As a result of chemical, temperature or pressure drivers, perovskite-like materials (with general chemical formula ABX$_3$) can adopt a wide range of different structural distortions away from the aristotype cubic structure. The structure may be distorted via three routes; a) distortion of the BX$_6$ octahedra (for example, a Jahn-Teller distortion), b) a tilt (or rotation) of the rigid BX$_6$ octahedral units and c) A-site cation displacements. These distortion mechanisms drive many of the resultant electronic, magnetic, and other physical properties of these materials. By application of temperature or pressure it is possible to drive even further the structural distortions to both higher and lower symmetry. Perovskite-like materials undergo a series of structural transitions with either a drive towards higher or lower symmetry as a function of temperature and pressure and the exact sequence can be understood by Landau theory and the direction of which can be predicted using qualitative methods.

Neutron diffraction provides a unique insight into the crystallographic structure of perovskite related materials at extreme conditions. It allows the accurate determination of atomic positions of generally lighter X elements in the presence of heavier A and B elements or when elements of similar atomic number are present in the same material. We present two studies of archetypal perovskites BaTiO$_3$ and LaCoO$_3$ in which we have determined the variation of crystallographic structure as a function of pressure and temperature.

We have mapped the phase diagram of BaTiO$_3$ more extensively than previous attempts using high-pressure neutron-powder diffraction [1]. The mapping of the phase diagram has been performed using isothermal compression at fixed temperatures (175, 225, 290, 480 K) within each of the known crystallographic phases, up to $\sim$6 GPa using a large volume press (Figure 1). The crystallographic structure of each phase has been measured, and the determined absolute atomic displacements of all atoms within the cell have provided detailed information on the order of the phase transitions observed, and the behaviour of the ferroelectric dipole moment.

We also report a high-pressure variable-temperature neutron diffraction study of LaCoO$_3$, from ambient to 6GPa at 120, 290, and 480 K [2]. We see no evidence for previously-reported discontinuities in the Co–O and La–O distances in the pressure and temperature ranges studied. Such discontinuities have previously been attributed to the well-documented spin-state transition of the Co$^{3+}$ cation, we conclude that manifestations of the electronic configuration of LaCoO$_3$ are not evident in the crystallographic structure upon pressurisation.