Growth and Characterization of L-Histidine Tetrafluoroborate Single Crystals as a New Laser Damage Resistant Material

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Abstract

L-Histidine tetrafluoroborate single crystals have been grown from the aqueous solution. The profitable pH value to grow large crystals, the relative flow rate to get clear crystals, crystal habit and the orientation of the obtained crystal have been clarified. We have also demonstrated that the LHBF crystal has very high damage threshold which is potentially good for generation of the phase conjugated waves.

1. Introduction

Semi-organic crystals which contain both organic and inorganic molecules in a unit cell have excellent mechanical properties compared to simple organic crystals. A typical example of this kind of nonlinear optical material is L-arginine phosphate monohydrate (LAP) crystal[1-4]. LAP crystal has been known to have an extremely high damage threshold for pulsed lasers. From this point of view, it can be said that LAP crystal is promising for generation of phase conjugated wave using the stimulated Brillouin scattering rather than generation of higher harmonic waves[5].

Recently, L-Histidine tetrafluoroborate (LHBF) has been reported as a new semi-organic nonlinear material to obtain a radiation in ultraviolet region by the higher harmonic generation[6]. It has a monoclinic structure (space group $P2_1$) which is the same as LAP crystal. However, analogizing from the characteristics of LAP crystal, it is expected that LHBF also has a high damage threshold and is suitable for generation of phase conjugated waves.

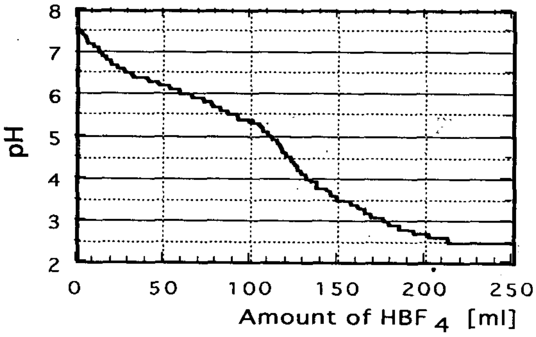

Fig. 1 . The titration curve of dilute (approx. 1%) L-histidine solution by tetrafluoroboric acid solution(0.15%).

In this work we tried to performed the preliminary experiments of growth of

LHBF from aqueous solution, namely the synthesis, the measurement of the solubility, the structure analysis, crystal habit and orientation. The laser damage threshold of the grown crystals was also evaluated.

2. Experimental

2.1. Synthesis

LHBF can be synthesized by reacting L-histidine and tetrafluoroboric acid in water. Since L-histidine is an amino acid and indicates a basic characteristic in water, this reaction is one of neutralization reaction. Fig. 1 shows the results the titration of dilute L-histidine solution by tetrafluoroboric acid solution. From this figure, the pH value of the neutralization point is determined as approximately 4.5.

By changing the pH value of the solution from 2.5 to 6, precipitation or nucleated small crystals (about 1-2 mm) ware obtained by evaporation method at constant temperature (30℃). At pH 6, any precipitation has not been observed. At pH 2.5, very fine powder-like precipitation was obtained. Crystalline nucleations were observed at pH value from 3.8 to 5.3. So the lattice parameters of these obtained crystals were measured by a four-axis x-ray diffractometer. The results were summarized in Table I.

From these results it can be said that the nucleated crystal from the solution of pH 4.5 is most closed-packed, mainly because the *c*- axis is the shortest among the performed conditions. Furthermore, the averaged grain sizes of the obtained crystals at pH 4.5 were somewhat larger than that at pH 5.3 and 3.8, as shown in Table II. Therefore, we performed following growth experiments using the solution at pH 4.5.

Table I. Change of lattice parameter of nucleated crystals as a function of pH value of the mother liquours.

	a (Å)	*b* (Å)	*c* (Å)	*β* (deg.)
pH 6.0	No preciptation			
pH 5.3	5.0334	9.0896	10.2294	93.55
pH 4.5	5.0260	9.0881	10.2035	93.54
pH 3.8	5.0263	9.0902	10.2256	93.50
pH 2.5	Fine powder-like precipitation			

Table II. Averaged crystal sizes and their standard deviation of nucleated crystal from the mother liquor of different pH values.

	Axis	Ave. size (mm)	SD (mm)
pH 5.2 pH 3.8	*a*	1.89	0.35
	b	1.29	0.23
	c	0.82	0.26
pH 4.3	*a*	2.77	0.49
	b	1.91	0.34
	c	1.05	0.38

2.2. Growth of LHBF

Crystal growth experiments were performed by conventional temperature falling method. A saturated solution at 30℃ was prepared as a mother liquor.

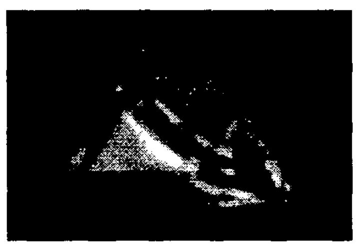

Fig. 2 . A photograph of typical LHBF crystal grown in the present experiment.

The amount of the mother liquor was 1 ℓ . The prepared solutions were filtered through a 0.45 μm membrane before starting crystal growth. From our solubility measurement, it was found that the temperature gradient of the solubility was 0.003 g/°C· mℓ.

A typical size of the grown crystals is 16 mm X 25 mm X 6 mm. The photograph of typical crystal obtained by this experiment is show in Fig. 2. Generally, in solution growth, the stirring speed of the solution is very important to obtain the clear crystals without the liquid inclusion. In the present experiment, it was found that the relative flow rate of more than 70 cm/sec is necessary to obtain the clear LHBF crystals.

The facets and edges of the grown crystals were very clear, so orientation of the crystal was not too difficult. For this purpose, we used the Laue method and a θ-2θ x-ray diffractometer. The results were summarized in Fig. 3. In Fig. 3, the crystallographic orientations as well as some optically important axes which have been determined by using crossed polarizers, He-Ne laser, and the second harmonic generation of Nd:YAG lase, were denoted.

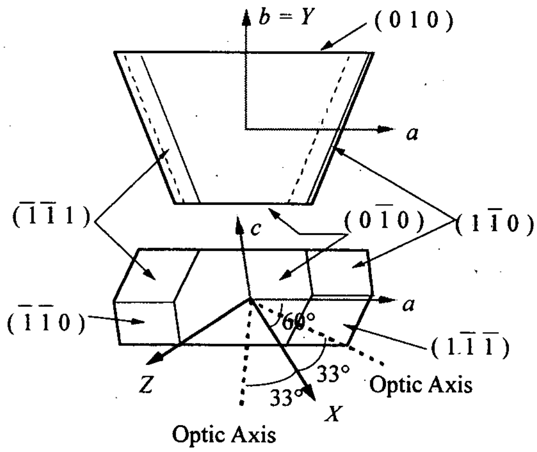

Fig. 3. The crystal orientation, Miller indices and dielectric axes of LHBF crystal.

2.3. Damage Threshold of LHBF

We used a linearly polarized Q-switched Nd:YAG laser (1.064 μm) operating in a transverse single mode. The pulse width was 7 ns and the energy of a pluse was 10 mJ/pulse. Samples were prepared by carefully cleaving the crystals in the *a-b* plane. The thickness of the samples was less than 1 mm. The laser beam was focused with a lens of which focal length was 90 mm. By changing the distance between the lens and the sample, the laser intensity through the sample was changed. As a result, no damage has been observed even when the sample was located at the focal point. The estimated intensity at the focal point was approximately 60 GW/cm^2. In Fig. 4, this value has been plotted with the damage threshold of LAP, deuterated LAP (DLAP) crystals and so on which have been reported in Ref. 3.

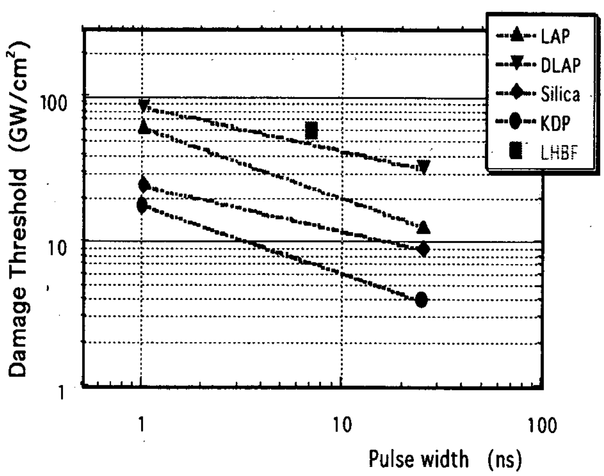

Fig. 4. Laser intensity which can pass through LHBF crysrals without inducing the optical damage. The damage thresholds of LAP, DLAP, fused silica and KDP (potassium dihydrogen phosphate) [3] were also plotted for comparison.

From these results, it can be said that the damage threshold of LHBF crystal is same or higher than that of LAP crystal.

3. Summary and conclusion

We have investigated the growth technique and characterization of LHBF as a highly damage resistant crystal which is potentially useful to generate the phase conjugated waves. The profitable pH value to grow a large crystal, the relative flow rate to get clear crystals, crystal habit and the orientation of the obtained crystal have been clarified. We also have demonstrated that the LHBF crystal has damage threshold as same as or higher than LAP and DLAP crystals which are known to have extremely high damage thresholds and very good materials for generation of the phase conjugated waves.

At this moment, we do not understand why semi-organic crystals have such a high damage threshold. Mechanical properties of these crystals may have some relationship with the damage mechanism. We can conclude that LHBF crystal is very promising for generation of the phase conjugated waves.

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