Study on Structural, Spectral and Optical properties of Barium Nitrate L-Methionine Semiorganic Crystal

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ABSTRACT

L-Methionine Barium Nitrate LM+BN crystal a nonlinear optical material is semiorganic type. It has been grown by slow evaporation solution technique. LM+BN crystal is sufficiently good for SHG. To get high optical perfection it is recrystalized by SEST at elevated temperature (40°C), from supersaturated solution by stirring it for several hours. LM+BN with cubic crystal system is fairly suitable for NLO applications because of its wide optical transparency.

Keywords
Crystal growth, LM+BN, Optical transparency, SEST at 40°C

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Introduction

Recently in optoelectronics technologies second order nonlinearity of Non-linear optical materials have importance. Individually organic and inorganic nonlinear optical materials have their own advantages and disadvantages. The inorganic nonlinear optical crystals are easy to grow into large size using the conventional solution growth technique, generally these crystals have high mechanical strength. But lower nonlinear efficiency compared to their organic counterparts. The organic materials are difficult to grow and have less mechanical strength. In spite of these drawbacks, the organic materials have high nonlinear activity. To grow crystals with high optical nonlinearity and mechanical strength, the organic and inorganic materials are admixtured. These are known as semiorganic crystals. This new class of crystals are important in the fabrication of optoelectronics device. [1]. In recent years, because of the metal-organic complexes incorporated in the semi-organic NLO materials has attracted the researchers. Organic materials like amino acids are useful for optical applications. Designing and fabrication of opto-electronic devices is possible with organic and hybrid semiconducting materials, which are emerged as alternatives to the traditional semiconductors due to their appealing features, these devices show improved nonlinear polarization due to use of donor-acceptor (DA)-type structured organic molecules also known as Dipolar (Zwitterions). A series of amino acid particularly l-arginine, l-threonine, l-asparagine, and l-leucine, l-cystine, ß-alanine based crystals were grown by admixing it with some inorganic salts like [2].

Literature survey reveals the characterization studies of new semiorganic materials of L-Glycine Sodium Nitrate (GSN) [3], further undoped GSN and LiNO3 doped GSN [4], also bis(thiourea) barium nitrate (BTBN) for frequency conversion [5], further L-Valine Lithium Nitrate [6] are reported, but the growth and characterization of L-methionine doped with barium nitrate [LM+BN] have not been studied so far. For the first time the title compound was grown at 40°C and characterized using the following studies to understand the optical transparency property of the material.

Experimental

2.1. Material synthesis and crystal growth

Slow evaporation of a solution, which was prepared by dissolving in double distilled water, L-Methionine [$C_5H_{11}NO_2S$] and Barium Nitrate [$Ba(NO_3)_2$] (Loba Chemie) of analytical grade and stirred continuously for several hours. Further the solution is vacuum filtered by Whatman's filter paper and was evaporated by *SEST* (slow evaporation solution growth technique) at 40ºC temperature in PID controlled temperature bath for more than three weeks. The product was purified by recrystallization process, till well transparent and good quality crystals of LMBN with dimensions of 21 × 20 × 2 mm^3 were produced [**fig.-1**].

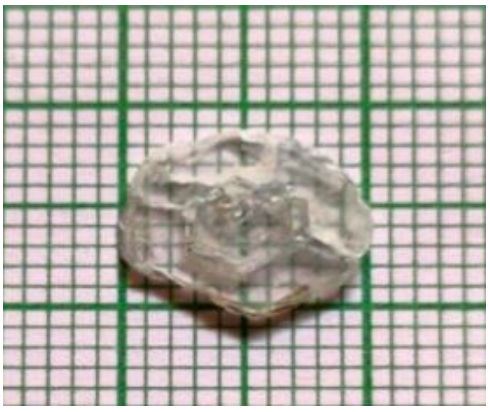

Fig. 1 LM+BN crystal

2.2. Characterizations

X-ray diffractometer (Rigaku UltraX18, 18kW, Germany, CuKα radiation of wavelength 1.5404 Å) used to record the XRD data in the range 2θ = 20° - 70°. The grown crystals were subjected to FTIR Spectroscopy and their optical properties (Linear and Non-Linear) were studied. Optical transmission of grown crystals was measured by UV-Visible spectrometer (JASCO UV/VIS/NIR Spectrophotometer MODEL-670) in the spectral range 190-1400 nm. The grown crystal exhibits very excellent transmission range. The SHG efficiency was measured by using Kurtz and Perry powder method.

Results and Discussion

3.1 Crystal Structure:

PowderX software is used to analyse XRD data of the LM+BN crystal (**fig. 2)**, The grown crystal is belonging to non-centrosymmetric space group P_{21} with cubic structure. The lattice parameters of the LM+BN crystal is a = 8.1246 Å, b = 8.1246 Å, c = 8.1246 Å, α = β = γ = 90° with unit cell volume = **535.38** $Å^3$. The values were compared with the crystallographic data of L-methionine and barium nitrate.
From the result it is observed (**Table No.: 1**) that there is change in structure of the L- methionine. The cell parameters of LM+BN confirms the admixing of barium nitrate into the L- methionine.

Table No. 1 Comparison of lattice parameters of LM+BN with the reported values of L-Methionine and Barium Nitrate.

Parameters	LM + BN	$C_5H_{11}NO_2S$	$Ba(NO_3)_2$
a (Å)	8.12	9.498	8.11
b (Å)	8.12	5.189	8.11
c (Å)	8.12	15.318	8.11
α (°)	90°	90°	90°
β (°)	90°	97.69°	90°
γ (°)	90°	90°	90°
Volume ($Å^3$)	535.38	754.94	533.41
Space group	P_{21}	P_{21}	P_{23}
Crystal system	Cubic	Monoclinic	Cubic

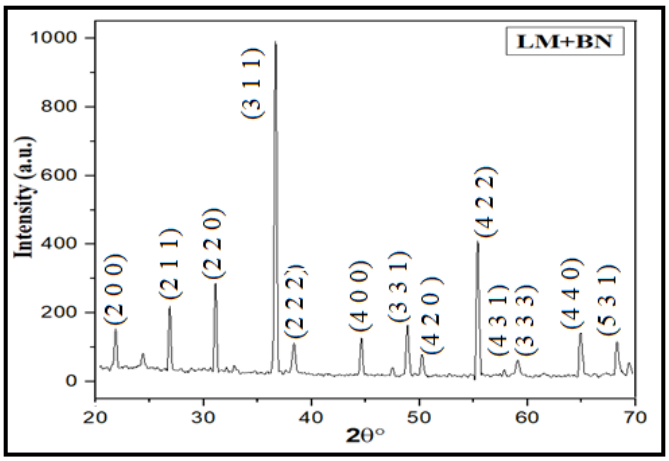

Fig. 2 Powder XRD pattern of LM+BN crystal

3.2 UV-visible-NIR spectroscopy

Figure 3 (a) shows that **t**he UV-Visible transmission spectrum of LM+BN. The UV-Visible spectral analysis shows that in the UV region crystal has lower cut off wavelength around 304 nm. In the entire visible region good transparency of the crystal is suitable for second harmonic generation devices. There is no prominent absorbance in the spectral range from 304 nm to 1200 nm. **Fig.: 3 (b)** shows absorbance spectrum of LM+BN. Optical transmittance is observed for 1.0 mm thin plates of and L-Methionine Barium Nitrate crystals grown at 40°C and is sufficiently good for SHG.

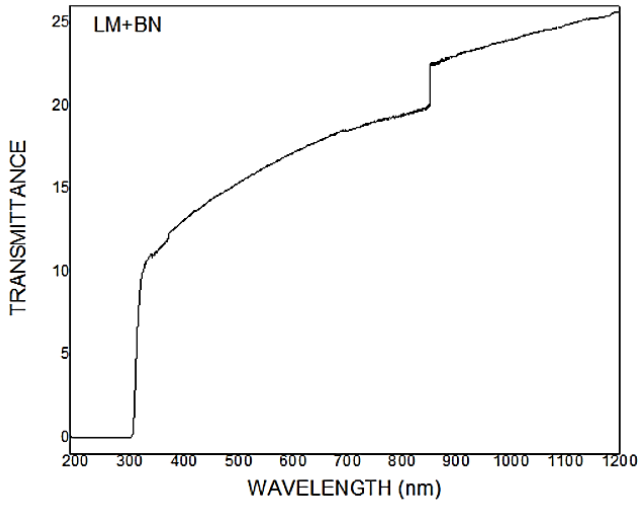

Fig.3(a)

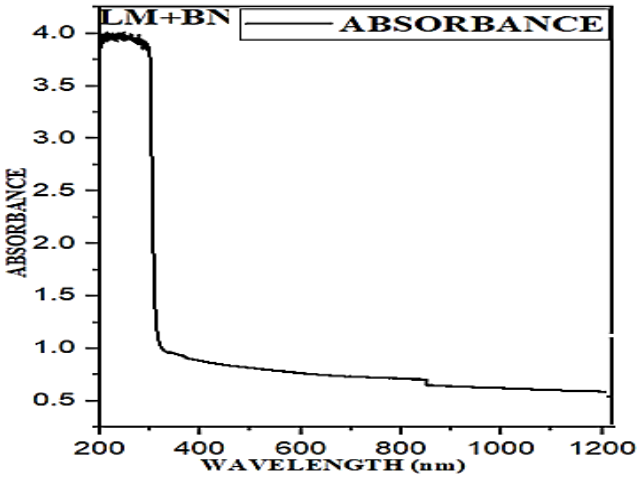

Fig.3(b)

Fig. 3 UV-VIS-NIR (a) transmission (b) absorption spectrum LM+BN crystal.

From the plot of variation of $(\alpha h\upsilon)^2$ vs. photon energy ($h\upsilon$) of LM+BN crystal the value of band gap energy (3.69 eV) of the grown LM+BN crystal was determined by extrapolating the linear portion [7] of the curve to zero absorption (**Fig. 4**).

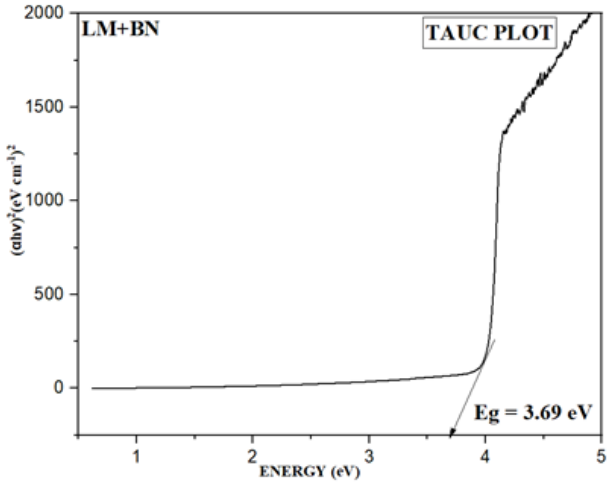

Fig. 4 Variation of $(\alpha h\upsilon)^2$ vs. photon energy ($h\upsilon$) of LM+BN crystal.

3.3 FTIR studies

Functional groups [***Table:*** **2**] that are present in L-Methionine and Barium Nitrate LM+BN crystal is identified from FTIR spectrum (ALPHA-II, Bruker, Japan) in the range between 4000 cm^{-1} to 400 cm^{-1}. **Fig. 5**.

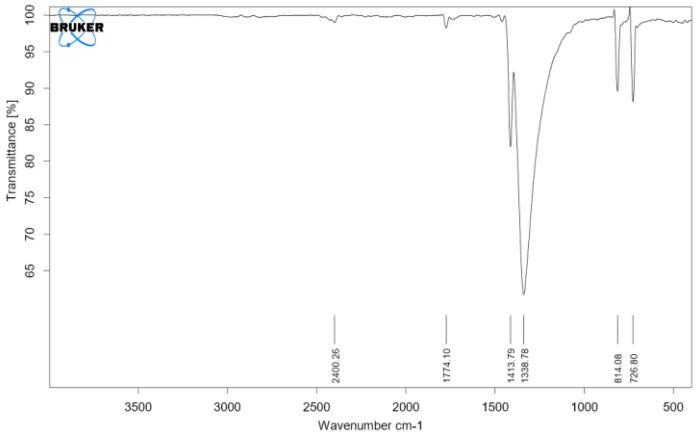

Fig. 5 FTIR spectrum LM+BN crystal.

Table: 2 Vibrational group assignment of LM+CS crystal

Wavenumber (cm^{-1})	Vibrational group
726.80	Ba-N contacts
814.08	N=O stretching
1338.78	C-N stretching
1413.79	S=O stretching
1774.10	C=O, C=C stretch
2400.26	N-H stretching

Presence of amino group confirmed due to N-H bond stretch indicates a weak medium which is somewhat of a narrow band. This weak medium is positioned at the left end of the spectrum, peak at 2400.26 cm^{-1}.

Also presence of dipolar (Zwitterions) L-methionine is confirmed, with carboxylic acid functional group of amino acid (as it has O-H, C=O bonds), The carboxylic acids shows weak and narrow band covering the C=O stretch and peak at 1774.10 cm^{-1}. At the same time, they also show the weak band towards right side of the spectrum at1413.79 cm^{-1} corresponding to S=O stretch. Similarly, the sharp U-shaped absorption peaks at 1338.78 cm^{-1} due to amine group C-N stretch and at 814.08 cm^{-1} is due to N=O stretch and also another at 726.80 cm^{-1} is due to Ba-N contacts [8].

3.4 SHG Measurements:

Analog setup of Kurtz and Perry powder method is used to identify the materials non-centrosymmetric crystal structure. Which consists of a: Quanta Ray Spectra Physics Model Q-switched mode locked Prolab 170 Nd: YAG laser beam of fundamental wavelength 1064 nm with an input power of 1.2 mJ and pulse width of 10 Hz was made to fall on the sample. The green radiation generated confirms the second harmonic signal generated in the crystalline sample. The emission of green light (λ = 532nm) from the LM+BN crystals confirmed their noncentrosymmetric crystal structure. The moderate output was measured with digital storage oscilloscope, The SHG efficiency of L-Methionine Barium Nitrate crystals decreased due to lower polarizing ability of the material.

Conclusions

A semi organic NLO crystal, LM+BN was grown by SEST method at constant 40̊ C temperature. Powder XRD method reveals the cubic crystal structure of the grown crystal. Identification of LM+BN functional groups are confirmed by FTIR analysis. Analyzed UV-VIS-NIR spectrum reveals the wide transparency of the crystal. The transparent nature of the crystal in the visible region makes the material important for NLO applications. The spectrum indicates that the crystal has a broad optical window in the visible region as there is no absorbance in this spectral range, it confirms L-Methionine Barium Nitrate with sufficient moderate efficiency crystals could be the good candidate for SHG applications.

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References

[1] N. Kalaimani , K. Ramya , R. Aarthi , C. Ramachandra Raja, “Synthesis, Growth, Investigation of Structural, Spectral and Optical Properties of Solution Grown Dipotassium Fumarate Dihydrate Crystal”, Int. J. Sci. Res. in Physics and Applied Sciences, Vol.6, Issue.5, pp.21-26, October (2018).

[2] P. Baskaran, et al, “Synthesis, growth and characterization of a nonlinear optical crystal: l-Leucinium perchlorate”, Journal of Taibah University for Science 11, pp. 11–17, (2017).

[3] S. Arockia Avila, (IJSRST), “Growth and Characterization of L-Glycine Sodium Nitrate Single Crystal for Electro-optic Applications”, Volume 3, Issue 11, November-December-2017.

[4] D. Dooslin Mary et al J. Chem. Pharm., “ Solution growth and studies of undoped and lithium nitrate added glycine sodium nitrate single crystals “, Res., 7(1):242-246, 2015.

[5] A. ANBARASI et al, Materials Science-Poland, “Synthesis, growth and characterization of semiorganic nonlinear optical single crystal bis(thiourea) barium nitrate (BTBN) for frequency conversion”, DOI:10.2478/ msp-2019-0039.

[6] K. A. Vijayalakshmi and S. Ramalakshmi, (IJESI), "Growth and Characterization of Semi-Organic NLO Material: L-Valine Lithium Nitrate, vol. 07, no. 06, pp 56-60, , 2018.

[7] A.K. Chawla, D. Kaur, R. Chandra, Opt. Mater., 995–998, 29 (2007).

[8] Tandel et al, Mat. Sci. Res. India, “Influence studies of doping on FTIR Spectra and Thermogravimetric Analysis of Barium Nitrate Crystals”, Vol. 15(1), 83-90 (2018).