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Progresses on the structural chemistry of the actinide phosphates

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Data on structure and properties of actinide phosphates are needed for the development of phosphate ceramics envisaged as possible hosts for long-term sequestration of actinides generated by the nuclear fuel cycle. In that aim an extensive study on the crystal structures, thermal stability, and thermodynamic properties on a number of crystalline trivalent and tetravalent actinide phosphates was undertaken.
PuPO₄ with monazite structure was obtained and characterized in terms of thermal stability and thermal expansion. The decomposition of PuPO₄ to Pu₂O₃ was observed at 1573 K. Its high-temperature heat capacity is to be measured up to 1500 K by drop calorimetry.
M^{II}Np(PO₄)₂ (M^{II}= Ca, Sr, Ba) were obtained by solid state reaction. The influence of ionic radius of M^{II} (M^{II}= Ca, Sr, Ba) on the crystal structure is further discussed. Pure phase of CaNp(PO₄)₂ with monazite structure (P2/n) was obtained by solid state reaction after several thermal treatments and readjustments in stoichiometry. The lattice parameters are a= 6.65085(3) Å, b= 6.83893(5) Å, c= 6.35378(3) Å, and β= 104.117(9) o. SrNp(PO₄)₂ seems to adopts an inedited double-monazite structure with a= 6.895 Å, b= 13.272 Å, c= 6.892 Å, and β= 99.22 o, probably due to the Sr/Np ordering responsible for the non-negligible reflections with k = 2n +1; in this case, the two cations seem too different in size to allow disorder, contrarily with CaNp(PO₄)₂. Pure BaNp(PO₄) with monoclinic C2/c was also obtained. Its structure was inferred with the one reported for RbEu(SO₄)₂, the lattice parameters being a= 12.69095(13) Å, b= 5.36179(6) Å, c= 9.40949(11) Å, and β= 102.516(68) o. The pattern looks similar with the one previously found for the Th-counterpart.

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