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Structural, vibrational and thermal characterization of phase transformation in L-histidinium bromide monohydrate single crystals

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HIGHLIGHTS

- -histidinium bromide single crystal was grown by slow evaporation technique.
- X-ray diffraction characterize the high-temperature phase transformation.
- The structural phase transformation occur due to loss of water of crystallization.
- The LHBr thermal expansion coefficients exhibit an anisotropic behavior.

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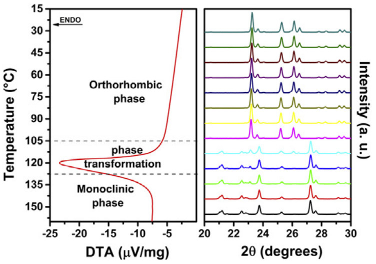
GRAPHICAL ABSTRACT



ABSTRACT

L-Histidinium bromide monohydrate (LHBr) single crystal is a nonlinear optical material. In this work the high temperature phase transformation and the thermal stability of single crystals of LHBr was investigated by X-ray diffraction, thermogravimetric analysis, differential thermal analysis, differential scanning calorimetry and Raman spectroscopy. The results showed the LHBr phase transformation of orthorhombic ($P2_12_12_1$) to monoclinic system ($P\ 1\ 2\ 1$) at 120 °C, with the lattice parameters $a = 12.162(1)$ Å, $b = 16.821(2)$ Å, $c = 19.477(2)$ Å and $\beta = 108.56(2)°$. These techniques are complementary and confirm the structural phase transformation due to loss water of crystallization.

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1. Introduction

Non-linear optical materials (NLO) have been the subject of intense research in the last few years. Semiorganic materials, which have features of both organic and inorganic materials, have been given much importance because of their applications, like parametric oscillators, wave guides, frequency conversion devices and second harmonic generation [1].

The first compound of L-histidinium bromide (LHBr) was obtained and characterized by Rajendran et al. [2] followed by Ittyachan and Sagayaraj [3]. Ittyachan et al. [4] reported the morphology, thermal properties, microhardness studies and microstructural imperfections of LHBr. Ramajothi and Dhanuskodi [5] have grown and characterized L-histidinium bromide crystals by

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various methods. Ahmed et al. [6] redetermined its structure by theoretically studying and investigating its geometric parameters, vibrational spectra and hyperpolarizability. Sajan et al. [7] also investigated theoretically vibrational spectra and NLO properties of LHBr. Joema et al. [8] reported growth and characterization of crystals of L-histidine bromide doped by urea. The results obtained show that doping leads to significant improvement in thermal properties, and the doped crystals are more thermally stable than pure crystals. In the literature, there is no structural analysis of phase transformation of L-histidinium bromide monohydrate crystal.

The aim of this work is to analyze the phase transformation behavior and the thermal stability of LHBr crystal at high temperatures using X-ray diffraction, thermal analysis and Raman spectroscopy.

2. Experimental

Large single crystals of L-histidinium bromide monohydrate were grown by slow evaporation method from aqueous solution with equimolar proportion of L-histidine (Sigma–Aldrich) and hydrobromic acid (Fluka). The synthesized compound was dissolved in deionized water using a magnetic stirrer, filtered to remove the suspended impurities in the solution and purified by repeated recrystallization process in water.

In order to characterize the LHBr at high temperatures, X-ray diffraction (XRD) measurements were carried out with an Empyrean powder diffractometer (Cu Kα radiation) operating at 40 kV/40 mA with an Anton–Paar TTK450 temperature chamber attached. The sample was heated between 30 and 130 °C, and the patterns were obtained in the 2θ interval ranging from 10 to 41° in steps of 0.02° with counting time of 2 s. The X-ray data of crystal were analyzed by Rietveld refinement using the GSAS program [9].

Thermogravimetry (TG) and differential thermal analysis (DTA) were performed in Shimadzu DTG-60 equipment. The measurements were performed between 0 and 450 °C at a rate of 10 °C/min, under nitrogen atmosphere. Differential scanning calorimetry (DSC) measurements of the sample were performed in a DSC 60 (Shimadzu) under constant heating rate of 5 °C/min, in the range of 0–450 °C under a nitrogen atmosphere.

Raman spectra were acquired using a Trivista 557 Princeton triple spectrometer operating in the subtractive configuration and equipped with a thermoelectric cooled charge coupled device (CCD) detector system. A helium-neon ion laser operating at 632.8 nm was used as an excitation source. The slits were set for a spectral resolution of 2 cm^{-1}. High temperatures were performed using a resistive furnace. A digital temperature controller with 0.1 °C stability monitored the temperature in the 30–130 °C range.

3. Results and discussion

3.1. Thermal analysis

The results of TG, DTA and DSC measurements are shown in Fig. 1. According to the TG curve, there is a weight loss between 100 and 200 °C that can be associated with the lattice water loss that was attributed to the first decomposition stage. The total weight loss of this stage corresponds to 7%. This is accompanied by major weight losses at 234.5 and 304.5 °C. The total weight loss of these stages between 200 and 240 °C corresponds to 35%. Hence, it is assigned to the decomposition stage of LHBr crystal. These results are compatible with those of Ittyachan et al. [4].

The DTA analysis showed sharp endothermic peaks at 120.8, 234.5 and 304.5 °C and all of these coincide with the decompositions shown in TG trace.

According to the DSC curve, there are sharp endothermic peaks at 119.1 °C and 233.2 °C, and an exothermic peak at 132.9 °C. These endothermic peaks are in good agreement with the peaks on the DTA trace. The exothermic peak on the DSC trace at 132.9 °C is attributed to crystalline transformation. The XRD measurements present some modifications in X-ray powder diffraction between 100 and 130 °C and DTA/DSC present modifications around that the same temperature range. Motivated by the results of thermal analysis, we performed X-ray diffraction and Raman spectroscopy as a function of temperature to characterize this phase transformation.

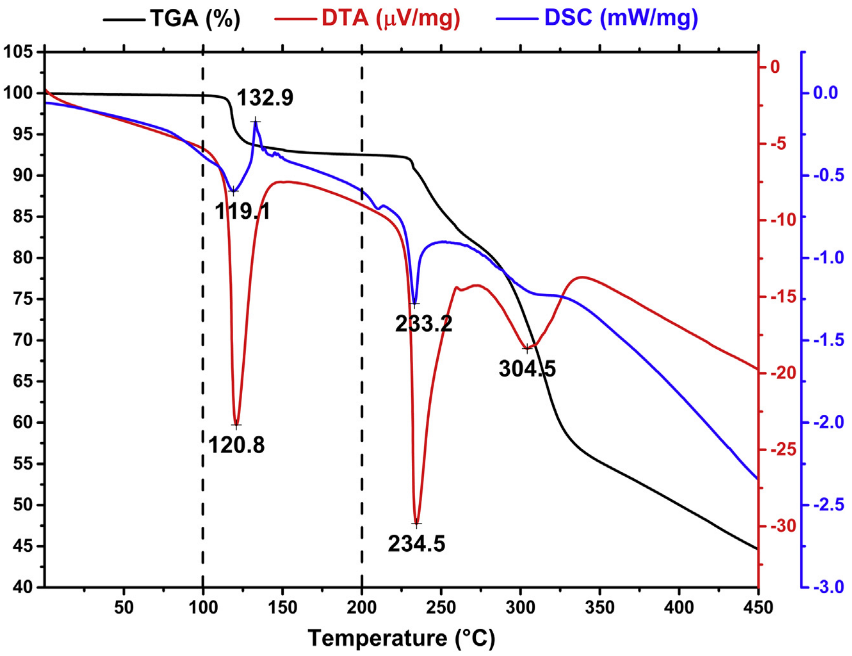

Fig. 1. TGA, DTA and DSC of the LHBr up to 450 °C.

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