ON THE EXISTENCE OF CERIUM(IV) ORTHOPHOSPHATE, "Ce₃(PO₄)₄"

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The present study is aimed to elucidate the existence of the ceric orthophosphate by synthesis and characterization of "Ce₃(PO₄)₄" and CePO₄. The results obtained indicate a mixed valence in both phosphates obtained, corresponding to nonstoichiometric compounds of cerium in an intermediate oxidation state (molar ratios P/Ce of 1.06 to 1.18). Based on the results obtained, the existence of other ceric phosphates synthesized at high temperatures is discussed.

INTRODUCTION

The lanthanoides are the fourteen 4f elements, placed in the periodic table immediately after lanthanum. Together with Sc, Y and La, are refereed in literature as "rare earths".[1] Their most common oxidation state is 3+, but there are also compounds in oxidation state 2+ (for La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Tm and Yb) or 4+ (for Ce, Pr, Nd, Tb and Dy). Stability of compounds with Ce(IV) is remarkable, bearing in mind the unoccupied $4f^0$ electronic configuration of this ion. Ceric compounds as CeF_4, CeO_2, $Ce(SO_4)_2 \cdot xH_2O$ (x = 0, 2, 4, 8), $(NH_4)_2Ce(SO_4)_4 \cdot 4H_2O$, are known as brightly colored; in reducing conditions, most of these compounds pass into the colorless cerous counterparts.

Because of this behavior, it is expected that cerium would be the perfect surrogate in inactive preliminary studies before working with very active actinoides, which frequently occur in 3+ and 4+ oxidation states (particularly, plutonium and americium). A class of interest in the conditioning of nuclear waste is that of orthophosphates; thus, it becomes obvious need to study the cerium phosphates in both oxidation states. The cerous monazite, $CePO_4$, is a widespread compound and

relatively easily obtained by chemical synthesis. Contrarily, the ceric counterpart "Ce₃(PO₄)₄" does not exists in nature and has not been synthesized and characterized to date. There are however other phosphates of Ce(IV) as $M^I Ce_2(PO_4)_3$ (M^I= Li, Na, K, Rb and Cs), $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$,[2,3] $Ce^{III}_{1-2x}Ce^{IV}_x M^{II}_x PO_4$ (M^{II} = Ba, Sr, x < 0.1),[4] and $M^{II}Ce(PO_4)_2$ (M^{II}= Mg, Ca, Sr, Ba, and Cd).[5-7] From all these compounds, only $Ce(PO_4)(HPO_4)_{0.5}(H_2O)_{0.5}$ is completely characterized in terms of crystallography. The remaining ones are obtained at high temperatures (above 900 K), temperature at which spontaneous reduction of Ce(IV) to Ce(III) in the presence of phosphate ion occurs, even in air.[8] Even if in the mentioned study "BaCe(PO₄)₂" is the target compound, the existence of all ceric phosphates obtained at high temperature is questionable.

Thus, the current study is aimed to elucidate the existence of "Ce₃(PO₄)₄". Therefore, we tried to synthesize cerous and ceric orthophosphates, and the obtained compounds were characterized by various experimental techniques.

RESULTS AND DISCUSSION

The results of the XRD and electron microscopy experiments of the two compounds indicates that in

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both cases we achieved single phases with monazitic structure, crystallizing in monoclinic group P2$_1$/n (**Fig. 1**). The crystallographic parameters are presented in **Table 1**.

Table 1

Lattice parameters of "Ce$_3$(PO$_4$)$_4$" and CePO$_4$

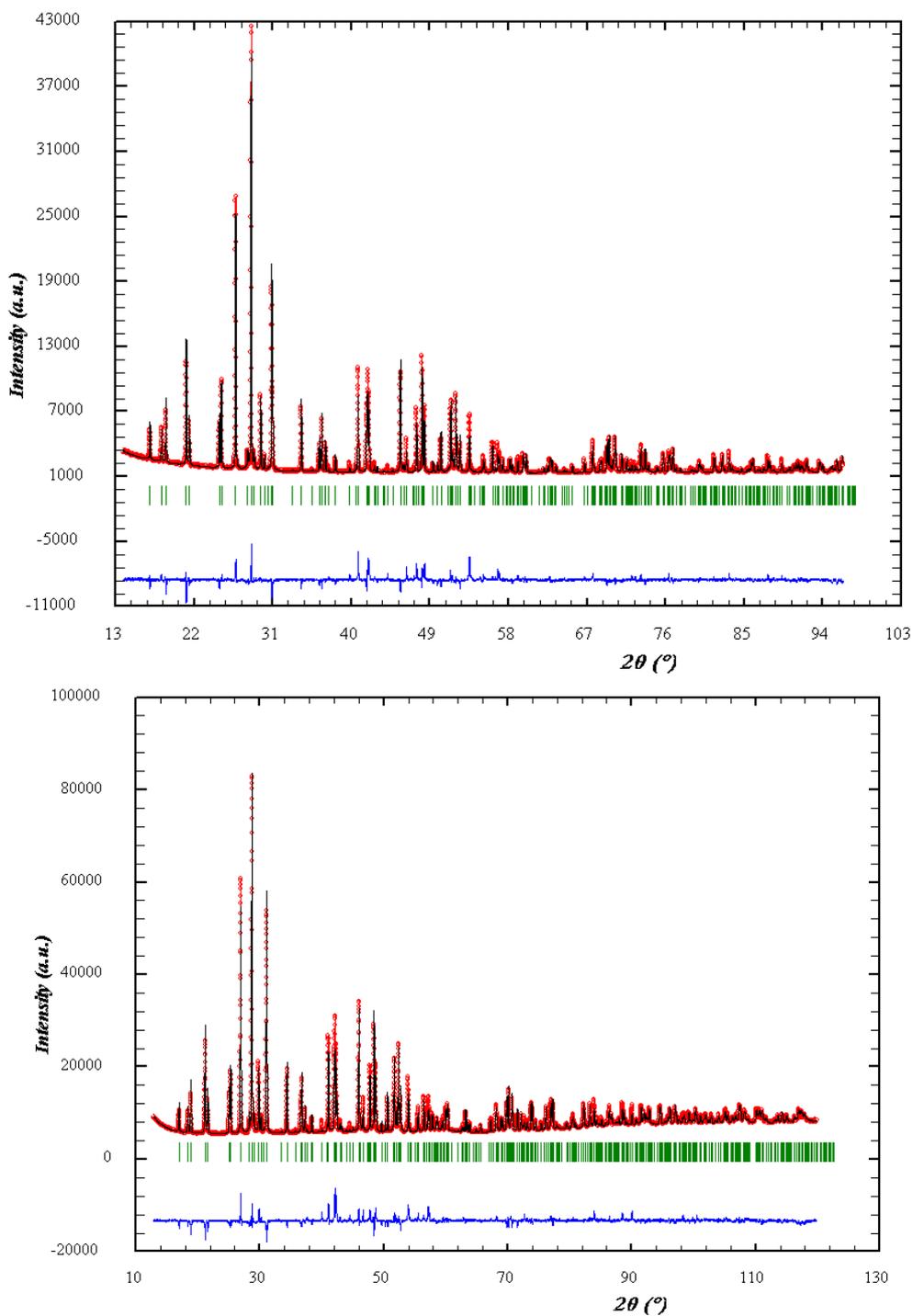| Compound	a, nm	b, nm	c, nm	β, °
"Ce$_3$(PO$_4$)$_4$"	0.6781	0.6996	0.6448	103.52
CePO$_4$	0.6800	0.7023	0.6471	103.46

Fig. 1 – Room-temperature Rietveld refinement plot of CePO$_4$ (a) and "Ce$_3$(PO$_4$)$_4$" (b), showing the observed (o), calculated (solid line), and difference pattern (lower). The vertical marks indicate the positions of allowed Bragg reflections.

All three lattice parameters of "$Ce_3(PO_4)_4$" are lower than for the ones corresponding to $CePO_4$, which might indicate that, in the first case, the "f" electron was assigned, with the formation of Ce^{4+} ion (ionic radius for coordination number IX being 0.102 nm, calculated as the average between the ionic radii in coordination VIII and X), smaller than Ce^{3+} ion (ionic radius for coordination number IX of 0.196 nm).[9] This behavior would explain the color differences of the two compounds, the "f" electron being responsible for optical properties of the ceric compounds.

From the EDX semiquantitative analysis it can be observed that the P/Ce molar ratios match in both cases nonstoichiometric compositions. For instance, the molar ratio P/Ce is 1.06 for $CePO_4$, (theoretical value: 1.00), while P/Ce is of 1.18 for "$Ce_3(PO_4)_4$" (theoretical value: 1.33). Thus, one can speak of deviations from stoichiometry and intermediate valence state in both cases, with cerium ions fluctuating between two states $4f^0$ and $4f^1$ electronic configuration. This result is in perfect agreement with that of XPS measurements summarized in Figure 9 of our previous publication,[8] in which we can observe a peak of 920 eV, corresponding to partial oxidation of Ce(III) from $CePO_4$ ($4f^1$ electronic configuration) to Ce(VI) ($4f^0$ electronic configuration).

The FT-IR spectra (**Fig. 2**) proved that both compounds are pure orthophosphates. The bans at 1000-950 cm^{-1} were assigned to stretching, while those at 620-530 cm^{-1} to bending vibrations of the PO_4^{3-} tetrahedra. Moreover, no vibration band in the range 800-700 cm^{-1} (associate to the P-O-P bridge characteristic of pyrophosphate or polytrioxophosphate groups) was observed. Raman spectra of the two compounds are shown in **Fig. 3** and indicates identical behavior of "$Ce_3(PO_4)_4$" and $CePO_4$. It can thus see clusters of four bans (two A_g and two B_g) in the 970-1080 cm^{-1} range corresponding to symmetric vibrations ν_1 and ν_3 of orthophosphate ion.[10] The only noticeable difference is in the intensity of the asymmetric band $\nu_2(PO_4)$, indicating a higher degree of disorder in "$Ce_3(PO_4)_4$", as a result of nonstoichiometry of this compound.

These data can be correlated with the results of the thermal analysis conducted on the reagents needed to obtain the "$Ce_3(PO_4)_4$" [$3CeO_2 + 4(NH_4)_2HPO_4$] (**Fig. 4**) and $M^{II}Ce(PO_4)_2$ [$M^{II}CO_3 + CeO_2 + 2(NH_4)_2HPO_4$, $M^{II} = Ca, Ba$). In all three cases we observed a weight loss in TG curves in the range 1000-1250 K, attributed the partial reduction of Ce(IV) to Ce(III) with the release of excess oxygen. This will lead to the formation of nonstoichiometric compounds, since the synthesis temperature of the orthophosphates exceeds 1200 - 1300 K.
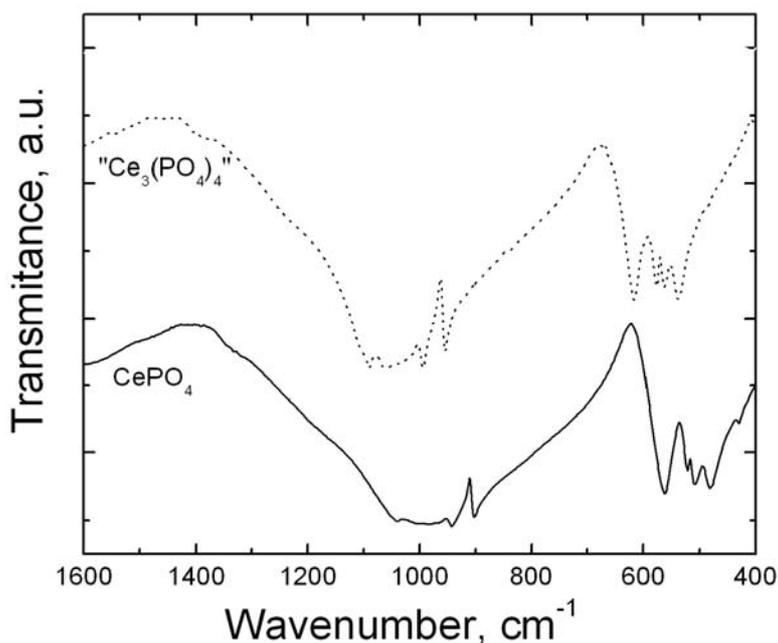

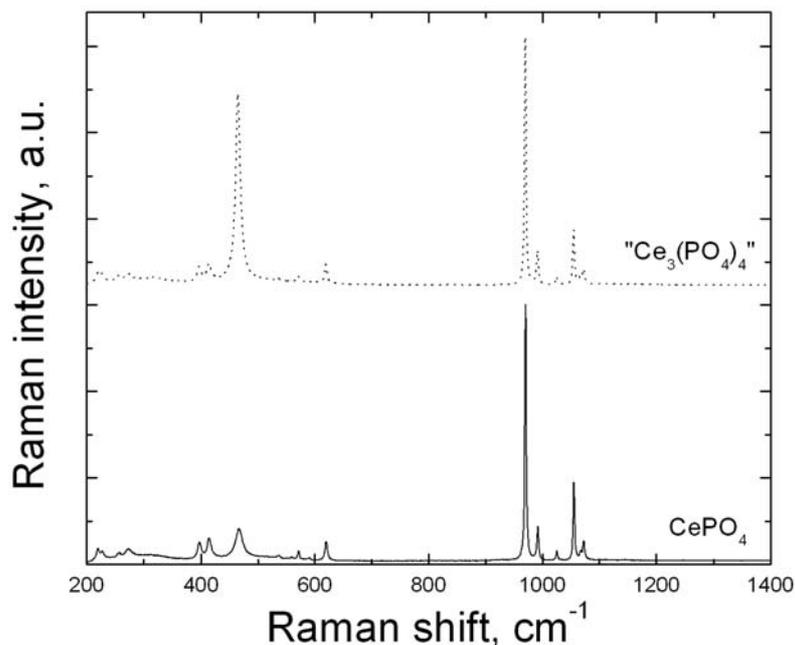Fig. 2 – The FT-IR spectra of $CePO_4$ and "$Ce_3(PO_4)_4$".
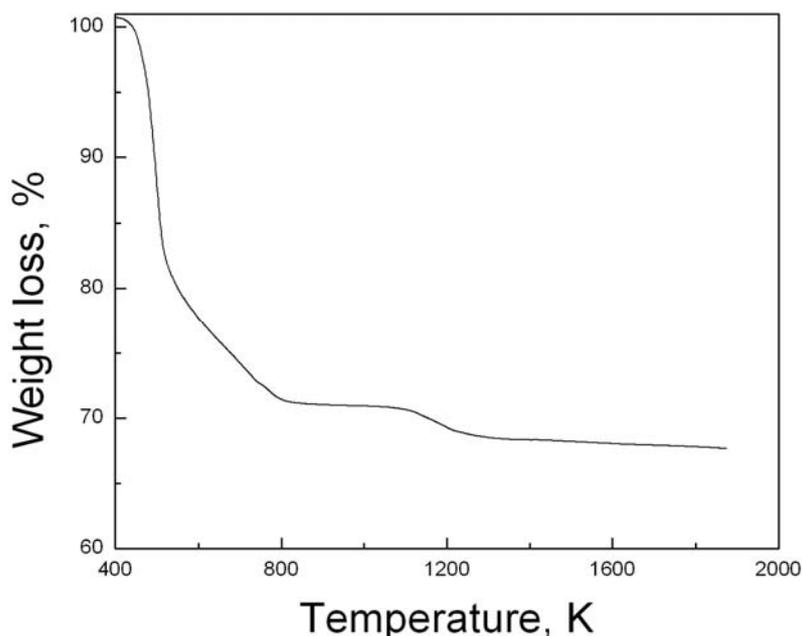
Fig. 3 – The Raman spectra of CePO$_4$ and "Ce$_3$(PO$_4$)$_4$".

Fig. 4 – The TG curve for the reagents mixture 3 Ce(SO$_4$)$_2$ + 4 (NH$_4$)$_2$HPO$_4$.

Consequently, ceric orthophosphates obtained at high temperature are relatively insufficient characterized in the literature and their existence can be questioned. Take the example of "CaCe(PO$_4$)$_2$": CaM^{IV}(PO$_4$)$_2$ type orthophosphate are known for M^{IV} = Zr, Ce, Th, U and Np (**Table 2**). Note that orthophosphate of calcium and cerium(IV) adopt a monoclinic structure, as for tetravalent actinoides. This behavior can be explained by the similarity in ionic radii coordination IX. In two previous papers it was questioned the existence of "M^{II}Ce(PO$_4$)$_2$"

(M^{II}= Ca and Ba) compounds based on the behavior of the redox couple Ce(IV)/Ce(III) at temperatures above 1000 K in this air.[8,13] In the absence of microscopic analysis for the compounds "M^{II}Ce(PO$_4$)$_2$" (M^{II} = Mg, Ca, Sr, Ba, Cd and Pb), the results previously reported[6,7] are not convincing. It seems that in all these cases binary systems are obtained, concentrating cerium on CePO$_4$ crystalline phase and the divalent ion in an amorphous one, as we demonstrated for "BaCe(PO$_4$)$_2$".[8]

Table 2

Lattice parameters for $CaM^{IV}(PO_4)_2$ compounds

Compound	Structure	Space group	a, nm	b, nm	c, nm	β, °	Reference
$CaZr(PO_4)_2$	orthorhombic	$P2_12_12_1$	1.4487	0.6721	0.6721	90.00	Fukuda *et al.* [11]
"$CaCe(PO_4)_2$"	monoclinic	$P2_1/n$	0.6759	0.6992	0.6438	103.43	Kitaev *et al.* [6]
$CaTh(PO_4)_2$	monoclinic	$P2_1/n$	0.6714	0.6921	0.6424	103.68	Raison *et al.* [12]
$CaU(PO_4)_2$	monoclinic	$P2_1/n$	0.6654	0.6841	0.6359	103.98	Bregiroux *et al.* [13]
$CaNp(PO_4)_2$	monoclinic	$P2_1/n$	0.6673	0.680	0.6375	104.11	Raison *et al.* [12]

EXPERIMENTAL

"$Ce_3(PO_4)_4$" and $CePO_4$ were obtained by starting from $Ce(NO_3)_3·6H_2O$ (Loba Chemie Wien) and $Ce(SO_4)_2$ (Alfa Aesar), respectively. By adding 25% H_3PO_4 (Loba Chemie Wien, 10% excess) and a few drops of NH_4OH (Merck), white suspensions were obtained. After 21 days, the precipitate formed was filtered and washed several times with distilled water. Both compounds were then subjected to heat treatment for 10 h at 1473 K in air. $CePO_4$ obtained was dark green, while "$Ce_3(PO_4)_4$" colorless.

The specimens were characterized by using powder X-ray diffraction measurement (Seifert X-ray diffraction goniometer type XRD 3003 PTS, in Bragg-Brentano geometry with Cu Kα radiation, in a step scan mode) and microscopic analysis (SEM515 from Philips with a Tracor northern EDX detector digitalized by SAMX). A complete structural analysis was performed for each sample by the Rietveld method with the Fullprof2k suite.

The thermal behavior was investigated by differential thermal analysis (Netsch STA 449C Jupiter) on a sample of 196.66 mg mixed reagents of stoichiometric amounts in alumina crucibles in an air atmosphere (50 ml·min^{-1}) up to 1873 K. The temperature was controlled by a Pt-PtRh (10 %) thermocouple. The applied heating and cooling rates were 20 K·min^{-1}.

FTIR spectra were recorded between 400 and 4000 cm^{-1} with a Perkin-Elmer FTIR 1730 spectrophotometer and a spectral resolution of 2 cm^{-1}. The samples were mixed with KBr and pressed into pellets containing 1-2% analyzed substance in KBr. Raman measurements were conducted at room temperature with a Perkin-Elmer Raman system using a Nd-YAG (532 nm) laser.

REFERENCES

1. V.S. Sastri, J.C. Bünzli, V. Ramachandra Rao, G.V.S. Rayudu and J.R. Perumareddi, "Modern aspects of rare earths and their complexes", Elsevier, Amsterdam, 2003.

2. M. Nazaraly, G. Wallez, C. Chanéac, E. Tronc, F. Ribot, M. Quarton and J.P. Jolivet, *Angew. Chem. Int. Ed.*, **2005**, *44*, 5691-5694.
3. M. Nazaraly, G. Wallez, C. Chanéac, E. Tronc, F. Ribot, M. Quarton and J.P. Jolivet, *J. Phys. Chem. Solids*, **2006**, *67*, 1075-1078.
4. J.G. Pepin, E.R. Vance and G.J. McCarthy, *Mat. Res. Bull.*, **1981**, *16*, 627-633.
5. A.I. Orlova, D.B. Kitaev, N.G. Kazantzev, S.G. Samoilov, V.S. Kurazhkovskaya and E.N. Vopilina, *Radiochemistry*, **2002**, *44*, 326-331.
6. D.B. Kitaev, Y.F. Volkov and A.I. Orlova, *Radiochemistry*, **2004**, *46*, 211-217.
7. M.P. Orlova, D.B. Kitaev, M.L. Spiridonova, N.V. Zubkova, Y.K. Kabalov and A.I. Orlova, *Crystallography Reports*, **2005**, *50*, 918-922.
8. K. Popa, D. Bregiroux, R.J.M. Konings, A.F. Popa, T. Gouder, T. Geisler and P.E. Raison, *J. Sol. State Chem.*, **2007**, *180*, 2346-2355.
9. R.D. Shannon, *Acta Crislalogr.*, **1976**, *A32*, 751-767.
10. E.N. Silva, A.P. Ayala, I. Guedas, C.W.A. Paschoal, R.L. Moreira, C.K. Loong and L.A. Boatner, *Optical Mater.*, **2006**, *29*, 224-230.
11. K. Fukuda, T. Iwata, A. Moriyama and S. Hashimoto, *J. Sol. State Chem.*, **2006**, *179*, 3870-3876.
12. P.E. Raison, R. Jardin, D. Bouexiere, R.J.M. Konings, T. Geisler, C.C. Pavel, J. Rebizant and K. Popa, *Phys. Chem. Minerals*, **2008**, *35*, 603-609.
13. D. Bregiroux, O. Terra, F. Audubert, N. Dacheux, V. Serin, R. Podor and D. Bernache-Assollant, *Inorg. Chem.*, **2007**, *46*, 10327-10382.