Indian J. Phys. **71A** (1), 57–60 (1997)

IJP A
- an international journal

Knoop hardness anisotropy on benzoic acid (001) cleavages

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Received 17 April 1996, accepted 13 June 1996

Abstract : Knoop microhardness studies were carried out on the (001) cleavage surfaces of benzoic acid single crystals The hardness variation with orientation showed the existence of a peak on going from the [010] direction to the [100] direction This behaviour confirms the symmetry of the plane and is not similar to that of anthracene and phenanthrene

Keywords : Knoop indentation, microhardness, benzoic acid

PACS Nos. : 81 40.Np, 62.20.Fe

Introduction

An important strength property of single crystals is their microhardness. Knoop microhardness anisotropy has been observed in aragonite, calcite, dolamite and magnesite [1,2]. Microhardness anisotropy in cubic crystals with different point groups has been studied [3]. Molecular structure and indentation hardness relationship have been reported in organic solids [4]. Vicker's microhardness behaviour with load has been reported by various workers in organic molecular solids [5–9]. Knoop hardness behaviour with load in benzoic acid single crystals has been recently reported [10].

Experimental techniques and results

Crystal growth :

Single crystals of benzoic acid were grown from the melt by the Bridgman method. The ting material was column chromatographed, twice vacuum sublimed and zone refined. The material was transferred to the crystal growth tubes without exposure to the atmosphere [11]. The crystals were cleaved in the usual manner using a sharp blade. Smooth (001) leavages were selected after optical examination. The crystals were indented on a Carl Zeiss NU 2 Universal Research Microscope.

Plate 1.

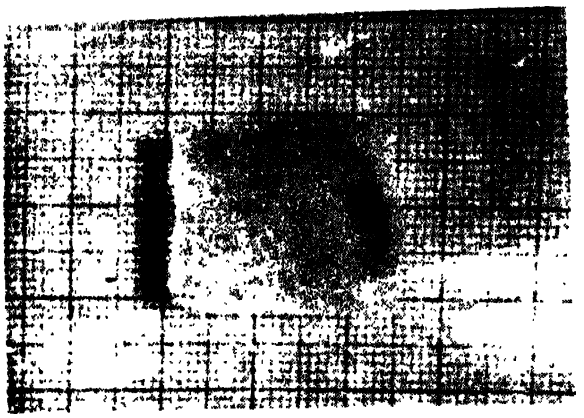

Plate 1. As-grown single crystal of benzoic acid

2.2. Microhardness :

The indents were made with a Knoop indenter. The load used was 2.5 gm. A number of indents were made at this load. The long diagonal length was used in calculating the Knoop hardness number (H_k) using the formula :

$$H_k = 14228.8 \times P/d^2 , \tag{1}$$

where P is the applied load in gm and d, the mean diagonal length in microns. The indentation time of 10s was kept constant as this time was adequate to minimize the vibration effects on the results. The crystal size was much larger than the indentation size, thus eliminating the boundary effects on the results. The distance between the indents was

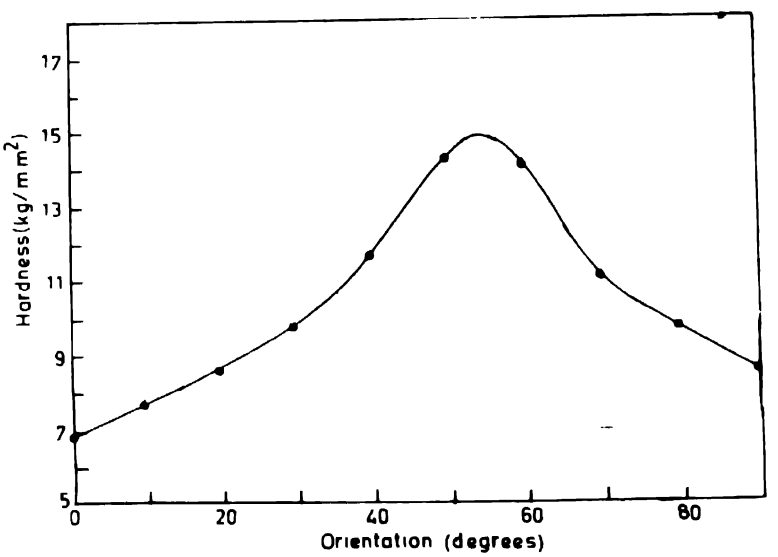

Figure 1. Hardness variation with orientation

five times the size of the largest indentation mark. The crystal thickness was relatively large such that the indenter did not sense the lower surface [12]. A number of crystals were indented.

Figure 1 shows the variation of the Knoop hardness with orientation for the crystals of benzoic acid. It is observed that the hardness is minimum when the long diagonal of the Knoop indenter is parallel to the [010] direction and the [100] direction with a peak occurring around 50°.

3. Discussion and conclusions

Benzoic acid crystallizes in the monoclinic structure. The lattice parameters are a = 5.440 Å, b = 5.180 Å and c = 20.800 Å with β = 97.5°. This compound has the structural formula (C_6H_5COOH) with 4 molecules per unit cell. They have the space group $P2_{1/c}$ and cleaves along the (001) plane [13].

The hardness depends on the plastic and elastic properties of the crystals. For anisotropic materials, the properties vary with crystallographic orientations. In the case of Knoop indentations, the elastic recovery takes place along the short diagonal only and the long diagonal does not change when the load is removed. When a loaded indenter penetrates a solid, the depth of penetration increases until the condition of the lattice immediately below the indenter, has the same characteristics as that of the specimen in which the saturation value of the compressive strain has been attained. The strain becomes progressively smaller with increasing distance from the centre of the material to a distance equal to the length of the long diagonal.

The microhardness properties are related to the crystal structure of the material or the way the atoms or molecules are packed together.

Indenting the (001) cleavage plane with the long axis of the Knoop indenter parallel to the [010] direction and rotating the long diagonal of the Knoop indenter, the microhardness values of benzoic acid single crystals increases till the long diagonal of the indentation mark is at about 50° to the [010] direction and then drops till the [100] direction is parallel to the long diagonal of the Knoop indenter.

The crystallizing unit in the case of benzoic acid is a dimer which consists of a pair of molecules held together by hydrogen bonds. The space group of this solid is $P2_{1/c}$ and contains four molecules per unit cell. If a complete rotation is done by measuring the Knoop hardness with orientation, then one should observe four peaks for the (001) planes which is observed in the present case confirming the symmetry of the plane.

Anthracene shows a maximum hardness value in the [010] direction and phenanthrene a minimum hardness value in this direction and opposite in the [100] direction. Both these solids have the same space group ($P2_{1/a}$) and crystal structure (monoclinic) and this type of behaviour has been explained in terms of the way the molecules are oriented and disposed in the unit cell [14].

The different behaviour of benzoic acid though it has the same crystal structure (monoclinic), is due to its different space group ($P2_{1/c}$) and to the dimer packed in the unit cell.

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