Possible Existence of Two Amorphous Phases of D-Mannitol Related by a First-Order Transition MEN ZHU, JUN-QIANG WANG, JOHN PEREPEZKO, LIAN YU, University of Wisconsin-Madison — We report that the common polyalcohol D-mannitol may have two amorphous phases related by a first-order transition. Slightly above Tg (284 K), the supercooled liquid (SCL) of D-mannitol transforms to a low-energy, apparently amorphous phase (Phase X). The enthalpy of Phase X is roughly halfway between those of the known amorphous and crystalline phases. The amorphous nature of Phase X is suggested by its absence of birefringence, transparency, broad X-ray diffraction, and broad Raman and NIR spectra. Phase X has greater molecular spacing, higher molecular order, fewer intra- and more inter-molecular hydrogen bonds than the normal liquid. On fast heating, Phase X transforms back to SCL near 330 K. Upon temperature cycling, it shows a glass-transition-like change of heat capacity. The presence of D-sorbitol enables a first-order liquid-liquid transition (LLT) from SCL to Phase X. This is the first report of polymorphism at 1 atm for a pharmaceutical relevant substance. As amorphous solids are explored for many applications, polymorphism could offer a tool to engineer the properties of materials. (Ref: M. Zhu et al, J. Chem. Phys. 2015, 142, 244504)