Thermodiffractometry study of (NH4)0.5Co1.25(H2O)2[BP2O8].(H2O)0.5 with CZP framework topology

Four CZP (chiral zincophosphate) zeolite topology compounds with the general formula MIMII(H2O)2[BP2O8].yH2O (MI = Na, NH4 and MII = Mn, Co, y = 0.5, 1) have been prepared under mild hydrothermal conditions (at 180 ℃). Such microporous compounds with aesthetically interesting crystal structures [1] can have interests in fields such as catalysis, storage, separation and ion-exchange. One compound of this family, (NH4)0.5Co1.25(H2O)2[BP2O8].(H2O)0.5, has been studied by variable temperature high resolution powder X-ray diffraction experiments carried out from 298 to 1073 K. Complete Rietveld refinements were achieved by combining stereochemical restraints of the powder diffraction data. At room temperature, this compound crystallizes in the P65 (No. 170) space group with Z = 4 belonging to the hexagonal system. The unit cell parameters obtained were: a = 9.4330(2) Å, c = 15.5203(2) Å, V = 1196.01(5) Å³. The crystal structure consists of a helical anionic framework, ∞[BP2O8]3−, composed of corner sharing BO4 and PO4 tetrahedra. Water and ammonia molecules are found within the helical channels running along the [001] direction. This compound undergoes a series of dehydration, de-ammoniation (analysis augmented by thermogravimetric experiments) and finally diminished sharp Bragg peaks indicating loss of long-range order. Total scattering analysis [2] was applied for the first time coupled to the above conventional structural refinement approach to further unravel this gaseous dissociation and temperature induced amorphization of the rigid host structure. Preliminary X-ray PDF analysis indicates that the local coordination environment found in the low temperature crystalline phases also persists in the amorphous phase.


Keywords: borophosphates, high-temperature, in-situ synchrotron XRPD

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