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Revealing Dislocations in m- Toluenediamine Single Crystals by a Selective Etch-Pit Technique

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Revealing Dislocations in *m*-Toluenediamine Single Crystals by a Selective Etch-Pit Technique

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The etchant (benzene + 10% aniline) has been found for revealing dislocations in a new non-linear single crystal of *m*-toluenediamine. The etchant reveals "as-grown" dislocations on the (010) and (001) planes as well as "fresh" ones (on the (010) plane). Kinetic observations on the (010) plane have been carried out using the selective etch-pit technique. Microhardness of the crystals and mean free path of dislocations as functions of the force acting on the indentor have also been determined.

Investigation into the nature and properties of linear defects in organic molecular solids is rather urgent. Firstly, the way the dislocation affects physical and chemical properties in organic crystals is of great interest. It is well known the dislocations in inorganic compounds may not only affect some crystal properties but in certain cases be responsible for complete changes of these properties.

Secondly, the investigation of dislocations in low-symmetry systems to which organic solids usually belong, is of special interest from the viewpoint of the physical nature of the imperfections. It is known that the current theory of dislocations has been developed only for high-symmetry crystals.

Thirdly, by knowing the conditions under which dislocations occur it is possible to obtain single crystals of high perfection suitable for physical investigations.

There have been only a few reports on dislocations in molecular solids in contrast to the amount of similar publications on other crystal types. These papers in general deal with revealing the dislocation type and behaviour in monoclinic crystals of naphthalene, anthracene, tetracene, pyrene and diphenyl[1,2] and benzoic acid.[3] Influence of dislocations in organic solids on some chemical and physical properties has been analysed in papers.[4,5]

The present paper deals with the investigation of the dislocation structure in single crystals of *m*-toluene-diamine $C_7H_{10}N_2$ (TDA), which is a non-linear transformer of laser radiation.[6] It is known that in the case of inorganic transformers, e.g. KDP and ADP lattice imperfections can considerably affect optical properties of those solids.[7] So far we have not known any publications on similar investigations in the field of organic solids. The data on the TDA dislocation structure are not available in literature either. Therefore it was necessary to develop the technique of the dislocation revealing and to study their distribution crystallography. The present investigation is the first step in studying interrelations between optical properties of the TDA crystal and its real structure.

EXPERIMENTAL

The TDA single crystals belong to orthorombic symmetry space group Pna 2_1 with parameters of the unit cell $a = 8{,}359$ Å, $b = 12{,}406$ Å, $c = 6{,}225$ Å.[8]

The experiments for revealing dislocations on the (010) and (001) planes have been carried out. The TDA single crystals grown from the melt of the powder previously refined† have been investigated. The crystallographical planes required were mechanically ground and polished before etching. The single crystal orientation was effected by α-ray technique. Etching and polishing were performed at room temperature, the solutions being continually stirred. Depth and width of pits were measured by the interferometer. The depth measurements were taken by means of interferential rings with a green optical light filter ($\lambda = 0.54$ μ).

SELECTION OF POLISHING AND ETCHING SOLUTIONS

20 % methanol in ethanol, producing a smooth surface on polishing, has been selected as a result of multiple tests. Normal polishing rates for (010) and (001) planes are $0.5 \cdot 10^{-4}$cm/sec and $1.2 \cdot 10^{-4}$ cm/sec respectively. But in case when pure ethanol is used for polishing it gives rise to etch pit patterns that rapidly diffuse.

Regarding the fact that the etchant base is to slightly dissolve the crystal.[9] solubility of the *m*-TDA in different organic compounds was determined. As a result, it was stated that in saturated hydrocarbons starting with octane, the TDA is practically not soluble; it dissolves in polar solvents—water, spirits,

† The purification and growth technique will be published elsewhere.

ketones, chlorinated hydrocarbons; it is slightly soluble in aromatic hydrocarbons, benzene, toluene.

From the etchants above, benzene has been selected as a base, since in this case only crystallographically oriented etch pits can be produced on etching. The process of etching is simultaneously accompanied by the surface polishing. Normal polishing rates on etching for (010) and (001) planes are $0.5 \cdot 10^{-4}$ cm/sec and $7 \cdot 10^{-5}$ cm/sec, respectively.

On etching in benzene the etch pit depth doesn't change after 20 sec and is 1,2 μk, i.e. the normal rates of the crystal dissolution on a free surface and within the dislocation itself practically coincide. In order to increase the dissolution normal rate some quantities of cyclic ethers (tetrahydrofuran), amides (dimethylformamide) and amines (aniline) were added to the etchant base. The best quality of etching was observed in the case of the 10% aniline solution in benzene. The etch pit pattern on the (010) and (001) planes in this etchant is given in Figure 1. Conformity of etch pit positions with the dislocation positions was determined according to the reproduction of the etch pit distribution on two cleavage planes (Figure 2) and to the repeated etching as well. Typical curves of dependence of etch pit sizes (l) on time of etching (t) are shown in Figure 3. On etching the TDA using benzene with some other additions the surface turns out to be rough.

REVEALING DISLOCATIONS BY SELECTIVE ETCHING

Investigations on the TDA single crystal etching demonstrated the selected etchant to reveal "as-grown" dislocations and fresh ones on the (010) planes. The etch pits of larger size correspond to the former dislocations. They remain

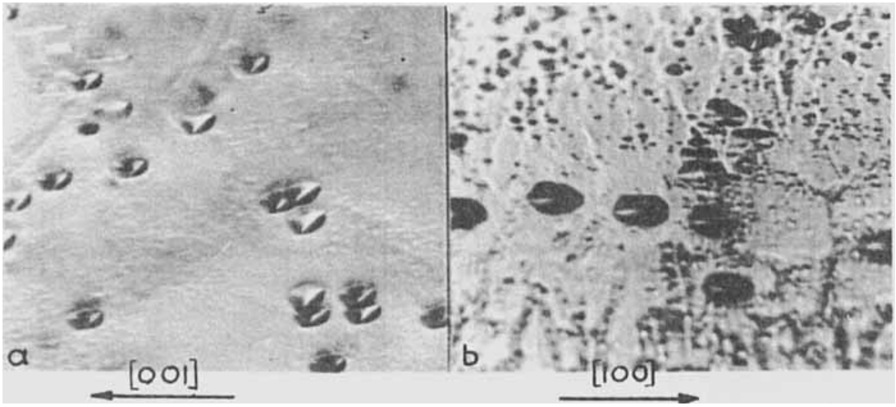

FIGURE 1 The etch pit shapes in the TDA crystals after etching by 10% aniline in benzene. (a) the (010) plane; (b) the (001) plane.

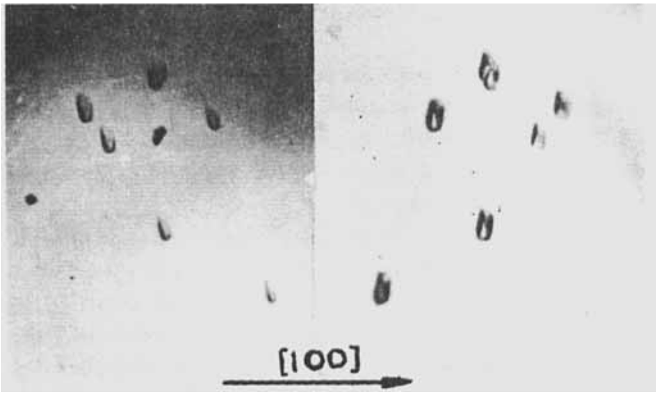

FIGURE 2 Two cleavage faces in the (010) plane.

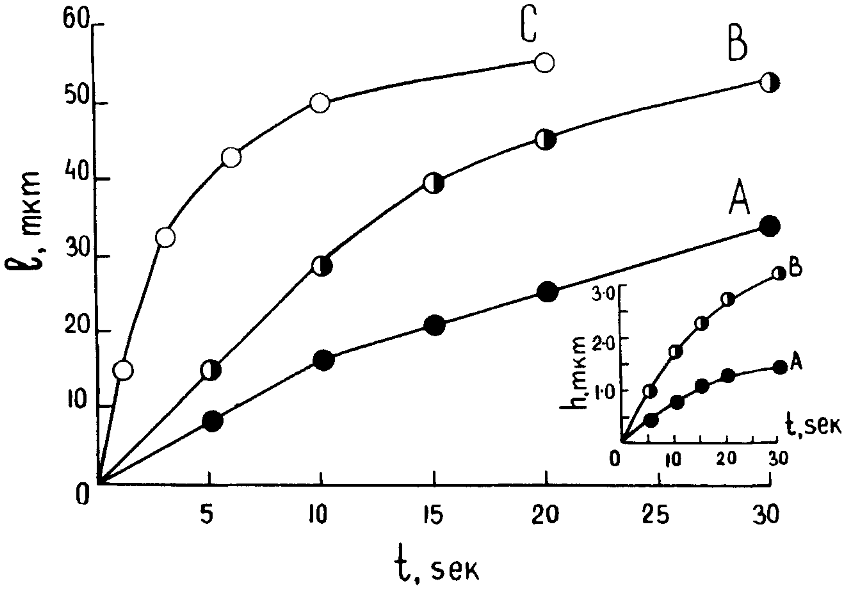

FIGURE 3 The dependence of the etch-pit width (l) and depth (h) on time (t) of etching in the (010) plane. (a) benzene (b) the 10% aniline solution in benzene (c) aniline.

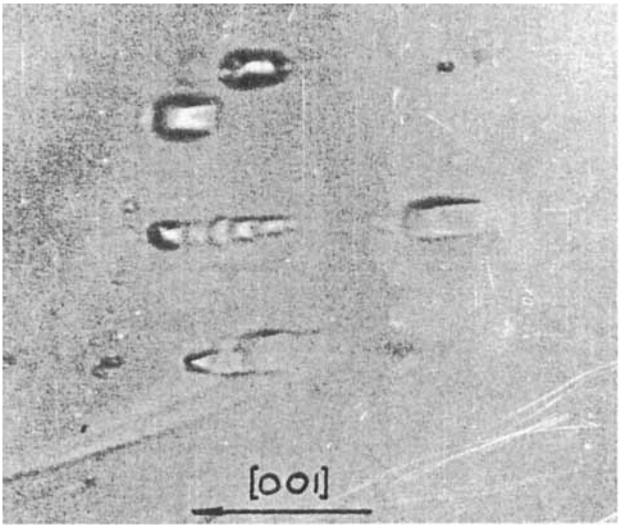

FIGURE 4 The dislocation movement on etching (× 480).

during the whole process of etching. However, this etchant failed to reveal "fresh" dislocations in the (001) plane.

Mean density of "grown-in" dislocations on the investigated crystals accounts for $10^4 - 10^5$ cm^{-2}. Developing and moving of "fresh" dislocations on the (010) plane were observed at compressing crystals during the etching process. The path of dislocations could be observed by successive disposition of flat-bottomed etch pits of dimishing size. A small sharp-bottomed etch pit corresponds to the final position of the dislocation (Figure 4). The obtained result enables one to expect that the dynamics of dislocation in the single crystals of TDA may be investigated.

The indentation traces of (010) plane of investigated crystals have been studied by the same technique. While using the etch-pit technique on this plane at room temperature it was discovered that some lines having dislocation etch-pits, appear from the indented trace in the (001) direction (Figure 5).

The direction and length of the lines do not depend on the indentor shape. With the increase of load on the indentor (from 2 up to 100 gr) microhardness ($H = P/S kg/mm^2$) drops and the line length (L) increases (Figure 6). Changes in etch-pits disposition along the lines at multiple polishing and etching of the same indentation trace point to the fact that glide planes in TDA single crystals might be the (100) or (110) planes. This is consistent with the TDA crystallic structure.[8] At the indentation of dislocations on the (001) plane no lines were detected.

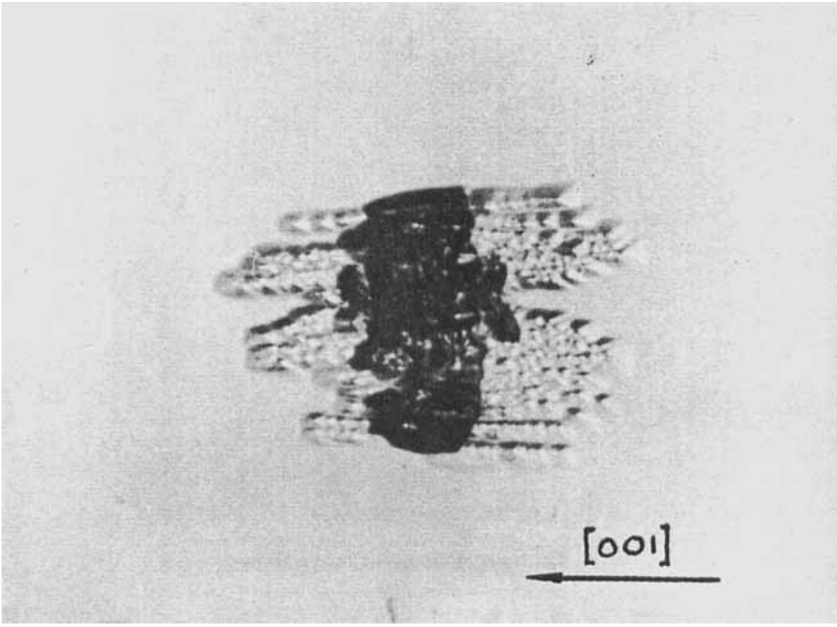

FIGURE 5 The indentation trace shape (loading 5 gr) on the (010) plane after etching (×400).

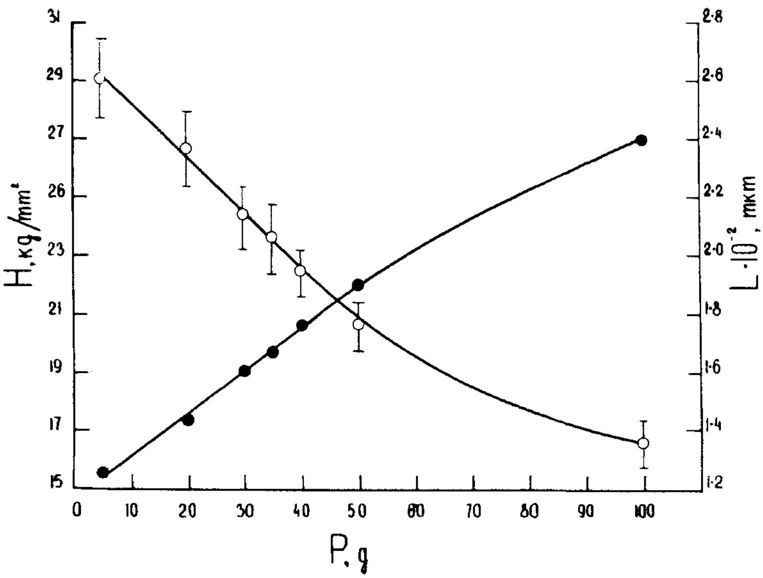

FIGURE 6 Dependence of the dislocation microhardness (H) and mean path (L) on the indentor loading. —O— = H; —●— = L.

Acknowledgements

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