Electronic Supplementary Material (ESI) for CrystEngComm.

On the loading rate sensitivity of plastic deformation in molecular crystals

Devaraj Raut, Mangalampalli S. R. N. Kiran, Manish Kumar Mishra, Abdulla M. Asiri and Upadrasta Ramamurty*

Supplementary Information

Estimation of hardness by Oliver-Pharr method:

The hardness of materialis defined as its resistance to local plastic deformation.[1,2] Thus, indentation hardness, H, can be determined from the maximum indentation load, $P_{\max}$, divided by the contact area, A:

$$H = P_{max} / (A) \qquad (1)$$

Where the contact area (A) is a function of the penetration depth, h, and can be determined by the following equation:

$$A\ (h) = C_0h^2 + C_1h + C_2h^{1/2} + C_3h^{1/4} + \ldots\ldots.. + C_8h^{1/128} \qquad (2)$$

It may be noted that only the constant C_0 is used if it is assumed that a Berkovich indenter has a perfect tip. However, for imperfect tips, higher-order terms have to be taken into account, and these are obtained from the tiparea function curve fit for a given tip. The elastic modulus, E, of the organic crystals can be obtained using the following equation:

$$1/ E_r^* = [(1- v_i^2)/E_i] + [(1- v_s^2)/E_s] \qquad (3)$$

Where v and E are Poisson's ratio and elastic modulus, respectively; and the subscripts i and s refer to the indenter and test material, respectively. The indenter properties used in this study are E_i=1140 GPa, and Poisson's ratio for the indenter is v_i=0.07E_r* is the reduced modulus that accounts for the fact that elastic deformation occurs in both the sample and the indenter, and it can be determined from the equation

$$E_r^* = \{(\pi)^{1/2} / \beta\ S\} / 2\ (A)^{1/2} \qquad (4)$$

Where S is the stiffness of the test material, which can be obtained from the initial unloading slope by evaluating the maximum load and the maximum depth, i.e., $S = dP/dh$. β is a shape constant that depends on the geometry of the indenter and is 1.034 for the Berkovich tip. The contact depth can be estimated from the load-displacement data using

$$h_c = h_{max} - (\varepsilon\, P_{max} / S) \qquad (5)$$

Where ε is a constant that depends on the indenter geometry (ε = 0.75 for Berkovich indenter) and h_{max} the displacement at the peak load.

The loading curve can be fitted with the following power-law relation,

$$P = \alpha\, h^{\mathrm{m}} \qquad (6)$$

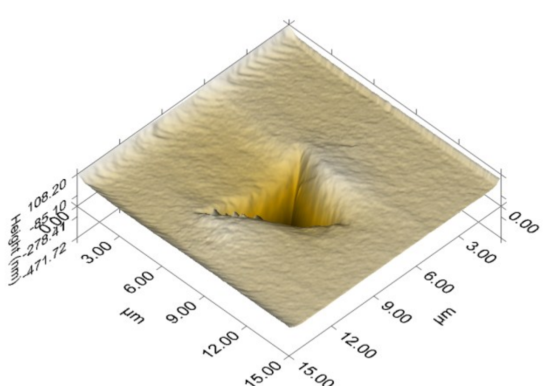
and unloading curve can be expressed as

$$P = \alpha\, (h - h_f)^{\mathrm{m}} \qquad (7)$$

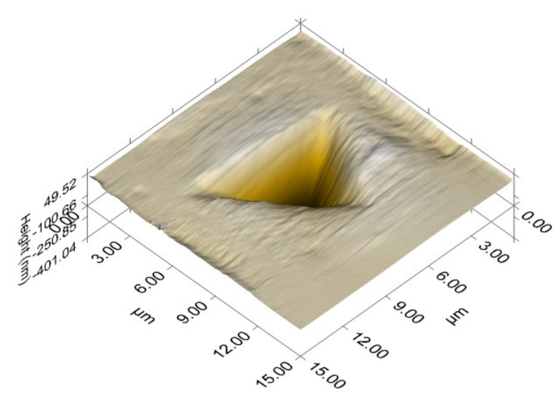
Where P is the indenter load, h is the elastic displacement of the indenter; h_f is the final depth, α and m are fitting constants. The value of m for Berkovich tip will usually be 1.5.

1. W. C. Oliver, G. M. Pharr, *J. Mater. Res.*, **7**, 1564 (1992)
2. W. C. Oliver, G. M. Pharr, *J. Mater. Res.*, **19**, 3 (2004)

L-alanine



p-Nitroaniline



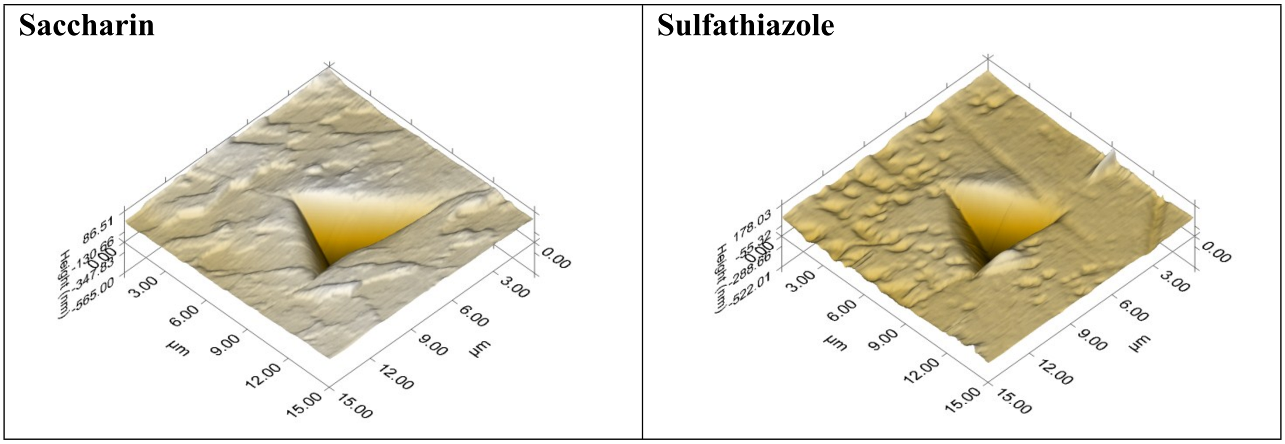


Figure S1: Residual indent impressions of the Berkovich indents on various crystals studied in the present study.