

## On the existence of cerium (IV) orthophosphate, ‘Ce<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>’

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The most common oxidation state of the lanthanoides 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<sup>0</sup> electronic configuration of this ion. Ceric compounds as CeF<sub>4</sub>, CeO<sub>2</sub>, Ce(SO<sub>4</sub>)<sub>2</sub>·xH<sub>2</sub>O (x = 0, 2, 4, 8), (NH<sub>4</sub>)<sub>2</sub>Ce(SO<sub>4</sub>)<sub>4</sub>·4H<sub>2</sub>O, 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 occurs in 3+ and 4+ oxidation states (particularly, Pu and Am). 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<sub>4</sub>, is a widespread compound in nature and relatively easily obtained by chemical synthesis. Contrarily, the ceric counterpart ‘Ce<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>’ does not exist in nature and has not been synthesized and characterized to date. There are however other phosphates of Ce(IV) as Ce(PO<sub>4</sub>)(HPO<sub>4</sub>)<sub>0.5</sub>(H<sub>2</sub>O)<sub>0.5</sub>, M<sup>I</sup>Ce<sub>2</sub>(PO<sub>4</sub>)<sub>3</sub> (M<sup>I</sup>= Li, Na, K, Rb, and Cs), Ce<sup>III</sup><sub>1-2x</sub>Ce<sup>IV</sup><sub>x</sub>M<sup>II</sup><sub>x</sub>PO<sub>4</sub> (M<sup>II</sup> = Ba, Sr, x < 0.1), and M<sup>II</sup>Ce(PO<sub>4</sub>)<sub>2</sub> (M<sup>II</sup>= Mg, Ca, Sr, Ba, and Cd). From all these compounds, only the first 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. Even if in the mentioned study ‘BaCe(PO<sub>4</sub>)<sub>2</sub>’ is the target compound, the existence of all ceric phosphates obtained at high temperature is questionable.

In order to elucidate this behaviour, ‘Ce<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>’ and CePO<sub>4</sub> were obtained by starting from Ce(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (Loba Chemie Wien) and Ce(SO<sub>4</sub>)<sub>2</sub> (Alfa Aesar), respectively. By adding 25% H<sub>3</sub>PO<sub>4</sub> (Loba Chemie Wien, 10% excess) and a few drops of NH<sub>4</sub>OH (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<sub>4</sub> obtained was dark green, while ‘Ce<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>’ colorless.

The results of the XRD and electron microscopy experiments of the two compounds indicates that in both cases we achieved single phases with monazitic structure, crystallizing in monoclinic group P2<sub>1</sub>/n. All the lattice parameters of ‘Ce<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>’ (a= 0.6781 nm, b= 0.6996 nm, c= 0.6448 nm, β= 103.52 °) are lower than for the ones corresponding to CePO<sub>4</sub> (a= 0.6800 nm, b= 0.7023 nm, c= 0.6471 nm, β= 103.46 °), which might indicate that, in the first case, the ‘f’ electron was assigned, with the formation of Ce<sup>4+</sup> 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<sup>3+</sup> ion (ionic radius for coordination number IX of 0.196 nm). 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 compounds. For instance, the molar ratio P/Ce is 1.06 for CePO<sub>4</sub>, (theoretical value: 1.00), while P/Ce is of 1.18 for ‘Ce<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>’ (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<sup>0</sup> and 4f<sup>I</sup> electronic

configuration. This result is in perfect agreement with that of XPS measurements summarized in figure 9 of [1] in which it was observed a peak of 920 eV, corresponding to partial oxidation of Ce(III) from CePO<sub>4</sub> (4f<sup>1</sup> electronic configuration) to Ce(VI) (4f<sup>0</sup> electronic configuration).

The FT-IR spectra proved that both compounds are pure orthophosphates. The bands at 1000-950 cm<sup>-1</sup> were assigned to stretching, while those at 620-530 cm<sup>-1</sup> to bending vibrations of the PO<sub>4</sub><sup>3-</sup> tetrahedra. Moreover, no vibration band in the domain 800-700 cm<sup>-1</sup> (associate to the P-O-P bridge characteristic of pyrophosphate or polytrioxophosphate groups) was observed. Raman spectra of the two compounds indicates identical behavior of 'Ce<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>' and CePO<sub>4</sub>. It can thus see clusters of four bands (two A<sub>g</sub> and two B<sub>g</sub>) in the 970-1080 cm<sup>-1</sup> domain corresponding to symmetric vibrations ν<sub>1</sub> and ν<sub>3</sub> of orthophosphate ion. The only noticeable difference is in the intensity of the asymmetric band ν<sub>2</sub>(PO<sub>4</sub>), indicating a higher degree of disorder in 'Ce<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>', 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<sub>3</sub>(PO<sub>4</sub>)<sub>4</sub>' [3CeO<sub>2</sub> + 4(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>] and M<sup>II</sup>Ce(PO<sub>4</sub>)<sub>2</sub> [M<sup>II</sup>CO<sub>3</sub> + CeO<sub>2</sub> + 2(NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, M<sup>II</sup> = 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.

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<sub>4</sub>)<sub>2</sub>': CaM<sup>IV</sup>(PO<sub>4</sub>)<sub>2</sub> type orthophosphate are known for M<sup>IV</sup> = Zr, Ce, Th, U, and Np (Table 1).

**Table 1.** Lattice parameters for CaM<sup>IV</sup>(PO<sub>4</sub>)<sub>2</sub> reported compounds.

Compound	Structure	Space group	<i>a</i> , nm	<i>b</i> , nm	<i>c</i> , nm	β, °	Ref.
CaZr(PO <sub>4</sub> ) <sub>2</sub>	orthorhombic	P2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	1.44876	0.67213	0.67213	90.00	[3]
'CaCe(PO <sub>4</sub> ) <sub>2</sub>	monoclinic	P2 <sub>1</sub> /n	0.6759	0.6992	0.6438	103.43	[4]
CaTh(PO <sub>4</sub> ) <sub>2</sub>	monoclinic	P2 <sub>1</sub> /n	0.6714	0.6921	0.6424	103.68	[5]
CaU(PO <sub>4</sub> ) <sub>2</sub>	monoclinic	P2 <sub>1</sub> /n	0.6654	0.6841	0.6359	103.98	[2]
CaNp(PO <sub>4</sub> ) <sub>2</sub>	monoclinic	P2 <sub>1</sub> /n	0.6673	0.680	0.6375	104.11	[5]

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<sup>II</sup>Ce(PO<sub>4</sub>)<sub>2</sub>' (M<sup>II</sup>= Ca, Ba) compounds based on the behavior of the redox couple Ce(IV)/Ce(III) at temperatures above 1000 K in air [1,2]. In the absence of microscopic analysis for other compounds 'M<sup>II</sup>Ce(PO<sub>4</sub>)<sub>2</sub>' (M<sup>II</sup> = Mg, Ca, Sr, Ba, Cd, and Pb), the results previously reported are not convincing. It seems that in all these cases binary systems are obtained, concentrating cerium on CePO<sub>4</sub> crystalline phase and the divalent ion in an amorphous one, as it was demonstrated for 'BaCe(PO<sub>4</sub>)<sub>2</sub>' [1].

## References

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