals.

Atom	Pure 4MLBA chemical shift in ppm (δ)	4MLBACH chemical shift in ppm (δ)	Assignments
H4, H5, H6, H7	6–8	7.213, 7.223, 7.320 and 7.340	H in aromatic ring
H8, H9	3.795	4.015, 4.002	CH_2
H1, H2, H3	2.320	2.311	CH_3
H10, H11, H12	1.42	8.278	NH_3

The aromatic ring hydrogen signal is found as a multiplet between 7.213 and 7.340 ppm. The position of the hydrogen atom in the structure of the molecule is represented in figure 6.

**Figure 6.** Structure of 4MLBACH representing the position of carbon and hydrogen atoms.

3.6 ^{13}C NMR spectral analysis

The ^{13}C NMR profile is depicted in figure 7. The chemical shifts and the assignments for the different carbon atoms are presented in table 2. The aromatic carbon attached to the methylene group shows a sharp peak at 138.31 ppm. The peaks observed at 129.25, 129.62 and 131.36 ppm were due to the other C atoms attached to the ring [22]. The signal at 42.60 ppm is due to the CH_2 group bonded with NH_3 . In the case of pure 4-methylbenzylamine the CH_2 peak is present at 46.21 ppm. The coordination of H^+ cations and Cl^- anions with 4-methylbenzylamine was confirmed by this peak at 42.60 ppm which in turn establishes the $\text{N}-\text{H}\cdots\text{Cl}$ interaction. The signal for carbon present in the methyl group peak is observed at 21.18 ppm.

3.7 Z-Scan analysis

Sheik Bahae *et al* [23] introduced and employed a Z-scan analysis method to determine the nonlinear refractive

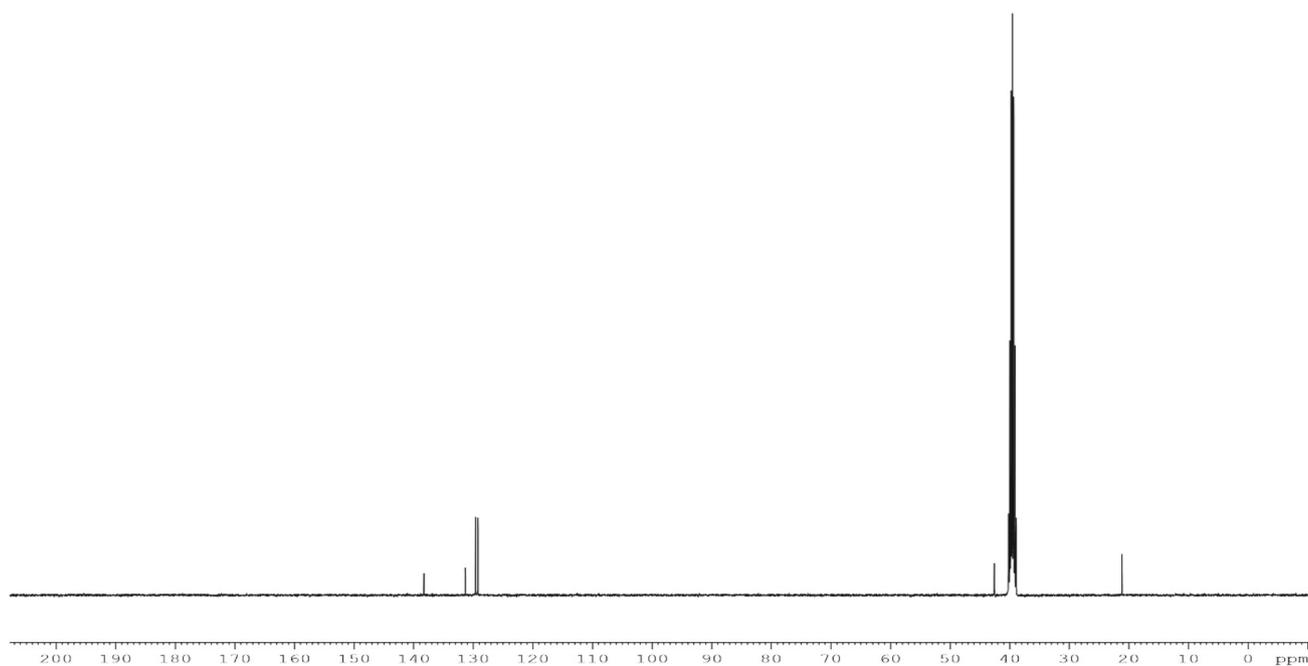
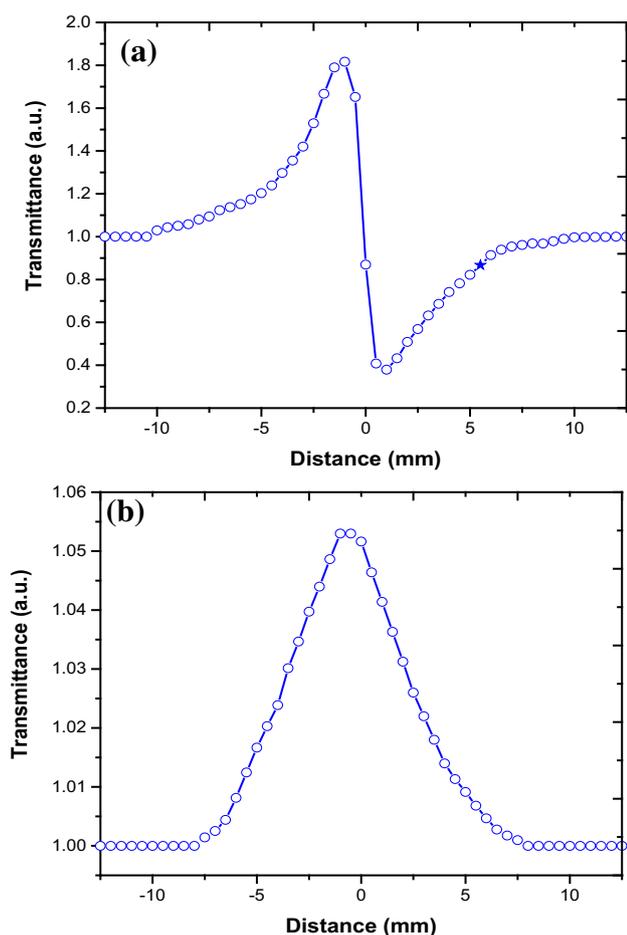
**Figure 7.** ^{13}C NMR chemical shifts (ppm) of 4MLBACH crystals.

Table 2. ^{13}C NMR chemical shift values and assignments of 4MLBACH crystals.

Atom	Pure 4MLBA chemical shift in ppm (δ)	4MLBACH chemical shift in ppm (δ)	Assignments
C1	20.97	21.18	CH ₃
C2	140.47	138.31	CH
C3	129.10	129.62	CH
C4	136.09	131.36	CH
C5	126.95	129.25	CH
C6	136.09	131.36	CH
C7	129.10	129.62	CH
C8	46.21	42.60	CH ₂

**Figure 8.** (a) Z-Scan closed aperture trace of 4MLBACH crystals. (b) Z-Scan open aperture trace of 4MLBACH crystals.

index (n_2), absorption coefficient (β) and third-order NLO susceptibility (χ^3).

This study was carried out for the 4MLBACH crystals using a single-beam Z-scan technique equipped with a Nd-YAG laser with an intensity of 5 mW ($\lambda = 532$ nm), focussed by a lens with a focal length of 3.5 cm. This method is a usual and simple method to determine the NLO parameters such as the refractive index (n_2), absorption coefficient (β) and third-order NLO susceptibility (χ^3) by closed and open aperture mode very accurately using the formula reported in the literature [24]. Measurements of the closed aperture and the open aperture as a function of the sample position Z have been performed for the 4MLBACH crystal and illustrated in figure 8a and b, respectively. The pre-focal peak followed by the post-focal valley nature of the closed aperture curve enunciates that the crystal is pronounced to negative n_2 which is due to the occurrence of the self-defocussing effect. The negative nonlinearity contributes to high-laser damage threshold [25]. This finds application in optical sensors like night vision devices [26]. The open aperture Z-scan curve suggests that the sample exhibits the larger transmission near the focus ($Z = 0$) which is due to the saturable absorption of the 4MLBACH crystal [24]. The primary applications of saturable absorption are Q switching of lasers that generate short optical pulses, passive mode locking to obtain ultrashort pulses and optical bistability applied in optical memory, optical transistor, optical switching and also useful for cleaning up pulse shapes [27–30]. The value of third-order NLO susceptibility χ^3 of the crystal was found to be 3.57×10^{-6} esu (table 3). The crystal structure is constructed by N–H \cdots Cl and C–H \cdots Cl interactions which results in the formation of hydrogen bonds as reported by the authors [11]. These hydrogen bonds change the electronic distribution and enhance the

Table 3. Third-order NLO parameters of 4MLBACH crystals.

Nonlinear refractive index (n_2)	$7.02 \times 10^{-8} \text{ cm}^2 \text{ W}^{-1}$
Nonlinear absorption coefficient (β)	$0.04 \times 10^{-4} \text{ cm W}^{-1}$
Real part of third-order susceptibility [$\text{Re}(\chi^3)$]	3.56×10^{-6} esu
Imaginary part of third-order susceptibility [$\text{Im}(\chi^3)$]	0.24×10^{-6} esu
Third-order nonlinear susceptibility (χ^3)	3.57×10^{-6} esu

Table 4. Comparison of the χ^3 value of 4MLBACH with some third-order NLO crystals.

Name of the crystal	Third-order optical susceptibility (χ^3) (esu)	Reference
4MLBACH	3.57×10^{-6}	Present work
VMST	9.6963×10^{-12}	[33]
MMST	2.29×10^{-7}	[34]
KDNB	3.02×10^{-8}	[35]

molecular polarization. This could be the reason for the large third-order susceptibility exhibited by the title crystal [31,32]. The χ^3 value of 4MLBACH was compared with the values of some reported NLO crystals and are presented in table 4.

4. Conclusions

The title crystal was grown using a solvent evaporation technique. The colourless good quality crystals were harvested in 15 days. They crystallize in the monoclinic crystal system with the $C2/c$ space group. The wide transparency width of the title crystal was ascertained by the transmission spectrum. Vibrational spectroscopy was employed to analyse the functional group of 4MLBACH single crystals. The protonated molecular structure is once again confirmed by ^1H and ^{13}C NMR spectroscopy. It is found that the hydrogen bond is responsible for the larger third-order susceptibility values.

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References

- [1] Ruiz B, Yang Z, Gramlich V, Jazbinsek M and Gunter P 2006 *J. Mater. Chem.* **16** 2839
- [2] Suresh S and Arivouli D 2011 *J. Optoelectron. Biomed. Mater.* **3** 63
- [3] Ferguson B and Zhang X C 2002 *Nat. Mater.* **1** 26
- [4] Bordui P F and Fejer M M 1993 *Annu. Rev. Mater. Sci.* **23** 321
- [5] Kubodera K and Kobayashi H 1990 *Mol. Cryst. Liq. Cryst.* **182** 103
- [6] Jiang M H and Fang Q 1999 *Adv. Mater.* **11** 1147
- [7] Kimizuka N and Kunitake T 1996 *Adv. Mater.* **8** 89
- [8] Mitzi D B, Chondroudis K and Kagan C R 2001 *IBM J. Res. Dev.* **45** 29
- [9] Santos S N C, Almeida J M P, Paula K T, Tomazio N B, Mastelaro V R and Mendonça C R 2017 *Opt. Mater.* **73** 16
- [10] Karthick N, Sankar R, Jayavel R and Pandi S 2009 *J. Cryst. Growth* **312** 114
- [11] Aarthi R, Thiruvalluvar A and Ramachandra Raja C 2017 *IUCrData* **2** x1712
- [12] Bharath D and Kalainathan S 2014 *Spectrochim. Acta. A* **120** 32
- [13] Natarajan S, Shanmugam G and Martin Britto Dhas S A 2008 *Cryst. Res. Technol.* **43** 561
- [14] Barth A 2000 *Prog. Biophys. Mol. Biol.* **74** 141
- [15] Brittain H G 2011 *Cryst. Growth Des.* **11** 2500
- [16] Grayson M 2003 *Internet Electron. J. Mol. Des.* **2**
- [17] Brittain H G 2009 *Cryst. Growth Des.* **9** 3497
- [18] Gunasekaran S, Sailatha E, Seshadri S and Kumaresan S 2009 *Indian J. Pure Appl. Phys.* **47** 12
- [19] Karthiga S, Kalainathan S, Hamada F, Yamada M and Kondo Y 2016 *RSC Adv.* **6** 33159
- [20] https://sdfs.db.aist.go.jp/sdfs/cgi-bin/direct_frame_top.cgi
- [21] Beecher C N and Larive C K 2015 *Anal. Chem.* **87** 9842
- [22] Kefi R, Jeanneau E, Lefebvre F and Nasr C B 2011 *Acta Cryst.* **C67** m126
- [23] Sheik-Bahae M, Said A A, Wei T H, Hagan D J and Van Stryland E W 1990 *IEEE J. Quantum Electron* **26** 760
- [24] Sangeetha P, Jayaprakash P, Nageshwari M, Rathika Thaya Kumari C, Sudha S, Prakash M *et al* 2017 *Physica B* **525** 164
- [25] Gupte S S, Marcano O A, Pradhan R D, Desai C F and Melikechi N 2001 *J. Appl. Phys.* **89** 4939
- [26] Zhou Y S, Wang E B and Peng J 1999 *Polyhedron* **18** 1419
- [27] Fan H-L, Ren Q, Wang X-Q, Li T-B, Sun J, Zhang G-H *et al* 2009 *Nat. Sci.* **1** 136
- [28] Nihei H and Okamoto A 2001 *Proc. SPIE* **4416** 470
- [29] Assanto G, Wang Z, Hagan D J and Vanstryland E W 1995 *Appl. Phys. Lett.* **67** 2120
- [30] Mazurenko D A, Kerst R, Dijkhuis J I, Akimov A V, Golubev V G, Kurdyukov D A *et al* 2003 *Phys. Rev. Lett.* **91** 213903
- [31] Lei C, Yang Z, Zhang B, Lee M-H, Jing Q, Chen Z *et al* 2014 *Phys. Chem.* **16** 20089
- [32] Gomathi R, Madeswaran S and Rajan Babu D 2017 *J. Mater. Sci.: Mater. Electron* **28** 11374
- [33] Krishna Kumar M, Sudhar S, Pandi P, Bhagavannarayana G and Mohan Kumar R 2014 *Opt. Mater.* **36** 988
- [34] Kumar M K, Sudhar S, Silambarasan A, Sornamurthy B M and Kumar R M 2014 *Optik* **125** 751
- [35] Karuppasamy P, Sivasubramani V, Senthil Pandian M and Ramasamy P 2016 *RSC Adv.* **6** 109105