Understanding the behaviour of phase transitions at high pressure is important experimentally, as high levels of theory are required to predict possible phase boundaries for even simple materials. One material with important real-world applications and little information on its phase boundaries is methanol. Previously, there were three known crystalline structures of methanol, the α and β polymorphs are found at ambient pressure and low temperatures, and the γ polymorph is found at ambient temperature and high pressure.[1-3] The γ phase forms crystallites in liquid methanol at 7 GPa, and through pressure and temperature cycling, a single crystal was determined at 4.01 GPa, crystallising in the P-1 space group. Recently, we identified a new crystalline structure of methanol, found in the monoclinic P21/c space group at 5.09 GPa.[4] This phase, named the ε phase was grown in a diamond anvil cell (DAC) with a single crystal of tetraphenylethylene (TPE) which we believe to have acted as a crystallisation seed, although the specific mechanism is undetermined. The ε-polymorph of methanol is unique, as it is the first determined structure of methanol to feature a 4-membered hydrogen bonded ring motif. This is notable, as in the gas phase methanol primarily exists within a 3-membered ring structure, and although previously ring structures in the solid state have been proposed through ab initio calculations, the α, β, and γ polymorphs do not contain any hydrogen bonded ring motifs.

Using a crystallisation seed, methanol was able to crystallise at a lower pressure than the pressure required to form crystallites for the γ phase, and formed as a large single crystal that filled the entire sample chamber of the DAC. The experiment was repeated multiple times, with methanol reliably crystallising at pressures between 5 and 6 GPa, using either TPE or a piece of glass as the crystallisation seed, showing that the composition of the seed did not affect the crystallisation pressure. This new method of growing a crystal of a low melting compound is useful, as being able to lower the crystallisation pressure allows thermal cycling of the material to form a single crystal to be conducted at lower temperatures. This will allow for the structure determination of materials that have low decomposition temperatures, which may decompose while thermal cycling. This could prove useful in the liquid natural gas industry and in astrochemistry, as the formation of crystals of low melting compounds occur frequently in these fields.