Available online at www.sciencedirect.com
SCIENCE DIRECT
Materials Letters 59 (2005) 1400–1404
materials letters
www.elsevier.com/locate/matlet

Studies of microhardness anisotropy and Young's modulus of nonlinear optical crystal L-arginine hydrochlorobromo monohydrate

Tanusri Pal, Tanusree Kar*

Department of Materials Science, Indian Association for the Cultivation of Science, Jadavpur, Kolkata 700032, India

Received 29 January 2004; accepted 8 March 2004
Available online 29 January 2005

Abstract

In this communication hardness anisotropy of first order and second order has been studied for a new nonlinear optical crystal L-arginine hydrochlorobromo monohydrate (LAHClBr). We have employed Vickers and Knoop indentation method for the measurement of microhardness and Young's modulus of LAHClBr. The results are also verified by ultrasonic velocity measurement. Both the values of microhardness and Young's modulus reveal that (100) plane is the softest one and (100)<010> is identified as one of the slip system. Overall studies also show that LAHClBr belongs to the soft crystal category.

Keywords: Optical materials; Crystal growth; Hardness; Elastic properties

1. Introduction

Semiorganic nonlinear optical materials are found to possess better mechanical strength compared to organic materials. L-Arginine hydrochlorobromo monohydrate, $C_6H_{14}N_4O_2HClBr$, H_2O abbreviated as LAHClBr is a new semiorganic nonlinear optical material as reported in our earlier publication [1]. LAHClBr possesses high value of damage threshold and hardness compared to other complexes of L-arginine [1–3] so far reported. The high value of hardness of LAHClBr, which is very important as far as fabrication of devices is concerned, inspired us to study the microhardness of LAHClBr in greater details. Microhardness measurement of single crystals using conventional pyramidal indentors is influenced by basic anisotropic properties of the crystals. The cause of underlying hardness anisotropy (first order and second order) is due to interatomic forces that generally vary with crystallographic directions. Hardness anisotropy of first order, which is defined as the variable hardness in different crystallographic directions, could be measured on one crystal face or section by change of orientation of the indentation. Hardness anisotropy of second order is defined as the variable hardness in different faces or sections of the same crystal and is measured by performing hardness measurement on different faces of the same crystal. In this present communication hardness anisotropy of both first and second order has been studied for a new nonlinear optical crystal, L-arginine hydrochlorobromo monohydrate (LAHClBr). Results of these studies have been used to calculate the Young's modulus of different crystallographic planes and to get an idea about the slip systems prevailing in the single crystal of LAHClBr. The values of Young's modulus obtained from hardness measurement are also compared with the values calculated from the ultrasonic velocity data.

2. Experimental

Single crystals of nonlinear optical material LAHClBr were grown by slow evaporation as well by slow cooling methods from its aqueous solution. Detailed studies on synthesis, crystal growth were described elsewhere [1].

* Corresponding author. Tel.: +91 3324734971; Fax: +91 33 24732805.
E-mail address: mstk@mahendra.iacs.res.in (T. Kar).

0167-577X/$ - see front matter © 2005 Elsevier B.V. All rights reserved.
doi:10.1016/j.matlet.2004.03.056

Table 1
Microhardness parameters of LAHClBr crystal

Plane	Meyer's index "n"	Hardness value at 5 gm load H_v (GPa)	H_k (GPa)	Young's modulus E (GPa) From Marshall method	From Ultrasonic measurement
100	1.73428	1.1	0.8004	7.19	7.02
010	1.70898	1.2	0.8455	10.44	9.97
001	1.6172	1.8	1.3491	17.18	16.90

LAHClBr crystal belongs to the monoclinic system with space group $P2_1$. The typical growth habit is shown in Fig. 1. Crystals selected for the microhardness studies were free from cracks and visible inclusions. Thin plates of dimensions $10\times5\times5$ mm^3 and parallel to {100}, {010} and {001}planes were cut from the as-grown crystals with a wet thread and polished by gently rubbing the plates on a felt cloth wetted with ethanol. Second order hardness anisotropy of LAHClBr was determined using an mhp 160 microhardness tester fitted with Vickers diamond pyramidal indenter and attached to a Carl–Zeiss (Jenavert) microscope. The Vickers microhardness (H_v) was measured on the {100}, {010} and {001} faces for applied loads ranging from 5 gm to 50 gm for a dwell time of 10 s in all cases. Eight to ten indentations were made for each load, and the diagonal lengths of the indented impressions were measured using a calibrated micrometer attached to the eyepiece of the microscope. The Vickers microhardness number H_v was calculated using the relation

$$H_v = 1.8544\left(P/d^2\right) \text{ Pascal} \tag{1}$$

where P is the applied load in Newton and d is the average diagonal length in meter.

For the determination of Young's modulus, Knoop indentation was made on the cut plates with a Knoop diamond pyramidal indenter fitted to an mhp 160 microhardness tester attached to a Carl–Zeiss (Jenavert) microscope. Indentations were made with a fixed load for a dwell time of 10 s. Lengths of the long diagonal of the indentation as well as the width were measured with the help of a calibrated micrometer as mentioned earlier.

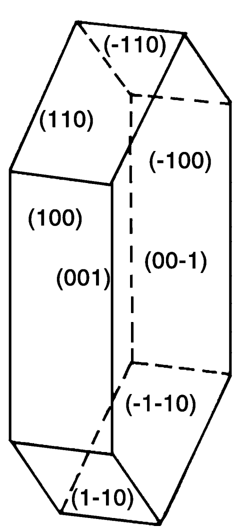

Fig. 1. Predicted morphology of LAHClBr crystal.

Knoop microhardness values were calculated from the formula

$$H_k = 14.299\left(P/d^2\right) \text{ Pascal} \tag{2}$$

where P is the applied load in Newton and d is the length of long diagonal of the Knoop indentation in meter. For calculation of Young's modulus from microhardness data we followed the method of Marshall et al. [4] and used the following formula

$$E = 0.45H_k/(0.1406 - b/a) \tag{3}$$

where H_k is the Knoop microhardness value at a particular load as calculated from Eq. (2), b and a are the shorter Knoop indentation diagonal and the longer Knoop indentation diagonal, respectively. Knoop hardness anisotropy of first order was determined only on the cleavage plane (100) of the LAHClBr crystal. The long diagonal of the indenter parallel to <001> was assumed to be 0°. Indentation was made at 0°, 30°, 45°, 60°, 90°, 120°, 135°, 150° and 180° at a load of 5 gm for a dwell time of 10 s. Knoop microhardness for different orientation was then calculated by using Eq. (2). To check the validity of Eq. (3) for our crystal, we compared the values of Young's modulus with that calculated from ultrasonic velocity data. From the longitudinal velocity v_l and transverse velocity v_t of ultrasonic waves, the elastic moduli of the present crystals were calculated by using [5]

$$v_l = (\lambda + 2\mu)/\rho \tag{4}$$

and

$$v_t = (\mu/\rho) \tag{5}$$

where λ and μ are Lame's elastic constants and ρ is the density of the sample. Finally the Young's modulus (E) is calculated from Lame's constants with the help of the relation [6]

$$E = \mu(3\lambda + 2\mu)/(\lambda + \mu) \qquad [6]$$

Table 1 compares the values of Young's modulus obtained by hardness and ultrasonic velocity measurement.