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Article

$SrNp(PO_4)_2$: an Original Ordered Modification of Cheralite

Karin Popa,[†] Gilles Wallez,*[,‡] Philippe E. Raison,[§] Damien Bregiroux,[‡] Christos Apostolidis,[§]
Patric Lindqvist-Reis,[⊥] and Rudy J. M. Konings[§]

[†]*Department of Chemistry, Al. I. Cuza University, 11 Carol I Boulevard, 700506 Iasi, Romania,* [‡]*Laboratoire de Chimie de la Matière Condensée de Paris, UPMC Université Paris 06, CNRS-UMR 7574, ENSCP-ParisTech, 11 rue Pierre et Marie Curie, 75231 Paris Cedex 05, France,* [§]*European Commission, Joint Research Centre, Institute for Transuranium Elements, P.O. Box 2340, 76125 Karlsruhe, Germany, and* [⊥]*Institute for Nuclear Waste Disposal, Karlsruhe Institute of Technology, Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany*

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The new compound $SrNp(PO_4)_2$ (orthorhombic *Cmca*) has been synthesized by a solid-state reaction and its crystal structure solved ab initio and refined by Rietveld analysis. Though chemically and structurally related to the cheralite $CaTh(PO_4)_2$, $SrNp(PO_4)_2$ shows alternate layers of SrO_{10} and NpO_8 polyhedra instead of a disordered array of 9-fold polyhedra. Raman and IR spectroscopic measurements also account for ordered cations. This novel structural type allows one to explain the boundaries of the cheralite domain in terms of the cation size and can be proposed as an archetype for a series of other actinide-bearing phosphate compounds.

Introduction

Under normal conditions, $M^{II}M'^{IV}(PO_4)_2$ double phosphates of medium- to large-size cations crystallize in two main families: layered yavapaiite-related structures made of $M^{II}O_{10}$ (M^{II} = Ca, Sr, Ba) and $M'^{IV}O_6$ polyhedra (M'^{IV} = Ge, Sn, Ti, Zr, Hf),[1−5] and cheralites, from the archetype $CaTh(PO_4)_2$.[6,7] A third form, observed only for $PbSn(PO_4)_2$, results from the stereochemically active lone pair of Pb^{II}.[8]

Formerly known as brabantite, cheralite is an analogue of monazite $CePO_4$ (also $P2_1/n$), made of a phosphate tetrahedron and a unique 9-fold polyhedron for disordered cations Ca^{II} and Th^{IV}.[9−11] The early work of Rose has evidenced several other $M^{II}Th(PO_4)_2$ cheralites with cations slightly smaller or larger than Ca^{II} (Cd^{II}, Sr^{II}, and Pb^{II}) but not with Ba^{II}, probably being too bulky.[6]

Because of their remarkable durability both thermally (up to 1200 °C)[12,13] and chemically[14−19] and the possibility of fabricating and sintering monazite−cheralite solid solutions,[20−24] these mineral derivates have been the subject of intensive studies during the past years and figure as interesting candidates for the long-term immobilization of minor actinide radwastes.

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*To whom correspondence should be addressed. E-mail: gilles.wallez@upmc.fr. Tel.: +33 153737946. Fax: +33 146347489.

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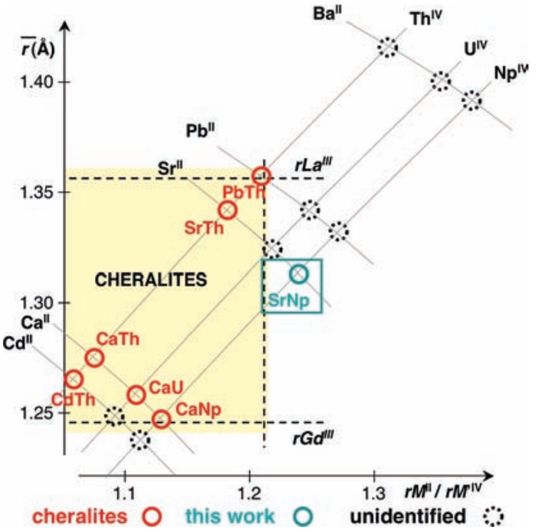

Figure 1. Steric criteria for $M^{II}M'^{IV}(PO_4)_2$ (M^{II} = Cd, Ca, Sr, Pb, Ba; M'^{IV} = Np, U, Th) evidencing the domain of cheralite structures.

As for the trivalent transuranium cations (Pu^{III}, Am^{III}, and Cm^{III}) in monazite, the partial substitution of 4-fold species (U^{IV}, Np^{IV}, and Pu^{IV}) for Th^{IV} has been shown to be feasible;[23,25–27] however, the only fully substituted cheralites known are $CaU(PO_4)_2$ and $CaNp(PO_4)_2$ (CNP). Tetravalent plutonium was only introduced in limited amounts in a $Ca(Np,Pu)(PO_4)_2$ solid solution because of its propensity to reduce to Pu^{III}.[28] As will be seen in the following, no other compositions synthesized to date yielded cheralites, and none of them could be characterized.

The dissimilarity between the yavapaiite and cheralite structures reflects the strong difference in terms of radius between the p- and d-block 4-fold cations, on the one hand ($r_C \leq 1.03$ Å in coordination IX, tending to VI, "crystal radius"), and that of Th^{IV} (r = 1.23 Å, IX), on the other hand.[29] Except for Ce^{IV} (1.16 Å, IX), which reduces spontaneously to Ce^{III} when combined with phosphate, only the above-cited transuranium elements (r = 1.15−1.19 Å, IX) occupy the intermediate zone of this size scale. For this reason, as well as for the very specific radiological working conditions, the crystal chemistry of transuranium-based $M^{II}M'^{IV}(PO_4)_2$ compounds remains poorly known and difficult to predict. To date, the most reliable predictive model for cheralites combines the two steric criteria reported in Figure 1: the mean radius $(r_{M^{II}} + r_{M'^{IV}})/2$, which must be comparable to those of the monazite-compatible lanthanides (La^{III}−Gd^{III}), and the $r_{M^{II}}/r_{M'^{IV}}$ ratio, whose maximum lies between the values of $PbTh(PO_4)_2$ (cheralite) and $SrU(PO_4)_2$ (non-cheralite).[9,10]

$SrNp(PO_4)_2$ (SNP), which has never been reported before, lies beyond this limit. The investigation of this compound has been undertaken with the double aim of exploring the actinide-loaded end member of a potential matrix for radioactive wastes and of improving the knowledge of the structural behavior of one of these rare cations.

Table 1. Main Acquisition Parameters, Refinement, and Crystallographic Data for SNP

temperature	20 °C
diffractometer, scan mode	Siemens D8, Bragg−Brentano
anode, monochromator	Cu Kα (40 kV, 40 mA), Ge(111)
detector	LinxEye
scan range, step, total time	$12.00 < 2\theta < 140.00°$, 0.00826°, 36 h
reflns measd	642
profile (model)/intensity-dependent parameters	11 (pseudo-Voigt)/27
conventional reliability factors	$R_p = 0.037$, $R_{wp} = 0.052$, $R_{exp} = 0.020$, $\chi^2 = 6.9$, $R_{Bragg} = 0.037$
space group, system	*Cmca* (No. 64), orthorhombic
cell parameters	a = 10.5045(2) Å b = 8.9360(2) Å c = 13.2752(2) Å
formulas per cell, calcd density	Z = 8, 5.489

Experimental Section

The experimental work was carried out in specifically designed gloveboxes for radioactive materials at the Institute for Transuranium Elements (Karlsruhe, Germany).

Synthesis. A total of 49.6 mg of reactor-grade $^{237}NpO_2$ was mixed and ground with 36.89 mg of $Sr(NO_3)_2$ (Alfa Aesar, a stoichiometric amount) and 55.25 mg of $(NH_4)_2HPO_4$ (Alfa Aesar, 20% excess) in an agate mortar under nitrogen and then heated for 24 h at 1108 °C under argon (purity 4.6, heating and cooling at 200 °C h^{-1}). The obtained powder was thoroughly ground and heated once more for 24 h at 1212 °C (at the same rate and atmosphere). We obtained 77.00 mg of final product.

X-ray Diffraction (XRD). Room temperature XRD was performed for structure analysis. The main acquisition parameters, refinement, and crystallographic data are reported in Table 1. To reduce the background, a silicon wafer was used as the holder for the sample (about 50 mg). A similar apparatus equipped with an Anton Paar HTK-2000 heating chamber fitted with a platinum heating strip and a 6° Braun detector was used for high-temperature XRD (HTXRD; room temperature to 1200 °C, every 100 °C), intended to observe possible phase transitions.

Despite some similarities with those of monazites and cheralites, the XRD pattern of SNP showed several other strong peaks that called for a reinterpretation of the lattice. The cell found using *Dicvol*[30] is orthorhombic, and the diffraction intensities, extracted with *Fullprof*[31] in Le Bail's mode, showed systematic extinctions consistent with space group *Cmca*. Patterson synthesis, performed using *SHELXS*,[32] revealed Np in a unique site, and then the other atoms were located by Fourier syntheses. Soft constraints were applied on the P−O distances during the Rietveld refinement. No impurity peaks stronger than $0.01I_{max}$ were observed. Bond lengths are reported in Table 2. Note the short Np−O12 distance due to the 2-fold coordination of O13, whereas all other oxygen atoms are bond to three or four cations.

IR Spectra. A Perkin-Elmer 2000 Fourier transform infrared (FT-IR) spectrophotometer was used to record IR spectra of SNP and CNP at room temperature. The samples were diluted in KBr or polyethylene and pressed to tablets for recording of mid- and far-IR spectra, respectively.

Raman Spectra. Raman spectra of SNP and CNP powders were measured at room temperature using a Bruker Senterra

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Table 2. Bond Lengths (Å) in SNP[a]

Sr−O11 (×2)	2.604(4)
Sr−O11 (×2)	2.702(4)
Sr−O13 (×2)	2.767(2)
Sr−O21 (×2)	2.712(4)
Sr−O22 (×2)	2.659(4)
Np−O11 (×2)	2.480(3)
Np−O12	2.175(3)
Np−O13	2.412(4)
Np−O21 (×2)	2.261(3)
Np−O22 (×2)	2.278(3)
P1−O11 (×2)	1.542(3)
P1−O12	1.564(3)
P1−O13	1.563(4)
P2−O21 (×2)	1.560(4)
P2−O22 (×2)	1.561(3)

[a] Sr−O distances are paired through a [001] 2-fold axis, Np−O and P1−O through a (100) mirror, and P2−O through a [100] 2-fold axis. P−O distances are under soft constraints.

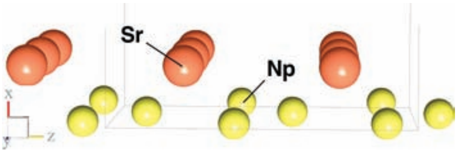

Figure 2. Arrays of Np^{IV} ($x = 0$) and Sr^{II} ($x = {}^1/_4$) in SNP.

dispersive Raman microscope at 785 nm and 25 mW. The spectral resolution was 4 cm^{-1}. For each compound, eight spectra were averaged and background-corrected using the *OPUS* software from Bruker.

UV/Vis/Near-IR Spectra. A Perkin-Elmer Lambda 9 UV/vis/near-IR spectrophotometer was used to record room temperature electronic absorption spectra of SNP and CNP. Small amounts of the samples were diluted in a polyethylene powder and pressed to tablets.

Results and Discussion

The structural determination evidences specific sites for Sr^{II} and Np^{IV}. To ascertain the difference with disordered cheralite, a complementary Rietveld refinement was made to introduce a disorder rate x as a variable in the two heavy-cation sites with occupation models $Sr_{1-x}Np_x$ and $Np_{1-x}Sr_x$, in accordance with the stoichiometry and supposing a 100% total occupancy of both sites. The result ($x = 0.017$) confirms the hypothesis of a fully ordered structure and allows one to locate Sr^{II} and Np^{IV} respectively in 10- and 8-fold oxygen polyhedra. Despite this, as well as a higher symmetry and a quadruple volume, the SNP unit cell is related to the monazite−cheralite one, with $a_{SNP} = a_{mon} - c_{mon}$, $b_{SNP} = a_{mon} + c_{mon}$, and $c_{SNP} = 2b_{mon}$.

Np and P1 share the mirror plane at $x = 0$; Sr and P2 (both on 2-fold axes) are nearly coplanar (respectively $x = {}^1/_4$ and 0.227). In these (100) layers, Np forms a pseudohexagonal array, whereas that of Sr is nearly rectangular (Figure 2).

Compared to the classical cheralite structure in which both big cations form equivalent MO_9 polyhedra,[11] SNP exhibits differentiated cation environments. Whereas the Ca/ThO_9 polyhedron is strongly elongated, with a capping oxygen 0.35 Å further from the cation than the outer corner,[11] SrO_{10} (symmetry C_2) and NpO_8 (symmetry C_v) are rather regular-shaped, with a clear distance gap between in- and out-of-polyhedron oxygen atoms (1.42 Å for Sr and 1.31 Å for Np). Conceivably, the Np site could also accommodate U^{IV} and Pu^{IV} cations because of their similar sizes and common occurrence in 8-fold coordination. According to Figure 1, several other actinide-bearing phosphates can be envisioned with the SNP archetype structure, namely, $PbU(PO_4)_2$, $PbNp(PO_4)_2$, and $SrU(PO_4)_2$.

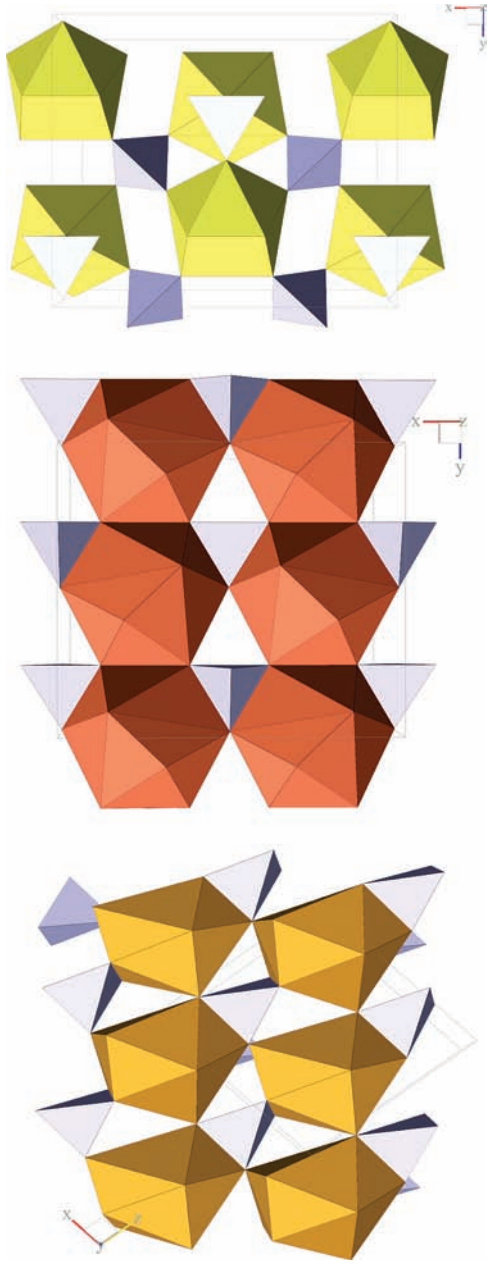

Figure 3. Charge and radius differences resulting in two different arrays for cations Sr^{II} and Np^{IV}, from top to bottom: (a) (001) SNP layer with SrO_{10} (yellow) and PO_4 (blue); (b) (001) SNP layer with NpO_8 (red) and PO_4; (c) (010) cheralite layer with Ca/ThO_9 (amber) and PO_4.

To allow an easy comparison with cheralite, the most convenient way to describe this structure is to consider a dense succession of Sr^{II} and Np^{IV} layers along the c axis. In the first ones (Figure 3a), the SrO_{10} polyhedra are connected together via edges and corners and in the same way to phosphate tetrahedra. This connection is allowed by the low charge and high radius of the cation; the resulting array is not very different from the (010) layer of $CaTh(PO_4)_2$ (Figure 3c).

Next along the c axis, Np^{IV}, smaller and having a higher charge, forms corrugated layers of independent NpO_8 polyhedra that share only corners with phosphates (Figure 3b). SrO_{10} and NpO_8 polyhedra of adjacent layers are connected by faces, building infinite zigzag chains, as the Ca/ThO_9 units do in cheralite.

The Inorganic Crystal Structure Data Base (Fachinformationzentrum Karlsruhe) was browsed in a search for other $MM'(XO_4)_2$ compounds (X = P, As, V, S) involving MO_{10} and $M'O_8$ polyhedra, but no isotype was found, revealing this structure as fully original. However, because of some similarities, and despite noticeable differences, SNP can be seen as an ordered modification of the cheralite type. (Further details of the crystal structure investigation may be obtained from Fachinformationzentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany [fax (+49)7247-808-666; e-mail crysdata@fiz-karlsruhe.de, weblink http://www.fiz-karlsruhe.de/request_for_deposited_data.html] on quoting CSD number 421421.) Because HTXRD did not reveal any phase transition between room temperature and 1100 °C, we can conclude that the $r_{Sr^{II}}/r_{Np^{IV}}$ ratio is high enough to block any disordering mechanism, thus accounting for a very stable crystal structure. The thermal expansion, measured by Rietveld analysis, appears to be roughly isotropic ($\alpha_a = 8.2 \times 10^{-6}\,°C^{-1}$, $\alpha_b = 7.1 \times 10^{-6}\,°C^{-1}$, and $\alpha_c = 9.3 \times 10^{-6}\,°C^{-1}$, with a mean linear $\alpha_l = 8.2 \times 10^{-6}\,°C^{-1}$, 30−1000 °C range). This value is somewhat lower than those of the typical cheralite $CaTh(PO_4)_2$ ($\alpha_l = 10.6 \times 10^{-6}\,°C^{-1}$) and monazite isotype $NdPO_4$ [$\alpha_l = 9.4 \times 10^{-6}\,°C^{-1}$; $r_{Nd^{III}} \approx (r_{Sr^{II}} + r_{Np^{IV}})/2$].[13,33]

To our knowledge, the only ordered form of cheralite observed to this date is the low-temperature modification of $CaU(PO_4)_2$,[34] a monazite-like array in which the cation environments remain very similar to each other but with a lower coordination (CaO_8 and UO_8) and shared edges in the (010) layers. This results obviously from the low mean radius of Ca^{II} and U^{IV}, which places the compound near the lower limit of the cheralite domain (Figure 1). The ordering in that compound is probably charge-driven, different from that of SNP, which seems to be size-driven.

The nearest parent of SNP in terms of cation size is its uranium counterpart, $SrU(PO_4)_2$, reported by Kitaev et al., who observe "additional reflections of impurity phases" in the cheralite-like diffraction pattern, even after prolonged heating (800 °C, 400 h).[35] Besides, $BaTh(PO_4)_2$, first prepared by Volkov et al., has been later reported by Brandel et al. and Montel et al.[7,36,37] The latter authors proposed a "double monazite" (doubled *a* parameter) of unknown structure, different from that of Orlova, who considered a non-monazite structure with a highly probable ordered accomodation of Ba and Th. Volkov et al. and Orlova also reported a complex polymorphism, with no less than four modifications in the temperature range 650−1550 °C.[36,38] So, these still unidentified compounds in which the cations do not comply with the above-mentioned steric criteria present cheralite-like diffraction patterns with extra peaks that could be nothing but hints for some form(s) of ordering, similar to or different from SNP. Actually, an in-depth structural analysis should be undertaken to identify these modifications and allow global insight into this family of compounds.

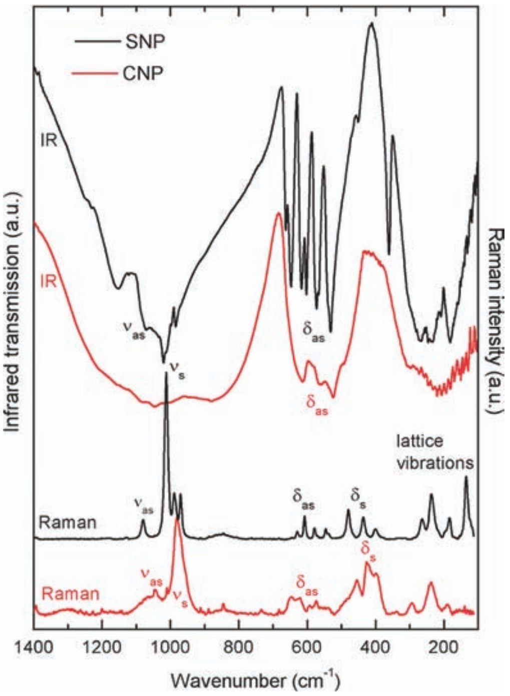

Figure 4. Room temperature IR and Raman spectra of SNP and CNP.

IR, Raman, and Np^{4+} ($5f^3$) electronic absorption spectroscopic methods have been used to learn more about differences and similarities between the cheralite structure, CNP, and its ordered modification, SNP. The IR and Raman bands of these compounds (Figure 4) result largely from internal vibrations of the phosphate groups and lattice vibrations, several of which are both IR- and Raman-active, in agreement with the compounds' relatively low crystal symmetry. We assign the intense band at 1012 cm^{-1} in the SNP Raman spectrum to the symmetric stretching mode (ν_s), the weak band at 1080 cm^{-1} to the antisymmetric stretching mode (ν_{as}), and the bands in the regions 400−480 and 530−665 cm^{-1} to the symmetric (δ_s) and antisymmetric (δ_{as}) bending modes, respectively. The lattice vibrations below ~360 cm^{-1} involve different SrO_{10} and NpO_8 vibrational modes. The assignment for CNP is analogous, although the bands are appreciably broader and some of them notably shifted compared to the corresponding bands of SNP. It should be noted, however, that the CNP spectra are almost identical with those of $CaTh(PO_4)_2$ and $CaU(PO_4)_2$, both monoclinic, and with the cheralite structure.[11,20]

In a previous study, it was concluded that the broadening of the ν_s and ν_{as} bands of $CaTh(PO_4)_2$ was due to a distortion of the tetrahedral geometry of the PO_4^{3-} groups caused by the substitution of Ca^{2+} and Th^{4+} for the rare-earth ions of monazite.[11] This explanation would account for the equally broad bands of CNP, which also feature a significant distortion of the PO_4^{3-} ions, as can be seen by the large range of P−O distances, 1.52−1.57 Å. Consequently, the comparatively small distortion in SNP is consistent with its narrow IR and Raman bands (cf. Table 2 and Figure 4).

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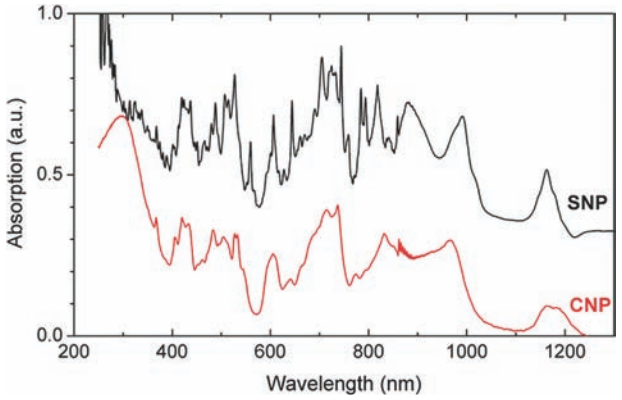

Figure 5. Room temperature Np^{4+} $5f^3$ electronic absorption spectra of SNP and CNP.

The absorption bands of SNP and CNP in the region 300−1300 nm (Figure 5) are entirely due to the $5f^3$ electronic transitions of Np^{4+} in these compounds. This was checked by recording spectra of the corresponding Th^{4+} $5f^0$ compounds, which showed negligible absorption in this region. Overall, the two spectra are comparable; they contain the characteristic Np^{4+} bands present in the Np^{4+}(aq) spectrum, for example;[39] however, SNP has much narrower bands than CNP, in analogy with the IR and Raman results. Because the $5f^3$ electronic absorption spectra monitor the local NpO_8 and NpO_9 structures in SNP and CNP, respectively, the rather broad bands of CNP may therefore be due to the presence of NpO_9 moieties with slightly different cation environments, whereas the narrow bands of SNP account for NpO_8 moieties of very similar or identical geometries in a highly ordered structure.

Actually, $CaTh(PO_4)_2$ seems to be the only thorium-based cheralite that preserves its structure after substituting An^{IV} minor actinides for Th^{IV}, as a result of a good steric compatibility of Ca^{II} with An^{IV}, and even Pu^{IV} in limited rates. Nevertheless, the discovery of this new ordered modification, just beyond the expected boundary of cheralites, opens perspectives for the improvement of this material. The existence of specific environments for both cations, likely increasing the stability, could lead to the design of new host matrixes for actinides. However, the structure of SNP appears less compact (155.7 $Å^3$ per formula) than that of $NdPO_4$ (145.6 $Å^3$ per two formulas) despite a mean radius of cations of 1.31 Å (Sr^{II}, 1.45 Å; Np^{IV}, 1.17 Å; extrapolated value) similar to that of Nd^{III}, 1.30 Å.[40]

At last, because SNP is structurally different from its thorium counterpart, significant differences in physical and chemical properties can be expected. So, from a crystal chemistry point of view, this study highlights the limitation of Th^{IV} as a low-radioactive surrogate for An^{IV} minor actinides in phosphate compounds because of its larger radius. Unfortunately, whereas a size-matching rare-earth surrogate can be found for each An^{III} cation, stable and inert M'^{IV} species with radii comparable to those of An^{IV} simply do not exist. This calls for further investigations.

Conclusion

The difference in size between Sr^{II} and Np^{IV} appears as the driving force that orders the cations in SNP, making this unique structure clearly suitable for tetravalent minor actinides, perhaps more than the true cheralite form. Further investigations will be carried out to improve our knowledge of this compound. Should they be successful, a careful exploration of the terra incognita that lies beyond the borders of true cheralites could prove highly interesting and reveal isotypes of SNP.

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