Crystal Structure of a Cerium(IV) bis(phosphate) Derivative

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Electronic Supplementary Information

Synthesis of $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$. The synthesis was performed under hydrothermal conditions in a stainless steel Teflon-lined vessel (100 mL) under autogenous pressure, with a molar composition ratio of $1\text{CeO}_2\text{-}12\text{CO}(\text{NH}_2)_2\text{-}25\text{H}_3\text{PO}_4\text{-}25\text{H}_2\text{O}$. The reaction mixture was then sealed and heated to 180 °C for 5 days. The obtained products were filtered, washed with distilled water and dried at ambient temperature. The phosphorus and cerium contents of the yellow powder product was determined using a SpectraSpectrometer DCP-AEC after dissolving a weighed amount of sample in $\text{HF}(\text{aq})$, and the nitrogen content was obtained on a C-H-N Perkin-Elmer model 2400B elemental analyser. The result showed that the product contains: 36.1, 15.9 and 6.9 mass % for Ce, P and N, respectively (calculated for $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$: 36.5 % Ce, 16.2 % P, 7.3 % N).

Thermal analysis data. A Mettler-Toledo TGA/SDTA851^e was used for the thermal analyses under a dynamic nitrogen atmosphere (50 mL/min) at a heating rate of 10 °C/min, and a Pfeiffer Vacuum ThermoStarTM GSD301T mass spectrometer was used to determine the evacuated vapours. The masses 18 (H_2O), 15 (NH_3), and 32 (O_2) were tested using a C-SEM detector, operating at 1400 V, with a time constant of 0.5 s.

Thermal decomposition data for $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$: a) TG (solid line) and DTG (dotted line) curves, and b) mass spectrometry analysis of evacuated H_2O (solid line), NH_3 (dotted line) and O_2 (dashed line).

Powder XRD data and structural details. X-ray powder diffraction patterns were recorded at Oviedo University SCT facilities using a Seifert XRD3000 operating in Bragg-Brentano θ - θ geometry at 50 kV and 40 mA with graphite monochromated $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). The samples were gently ground in an agate mortar and size-loaded in order to minimize the preferred orientation. All data were collected at room temperature over the angular 2θ range 11 - 110° with a step of 0.02° and a counting time of 10 s/step. The pattern was indexed using the program TREOR (Werner, P.E.; Eriksson, L.; Westdahl, M. *J. Appl. Crystallogr.* **1985**, *18*, 367) in the tetragonal system with lattice parameters $a = 6.890(2) \text{ \AA}$, $c = 17.76(1) \text{ \AA}$ and figures of merit: $M_{15} = 13$, $F_{15} = 15$ (0.02, 50). Systematic absences were consistent with the space group $I4_1/amd$. A proposed structure in this group was obtained by a direct space search using the program FOX (Favre-Nicolin, V.; Cerný, R. *J. Appl. Crystallogr.* **2002**, *35*, 734) with a starting configuration composed of one cerium atom, one idealized phosphate group and one nitrogen atom in random positions and orientations. However, the proposed structure was affected by a severe disorder of the phosphate group. Moreover, the refinement of the structure of this group led to a poor pattern fitting. For this reason, the refinement was attempted in the two maximal subgroups that duplicate the phosphate sites, $I-4m2$ and $Imma$. Only the refinement in $Imma$ was stable and led to a reasonable pattern fitting although it was clear at this point that the initial observed disorder was only partially described in the new space group. The water molecule cannot be located by difference Fourier synthesis in a unique site, but rather it seemed to be severely disordered around the ideal position 0, 1/4, 7/8 (a special position in the related supergroup). The structure refinement including this position led to lower reliability factors but a very high displacement parameter for the oxygen of the water molecule. Accordingly, the water molecule was omitted from the refinement. The final structure refinement in $Imma$ was carried out using the Rietveld method as implemented in the program GSAS (Larson, A.C.; Von Dreele, R.B. *General Structure Analysis System (GSAS)*; Los Alamos National Laboratory, Report LAUR, 1994; p 86), including a preferred orientation correction using a spherical-harmonics function (Von Dreele, R.B.; Lujan Jr, M. *J. Appl. Cryst.* **1997**, *30*, 517). The isotropic displacement factors of each discrete atom type were constrained to have the same value. Owing to the low electron weight of the PO_4 units, the P-O distances and O-P-O angles had to be put under soft constraints. Finally, 40 parameters were refined and gave acceptable reliability factors bearing in mind the limitations imposed by the fact of being a disordered structure ($R_p = 0.14$, $R_{wp} = 0.18$, $R_{exp} = 0.078$, $R(F^2) = 0.15$ and $\chi^2 = 5.11$). See “Ce(IV)P-Oviedo-JACS.cif” file.

In order to check the correctness of the $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2 \cdot \text{H}_2\text{O}$ structure, a theoretical calculation within the density-functional theory (DFT) method and the local density approximation (LDA) has been carried out. The ABINIT code (Gonze, X.; Beuken, J.M.; Caracas, R.; Detraux, F.; Fuchs, M.; Rignanese, G.M.; Sindic, L.; Verstraete, M.; Zerah, G.; Jollet, F.; Torrent, M.; Roy, A.; Mikami, M.; Ghosez, P.; Raty, J.Y.; Allan, D.C. *Comp. Mater. Sci.* **2002**, *25*, 478.) with the HGH pseudopotentials (Hartwigsen, C.; Goedecker, S.; Hutter, J. *Phys. Rev. B* **1998**, *58*, 3641) has been used. A plane wave kinetic energy cutoff of 800 eV was used in the calculations. Starting from the $(\text{NH}_4)_2\text{Ce}(\text{PO}_4)_2$ experimental structural data, the geometry of $\text{K}_2\text{Ce}(\text{PO}_4)_2$ model compound has been optimized in the $I4_1/amd$ space group. The obtained results indicates that the ideal ordered optimized geometry have similar features that the experimental one. For further details on the theoretically optimized crystal structure see “Ce(IV)P-theor-Oviedo-JACS.cif” file.