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Studies on the microstructure and microhardness of L-alaninium oxalate single crystals for optical devices

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L alaninium oxalate, a potential non linear optical material (NLO) has been grown by slow evaporation method at ambient temperature. The basal surfaces are examined using optical microscopy technique to understand growth and defect features which can influence the performance of a crystal for device applications. Three novel dislocation etchants are introduced and used in the present work. Etch pits of various shapes and densities are observed. Dislocation studies suggest that the crystal growth is effected by a 2D growth mechanism. Micro hardness studies are carried out to reveal the suitability of the material for device fabrication.

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1. Introduction

Metallography is dependent upon the time consuming and pain staking identification, by trial and error of effective etchants which reveal a host of information about the microstructures. The microstructural aspects of crystals have deleterious effects on the performance of devices as they affect plasticity and crystal strength, electronic and ionic conductivity and diffusion properties [1].

There are several models of crystal growth and each crystal grows by one of these mechanisms. A complimentary approach of understanding the growth mechanism is to study the features on free and etched surfaces of the crystals. Patterns observed on surfaces like spirals, hillocks, slip pattern…etc yield valuable information on the growth process and perfection in the crystal [2].

Hardness of a material is the measure of the resistance it offers to local deformation. General definition of indentation hardness which is related to the various forms of indenter is the ratio of applied load to the surface area of indentation [3]. In general, it comes from the intrinsic resistance of crystals and the resistance caused by imperfections in the crystals [4].

Organic nonlinear optical (NLO) materials have been actively studied for their use in nonlinear optics and devices [5, 6, and 7]. The superiority of organic NLO materials results from their versatility and possibility of tailoring their properties for particular device applications. Organic NLO materials have high nonlinear figure-of-merit for frequency conversion, high laser damage threshold and fast optical response time as compared with inorganic NLO materials [5, 8]. Crystals of amino acids and their salts are bio organic NLO materials with promising applications in lasers and non-linear optics [9]. L-alaninium oxalate (LAO), which is the charge transfer complex of L-alanine and oxalic acid, is an interesting non linear optical material [10].

The goal of the present work is to understand the growth mechanism and structural defects in the crystal and to estimate microhardness which is important as far as the fabrication of devices is concerned.

2. Experimental

Good optical quality crystals of LAO grown by solvent evaporation technique are used for the present study. The surface features on the as grown crystal surfaces and on the etched surfaces, etched with the dislocation etchants developed for the present study are examined using a Leica Q win Microsystems metallurgical microscope attached to a computer for easy viewing of surface patterns. N-propyl alcohol (60%) is used as the chemical polishing agent.

Microhardness measurement on the [100] surface of the crystal is done for applied loads from 5 g to 100 g with a dwell time of 5seconds using Leitz Miniload Hardness tester.

3. Results and discussion

3.1 Features on free and etched surfaces

The chemical etching studies are carried out on the as grown single crystals of LAO to study the symmetry of the crystal face from the shape of etch pits, and the distribution of structural defects in the grown crystals .

An observed layer structure of the crystal is shown in Fig. 1 (a). Fig. 1 (b) shows the striation pattern observed on the surface, due to the thermal strain that may occur during growth. Secondary nucleation and overgrowth patterns on the growth surface are shown in Fig. 1(c).

According to Buckley [11], overgrowth patterns are formed due to interruption in the continuity of deposition of material which in turn is due to change in growth conditions.

When etched with water bunch pattern are formed as shown in Fig. 1 (d). This is due to the fast dissolution of the surface the shape of which depends on the disorientation of the exposed crystallographic plane. Development of bunches is determined by the directions of the operating etching vectors on crystal surface which are determined from an energy consideration involving the breaking of the lowest number of bonds. When the etch rate is high bunching will develop not only on the surface but also at the dissolution steps generated by dislocations [12].

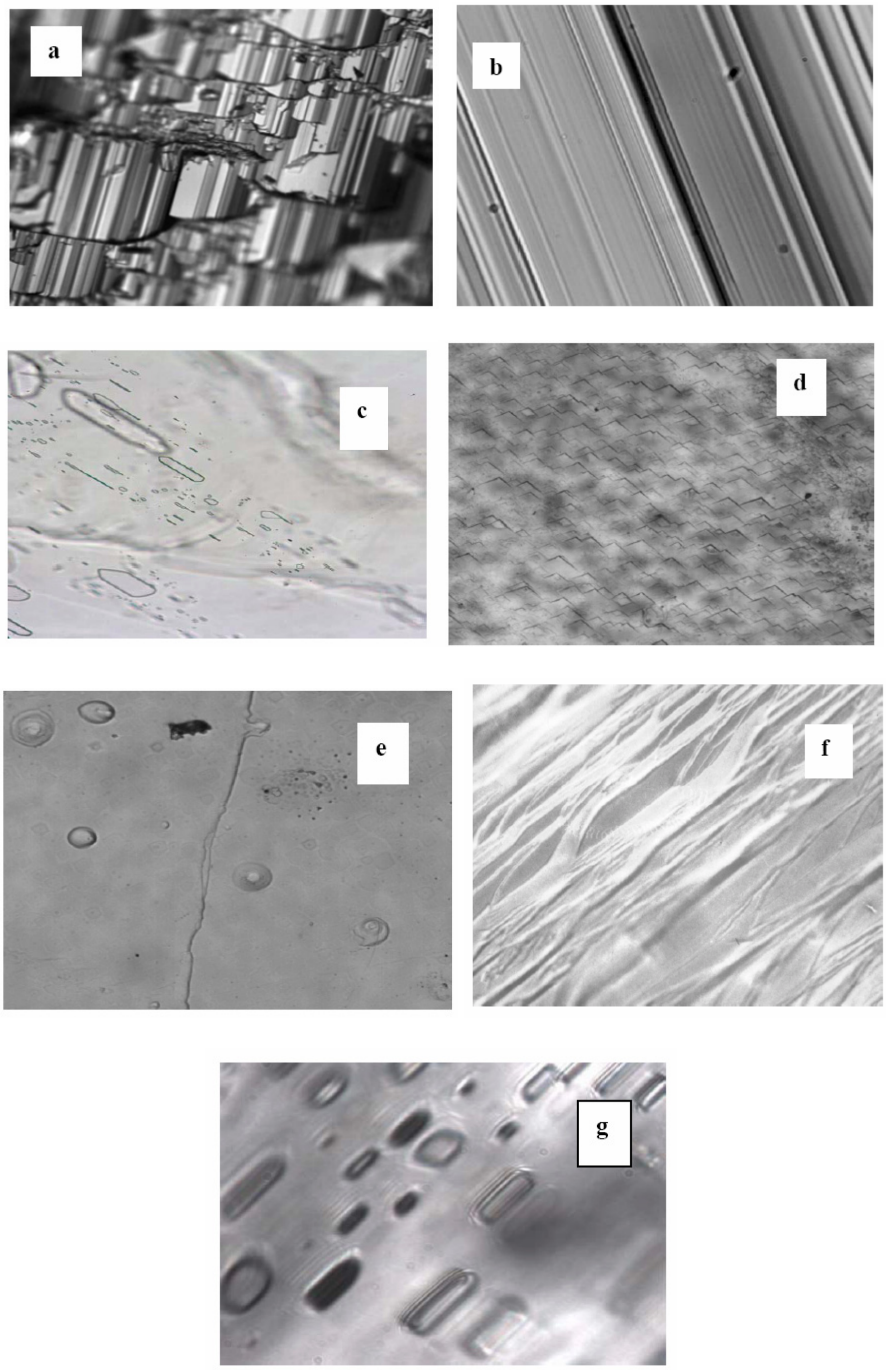


Fig.1. (a) layer structure (b) striation pattern (c) overgrowth (d) bunch pattern (e) etch hillock (f) lamellar structure (g) rectangular etch pits.

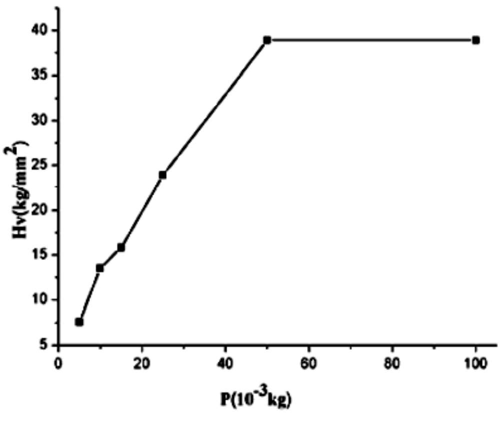
Fig. 1 (e) shows the terraced etch hillocks formed on the [101] face by etching with acetone and water taken in the ratio 1:2. When the surface dissolution is low, the surface is smooth, and the increased dissolution at dislocations can lead to terraced etch hillocks. The fractograph shown in Fig.1 (f) illustrates the pattern which strongly presents the lamellar structure.

A composition of water in methanol in the volume ratio 1:5 is found to be produce rectangular etch pits (Fig. 1 (g)) on the [100] surface when etched for 5-10 seconds. On successive etching no spurious development of pits are observed which suggests that etch pits are produced at the emergence of dislocation. The flat bottomed and shallow pits appear and disappear on successive layer etching indicating that they are due to dislocations which extend only a few molecular layers.

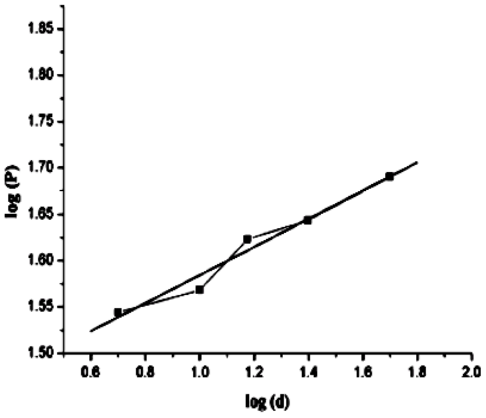
Micro topographical analysis suggests that the growth of these crystals is due to 2D nucleation and spreading of layers.

3.2 Microhardness studies

Good quality crystals with excellent optical performance and mechanical behviour are needed for device applications. In single crystals, second harmonic generation is always lower from the defective sectors compared to that from the more perfect sectors [13, 14].



(a)



(b)

Fig. 2 (a) Vicker's hardness profile (b) Mayer's plot.

Microhardness measurement on the (100) surface of the crystal is done for applied loads (P) from 5 g to 100g with a dwell time of 5 seconds using Leitz Miniload Hardness tester and the average indentation diagonal length(d) is measured. Vicker's micro hardness profile of the crystal (Fig. 2. a) calculated using the formula

$$\mathbf{H_v} = 1.8544\ P/d^2\ \text{Kg/mm}^2$$

Increase in microhardness with increase of load in the low load region can be attributed to the heaping up of material at the edges of impression made by the indentor [3] due to the slipping of layers at the indentation centre since at this region it is plastic. Increase in load enables the defects to move and pin upon the boundaries. At higher loads, slipping of layers stops which in turn harden the crystal. This is shown in the region between 50 g and 100 g. If we increase the load beyond 100 g crystal is found to be ruptured. The maximum hardness is found to be 38.9 Kg/mm^2. Mayer's plot of log P versus log d is shown in Fig (2.b), the slope which gives the value of work hardening coefficient (n). The value of n for LAO is found to be equal to2.43 which is as expected for soft organic materials [15].

4. Conclusions

Single crystals of the nonlinear optical material L-alaninium oxalate has been grown by solvent evaporation technique at room temperature. Surface studies on the as grown and etched surface reveals that the crystal growth is by 2D nucleation and subsequent spreading of layers. Shallow and flat bottomed etch pits, which disappear on subsequent etching suggests that the defect is mainly due to edge dislocations. The absence of patterns like growth spirals, slip bands…etc also support this. The low dislocation density found in the present study suggests that crystals grown by solvent evaporation method can be utilized for optical device applications.

From the microhardness studies it is seen that l-alaninium oxalate possesses a relatively high value of microhardness of 38.9 kg/mm^2 which is also quite suitable for fabrication of optical devices.

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