Solid-state refrigeration technology based on caloric effects is promising to replace the currently used vapor compression cycles, due to its numerous potentials for reducing electricity consumption and worldwide emission of greenhouse gases. Recent high-pressure experiments have reported that plastic crystal neopentylglycol (NPG) exhibits colossal barocaloric effects (CBCEs) with record-high entropy changes near room temperature, offering exciting prospects for the field of solid-state cooling through the application of moderate pressures. However, the complete microscopic mechanism remains unestablished so as to further push forward the development and application. Here, we conduct a comprehensive study combing density functional theory calculations (DFT) and molecular dynamical simulations (MD), along with Raman spectroscopy and neutron inelastic scattering measurements on NPG plastic crystals. We reveal that the formation of intermolecular hydrogen bond ladder plays a key role in the orientational order of NPG molecules in monoclinic phase, and the activation barrier of orientational disorder is prominently suppressed owing to the hydrogen bond broken in cubic phase, contributing significantly to the entropy changes which substantially lowers the total Gibbs free energy in the monoclinic-to-cubic phase transition. Furthermore, external pressure affect the vibrational frequencies of O-H stretch mode which directly correlates the strength of hydrogen bond, emerging as a promising strategy of tuning the orientational order-to-disorder that leads to CBCEs at desired temperature range. Our study establishes the atomic-scale origin of plastic crystals with CBCEs and provides important guidance to the design of next-generation solid-state refrigeration technology for practical application.