International Journal of ChemTech Research
CODEN (USA): IJCRGG, ISSN: 0974-4290, ISSN(Online):2455-9555
Vol.13 No.03, pp 274-282, 2020

Studies on Optical Constants and Solid State Parameters of a Semi-organic Nonlinear Optical Material L-Methioninium Nitrate for Optoelectronic Device Fabrication

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Abstract : Semi-organic nonlinear optical material L-methioninium nitrate have been synthesized by the slow evaporation technique at room temperature. The synthesized crystal structure lattice parameters are found to be a = 10.68 (2) Å, b = 5.47 (2) Å, c = 16.725.47 (2) Å; α = γ = 90º, β = 100.7º by single crystal X-ray diffractometer. The grown crystal belongs to a monoclinic structure and non-centrosymmetric space group $P2_1$. Optical properties were determined from optical absorption studies to compute the absorption range, band gap, refractive index and electrical susceptibility of L-methioninium nitrate. Dielectric parameters of the sample carried out at different temperature in the frequency range from 100 Hz to 5 MHz. The solid parameters such as plasma energy, Penn gap, Fermi energy and polarizability of L-methioninium nitrate have been determined using dielectric studies. The second harmonic generation efficiency of the grown crystal has been confirmed by Kurtz and Perry technique. These preliminary investigations suggest that the present compound L-methioninium nitrate can serve as a potential material for optoelectronic device fabrication.
Keywords : Nonlinear Optical Material, Optical studies, Solid state parameters, NLO test and L-Methioninium Nitrate.

1. Introduction

Semi-organic based single crystals have paid attention towards the researchers because many of the non-linear optical materials are presently used in the fabrication of optoelectronic devices [1]. Usually potassium dihydrogen phosphate (KDP) is broadly used as a laser frequency doubler and Lithium Niobate ($LiNbO_3$) crystal is employed as electronic modulator. Broadly, the non-linear optical properties of the crystal have played an important role in second harmonic generation, frequency mixing, optical switching, electro optic

P. Vasudevan et al /International Journal of ChemTech Research, 2020,13(3): 274-282.

DOI= http://dx.doi.org/10.20902/IJCTR.2019.130325

modulation, optical parametric oscillation, optical bistability, telecommunication, signal processing, etc., [2, 3] for that study of optical and electrical properties of the crystal are necessary. Naturally, amino acids have capable to exhibits nonlinear optical properties due to their donor NH_2 and acceptor COOH and also charge transfer is possible [4]. This type of crystals has poor mechanical and thermal stability. To overcome these difficulties and find a new class of crystals, researchers focusing study of semi-organic single crystals. Moreover amino acids have large nonlinear susceptibilities which improve the chemical stability, laser damage threshold, linear and nonlinear optical properties [5]. Therefore, we have chosen L-methionine is an organic compound under amino acid group. It is one among two sulphur containing proteinogenic amino acids, the other one being cystein for forming amino acid complexes. Several new complexes incorporating L-methionine have been recently crystallized and their structural, optical, electrical, mechanical and thermal properties have been investigated, such as bis (L-methioninium) sulfate, L-methionine L-methioninium perchlorate, etc. [6-9]. In this manner, Pandiyarajan et al and Vasudevan et al have reported only the crystal structure, vibrational spectral studies, mechanical and thermal studies of L-methioninium nitrate (LMN) [10, 11]. The literature survey reveals that other properties of LMN have not reported till date. Hence, in the present study, LMN single crystal grown by the slow evaporation technique at room temperature. Optical properties such as optical absorption range, band gap, refractive index and electrical susceptibility of LMN were computed to understand optical properties. Dielectric studies were extensively studied to evaluate the polarizability for assessing the second harmonic generation (SHG) efficiency of the grown crystal. Also, the solid parameters such as plasma energy, Penn gap, Fermi energy and polarizability of L-methioninium nitrate have been determined using dielectric studies for the first time.

2. Experimental

2.1 Synthesis

Analytical grade of L-methionine and nitric acid were taken as the starting materials for synthesizing LMN. A solution was prepared by dissolving L-methionine and nitric acid in water with 1:1 molar ratio and stirred using a magnetic stirrer to get homogeneous solution. The solution was then allowed for slow evaporation at room temperature. As a result, the solution gradually reached supersaturation leading to nucleation phenomenon followed by the growth mechanism. Well transparent and colourless crystals of LMN with dimensions of $10 \times 5 \times 3$ mm^3 were harvested after a period of 20 days. The as-grown LMN crystal is shown in Fig.1. The product was then purified by recrystallization process. The reaction for the synthesized crystal is given as follows:

$$C_5H_{11}NO_2S + HNO_3 \rightarrow C_5H_{12}NO_2S^+ . NO_3^- \quad (1)$$

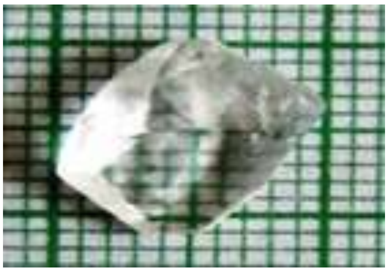

Fig. 1 As-grown LMN crystal

Table 1 Optimized growth conditions for LMN single crystal

Method of Growth	Slow evaporation technique
Solvent used	Deionized water
Molar ratio (L-Methionine: Nitric acid)	1:1
Temperature for growth	Room temperature (30ºC)
Period of growth	20-30 days
Dimension	$10 \times 5 \times 3$ mm^3

2.2 Characterization Details

Single crystal XRD studies were carried out using Bruker Kappa APE XII single X-ray diffractometer to determine the lattice parameters and the space group of the grown LMN crystal. Optical absorption measurements were made using Perkin Elmer Lamda 35 UV-VIS-NIR spectrophotometer with a resolution of 2 nm in the region from 200 nm to 1200 nm to measure the absorption range of the crystal. Dielectric parameters were calculated with an accuracy of 2 % using an HIOKI LCR Hitester varying the temperatures in the frequency range from 5 Hz to 5 MHz. Nonlinear optical property of LMN crystals was confirmed by the Kurtz and Perry powder technique using Q-switched high energy Nd:YAG laser (QUANTA RAY model LAB-170-10).

3. Results and Discussion

3.1 Single Crystal XRD

Single crystal XRD analysis reveals that the grown crystal belongs to monoclinic structure with non-centrosymmetirc space group $P2_1$. The crystal lattice parameters were found to be a = 10.68 (2) Å, b = 5.47 (2) Å, c = 16.72 (6) Å; $\alpha = \gamma = 90^o$, $\beta = 100.7^o$ with unit cell volume V = 983.3 $Å^3$. These lattice parameters are found to be in good agreement with the reported values [12]. The non-centrosymmetric nature of the grown crystal fulfills the important criterion for an NLO material.

3.2 Optical Studies of LMN

Optical absorption measurements were made using Perkin Elmer Lamda 35 UV-vis-NIR spectrophotometer with a resolution of 2 nm in the region from 200 nm to 1200 nm to measure the absorption range of the crystal. The recorded absorption spectrum is as shown in Fig. 2. From the observed spectrum, the lower cut-off wavelength is found to be 325 nm and there is no absorption peak in the visible region and near the infrared region which indicates the absence of overtones [13]. An absorption peaks obtained in the range between 200 and 350 nm shows n to π^* transitions of the carbonyl group [14]. The absence of absorption in the near infrared region provides the access to the laser wavelength of 1064 nm from Nd: YAG source for second harmonic generation [15].

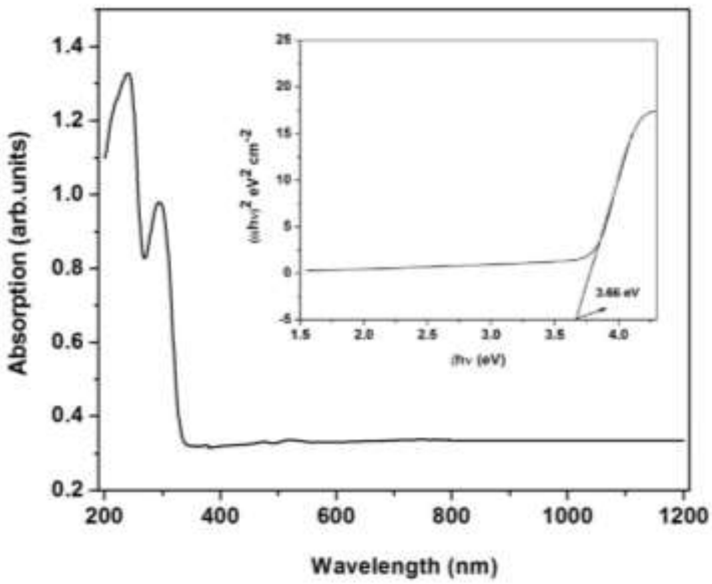

Fig. 2 UV-vis-NIR absorption spectrum and band gap of LMN crystal

Hence, UV absorption studies reveal that the grown LMN crystal is one of the suitable materials for exhibiting second harmonic generation in the entire visible and near infrared region. The Tauc's plot of $(\alpha h\nu)^2$ against the photon energy (hν) at room temperature (Fig. 2) shows a linear behaviour, (α-absorption coefficient and h-Planck's constant) which can be considered as an evidence of the indirect transition. Using Tauc's plot, the band gap of the LMN crystal was found to be 3.66 eV.

The relation between refractive index (n) and energy gap (E_g) is given by Reddy et al [16] as,

$$E_g e^n = 36.3 \qquad (2)$$

After finding the refractive index, the reflectance (R) of the crystal was calculated using the expression,

$$R = \left(\frac{n-1}{n+1}\right)^2 \qquad (3)$$

The refractive index and reflectance of the crystal were calculated as 1.97 and 0.106 respectively in the transmission range. The high value of refractive index and low value of reflectance reveal that the grown crystal is more transparent to transmit the light from 325 to 1200 nm.

The electrical susceptibility (χ_c) was calculated using the following relation,

$$\chi_c = \varepsilon_r - 1 \qquad (4)$$

Or $$\chi_c = n^2 - 1 \quad (\because \varepsilon_r = n^2) \qquad (5)$$

Hence, $\chi_c = 2.88$

Since the electrical susceptibility is greater than 1, the material can be easily polarized due to irradiation with powerful laser beam.

3.3 Dielectric Studies of LMN

A rectangular grown material LMN of approximate thickness of 1.46 mm and area of cross section 32.33 mm^2 was used for dielectric study. The surface of the crystal was well polished and placed into the sample holder for dielectric measurements. This arrangement provides a good thermal insulation to the cell and ensures a uniform temperature over the bulk of the sample. The sample holder was heated at a slow rate from room temperature to 130ºC below the decomposition or melting temperature. The temperature of the LMN was permitted to become constant for a few minutes and then capacitance and dielectric loss values were recorded for different frequencies from 100 Hz to 5MHz. The dielectric constant and dielectric loss of the grown crystal have been calculated by using the relations:

$$\varepsilon' = \frac{cd}{A\varepsilon_o} \qquad (6)$$

$$\varepsilon'' = \varepsilon_r D \qquad (7)$$

where d is the thickness of the grown crystal, A is the area of the crystal and D is the dissipation factor. Figures 3 and 4 show the variation of dielectric constant and dielectric loss factor for LMN crystals as a function of frequency at different temperatures. At low frequencies, the dielectric constant is found to be maximum and then it decreases with increasing frequency. In high frequency region both dielectric constant and dielectric loss factors are fairly remaining constant as shown in Fig. 3 and 4. The high value of dielectric constant at low frequency is owing to the presence of all types of polarizations viz., electronic, ionic, orientation and space polarization. The space polarization will depend on the purity and perfection of the sample.

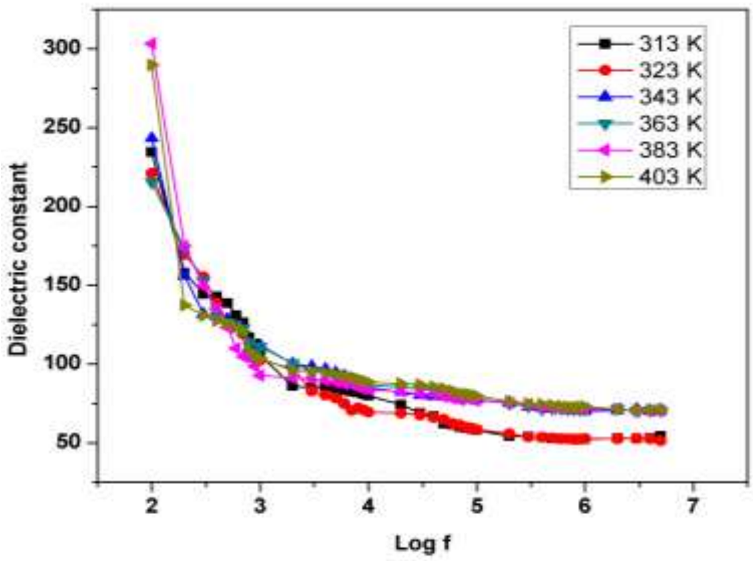

Fig. 3 Variation of dielectric constant with frequency for LMN crystal

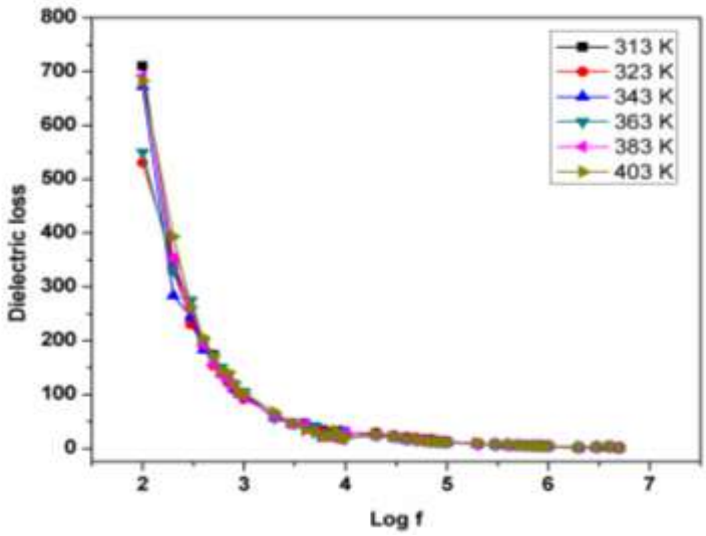

Fig. 4 Variation of dielectric loss with frequency for LMN

According to Miller rule, the low value of dielectric constant in the higher frequency region can enhance the SHG efficiency of the grown crystal [17]. The lower value of dielectric loss at high frequencies will guarantee that the grown crystal is free from major defects [18]. Dielectric measurements suggest that replacement of other materials in microelectronic industry may be possible with LMN crystals because of lower dielectric constant values at high frequencies.

3.4 AC Conductivity of LMN

The study of ac conductivity (σ_{ac}) gives an idea about the polarization mechanism in the crystal. The AC conductivity has been calculated from the following formula:

$$\sigma = \varepsilon_{\circ}\varepsilon_{r}\omega\tan\delta \qquad (8)$$

where $\varepsilon_{\circ}$ is the vacuum dielectric constant (8.85×10^{-12} F/m), ε_{r} is the relative dielectric constant of the LMN crystal and ω is the angular frequency $(\omega = 2\pi\upsilon)$ of applied field. The AC conductivity (σ_{ac}) of LMN crystal was calculated using the dielectric data. Figure 5 shows the variation of ac conductivity with various frequencies and temperatures. It is seen that the value of ac conductivity increases with increase in frequency.

The number of charge carriers is multiplied as the frequency of the applied field increases and hence the ac conductivity shows sharp increase at higher frequencies. At higher temperatures the thermal energy is sufficient to increase the number of charge carriers and hence the ac conductivity increases with the increase of temperature. The sudden increase of ac conductivity is due to the good response of the charge carriers with the applied field. The variation of ac conductivity with temperature follows the Arrhenius plot of equation as follows:

$$\sigma_{ac} = \sigma_{\circ} \exp\left(\frac{-\Delta E_a}{kT}\right) \tag{9}$$

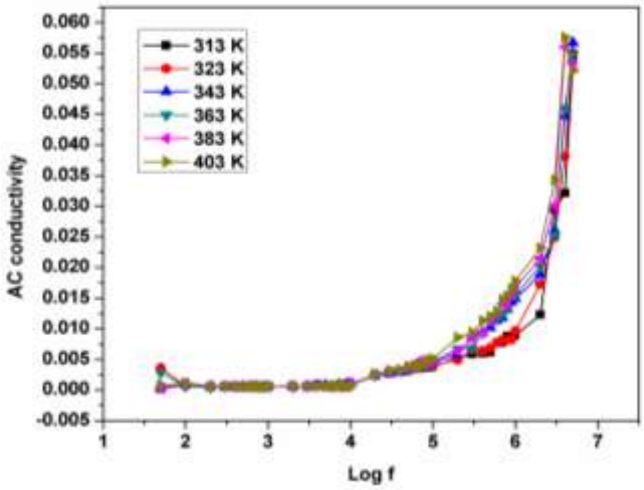

Fig. 5 AC conductivity of LMN crystal

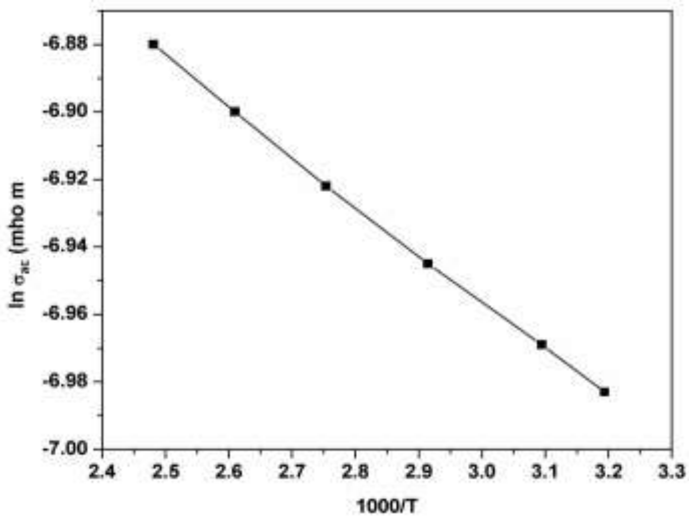

Fig. 6 Arrhenius plot of AC conductivity of LMN crystal

where ΔE_a is the activation energy, k is the Boltzmann constant and T is the temperature in Kelvin. Figure 6 shows the Arrhenius plot of ac conductivity of LMN crystal. The slope of the plot of ac conductivity versus temperature gives the activation energy required for the conduction process of the charge carriers. The value is found to be 0.145 eV and the lower value of the activation energy establishes that the crystal contains less number of defects. Hence, the material is useful for various microelectronic and nonlinear optical applications.

3.5 Solid State Parameters of LMN

Solid state parameters are necessary to analyze second harmonic generation efficiency of the title compound. From the single XRD data, the molecular weight of the grown crystal is M= 212.23g, and the total number of valence electron Z= 4. The density of the grown crystal was found to be ρ= 1.442 cm^{-3} and dielectric constant at 1 MHz is ε_∞= 52.25. The valence electron plasma energy,

$$\hbar\omega = 28.8\left(\frac{Z\rho}{M}\right)^{1/2} \tag{10}$$

where Z is the total number of valence electrons. The chemical formula of LMN is $C_5H_{12}N_2O_5S$, where, Z = (5 × Z_C) + (12 × Z_H) + (2×Z_N) + (5 × Z_O) +(1× Z_S) = 78, total number of valence electrons, ρ is the density and M is the molecular weight of the LMN single crystal. The plasma energy in terms of Penn gap and Fermi energy [19] as,

$$E_P = \frac{\hbar\omega_P}{(\varepsilon_\infty - 1)^{1/2}} \tag{11}$$

and

$$E_F = 2.948(\hbar\omega_P)^{4/3} \tag{12}$$

Polarizability, α is obtained using the relation

$$\alpha = \left[\frac{(\hbar\omega)^2 S_0}{(\hbar\omega_P)^2 S_0 + 3E_P{}^2}\right] \times \frac{M}{\rho} \times 0.396 \times 10^{-24} \tag{13}$$

Where $S_\circ$ is a constant for a particular material, and is given by

$$S_\circ = 1 - \left[\frac{E_P}{4E_F}\right] + \frac{1}{3}\left[\frac{E_P}{4E_F}\right]^2$$

The value of α is obtained agrees well with that of Clausius-Mossotti equation, which is given by,

$$\alpha = \frac{3M}{4\pi N_a \rho}\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \tag{14}$$

where the symbols have their usual meaning. N_a is the Avogadro number and calculated fundamental data on the grown crystal of LMN are listed in Table 2. The determined polarizability of LMN is found to be larger than that of standard material KDP. It is revealed that SHG efficiency of LMN is more than that of KDP. Hence, the grown material LMN has capable to improve SHG efficiency.

Table 2 Solid state parameters for LMN single crystal

Solid state parameters	**Values for LMN crystal**
Molecular weight	212.23
Density (g cm^{-3})	1.442
Plasma energy (eV)	20.96
Penn gap (eV)	2.92
Fermi energy (eV)	17.03
Polarizability by Penn gap (cm^3)	5.49× 10^{-23}
Polarizability by Clausius-Mosotti equation (cm^3)	5.51× 10^{-23}

3.6 Second Harmonic Generation of LMN

Nonlinear optical property of LMN crystals was confirmed by the Kurtz and Perry powder technique using Q-switched high energy Nd:YAG laser (QUANTA RAY model LAB-170-10) [20]. The as grown crystal LMN was powdered and packed in the capillary tube. A high intense beam of laser wavelength 1064 nm was allowed to illuminate the sample with a pulse width of 8 ns. The emissions of green radiation 532 nm from the LMN ensure that the material exhibits nonlinear optical property. The power of incident laser beam was measured as 0.68J. The output radiation from the given material was allowed to fall on a photomultiplier tube which converts the light signal into electrical signal. The output power of LMN was measured as 2.86mJ.

Table 3. Comparison of output power of amino acid derivative crystals with LMN crystal

Some amino acid derivative crystals	Output power in mJ
L-alanine	2.24
L-arginine bromide	2.04
L-phenyalaninium maleate	1.83
L-phenyalaninium nitrate	1.76
L-methioninium nitrate (Present work)	2.86

The measurements were made for some other amino acid derivatives too. LMN crystal is found to possess SHG efficiency more than that of L-alanine (2.24mJ), L-arginine bromide (2.04mJ), L-phenylalaninium maleate (1.83mJ) and L-phenylalaninium nitrate (1.76mJ). Moreover, the crystal has the advantage of combining thermal and mechanical robustness with high nonlinear behaviour required for nonlinear optical device fabrications. A comparison of output power of amino acid derivative crystals with that LMN crystal is listed in Table 5.6. LMN crystal is found to possess more SHG efficiency than other amino acid derivative crystals mentioned in the Table 3.

4. Conclusion

L-methioninium nitrate single crystal was successfully grown by slow evaporation technique at room temperature. Single crystal XRD study reveals that the LMN crystal belongs to monoclinic structure and non-centrosymmetric space group $P2_1$. The optical absorption spectral analysis reveals that the crystal is transparent in the entire UV-VIS-NIR region with the lower cut-off wavelength as 325 nm. Using Tauc’s plot, the band gap of the LMN crystal was found to be 3.66 eV. The high value of refractive index and low value of reflectance reveal that the grown crystal is more transparent to transmit the light from 325 to 1200 nm. The lower value of dielectric loss at high frequencies will ensure that the grown crystal is free from major defects. The activation energy is determined from the plot of ac conductivity against temperature is to be 0.145 eV and the lower value of activation energy establishes that the crystal contains less number of defects. The fundamental parameters such as plasma energy, Penn gap, Fermi energy and polarizability were calculated and tabulated. Kurtz and Perry powder technique confirms that LMN is one of the promising nonlinear optical materials with appreciable SHG efficiency. The above studies reveal that material is useful for optoelectronic device fabrication and nonlinear optical applications.

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