Phosphates

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The First Structure of a Cerium(IV) Phosphate: Ab Initio Rietveld Analysis of $Ce^{IV}(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$**

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Since the investigations by König and Alberti in the late 1960s and those by Clearfield in the 1970s, several studies have continued to show that cerium(IV) phosphates (CePs) are interesting inorganic materials for cation exchange, amine intercalation, trapping of radioactive elements, and proton conduction.[1–12] Very recently, cerium(IV) phosphate nanotubes have also been reported.[13] Compared with zirconium, titanium, and tin phosphates, which are well-documented materials used in various fields (ion exchange, intercalation, proton conduction, heterogeneous catalysis, molecular sorption),[14] CePs appear to be much more complex. While the former exhibit two well-characterized lamellar structures, that is, $Zr(HPO_4)_2{\cdot}H_2O$ (α-ZrP)[15] and $Zr(H_2PO_4)(PO_4){\cdot}2H_2O$ (γ-ZrP),[16] based on six-coordinate metal centers, cerium(IV) phosphates appear to adopt several crystalline structures, with P/Ce ratios ranging from 1.1:1 to 3.0:1.[1–12] Despite some efforts and evidences that the structures do not correspond to the α- or γ-ZrP types,[7,9] all these cerium(IV) phosphates structures have remained unknown until now. This lack of information has often made the interpretation of results much more difficult or even impossible. Moreover, in some cases, the chemical composition remains a matter of debate. Indeed, according to its powder X-ray diffraction pattern a unique crystalline compound has, depending on authors, been considered to be $Ce_2O(HPO_4)_3{\cdot}H_2O$, $(CeOH)_2(HPO_4)_3$, $Ce(HPO_4)(PO_4)_{0.5}(OH)_{0.5}$, or $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$.[1a,4a,6,7,9]

This peculiar CeP, which exhibits a P/Ce ratio of 1.5:1 has been described several times in the literature.[1a,3a,4a,6,7,9] A unit cell and possible space groups have even been proposed.[7,9] Moreover, its structure was supposed to be a layered one, even though no amine could be intercalated.[7] However no other structural details were available. As it has been obtained from various cerium(IV) salts (sulfate, ammonium nitrate) or derivatives (hydroxide, oxide) either under reflux or hydrothermal ageing in H_3PO_4 solutions, this crystalline compound seems to exhibit a high degree of thermodynamic stability and, therefore, should offer a relevant first entry in the field of CePs structures. Herein, the structure of $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ is solved by ab initio Rietveld analysis. It consists of $[Ce(PO_4)^+]_n$ slabs bridged by hydrogenphosphate tetrahedra. The chemical nature of the (hydrogen)phosphates is also unambiguously established from the P–O distances and ^{31}P NMR spectroscopy. Importantly, this is the first time a CeP structure is presented.

$Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ was synthesized from CeO_2, H_3PO_4, and H_2O. It consists of crystalline platelets a few microns long in the longest dimension. The compound was found to be monoclinic, with a strong cell elongation along the a axis, consistent with the (100) platelet habit of the crystallites. The unit cell parameters were refined from the X-ray powder diffraction data ($a = 21.0142(3)$, $b = 6.55082(7)$, $c = 6.94382(6)$ Å, $\beta = 91.983(1)°$, $V = 955.32(2)$ Å^3) and the results agreed with those reported.[7,9] The structure was solved with the space group $C2/c$ (No. 15). It can be described as dense $[Ce(PO_4)^+]_n$ slabs, extending parallel to the (b,c) plane, with cerium atoms on both surfaces (Figure 1). Each cerium atom is connected to four phosphate tetrahedra belonging to the same side and to one phosphate tetrahedron on the opposite surface of the slab. These slabs are bridged by HPO_4^{2-} units and water molecules are also present in the interslab region, which results in eight-coordinate cerium atoms. This structure bears absolutely no resemblance with the α- or γ-ZrP structures.[15,16] The $\{(P1)O_4\}^{3-}$ (slab) tetrahedron is regular (Figure 1), except for the outstandingly small O13-P1-O14 angle (97.1(8)°), which results from the sharing of the O13–O14 edge with a cerium atom. The long P2–O24 distance and the absence of Ce–O24 contact indicate that O24 is the protonated vertex of the $\{H(P2)O_4\}^{2-}$ hydrogenphosphate tetrahedron. The water molecule fills a structural cavity surrounded by eight oxygen atoms of (hydrogen)phosphates and one cerium atom.

Actually, the absence of superstructure peaks indicates some form of disorder in the array of the HPO_4^{2-} and H_2O units. The distances between an HPO_4^{2-} tetrahedron (e.g., the white one (P2) near the center of the cell in Figure 2) and its three closest equivalents (shaded in Figure 2) are too short to allow the occupation of these closest positions. Likewise, the occupation of an HPO_4^{2-} site precludes the presence of a water molecule in the closest H_2O site (d(P2)-O_W) 1.21(1) Å). These two conditions, along with the 50 % occupancy of the interslab sites, lead to consideration of two equiprobable sets of alternate HPO_4^{2-} and H_2O units, forming fully ordered zigzags along the c axis, shown in different tones in Figure 2. In terms of symmetry, each zigzag still obeys the c-mirror axis, but ignores the inversion center and the twofold symmetry. Although neighbor zigzags in the same (b,c) plane are far enough apart to prevent any overlapping of their sites, the b parameter is small and the interactions should be strong

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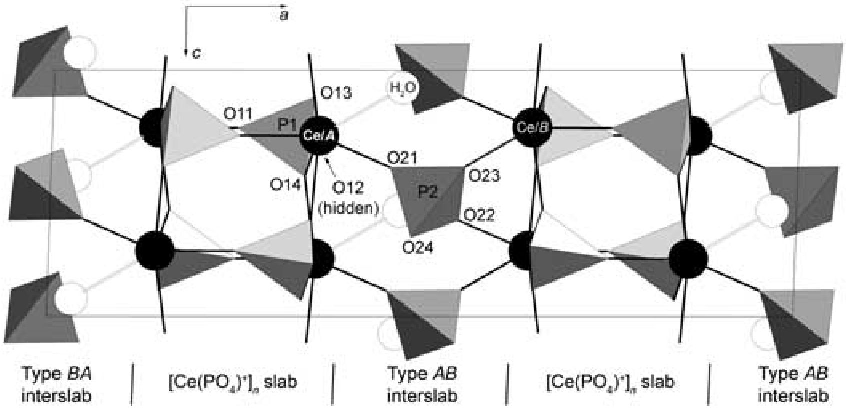

Figure 1. (010) projection of the $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ structure. The random succession of the interslab regions along the stacking *a* axis illustrates the disorder. P–O interatomic distances [Å]: P1-O11 1.543(6), P1-O12 1.518(9), P1-O13 1.52(1), P1-O14 1.53(1), P2-O21 1.50(1), P2-O22 1.51(2), P2-O23 1.52(2), P2-O24 1.61(2). Gray tetrahedra PO_4. The positions Ce/*A* and Ce/*B* are discussed in the text as are the *BA* and *AB* interslab units.

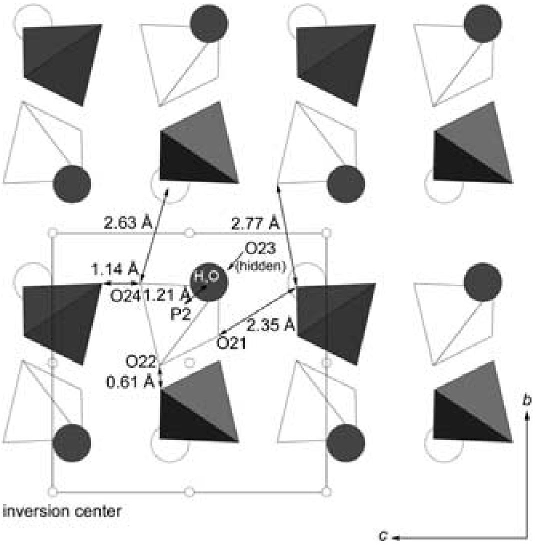

Figure 2. (100) projection of the interslab regions near $x=1/2$ for the $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ structure. White and shaded units ($H(P2)O_4^{2-}$ tetrahedra and O_w (water oxygen) atoms) represent the two possible and equipropable zigzag models.

enough to keep the structure ordered along the *b* axis (see distances in Figure 2). So, the whole interslab region obeys a *c* symmetry instead of 2/*c*. In contrast, the thickness of the $[Ce(PO_4)^+]_n$ slabs prevents the cerium atom from "seeing" both neighbor layers, thus reducing strongly the ordering interactions along the *a* axis. Indeed, the disorder is likely to affect the stacking axis. The drop of symmetry of the zigzags has repercussions for the cerium atoms. If a pair of cerium atoms that should be equivalent by a twofold symmetry operation is considered for example, Ce/*A* and Ce/*B* in Figure 1, Ce/*A* is linked to atom O21 and the water molecule, while Ce/*B* is connected to atoms O22 and O23 of two different HPO_4^{2-} tetrahedra. Therefore, two different environments must be taken into account for the cerium atoms. They are noted *A* and *B*, hereafter (Figure 3). Note that all cerium atoms on one side of a slab are of the same type, while those facing them on the nearest slab are of the other type. Therefore, each interslab layer has an "*A*" and a "*B*" side, but is randomly either of "*AB*" or "*BA*" type, as shown in Figure 1.

In the course of the Rietveld refinements, attempts were made to measure the effect on the slabs of the disorder in the interslab regions by splitting the cerium atom and the $\{(P1)O_4\}^{3-}$ tetrahedron onto two sites. The cerium atom appeared slightly delocalized along the *a* axis onto two positions, 0.169(5) Å apart, as could be guessed from the two environment types, while the split positions of the P1 and connected oxygen atoms remained very close, but with larger estimated standard deviations (esds). Because this model did not allow correlations between the environment and the position of a slab atom to be established, this model was abandoned. The cerium atom was simply modeled as lying on a single position, with anisotropic harmonic displacement factors, resulting in an *a*-axis elongated thermal ellipsoid (B_{11} 1.27(7), B_{22} 0.10(6), B_{33} 0.12(5), B_{12} 0.1(1), B_{13} 0.04(5), B_{23} 0.10(8) Å^2). Note that the cerium atoms are octacoordinate in both environments (Figure 3), and exhibit

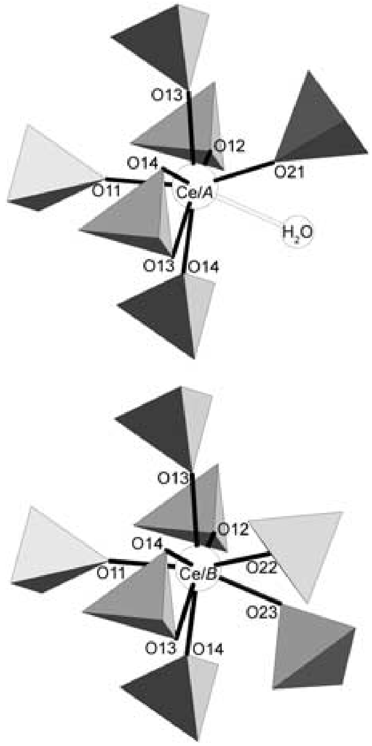

Figure 3. The two possible and equiprobable environments of the cerium atom (top: type *A*, bottom: type *B*) in the $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ structure. Ce–O interatomic distances [Å]: Ce*A*/*B*-O11$^{\mathrm{I}}$ 2.235(5), Ce*A*/*B*-O12$^{\mathrm{II}}$ 2.206(7), Ce*A*/*B*-O13 2.44(1), Ce*A*/*B*-O13$^{\mathrm{III}}$ 2.384(9), Ce*A*/*B*-O14 2.44(1), Ce*A*/*B*–O14$^{\mathrm{IV}}$ 2.334(8), Ce*A*-O21 2.22(1), Ce*B*-O22$^{\mathrm{V}}$ 2.32(2), Ce*B*-O23$^{\mathrm{VI}}$ 2.38(2), Ce*A*-O$_w$ 2.92(2) (with the following symmetry operations: I = 1/2−*x*, 1/2+*y*, 1/2−*z*; II = *x*, 1+*y*, *z*; III = *x*, 1−*y*, 1/2+*z*; IV = *x*, 1−*y*, *z*−1/2; V = 1−*x*, 1−*y*, 1−*z*; VI = 1−*x*, *y*, 1/2−*z*).

nearly equal valences (3.35 and 3.51 for A and B type cerium, respectively).[17] The slight but non-negligible contribution of the O_W atom in environment A accounts for a structural role of the water molecule.

This very same compound, according to its X-ray powder diffraction, has been described in previous works as a cerium(IV) hydroxy(hydrogen)phosphate with the formula $Ce(HPO_4)(PO_4)_{0.5}(OH)_{0.5}$.[4a,6,7] The present structure, and especially the P–O distances, indicate quite clearly that the compound is in fact a cerium(IV) (hydrogen)phosphate hydrate, with the formula $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$. The nature of phosphate units was however confirmed by ^{31}P MAS and CP-MAS NMR spectroscopy (CP-MAS = cross polarization magic-angle spinning), a result of the high sensitivity of such techniques to phosphorus environment.[18,19] The ^{31}P MAS NMR spectrum of $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ (Figure 4) shows three resolved resonance signals at $\delta = -15.7$, -27.3, and -29.2 ppm, with an intensity ratio of 1:1:1. A similar spectrum was previously reported but incorrectly interpreted.[6] Variation of the contact time in ^1H–^{31}P CP-MAS NMR (Figure 4) spectra shows that the signal at $\delta = -15.7$ ppm has a steep magnetization build up, while the two others ($\delta = -27.3$ and -29.2 ppm) have slower ones. From these results it can be inferred that the signal at $\delta = -15.7$ ppm corresponds to a hydrogenphosphate while the others correspond to fully deprotonated phosphates. Accordingly the amount of phosphate is twice the amount of hydrogenphosphate and the formula $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ must be considered. These ^{31}P chemical shifts fall within the regions found for the α- and γ-$M^{IV}P$ structures (M = Zr, Ti) and agree with the generally observed highfield shift of about 10 ppm for the removal of one proton.[19] While there is only one fully deprotonated phosphate environment in the structure, $\{(P1)O_4\}^{3-}$, ^{31}P NMR spectroscopy indicates two similar but different environments. This feature can be related to the occupancy in the interslab region. Indeed, depending on the surface of the slab, that is, corresponding to type A or type B cerium atoms, P1 has two possible and equiprobable environments which also exhibit different magnetization sources for CP experiments. A P1 atom belonging to a type A plane has one $H(P2)O_4$ tetrahedron (P1-O24 3.50 Å) and one water molecule (P1-O_W 3.68 Å) in its near environment, while a P1 atom in a type B plane has only one more remote H(P2)O4 tetrahedron (P1-O24 4.07 Å). Accordingly, the signal with the slower magnetization build up ($\delta = -29.2$ ppm) can be assigned to the phosphates in the type B planes which have the less-protonated environment.

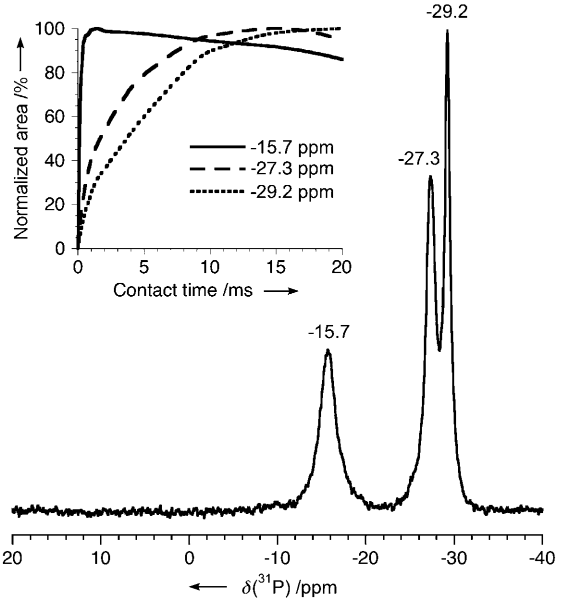

Figure 4. ^{31}P MAS NMR spectrum of $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ ($\nu_{MAS} = 14$ kHz). The inset shows the area of each signal versus the contact time in ^1H–^{31}P CP-MAS NMR experiments.

In conclusion, $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ can be considered to have a layered structure, as previously proposed from sedimentation experiments.[7] However, the bridging hydrogenphosphates hold the slabs tightly together and this simply explains why amine could not be intercalated in such a compound. Of note is that $U_2(PO_4)_2(HPO_4)\cdot H_2O$ and $Th_2(PO_4)_2(HPO_4)\cdot H_2O$, which both exhibit a powder diffraction pattern similar to the one of the homologous compound $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ studied here,[9] must have an identical structure to this first reported CeP structure.

Experimental Section

$Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$: Cerium oxide nanoparticles (2.6 g)[20] were dispersed in 1.96 M H_3PO_4 (15 mL; $PO_4/Ce \approx 2.4$). The preparation was then treated hydrothermally at 200 °C for 5 h. The yellow product obtained was collected by filtration, washed several times with distilled water, and dried under a flow of nitrogen.

X-ray powder diffraction (XRD) patterns were recorded on the BM01B line of the European Synchrotron Radiation Facility (Grenoble, France). The instrument parameters were previously refined from a LaB_6 pattern. The powder sample was placed in a 0.3 mm capillary and the data were collected at 293 K, using a wavelength of 0.69947 Å and a Ge(111) rear monochromator. The data were scanned between 4.062 and 55.488° (2θ), with a step of 0.006°, and 1247 reflections were observed. Assuming, as a rule of thumb, a rough 20 $Å^3$ volume per oxygen atom, the number of formula units in the cell was found to be $Z = 4$. Systematic extinctions led space groups Cc and $C2/c$ to be considered, and the structure resolution was initiated with the Cc. FullProf.2k[21] was run in profile-matching mode to extract the diffracted intensities and to correct them from absorption. The broadening of the h-dependent peaks, resulting from the crystallite shape (platelet), was taken into account when modeling the peaks shapes. The background fitting was made by interpolation between selected points. Eight positions and profile parameters were used. The profile model was a Thompson–Cox–Hasting with anisotropic size and strain effect. A Patterson synthesis performed with Shelx-97[22] allowed the cerium atoms to be located, the other atoms were found by observation of the Fourier maps.[23] The cerium atoms and some of the phosphates appeared to form dense $[Ce(PO_4)^+]_n$ blocks extending parallel to the (b,c) plane. At this point, the presence of a twofold symmetry between the cerium atoms, as well as between the electron densities became so obvious that the space group was changed for $C2/c$. HPO_4^{2-} units and the oxygen atom O_W of the H_2O molecules were found in the interblock spaces, on half-occupied sites in agreement with the stoichiometry and the symmetry (indeed, a joint refinement gave a 0.47(1) occupancy for the interblock sites). To reduce the number of parameters, anisotropic thermal factors were only used for the cerium atom. A single isotropic displacement factor was used for both phosphorus atoms and an other isotropic displacement factor for all the oxygen atoms. Finally, 44 parameters were refined and gave satisfactory reliability factors ($R_P = 0.060$, $R_{WP} = 0.084$, $R_{Bragg} = 0.055$, $R_{exp} = 0.053$, $R_F = 0.029$, and $\chi^2 = 9.5$).[24] Note that because of the low electron weight of the HPO_4^{2-} unit, the O-P-O angles and P–O distances had to be put under soft constraints, taking those of K_2HPO_4 as reference.[25]

^{31}P MAS NMR spectroscopy was performed at 121.5 MHz on a Bruker Avance 300 spectrometer, using a 4-mm locked Bruker probe. Chemical shifts are quoted relative to 85 % H_3PO_4.

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[1] a) K. H. König, E. Meyn, *J. Inorg. Nucl. Chem.* **1967**, *29*, 1153–1160; b) K. H. König, E. Meyn, *J. Inorg. Nucl. Chem.* **1967**, *29*, 1519–1526; c) K. H. König, G. Eckstein, *J. Inorg. Nucl. Chem.* **1969**, *31*, 1179–1188; d) K. H. König, G. Eckstein, *J. Inorg. Nucl. Chem.* **1972**, *34*, 3771–3779.

[2] E. M. Larsen, W. A. Cilley, *J. Inorg. Nucl. Chem.* **1968**, *30*, 287–293.

[3] a) G. Alberti, U. Costantino, F. Di Gregorio, P. Galli, E. Torracca, *J. Inorg. Nucl. Chem.* **1968**, *30*, 295–304; b) G. Alberti, U. Costantino, L. Zsinka, *J. Inorg. Nucl. Chem.* **1972**, *34*, 3549–3560.

[4] a) R. G. Herman, A. Clearfield, *J. Inorg. Nucl. Chem.* **1975**, *37*, 1697–1704; b) R. G. Herman, A. Clearfield, *J. Inorg. Nucl. Chem.* **1976**, *38*, 853–858; c) R. G. Herman, A. Clearfield, *J. Inorg. Nucl. Chem.* **1977**, *39*, 143–146.

[5] M. Tsuhako, M. Danjo, Y. Baba, M. Murakami, H. Nariai, I. Motooka, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 143–148.

[6] H. Hayashi, K. Torii, S. Nakata, *J. Mater. Chem.* **1997**, *7*, 557–562.

[7] M. Kaneyoshi, W. Jones in *Advances in Ion Exchange for Industry and Research* (Eds.: P. A. Williams, A. Dyer), The Royal Society of Chemistry, Cambridge, **1999**, pp. 176–186.

[8] H. Nakayama, A. Hayashi, M. Tsuhako, T. Eguchi, N. Nakamura, *Phosphorus Res. Bull.* **1998**, *8*, 89–94.

[9] V. Brandel, N. Clavier, N. Dacheux, *J. Solid State Chem.* **2005**, *178*, 1054–1063.

[10] P. Barboux, R. Morineau, J. Livage, *Solid State Ionics* **1988**, *27*, 221–225.

[11] Y. Xu, S. Feng, W. Pang, G. Pang, *Chem. Commun.* **1996**, 1305–1306.

[12] S. Pajkoff, *Monatsh. Chem.* **1968**, *99*, 1400–1408.

[13] C. Tang, Y. Bando, D. Goldberg, R. Ma, *Angew. Chem.* **2005**, *117*, 582–585; *Angew. Chem. Int. Ed.* **2005**, *44*, 576–579.

[14] a) G. Alberti in *Inorganic Ion Exchange Materials* (Ed.: A. Clearfield), CRC, Boca Raton, FL, **1982**, chap. 2; b) A. Clearfield in *Inorganic Ion Exchange Materials* (Ed.: A. Clearfield), CRC, Boca Raton, FL, **1982**, chap. 1; c) G. Alberti, U. Costantino in *Intercalation Chemistry* (Eds.: M. S. Wittingham, A. J. Jacobsen), Academic Press, New York, **1987**, pp. 147–180.

[15] J. M. Troup, A. Clearfield, *Inorg. Chem.* **1977**, *16*, 3311–3314.

[16] D. M. Poojary, B. Shpeizer, A. Clearfield, *J. Chem. Soc. Dalton Trans.* **1995**, 111.

[17] N. E. Brese, M. O'Keeffe, *Acta Crystallogr. Sect. B* **1991**, *47*, 192.

[18] a) A. R. Grimmer, U. Haubenreisser, *Chem. Phys. Lett.* **1983**, *99*, 487; b) T. M. Duncan, D. C. Douglas, *Chem. Phys.* **1984**, *87*, 339; c) A. K. Cheetham, N. J. Clayden, C. M. Dobson, R. J. B. Jakeman, *J. Am. Chem. Soc.* **1985**, *107*, 6249–6252; d) R. J. B. Jakeman, A. K. Cheetham, N. J. Clayden, C. M. Dobson, *J. Chem. Soc. Chem. Commun.* **1986**, 195–197.

[19] H. Nakayama, T. Eguchi, N. Nakamura, S. Yamaguchi, M. Danjyo, M. Tsuhako, *J. Mater. Chem.* **1997**, *7*, 1063–1066.

[20] Cerium oxide was provided by Rhodia in the form of crystalline nanometric particles (diameter ≈ 6 nm) that can be easily redispersed in water. Its formula corresponds to $CeO_{1.8}(NO_3)_{0.4}$-$(H_2O)_{1.1}$ ($M_w = 213.5\ g\,mol^{-1}$).

[21] J. Rodriguez-Carvajal, *FullProf.2k: Rietveld, profile matching and integrated intensity refinement of X-ray and neutron data, V 1.9c*, Laboratoire Léon Brillouin, CEA, Saclay, France, **2001**.

[22] G. M. Sheldrick, *Shelx-97: a program for crystal structure determination*, Göttingen, Germany, **1997**.

[23] J. Gonzalez-Platas, J. Rodriguez-Carvajal, *Gfourier: Fourier maps calculation program*, *V 3.20*, Universidad de La Laguna, Tenerife, Spain, and Laboratoire Léon Brillouin, CEA, Saclay, France, **2003**.

[24] $R_P = \Sigma\,|\,y^i_o - y^i_c\,|\,/\Sigma y^i_o$, $R_{WP} = \Sigma w^i\,|\,y^i_o - y^i_c\,|\,/\Sigma w^i y^i_o$, $R_{Bragg} = \Sigma\,|\,I^i_o - I^i_c\,|\,/\Sigma I^i_o$, $R_{exp} = ((n-p)/\Sigma w_i y^i_o)^{1/2}$, $R_F = \Sigma\,|\,(I^i_o)^{1/2} - (I^i_c)^{1/2}\,|\,/\Sigma (I^i_o)^{1/2}$, $\chi^2 = (R_{WP}/R_{exp})^2$. Further details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), on quoting the depository number CSD-415465.

[25] T. Lis, *Acta Crystallogr. Sect. C* **1994**, *50*, 484.