In this work we present the synthesis and structure-property investigation of anhydrous low porosity borophosphates [1] BPO4 and porous (NH4)0.5M1.25(H2O)2)(BP2O8)(H2O)0.5 M = Co(II), Mn(II) and NH4Fe[BP2O8(OH)] phases. Cristobalite-type BPO4 crystallizes in the tetragonal lattice, space group I-4 (No. 82) [2]. Variable-Temperature Powder X-ray diffraction (VT-PXRD) patterns for these material were analysed by the sequential and parametric Rietveld refinement [3] protocols. Both methods were used to determine the temperature dependency of the lattice parameters and linear thermal expansion coefficient. Whereas the lattice parameters were refined freely in the sequential method, the individual cell parameters were described using an empirically derived function in the parametric method. Both refinement protocols reveal significant anisotropy along the a- and c- axis as a function of temperature, with thermal expansion coefficients of 10.6 x10-6 /°C and 2.83 x10-6 /°C, respectively. Structural changes accompanying this thermoresponsive behaviour will be discussed, including the variation of the interatomic distances and P-O-B (inter-polyhedral angle, figure 1) with temperature. The open framework (NH4)0.5M1.25(H2O)2)(BP2O8)(H2O)0.5 M = Co(II) (1a), Mn(II) (1b) and NH4Fe[BP2O8(OH)] (2) phases were synthesized under mild hydrothermal methods at 180°C. The crystal structure of the isostructural (1a) and (1b) phases were refined in the hexagonal lattice, space group P65 (no. 170) and compound (2) in the monoclinic lattice, space group P21/c (no.14). Both (1a) and (1b) phases consists of NH4+ and H2O molecules located within the helical channels running along the [001] direction with compound (2) consisting exclusively of NH4+ molecules located within the helical channels running along the [100] direction. Thermoresponsive investigation conducted by TGA analysis reveal a five, four and three step mass loss process for compounds (1a), (1b) and (2) respectively, with the final step observed at 500-700°C range. Preliminary VT-PXRD results of these compounds will also be presented.