SURFACE STUDIES ON AS-GROWN FACES OF BISTHIOUREA ZINC ACETATE CRYSTALS

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ABSTRACT
Single crystals of bisthiourea zinc acetate (BTZA) were grown from slow evaporation of their saturated solutions. Surface studies on as-grown (021) faces indicate that the crystals grow by 2D growth mechanism. The crystal surface was treated with suitable chemicals and several new etchants capable of revealing dislocations were developed. The variation of Vickers hardness with applied load has been studied and the results suggest that BTZA crystals exhibit reverse indentation size effect. The anisotropy in hardness is revealed through Knoop indentation studies. The surface laser damage studies suggest that the laser-induced damage is of thermal origin.

Keywords: Crystal growth, Growth mechanism, Defects; Microhardness, Damage threshold.


1. INTRODUCTION
Nonlinear optical (NLO) materials have attracted several researchers as they play an important role in technologies like lasers, optical communication, electro-optic modulation and data storage etc. [1,2]. Therefore, the search for compounds having high optical nonlinearity (as of organic crystals) and physical ruggedness (as of inorganic crystals) has led to the development of a class of compounds called semiorganics. It was found that metal complexes of thiourea include the advantages of both organic and inorganic part of the complex. They have large nonlinearity, high resistance to laser-induced damage, low angular sensitivity and good mechanical hardness [3,4] and they can be grown from aqueous solution in the form of large single crystals.

In view of these, thiourea complexes have attracted significant attention during the last decade. A variety of crystals of this class have been studied by several researchers viz. zinc...
tristhiourea sulphate (ZTS) [5], bisthiourea cadmium chloride (BTCC) [6], bisthiourea zinc chloride (BTZC) [7], bisthiourea bismuth chloride (BTBC) [8], potassium thiourea bromide (PTB) [1] and bisthiourea cadmium formate (BTCF) [9]. Many subsequent researchers have also taken up the growth and characterization of semiorganic crystals due to the encouraging results. The present authors have investigated on a variety of themes [10-16] in recent past and in this communication, growth and characterization of bisthiourea zinc acetate (BTZA) crystal has been taken up. BTZA, a semiorganic compound exhibiting some important properties, crystallizes in monoclinic system with space group $P2_1/c$. Literature suggests that there are reports on growth and characterization of these crystals [17,18]; however, there are no clear reports on the surface studies. Such studies give useful information about the growth mechanism, dislocation density (defect content), hardness and laser damage threshold, which are necessary to exploit a crystal for device applications. The results of the above studies are presented in the following sections.

2. CRYSTAL GROWTH
TZA was synthesized using zinc acetate and thiourea in the ratio 1:2. The known amounts of these salts were dissolved in deionized double distilled water and the solution is continuously stirred at least for four hours using a magnetic stirrer to ensure complete miscibility and dissolution of the salt. The saturated solutions were prepared and are allowed for slow evaporation. All the growth experiments were performed in a constant temperature bath at 35°C. The self-nucleated seed crystals collected from the slow evaporation were allowed to grow on the base of the beaker. Colorless and transparent crystals of dimensions $13 \times 4 \times 3$ mm$^3$ were obtained in three weeks. The average growth rate of the crystals along the longer edge of the crystal face is 0.6 mm/day. Figure 1a shows, the grown crystals with different dimensions. The morphology of the well-developed faces of these crystals is shown in figure 1b, which is in agreement with the literature [18].

![Figure 1](image1.png)  
**Figure 1** a) As-grown crystals of BTZA and b) morphology of BTZA.

3. RESULTS AND DISCUSSION

3.1. Growth Mechanism
The growth and dissolution of crystals take place exclusively on solid-liquid interface. Therefore the surface microtopography of crystal faces represents the final stage of growth or dissolution of a crystal and this is more appropriate for crystals grown from solution. It is well known that certain growth features such as spirals, hillocks, and striations are seen on well-developed as-grown faces of some crystals when observed under a microscope. Many workers have undertaken
such studies on different crystals as these features reveal important information about the growth history of the crystals. With the development of spiral growth theory, the importance of such surface studies has increased. Hence, to understand the possible growth mechanism of these crystals, surface studies were carried out on about 20 as-grown (021) faces of these crystals using a Magnus MLX microscope fitted with Motic (1000) camera.

Most of these faces reveal typical striations (Figure 2a), which are parallel to the longer edge of the crystals and they propagate from one end to other. In some cases, the striations appeared perpendicular to longer face (Figure 2b). From the present observations, it appears reasonable to attribute the growth mechanism of BTZA crystals to 2D growth process [19]. Figure 2c shows a typical interlaced pattern observed on BTZA crystal, whose steps are parallel to the edges between (201) and (021) faces and that between (122) and (021) faces. The reason for the formation of interlacing steps appears to be due to nucleation and propagation of steps from two 2D sources (S₁, S₂) resulting in interlacing pattern (Figure 2d) as they intersect with each other [20].

Figure 2 Typical striations a) parallel to longer face b) perpendicular to longer face c) interlacing pattern and d) line diagram of interlacing steps.

3.2. Chemical Etching

For the fabrication of devices, one requires good quality crystals possessing minimum defects. Hence in the present studies, chemical etching technique has been employed to study the density and distribution of dislocations in BTZA crystals using an optical microscope. The present etching work has been confined to the as-grown faces only. In view of the meager information available on the etching of these crystals [21, 22], a number of etchants were tried and new etchants capable of revealing dislocations were developed as shown in table 1. Figure 3 shows the etch pattern observed with some of the etchants at a particular etching time. From these figures, it is evident that the shape of the etch pits is elongated rectangular, whose longer sides are parallel to the longer edge of the crystal (with all the etchants).
Further, a careful observation on a number of crystals suggests that the distribution of etch pits is not uniform, the density is more at the edges than at other regions of the crystal surface. The average density of dislocations is about $6.5 \times 10^3$/cm$^2$. As BTZA crystals growth with different faces (from Figure 1), they possess growth sector boundaries and it is known that dislocations can originate from these growth sector boundaries [23, 24]. This might be the reason for more density of etch pits at the edges.

**Figure 3** Etch pit pattern observed on $\langle 021 \rangle$ face of BTZA crystal etched with a) water (e.t 15 sec) b) methanol (e.t 50 sec) c) ethanol (e.t 30 sec) d) propanol (e.t 50 sec) e) acetic acid (e.t 30 sec) and f) acetic+formic (2:1) (e.t 20 sec).
Table 1 Action of various etchants on BTZA crystal.

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Etching action</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>Well-defined etch pits</td>
</tr>
<tr>
<td>Methanol</td>
<td>Well-defined etch pits</td>
</tr>
<tr>
<td>Ethanol</td>
<td>Well-defined etch pits</td>
</tr>
<tr>
<td>Propanol</td>
<td>Well-defined etch pits</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>Well-defined etch pits</td>
</tr>
<tr>
<td>Formic acid</td>
<td>Well-defined etch pits</td>
</tr>
<tr>
<td>Acetic + Formic acid (2:1)</td>
<td>Well-defined etch pits</td>
</tr>
<tr>
<td>Acetic + Formic acid (1:2)</td>
<td>Etching action increases and surface becomes rough</td>
</tr>
<tr>
<td>Propionic acid</td>
<td>Ill-defined etch pits</td>
</tr>
<tr>
<td>Xylene</td>
<td>Polishing action</td>
</tr>
</tbody>
</table>

3.3. Vickers Microhardness

Microindentation hardness testing provides useful information on the mechanical strength and deformation characteristics of a material. Hence, to understand the strength of BTZA crystal, which is a useful parameter for device fabrication, microhardness measurements were made using Leitz-Wetzlar (miniload 2) microhardness tester equipped with a Vickers diamond pyramidal indenter. For these studies, samples with smooth plane surfaces were chosen and loads ranging from 10 to 100 g were used with a constant indentation time of 15 sec in all cases. Hardness values \( H_v \) are estimated from the relation

\[
H_v = 1854.4 \left( \frac{P}{d^2} \right)
\]  

Where \( P \) is the load applied on the indenter in g, \( d \) is mean diagonal length of the square impression formed on the crystal surface in \( \mu \)m and hardness is in kg/mm\(^2\). Figure 4a shows the variation of hardness with the applied load on as-grown face of BTZA crystal. From the figure, it is observed that with the increase in load up to 50 g, the hardness value increases and thereafter attains a steady value of 105 kg/mm\(^2\). The initial increase in hardness with the applied load for BTZA crystals is termed as reverse Indentation Size Effect (reverse ISE). Further, it is important to notice that cracks appear at the corners of indentation mark from \( P = 50 \) g (Figure 4b), which may be due to the release of internal stress (perhaps tensile) generated locally by indentation.

Various explanations have been given on reverse ISE on different crystals. Pandya et al. [25] and Arora et al. [26] pointed out that at low loads the indenter pierces only the top surface layers, which results in the increase in hardness in this region. Further, they attributed the load independence of hardness at higher loads to rearrangement of dislocations. Sangwal [27] attributes reverse ISE on PbS and BaFCl due to nucleation and multiplication of dislocations at low loads and to the active participation of two sets of slip planes of a particular slip system at higher loads. Hence it is felt in the present studies that the reverse ISE mechanism in the crystals under study appears to be due to i) generation and easy propagation of dislocations; which results in a low value of hardness at initial loads, ii) dislocation interaction which slows down the motion of dislocations resulting in the gradual increase of hardness with load and iii) the mutual interaction or rearrangement of dislocations at higher loads, which can be attributed to the load independence of hardness [10,27,28]. However, as the crystals studied do not reveal indentation dislocation rosette (IDR) patterns, the explanation for ISE based on the development and motion of dislocations around the indentation mark cannot be established experimentally.
3.4. Hardness Anisotropy

It is well known that Vickers microhardness measurements are not so sensitive to study the anisotropic nature of hardness in crystals. Hence, indentation studies were also carried out with Knoop indenter to understand the anisotropic nature of BTZA crystals. The Knoop hardness $H_k$ was calculated using the expression

$$H_k = 14230\left(\frac{P}{a^2}\right)$$  \hspace{1cm} (2)

Where $H_k$ is in kg/mm$^2$ and $a$ is the longer indentation diagonal length in µm. The samples were mounted on a laboratory made mini-circular stage with which the angular position could be determined with an accuracy of 0.5°. Measurements were made at various orientations of $\theta$ ranging from 0 to 180°, where $\theta$ is the angle made by the long axis of the Knoop indenter with the longer edge of the crystal. Further, measurements were made at a single load (15 g), which gives a Knoop impression of reasonable dimensions.

Figure 5 shows the Knoop hardness anisotropy on BTZA crystals. It is interesting to note from the graph that the hardness value reaches a maximum and minimum value with respect to crystal orientation. The crystal structure and slip system play an important role in the observed variation of hardness with crystal orientation [10, 29]. The variation of size of the impression with orientation appears to depend on the participation of slip system at different angles. The larger impressions appear when the resolved shear stress is sufficiently high and smaller impressions when it is low. These studies suggest the anisotropic nature of BTZA crystal faces exhibiting hard and soft directions.
3.5. Laser Damage Threshold (LDT)

One of the most important considerations in the choice of material for optical applications is its optical damage tolerance as the operation of nonlinear devices involves the exposure of material to a high power laser source. The efficiency of conversion is strongly dependent on the incident power level for harmonic generation. Further, high optical intensities are involved in nonlinear processes; the materials must be able to withstand high power intensities [30]. Hence, high damage threshold is a significant parameter for NLO materials, which makes them suitable candidates for frequency conversion devices. A flash lamp pumped Q-switched Nd:YAG Innolas laser operating in TEM\textsubscript{00} mode with a pulse width of 7 ns (FWHM) and 10Hz repetition rate was used as the source for the LDT studies. The surface damage patterns (Figure 6b) of these crystals show tiny blobs surrounding the core of the damage. Hence, we can expect the damage to be of thermal origin [31]. The surface damage threshold of the crystals was calculated using the expression,

\[
\text{Power density (P_d)} = \frac{E}{\tau \pi r^2}
\]  

Where \(E\) is the energy (mJ), \(\tau\) the pulse width (ns) and \(r\) the radius of the spot (mm). The experimental results indicate that the average surface damage threshold for BTZA crystals is 0.39 Gw/cm\textsuperscript{2} and this value is comparable to other NLO crystals like KDP and ZTS. The present damage threshold values of BTZA crystal are higher than those reported in the literature [18].

Figure 5 Hardness anisotropy in BTZA crystals.

Figure 6 Surface pattern of BTZA crystal a) before and b) after laser damage.
4. CONCLUSIONS

As-grown faces of BTZA crystals reveal striations, which suggest that these crystals grow by the 2D growth process. Several new etchants were developed to reveal dislocations. The shape of the etchpits is elongated rectangular and the average dislocation density is about $6.5 \times 10^3$/cm$^2$. The hardness studies indicate that the crystal exhibits reverse ISE and the surface stresses released by indentation are perhaps tensile. The load independent hardness value of BTZA crystal is 105 kg/mm$^2$. Knoop hardness studies indicate the presence of hard and soft directions on the crystal face. The laser-induced damage is of thermal origin and the average damage threshold value is 0.39 Gw/cm$^2$.

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