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Synthesis, structure, crystal growth and characterization of a novel semiorganic nonlinear optical L-proline lithium bromide monohydrate single crystal

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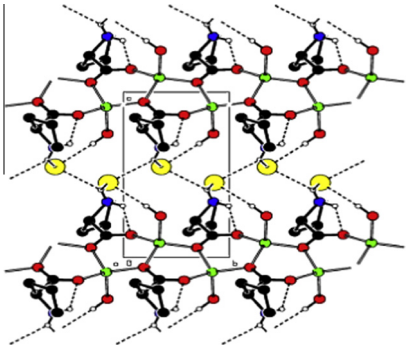
HIGHLIGHTS

- L-Proline lithium bromide monohydrate (LPLBM) crystal is grown.
- LPLBM crystal belongs to monoclinic system with space group $P2_1$.
- Mechanical, thermal, dielectric, linear and nonlinear optical properties are reported.
- Presence of Br^- is confirmed from energy dispersive X-ray analysis.

GRAPHICAL ABSTRACT

L-Proline lithium bromide monohydrate (LPLBM), a semiorganic nonlinear optical material was grown from slow evaporation technique at room temperature. The grown single crystals were characterized by XRD, spectral, thermal, optical, Vickers microhardness, dielectric, SEM–EDAX technique and for second order nonlinear optical properties. The grown LPLBM crystallizes into monoclinic system with the space group of $P2_1$. The modes of vibrations of different molecular groups present in LPLBM were identified by FT–IR and FT–Raman spectral studies. The optical transparency of the grown crystal was investigated by UV–Vis–NIR spectrum. The scanning electron microscope (SEM) study was carried out to determine the surface morphology of the grown crystal. The thermal stability of the grown crystal was investigated using thermogravimetric (TG) and differential scanning calorimetry (DSC). Second harmonic generation (SHG) efficiency was found to be 0.3 times that of urea. Crystal packing of the LPLBM projected along the *bc* plane.



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ABSTRACT

L-Proline lithium bromide monohydrate (LPLBM), a promising semiorganic nonlinear optical material, was synthesized and single crystals of LPLBM were grown from solution by slow evaporation technique. Single crystal X-ray structure solution reveals that the grown crystal belongs to monoclinic system with space group $P2_1$. Presence of various functional groups was identified by FT-IR and FT-Raman spectral analyses. UV–Vis–NIR spectroscopic study shows that the LPLBM crystal possesses 90% of transmittance in the range of 250–1100 nm. Vickers microhardness values, the dielectric constant and dielectric loss of the LPLBM crystal were reported. Elemental analysis by energy dispersive X-ray analysis shows the presence of carbon, nitrogen, oxygen and bromine. The surface morphology of the crystal was investigated using scanning electron microscopic study. The thermal stability of the LPLBM crystal was studied from

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Nonlinear optical material
Thermal characterization
SHG

TGA and DSC analysis. Second harmonic generation efficiency of the LPLBM crystal measured by Kurtz and Perry powder technique using Nd:YAG laser is about 0.3 times that of urea.

Introduction

Nonlinear optical (NLO) crystals find applications in the areas, such as optical modulation, frequency shifting, opto-electronics, signal processing, sensing and fiber optics communications [1]. Organic materials possess large nonlinear optical coefficients and structural diversity or flexibility when compared to that of the inorganic compounds [2]. However, most of the organic NLO crystals are constituted by weak van der Waals and hydrogen bonds with conjugated π electrons [3]. Hence, the organic materials are soft in nature and difficult to grow large size optical quality crystals. They show poor physico-chemical stability and low mechanical strength. Hence there has been considerable interest in the last few decades to synthesis and growth of semiorganic materials compared to organic crystals, since semiorganic crystals exhibit relatively high mechanical and thermal stability [4]. As a result, the search for novel nonlinear optical semiorganic materials exhibiting large nonlinearity and high resistance to laser induced damage [5–7] has become active. In this regard, amino acid family materials have drawn the attention of many researchers, because they possess high nonlinearity, wide transmission range, high conversion efficiency and high laser damage threshold.

Proline, one of the naturally occurring amino acids, is having a unique structure due to the pyrrolidine ring with α-carbon. Proline is abundant in collagen and is exceptional among the amino acids because the amino group is a part of a pyrrolidine ring, thus making it rigid and directional in the biological systems despite of its conformational flexibility [8]. Single crystals of L-proline belongs to noncentrosymmetric crystal structure and its NLO coefficients have been examined by Boomadevi and Dhanasekaran [9]. Proline combines with $CdCl_2$ [10], $ZnCl_2$ [11], $MnCl_2$ [12,13], $SrCl_2$ [14], $HgCl_2$ [15] and KCl_2 [16] to form semiorganic single crystals. Uma Devi et al. [17] have reported synthesis, growth and characterization of L-proline lithium chloride monohydrate. Recently Mohd. Shkir et al. [18] reported synthesis, growth, crystal structure, energy dispersive X-ray analysis (EDAX), UV–Vis–NIR, Differential Scanning Calorimetry (DSC) studies of L-proline lithium bromide monohydrate (LPLBM). We have also simultaneously carried out the work on the synthesis and growth of LPLBM material and we report on the properties that are not investigated by Mohd. Shkir et al. [18].

Experimental procedure

Synthesis

L-Proline lithium bromide monohydrate salt was synthesized by dissolving analar grade lithium bromide (LiBr – LOBA Chemie) and L-proline ($C_5H_9NO_2$ – LOBA Chemie) in stoichiometric ratio in double distilled water at room temperature and continuously stirred well using magnetic stirrer. Slow evaporation of the solvent at room temperature yielded LPLBM salt in about three days. The purity of the synthesized salt was improved by successive recrystallization process. The reaction mechanism of the synthesis of LPLBM material is shown in Scheme 1.

Crystal growth

The solubility of LPLBM was determined at four different temperatures, viz., 38 °C (51.5 g/100 ml), 45 °C (61.1 g/100 ml), 50 °C (68.3 g/100 ml) and 55 °C (76.1 g/100 ml) by following gravimetric analysis [19]. The material exhibits positive coefficient of solubility and the value of solubility, given in parenthesis, increases linearly with temperature. Saturated aquasolution of LPLBM was prepared at room temperature using the recrystallized salt and the solution was filtered using Whatman filter paper. Filtered solution was taken in a beaker, which was tightly closed with thick polythene paper and a few perforations were made on it. Slow evaporation of the solvent at room temperature yielded transparent LPLBM single crystals of $20 \times 4 \times 3\ mm^3$ dimensions in a growth period of three days. Harvested LPLBM single crystals are shown in Fig. 1. As the solubility of the LPLBM material is sufficiently high slow evaporation of the solvent yields relatively larger size crystals in a growth period of three days. Further, it is also evident from the solubility data that controlled slow evaporation of the solvent shall lead to the growth of transparent bulk crystals.

Results and discussion

Single crystal X-ray diffraction study

The crystal structure of LPLBM was determined from single crystal X-ray diffraction analysis. The X-ray intensity data for the title salt was measured on an Enraf Nonius CAD4-F diffractometer with graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Since the LPLBM is isomorphous with its chloride analogue [17], it was refined with the co-ordinates of the chloride analogue after removing chloride anion and H atoms using SHELXL-97 [20]. The position of the bromide anion was located from a difference Fourier map and refined anisotropically. The H atoms bound to C atoms were placed in geometrically idealized positions (C—H = 0.97–0.98 Å) with $U_{iso}(H) = 1.2U_{eq}(C)$ and constrained to ride on their parent atoms. The H atoms of amino group and water molecule were located from a difference Fourier map and refined using DFIX option with N—H = 0.85(2) Å, water O—H = 0.95(2) Å and water H...H distance restrained to 1.55(2) Å. The details of data collection and refinement statistics are presented in Table 1. CCDC 1011575 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. As shown in the ORTEP diagram (Fig. 2), the asymmetric unit contains a proline molecule, one Li cation, one Br^- anion and a water molecule. The Li cation has a distorted tetrahedral geometry and surrounded by a water molecule and three carboxylate oxygen atoms of the amino acid molecule as observed in chloride analogue of the title compound and in *catena*-Poly[[[aqua(glycine-κO)lithium]-μ-glycine-κ^2O:O]bromide] [21]. Selected intermolecular bond lengths and angles are given in Table 2. The conformation of the pyrrolidine ring of the proline residue can be described by five endo-cyclic torsion angles χ1 (N1—C2—C5—C4) = 23.2(7)°, χ2 (C2—C5—C4—C3) = −37.5(7)°, χ3 (C5—C4—C3—N1) = 36.4(9)°, χ4 (C4—C3—N1—C2) = −22.3(10)° and χ5 (C3—N1—C2—C5) = −0.8(8)°. The pyrrolidine ring adopts envelope conformation on atom C4 with a pseudo-rotation angle $\Delta = 268.9°$ and a maximum torsion angle $\varphi_m = 38.8°$ [22]. The hydrogen-bonding parameters are listed in Table 3. As shown in Fig. 3, the carboxylate group of proline residue acts as a bridging ligand connecting neighbouring Li ions to an infinite chain parallel to the *b* axis. The amino group of the proline is involved in an