Effect of pH on the morphology, mechanical and optical properties of L-arginine monohydrobromide monohydrate (LAHBr) single crystals

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Abstract. L-arginine monohydrobromide monohydrate (LAHBr) single crystals were grown from two molar mixtures of L-arginine and HBr acid in 1 : 2 and 1 : 3 ratios. The solution pH of the above molar ratios was measured to be 7.2 and 1.8, respectively. This drastic change in pH has modified the morphology of LAHBr single crystal and influenced the mechanical stability, optical transparency, refractive index, birefringence and laser damage threshold. The decrease in pH from 7.2 to 1.8 has enhanced the optical transparency and laser damage threshold of LAHBr crystal.

Keywords. pH effect; growth from solutions; crystal morphology; X-ray diffraction; nonlinear optical materials; mechanical stability.

1. Introduction

A crystal can have striking device applications if the physical properties of it are reliable and if it is chemically, mechanically and environmentally stable. The physical properties of the crystals depend upon the nature of molecules involved and the interactions between the molecules. Even if a crystal has good physical properties, poor crystal quality can certainly limit its applications in devices. Hence, the reliability of the physical properties of a crystal depends upon the quality of the crystal. Both the real and artificial crystals have variety of defects and thus every crystal grower has necessarily to optimize the conditions to minimize the defects and try to grow good quality crystals. There are many ways to minimize the crystal defects during growth; it starts from proper solution saturation and includes the following, *viz.*, minimizing the thermodynamical fluctuations, selecting the solvent,[1] changing the pH of the saturated solution,[2] introducing metal dopants that restricts the inclusions of impurities entering into the crystal lattice from solution,[3] annealing the crystals after growth[4] and using different growth methods[5] for the growth of a crystal.

With this in view, L-arginine monohydrobromide monohydrate (LAHBr) single crystals are grown from two different molar ratios (1 : 2 and 1 : 3) of L-arginine and HBr acid in order to analyse the growth morphology and changes in physical properties of the crystal. The crystal structure of LAHBr was reported[6] and various physical properties were studied elsewhere.[7–12] In the present work, LAHBr was formed from solutions with 1 : 2 and 1 : 3 molar ratios. The unit cell parameters were confirmed by single-crystal X-ray diffraction studies. The two crystals grown from 1 : 2 and 1 : 3 solutions were studied for their differences in crystal morphology, mechanical stability, optical transparency, refractive index, birefringence and laser damage threshold. Increase in HBr acid concentration in 1 : 3 molar ratio has decreased the solution pH to 1.8 and enhanced the optical quality of LAHBr crystal when compared to that of the crystal grown from solution with pH 7.2 containing L-arginine and HBr in 1 : 2 molar ratio. Hence, in this work, the effect of pH in enhancing the optical property of LAHBr single crystal is discussed.

2. Growth

L-arginine and HBr acid were taken in different molar ratios (1 : 2 and 1 : 3) and dissolved in water (solvent). The pH of the solution measured upon the saturation level was 7.2 for 1 : 2 molar ratio (LAHBr1) and 1.8 for 1 : 3 molar ratio (LAHBr2). The saturated solution was then allowed for slow evaporation at room temperature, which created spontaneous nucleation and growth of LAHBr single crystals. The grown crystals are shown in figure 1a and 1b, and their dimensions are $47 \times 42 \times 8$ mm^3 (LAHBr1) and $23 \times 7 \times 6$ mm^3 (LAHBr2). Growth period of LAHBr1 was 60 days and that of LAHBr2 was 45 days.

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3. Results and discussion

3.1 *X-ray diffraction studies*

The unit cell parameters of the crystals were determined by single-crystal X-ray diffraction studies and are given in table 1. The unit cell parameters of LAHBr1 and LAHBr2 are in agreement with the reported unit cell parameters of LAHBr single crystal grown from the solution containing 1 : 1 molar ratio of L-arginine and HBr.[9] The obtained unit cell parameters of both the crystals confirm that the grown crystals are LAHBr.

3.2 *Crystal growth habit*

The morphology of LAHBr1 crystal grown (figure 1a) from solution with pH 7.2 is effectively modified from the crystal grown from solution with pH 1.8. The morphology of LAHBr1 crystal grown from solution pH 7.2 matches with the reported morphology.[10] However, LAHBr2 crystal grown from solution with pH 1.8 is

Figure 1. (**a**) LAHBr1 and (**b**) LAHBr2 single crystals.

different with restricted growth along the '*c*'-axis. Due to this restricted growth, the (110), (–110), (011) and (0–11) faces were nearly equal and establishes a pyramidal shape at one end of the crystal and the length of two faces at the other end is reduced (figure 1b). Thus, the influence on the growth morphology is due to the drastic change in pH of the solution. However, no additional crystallographic faces have appeared due to change in pH. The Br⁻ ion interaction with solvent and LAHBr molecules are different along different directions of the growing crystal.[13] Hence, the growth rate along different directions is influenced by the increase in Br⁻ when HBr acid concentration increases in the solution prepared from 1 : 3 molar ratio (pH 1.8).

3.3 *Mechanical stability and optical studies*

Figure 2 shows the microhardness of the LAHBr1 and LAHBr2 crystals as a function of applied load along the ⟨010⟩ direction. For both the crystals, the Vickers microhardness value (H_v) increases with increasing load and above 100 g, cracks were started to develop around the indentation. It is observed from figure 2 that LAHBr1 is approximately 2 times harder than that of LAHBr2 for all loads. And the optical transmittance (along the ⟨010⟩
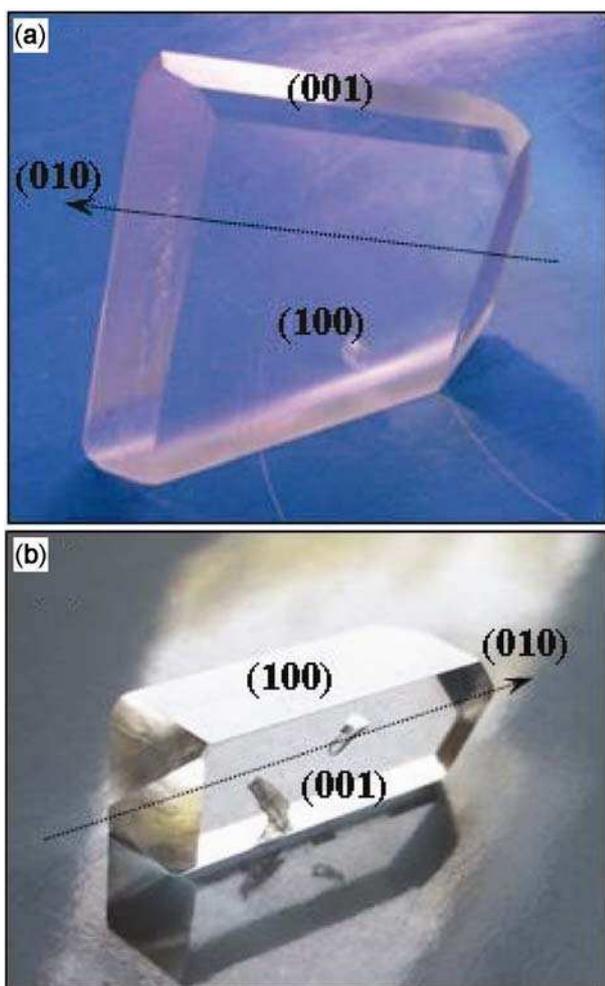
Table 1. Unit cell parameters of LAHBr single crystals.

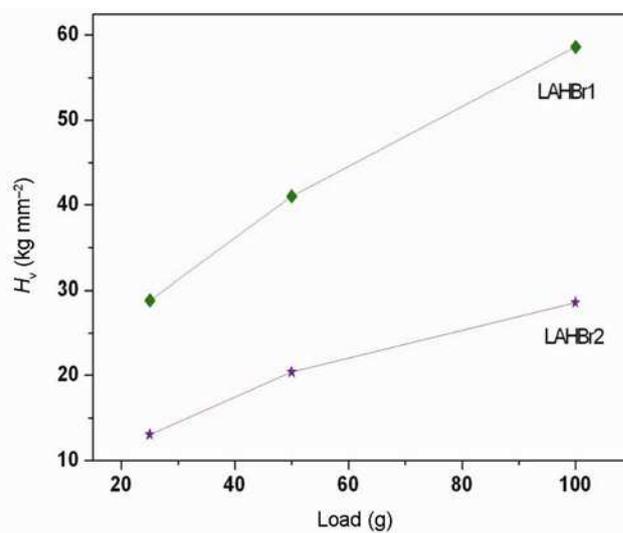| Cell parameters	LAHBr[9]	LAHBr1	LAHBr2
a (Å)	11.26	11.212(2)	11.189(5)
b (Å)	8.65	8.625(1)	8.602(3)
c (Å)	11.25	11.236(4)	11.206(3)
β (deg)	91.5	91.65(2)	91.97(2)

Figure 2. Microhardness of LAHBr single crystals with load.
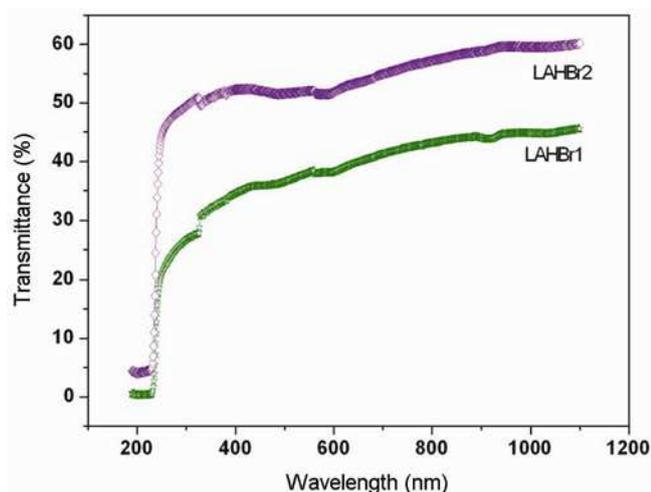
Figure 3. Optical transmittance of LAHBr single crystals.

Table 2. Refractive index and birefringence of LAHBr single crystals.

Properties	LAHBr1	LAHBr2
Refractive index n_y	1.6447	1.6128
Birefringence	0.00536	0.00551

direction) is low for LAHBr1 crystal when compared to that of LAHBr2 (figure 3). Crystals of 1 mm thickness were used for the optical study. The maximum difference in transmittance between the crystals is nearly 15%. However, both the crystals have same lower cutoff at 231 nm. On the other hand, the measured refractive index n_y of LAHBr1 is higher than that of LAHBr2 crystal (table 2). Further, the measured birefringence Δn does not differ much between LAHBr1 and LAHBr2 crystals (table 2).

The reason for the above three results may be attributed to the strong interaction of hydrogen bonds. The changes in solution pH affect the adsorption of LAHBr molecules at the LAHBr crystal sites (section 3.2). Hence, it affects the interaction and bonding of each LAHBr molecule that adsorb on the LAHBr crystal sites inside the solution. These changes along the ⟨010⟩ direction might be the reason for decreased H_v and refractive index and increased optical transmittance of LAHBr2 single crystal. The changes in physical properties of crystals due to the effect of pH were already reported in literatures.[2,13]

3.4 *Laser damage threshold (LDT) studies*

The laser beam absorbed by the crystals damages the crystal surface depending upon the laser wavelength, laser intensity, pulse width and the plane of the crystal being irradiated. Nd:YAG laser of wavelength 1064 nm with pulse width 10 ns was used for the determination of 'multiple-shot laser damage threshold' of LAHBr1 and LAHBr2 single crystals. The laser beam diameter was 1 mm and the focal length (f) of the convex lens used to focus the laser beam was 300 mm. In the present work, 20 laser shots (pulses) were required to create the multiple-shot damage. The laser beam spot on the sample (d') calculated was 203 μm using the formula

$$d' = \frac{1.27\lambda f}{d},\tag{1}$$

where d is the thickness of the sample and λ the wavelength of laser source. The laser damage threshold was calculated using the formula[14]

$$P = \frac{E}{\tau\pi r'^2},\tag{2}$$

where P is the power density, E the energy (mJ), τ the pulse width (ns) and r' the radius of the laser beam spot (μm). The calculated laser damage thresholds for LAHBr1 and LAHBr2 are 18.6 and 23.25 GW cm^{-2}, respectively. The damage threshold is high for LAHBr2 single crystal when compared to that of LAHBr1 single crystal. This can be explained on the basis of electron–hole pair trapping process.[15] The electron–hole pair can be easily produced by the intense laser during multi-photon absorption. The scattering centres and lattice defects trap the produced electron–hole pairs that cause the crystal to damage faster.[16,17] The LAHBr1 single crystal must have more number of defects and thus can absorb electron–hole pairs and decreases the damage threshold of the crystal when compared to that of LAHBr2 single crystal. It is noteworthy here that the LDT of LAHBr1 and LAHBr2 single crystals is high compared to that of standard KDP crystal which is 14 GW cm^{-2} under same laser parametric conditions.[18] The measured laser damage thresholds of LAHBr1 and LAHBr2 single crystals are higher than that of deuterated L-arginine phosphate monohydrate (9–13 GW cm^{-2}) and L-arginine phosphate monohydrate (10–13 GW cm^{-2}).[19]

4. Conclusions

LAHBr single crystals were grown from aqua solution containing L-arginine and HBr acid in different molar ratios of 1:2 and 1:3. The drastic change in the pH of solution influenced the morphology of LAHBr crystals obtained in this work. In addition, LAHBr1 single crystal has high mechanical stability and refractive index, but low optical transmittance. The low laser damage threshold of LAHBr1 single crystal reveals that the crystal has more number of defects. But, LAHBr2 single crystal has high optical transmittance and exhibits high laser damage threshold.

Acknowledgements

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