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Synthesis and Crystal Structure of NZP-Type Thorium−Zirconium Phosphate

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Microcrystals of $Th_{1/4}Zr_2(PO_4)_3$ were synthesized by thermal treatment (900 °C) of the material obtained using sol−gel technology (including organic complex formation and etherification). Their structure [hexagonal, $P\bar{3}c$, $a = b = 8.7311(4)$ Å, $c = 23.309(2)$ Å] includes the three-dimensional $[Zr_2(PO_4)_3]^-$ NASICON-type network and extraframework 6-fold-coordinated thorium(IV) cations.

The immobilization in ceramic materials for an underground repository can be considered one of the options for the management of long-lived and highly active radionuclides.[1−3] In this field, our research group recently reported both the synthesis and structural characterization of the first inner-transition-metal monohydrogenphosphate, $Th(HPO_4)_2 \cdot H_2O$,[4] following an experimental procedure (hydrothermal synthesis with H_3PO_3 as the source of phosphorus) similar to the one that we used previously in the well-crystallized $Th_2(PO_4)_2(HPO_4) \cdot H_2O$ preparation,[5] which is the precursor (by thermal treatment) of β-$Th_4(PO_4)_4P_2O_7$.[6,7] This material is a promising ceramic for the specific immobilization of tetravalent actinides because it allows the incorporation of large amounts of uranium, neptunium, or plutonium by the substitution of thorium into its crystal structure,[8,9] exhibits a valuable sintering capability,[10] and has an interesting long-term behavior (including resistance to dissolution and/or irradiation).[11−13] More recently, by using a very simple experimental strategy, we reported the synthesis of the first structurally described ammonium−thorium phosphates, $(NH_4)_2Th(PO_4)_2 \cdot H_2O$ and $NH_4Th_2(PO_4)_3$.[14] The structure of $NH_4Th_2(PO_4)_3$ is similar to their alkaline analogues $M^IM^{IV}{}_2(PO_4)_3$ (M^I = Li, Na, K, Rb, Cs; M^{IV} = Th, U, Np, Pu).[15−17] It is built with PO_4 monophosphate groups and ThO_9 polyhedra sharing their apexes and their edges, thereby forming a three-dimensional framework. This is a structure different from that adopted by the $NaZr_2(PO_4)_3$ structural family (NZP, NASICON-type) in which the transition metal is hexacoordinated.[18,19]

The NASICON family of ceramics is interesting because of their attractive physical and chemical properties.[20−22] They have received considerable attention because of their low thermal expansion, high temperature stability, and superionic conductivity and as ceramic materials for the immobilization of radionuclides.[23−26] The crystal structure of the prototype NZP[27] is constructed of a stable and flexible three-dimensional skeleton $[Zr_2(PO_4)_3]^-$, also built by tetrahedral PO_4 and octahedral ZrO_6 shared by their apexes, which allows numerous ionic substitutions at various lattice sites, giving as

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a result a large number of crystalline compounds, which contain atoms differing in the oxidation state (from 1+ to 5+ in the framework and from 1+ to 4+ in voids), electronegativity, and ionic radii of cations.[26] To our knowledge, only a limited number of NZP-type $M^IM^{IV}_2(PO_4)_3$ (M^{IV} = tetravalent actinide element) compounds are reported (M^I−M^{IV} = K−U, Rb−U, Rb−Np, K−Pu, Rb−Pu).[28−31] In addition, the existence of several NZP-type compounds with extraframework tetravalent actinides, $M^{IV}_{1/4}Zr_2(PO_4)_3$ (M^{IV} = Th, U, Pu), has also been proposed,[32] although their structural data have still not been reported. Therefore, it seems necessary to begin filling this scientific hole with thorium compounds (thorium is the actinide usually used for monitoring the behavior of transuranide elements with very high radioactivity on the basis of its lower specific activity and despite its simpler redox behavior). In this study, microcrystals of $Th_{1/4}Zr_2(PO_4)_3$ were obtained by a sol−gel experimental procedure. The structure of this compound, the first structurally reported NZP-type material with hexacoordinated extraframework actinide(IV) cations, was reached by synchrotron powder X-ray diffraction (XRD). Its hexagonal structure was refined in the space group $P\bar{3}c$ (No. 165) with the following final unit cell parameters: $a = b = 8.7311(4)$ Å, $c = 23.309(2)$ Å, $V = 1538.8(2)$ Å.[3]

The structure of $Th_{1/4}Zr_2(PO_4)_3$, illustrated in Figure 1, can be described as the classical three-dimensional $[Zr_2(PO_4)_3]^-$ NASICON-type network. The atomic distances are conventional (Zr−O = 1.86−2.35 Å; P−O = 1.51−1.54 Å). The thorium(IV) cations are surrounded by six oxygen atoms so that antiprism cavities are formed, which are created by the framework of the ZrO_6 octahedra and PO_4 tetrahedra. The Th−O distances observed (2.64 Å) are larger than the sum of the ionic radii (1.08 + 1.35 Å)[33] for a 6-fold-coordinated thorium(IV) cation, leading consequently at the same time to an anomalous high thermal factor [0.308(8)] and a low bond valence sum (the 1.7 value is obtained from the *VaList* program).[34] This situation, previously described in $M_{1/3}Zr_2(PO_4)_3$ (M = La, Eu, Yb) NZP-type compounds,[35−37] is related to the size of the O_6 cavity, which is too large to well accommodate the thorium(IV) cations whatever their size.

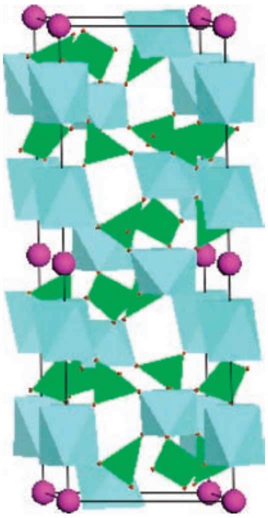

Figure 1. Projection of the structure of $Th_{1/4}Zr_2(PO_4)_3$ along the *a* axis with the *c* axis vertical (PO_4, tetrahedra; ZrO_6 octahedra; Th, purple circles).

In conclusion, giving the potential applications of actinide phosphates in the field of radionuclide immobilization, the structural characterization of this compound should encourage researchers to search for structural data from related compounds, in particular $M_{1/4}Zr_2(PO_4)_3$ (M = U, Np, Pu), sintering capability, and behavior during leaching tests or irradiation experiments.

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Supporting Information Available: Crystallographic data in CIF format, synthesis, experimental procedures, and details on the crystal structure. This material is available free of charge via the Internet at http://pubs.acs.org.

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