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Crystal growth and characterization of L-tyrosine bromide (LTB) nonlinear optical single crystals

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ABSTRACT

Single crystals of L-tyrosine bromide (LTB) have been grown by slow evaporation method from different solutions prepared with different normality of the solvent at ambient temperature. It has been observed that the growth rate along the crystallographic axes is considerably changed for different normality of solvent and remarkable morphological changes have been observed for the grown crystals. X-ray diffraction analysis, NMR and FTIR spectral analyses, thermo gravimetric (TG), and differential thermal analysis (DTA) have been employed to characterize the as-grown crystal. The UV cutoff (LTB) is below 300 nm and has a wide transparency window, which is suitable for second harmonic generation of laser in the blue region. Nonlinear optical characteristics of LTB have been studied using Q-switched Nd:YAG laser (λ=1064 nm). The second harmonic generation conversion efficiency of LTB is 1.2 times that of KDP. Hardness of the LTB crystal has also been determined. The laser damage threshold energy density has been found to be 625 MW/cm^2.

1. Introduction

Second order nonlinear optical crystals (NLO) are widely used to convert the frequency of coherent laser sources. Applications such as laser-based imaging, communication, remote sensing and counter-measure systems require improved nonlinear optical materials to accomplish such conversions. A strong need continues to exist for low cost, more efficient, higher average power materials for optical parametric amplifier operation and second harmonic generation (SHG) through the blue near-UV spectral region [1,2]. Ionic salt materials offer an important and extremely flexible approach for the development of new materials applicable over a very broad range of frequencies. For visible to near-UV wavelengths (0.25–1.4 μm), simple solution grown organic–inorganic complexes ('semi-organics') have been developed. In semi-organic crystals, high optical nonlinearity of a purely organic ion is combined with the favourable mechanical and thermal properties of an inorganic counter ion [3,4]. The growth of semi-organic DLAP crystal including the inhibition of microbes in the growth solution by adding H_2O_2 was reported [5]. Same problem has been solved by growing LAP crystal using controlled evaporation technique in the presence of sodium azide, and also reported no significant change in optical properties [6]. Mukerji and Kar [7] found new semi-organic crystal: L-arginine hydrobromide (LAHBr) and new analogs of LAP such as L-Arg · HCOOH, Arg · 2H_2PO_4, Arg · 2HCl and Arg · 2HBr · H_2O crystals have been completely characterized using infrared spectroscopy and X-ray diffraction analyses. However, no effort has been taken to grow these crystals in large size for their device application [8]. Rajan Babu et al. [9] reported the growth and optical properties of a new semi-organic L-alanine tetrafluroborate (L-ALFB) crystal by slow evaporation technique. Haja Hameed et al. [10] examined the growth of sulphate mixed L-arginine phosphate (LASP) crystals and Cu and Mg doped LAP crystals. L-histidinium bromide single crystals have been grown and identified as a suitable crystal for NLO application by several authors [11–13]. In these series, Srinivasan [14] first reported the crystal structure of L-tyrosine hydrogen bromide and Narayana Moolya and Dharmaprakash [15] reported the growth and optical property studies of L-tyrosine hydrobromide single crystals. In the present investigation, attempt has been made to grow single crystals of L-tyrosine bromide (LTB) by slow evaporation method from the solutions of different normality of the solvent, focusing on the growth conditions needed for growing relatively large size crystals of LTB and to study the structural, optical, mechanical and thermal properties of these crystals.

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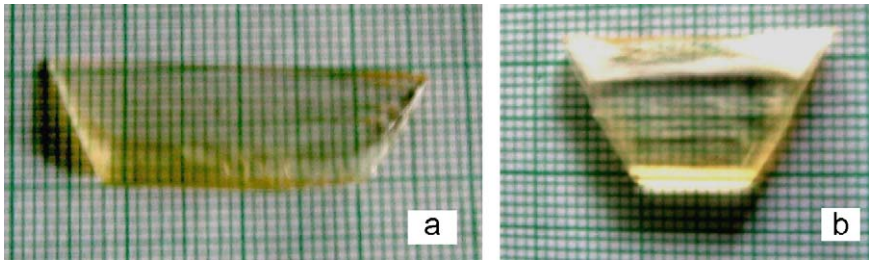

Fig. 1. L-tyrosine bromide single crystals grown from (a) 3 N and (b) 1 N solvents.

2. Experiment

2.1. Material synthesis

The analytical grade L-tyrosine and hydrobromic acid (HBr) have been taken as starting materials to synthesize L-tyrosine bromide (LTB). The calculated amount of hydrobromic acid has been dissolved first in the deionized water of resistivity 18.2 MΩ cm and then L-tyrosine has been added to the solution slowly with stirring. L-tyrosine bromide (LTB) salt has been synthesized according to the following reaction:

$$C_9H_{11}NO_3 + HBr \rightarrow C_9H_{12}NO_3Br$$

The prepared solution has been allowed to dry at room temperature. The purity of the synthesized salt has been improved by successive recrystallization process. To avoid decomposition, enough care is taken while heating the solution and maintained below a temperature of 75 °C. The material thus prepared has been analyzed by physical and chemical methods and then confirmed to be LTB. This compound has been used to grow bulk crystals.

2.2. Normality based growth of LTB crystals

Bulk growth of LTB single crystal has been carried out in aqueous solution by slow evaporation technique for different normality of solvent, using a constant temperature bath controlled to an accuracy of ±0.01 °C. The seed obtained from slow evaporation method has been used for the bulk growth. Fig. 1 shows the as-grown crystals of LTB with optimized solution for different normality (3 and 1 N) of solvent. It has been observed that unlike LAP solution, the microbes have not been found during the growth of LTB, which may be due to the presence of hydrobromic acid (HBr), which acts destructively on the growth of microbes. Bulk crystals of dimensions $30 \times 10 \times 7$ and $25 \times 16 \times 8$ mm^3 have been harvested after a month from the solution prepared from 3 and 1 N solvents, respectively. LTB crystals have grown in the shape of prism elongated in 'c' direction. LTB is stable at ambient temperature and is non-hydroscopic. The various planes of the as-grown LTB crystals (3 and 1 N) have been identified and are shown in Fig. 2a and b, respectively. The planes (0 0 1), (0 0 −1), (0 −1 1), (0 −1 −1), (1 1 0) and (−1 1 0) have been observed in the crystal grown from 3 N solvent and an additional (0 1 −1) plane has been observed in the crystal grown from 1 N solvent. It has been observed that the normality of the solvent influenced on the habit modification of the grown crystals. It has been observed that the growth rates along the three crystallographic axes are different for different normality of the solvent. Growth rates along the crystallographic axes have been determined by using Digital Vernier Calliper and are presented in Table 1.

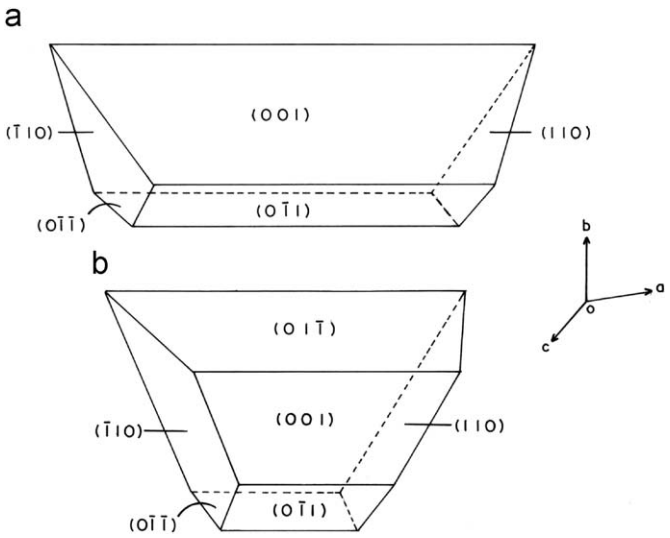

Fig. 2. Morphology of LTB crystals grown from (a) 3 N and (b) 1 N solvents.

Table 1
Growth rates of LTB crystals along the three crystallographic axes.

Solvent normality	Growth rates along a, b and c axes mm/day		
	a	b	c
1 N	0.83	0.53	0.26
3 N	1.0	0.33	0.23

2.3. Characterization

Single crystal X-ray diffraction analysis has been carried out using an ENRAF CAD-4 diffractometer with MoK$_\alpha$ (λ=0.7107 Å) radiation to identify the crystal system, to estimate the lattice parameter values and to find the morphology of the grown crystals. Powder X-ray diffraction analysis has also been carried out using a Rich Seifert diffractometer with CuK$_\alpha$ (λ=1.5418 Å) radiation to verify the correctness of lattice parameter values. The C^{13} NMR spectrum of LTB crystal has been recorded using JEOL GSX 400 instrument at 30 °C. The FTIR spectrum of LTB crystal has been recorded in the range 400–4000 cm^{-1} employing a Perkin–Elmer spectrometer by KBr pellet method in order to study the presence of various functional groups. Linear optical properties of the crystals have been studied using a Shimadzu UV–Visible spectrophotometer. To confirm the nonlinear optical property, the grown crystals have been subjected to Kurtz powder SHG test [16]. Hardness values have been determined on the prominent (0 0 1) plane. The LTB crystal of dimension $7 \times 4 \times 3$ mm^3 has been used for microhardness study. Indentations have