

Pressure-induced polymorphism of caprolactam: a neutron diffraction study

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Caprolactam, a precursor to nylon-6 has been investigated as part of our studies into the polymerization of materials at high pressure. It has been studied at ambient pressure and found to exist in only one polymorph.[1-2] Single crystal X-ray and neutron diffraction data have been used to explore the high-pressure phase behavior of caprolactam and we have observed two new high pressure solid forms. The transition between each of the forms requires a substantial rearrangement of the molecules and we observe that the kinetic barrier to the conversion can aid retention of phases beyond their region of stability. Form II of caprolactam shows a small pressure region of stability between 0.5 and 0.9 GPa with Form III being stable from 0.9 GPa to 5.4 GPa. The two high-pressure forms have a catemeric hydrogen-bonding pattern compared with the dimer interaction observed in the ambient pressure Form I. Neither of the high-pressure forms can be recovered to ambient pressure and there is no evidence of any polymerization occurring

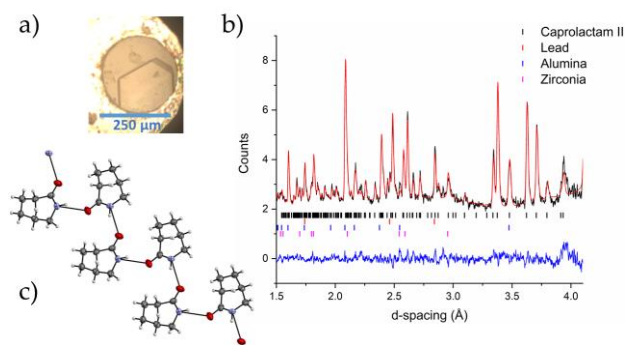


Figure 1. a) crystal of Form II grown from ethyl acetate from Form III crystals on decompression from 3.45 GPa to 0.55 GPa; b) The Rietveld fit of Form II to the data collected at 0.943(11) GPa in 1:1 pentane:isopentane (crystals recrystallized from ethyl acetate); c) The chain motif that is present in Form II of caprolactam.

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