Kinetically driven frowning of the crystal phase

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Keywords: high pressure, phase transition, negative-linear strain, amorphization.

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The fundamental techniques of controlling the growth of a desirable polymorph are based on the variations of the solvent, temperature conditions, the saturation of the solution, addition of impurities, surfactants, modification of the viscosity of the solution, etc. A relatively recent trend is vary pressure conditions. This includes (i) crystallization of liquids at high pressures, (ii) crystallization from solutions at high pressures, and (iii) pressure-induced solid-state polymorphic transformations. [1] Pressure has become an established highly-efficient tool for inducing strong structural transformations in various compounds. [2] Direct observation and structural characterization of a kinetic product and a thermodynamic product for crystal of 1,4-bis(pentyloxy)-2,5-bis(2-pyridineethynyl)-benzene (C5-PPB) are reported. [3]

An interesting phenomenon was observed in the crystal of C5-PPB. Under high hydrostatic pressure, depending on the velocity of compression, two phases of the same crystal could be observed. Single-crystal of C5-PPB was compressed both rapidly and slowly in the DAC and observed to undergo drastic visible changes. During compression, the two different following sets of effects were visually observed: (i) strong monotonic compression followed by the appearance of irregular "wrinkles" on the face; (ii) a transition front travelling along the crystal plane followed by abrupt shape change. These initially inconsistent observations were detected for the same crystal sample on subsequent experiments. The phase α can be monotonically compressed up to 0.8 GPa. Then, when the single crystal is compressed rapidly from 0.8 to about 1.2 GPa, a visible monotonic compression to new phase β is observed. However, when C5-PPB crystal is compressed slowly from 0.8 to 1.2 GPa, phase α is preserved. The further compression of such 'over-compressed' phase α results in irregular 'wrinkles' appearing on the crystal faces. This phenomenon occurs simultaneously with decrease in diffraction spots intensities, marking its gradual amorphization (Figure 1a). The transformation from phase α to phase β is associated with a giant negative-linear strain, visibly elongating the crystals in [100] direction (Figure 1b). This α-to-β phase transition can be classified as an isostructural phase transition, through maintained crystal symmetry and remained crystal integrity. This study demonstrates a new perspective of the compression rate in creating the phase diagrams of solids.

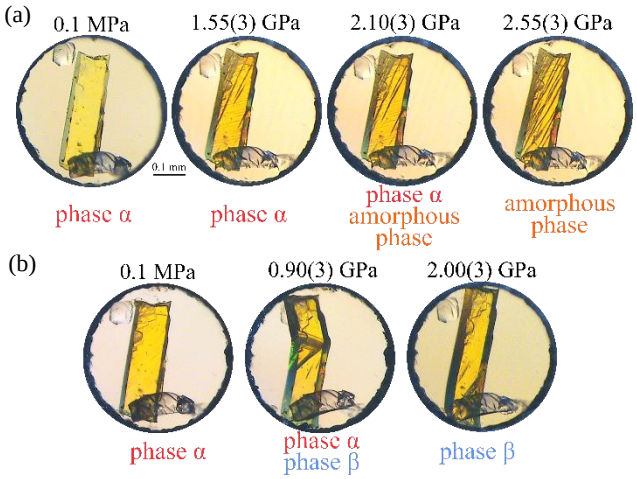

Figure 1. The sample C5-PPB single crystal (a) first compressed rapidly to 1.5 GPa, when the wrinkles mark the onset of amorphization, and then (b) after releasing pressure it was compressed again slowly to 0.9 GPa, where the transition to phase β starts and transition fronts travel through the sample, till it all transforms to the end.

Acknowledgments: This work was supported by funding from the Polish National Science Centre (OPUS 10 No. UMO-2015/19/B/ST5/00262) and by grant POWR.03.02.00-00-I026/16 co-financed by the EU European Social Fund under the Operational Program Knowledge Education Development.

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