

Synthesis and Characterization of Phosphates Containing Alkali Metals and Plutonium or Lanthanides*

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The compound $\text{Na}_3\text{Pu}(\text{PO}_4)_2$ has been synthesized and positively identified for the first time by X-ray diffraction, Raman spectroscopy, and absorption spectrophotometry. The literature on quaternary phosphates containing alkali metals (M) and lanthanides (Ln) or actinides (An) has been critically reviewed. Since the existence of compounds of the type $\text{M}_3(\text{Ln,An})_2(\text{PO}_4)_3$ appeared to be questionable, we conducted several replicate experiments with Ln = La to Gd. Our results did not reveal the existence of such compounds.

Introduction

As part of our research on plutonium phosphates, we were interested in the synthesis of $\text{Na}_3\text{Pu}(\text{PO}_4)_2$. Before we attempted the synthesis of this compound, the literature on quaternary phosphates was critically reviewed. This review revealed significant inconsistencies, and even possible errors, in the identification of postulated compounds; thus, several preparations, some duplicating reported methods, were undertaken to clarify the existence of selected quaternary phosphates. Because Raman spectroscopy had been particularly useful in the past for identifying crystalline phosphate-containing compounds, we used it extensively in this work.

Literature Review

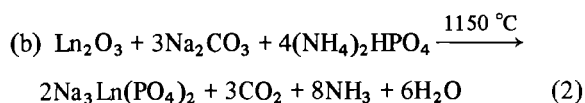
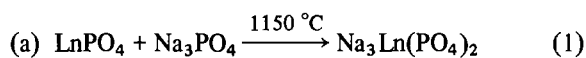
We arbitrarily divided the alkali metal (M)-lanthanide or actinide (Ln,An)-containing orthophosphates into the following types: I: $\text{M}_3(\text{Ln,An})(\text{PO}_4)_2$; II: $\text{M}_3(\text{Ln,An})_2(\text{PO}_4)_3$ and III: $\text{MAn}_2(\text{PO}_4)_3$. A review of the available information follows.

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Type I. $\text{M}_3(\text{Ln,An})(\text{PO}_4)_2$

Compounds of type (I), where M is either sodium or potassium, have been synthesized. Kizilyalli and Welch [1] prepared the corresponding sodium compounds of La, Ce, Nd, Gd and Y by means of several different reactions:

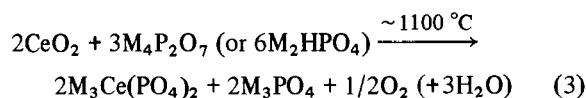


(c) Adding CeCl_3 or GdCl_3 solution to a considerable excess of Na_2HPO_4 solution, and, after drying, igniting the precipitate at 900°C .

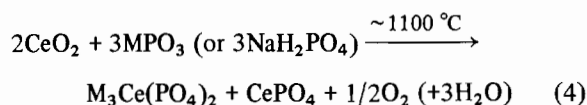
Kizilyalli and Welch [1] provided tables of X-ray diffraction intensities and 'd' values indexed in the (α) tetragonal system. A second type of structure, β or high temperature form, was described for Na–Gd and Na–Y compounds. This 'high' temperature form, which exhibits X-ray diffraction patterns only slightly different from the 'low' temperature form, was not actually obtained at higher temperatures. It was obtained by heating at the same temperature as the 'low' temperature form, but for longer heating periods followed by quenching.

Salmon *et al.* [2] used the method of eqn. 2 to prepare type I compounds containing Na and La, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er and Y, and provided a table of lattice parameters for the compounds assigned to the orthorhombic system. Salmon *et al.* [2] concluded that the structure of these compounds is related to and can be derived from that of $\beta\text{-K}_2\text{SO}_4$, and furthermore that the 'b' and 'c' parameters of the double phosphates are twice the size of those measured in the unit cell of $\beta\text{-K}_2\text{SO}_4$.

Bamberger *et al.* [3] prepared the Na–Ce and K–Ce compounds by means of the following reactions:



and



For $M = \text{Na}$, the compound gave an X-ray diffraction pattern that agreed with that of Kizilyalli [1]; for $M = \text{K}$, the compound was of a different structure which appeared to be neither tetragonal nor hexagonal. For $M = \text{Li}$, no double phosphate was formed, this observation was also made in 1979 by Loshchenov *et al.* [4].

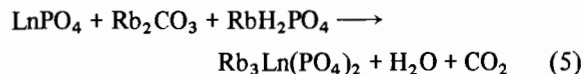
Mayer prepared the corresponding Na, -Pr, -Nd, -Sm, and -Gd compounds by reacting the lanthanide oxides with stoichiometric amounts of $\text{Na}_3\text{PO}_4 \cdot 12\text{H}_2\text{O}$ and $(\text{NH}_4)_2\text{HPO}_4$ at 1150°C and indexed their X-ray patterns in the orthorhombic system [5]. A comparison of the lattice parameters determined by Salmon [2] and by Mayer [5] reveals that they are the same but with b_0 and c_0 interchanged.

Mel'nikov *et al.* [6] prepared $\text{K}_3\text{Sc(PO}_4)_2$ by firing to 1150°C mixtures of what appears to be ScPO_4 and Na_3PO_4 in a ratio 1:4–5; the compound was assigned to the hexagonal system, and its diffraction pattern shows a resemblance to $\text{K}_3\text{Ce(PO}_4)_2$ [3] despite the significant difference in ionic radii of Sc and Ce.

Mel'nikov and Komissarova prepared the potassium compounds of Y and Gd to Yb and assigned them to the monoclinic system; the rubidium compounds of Y and Dy to Lu were assigned to the trigonal system while those of Gd and Lu were assigned to the monoclinic system [6a].

Hong and Chinn [7] synthesized single crystals of $\text{K}_3\text{Nd(PO}_4)_2$ by heating to 1400°C mixtures of $\text{K}_2\text{-CO}_3$, Nd_2O_3 and $\text{NH}_4\text{H}_2\text{PO}_4$ in the ratios 3:1:2, 3:2:3, 6:1:3 and 9:1:4. All these mixtures yielded crystals with isotypic monoclinic structures; an analysis of the structure indicated that the neodymium had a coordination number of 7.

Skiba *et al.* [8] synthesized three phosphate phases containing Na and Pu(III) by reacting PuCl_3 with Na_3PO_4 , both added to molten NaCl at 820°C . The phases were designated by the Roman numerals I to III depending on the molar ratio of Pu-to-phosphate initially added, which was, respectively, 1:1.5, 1:2 and 1:10. Phases I and II containing 58.2 and 60.1 wt.% Pu appeared to be similar; thus, only one listing of intensities and 'd' values were given. Phase III contained 47.0% Pu and its 'd' values and intensities were different from I and II. No attempt was made by the authors to assign stoichiometries to the compounds. As will be seen below, we have been able to elucidate those stoichiometries based on the work described in this paper. Mel'nikov *et al.* [9] have synthesized $\text{Rb}_3\text{Ln(PO}_4)_2$ where $\text{Ln} = \text{Gd to Lu, Y and Sc}$ by means of the reaction



at 600 to 700°C . The preparations were analyzed chemically and by X-ray powder diffraction. Mel'nikov *et al.* reported that the compounds containing Y and Dy to Lu are trigonal and those containing Gd and Tb are monoclinic, although the latter could be satisfactorily indexed as orthorhombic. Morozov *et al.* [10] have synthesized $\text{M}_3\text{-Ln(PO}_4)_2$ compounds, where $M = \text{Na, K, Rb or Cs}$ and $\text{Ln} = \text{Nd or Eu}$, using several of the reactions described above. The compounds were examined by infrared spectroscopy, and it was concluded that the data were in agreement with results from Raman spectroscopy reported in [1]. An additional, and more important, conclusion was that changing the alkali metal attached to the anion $\text{Ln(PO}_4)_2^{3-}$ has a larger effect on the IR spectra than changing the lanthanide.

Figure 1 shows the unit cell volume for $\text{Na}_3\text{Ln(PO}_4)_2$ compounds as a function of the effective ionic radius of the lanthanide element with coordination number 6 using Shannon's [11] estimates. The coordination number 6 was chosen arbitrarily over the more appropriate number 7 [7, 10] because not all the data needed were available.

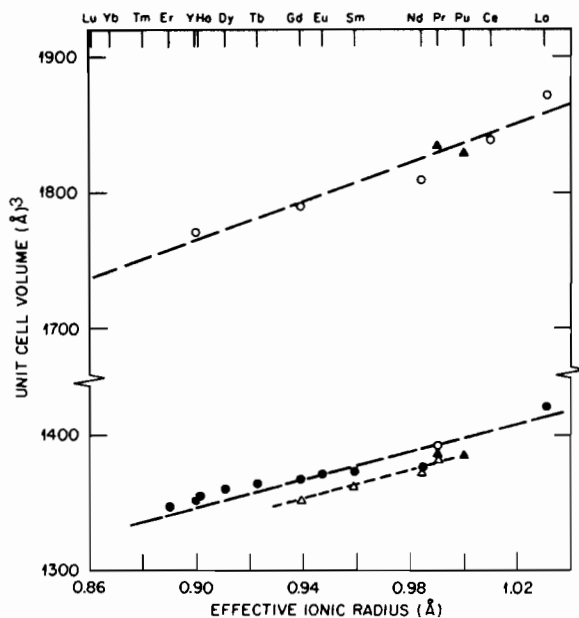


Fig. 1. Unit cell volume, in \AA^3 , of $\text{Na}_3\text{Ln(PO}_4)_2$ vs. effective ionic radii for coordination number 6 from [11]. Δ from [5], \circ from [1], \bullet from [2], \blacktriangle from this work.

Type II. $\text{M}_3(\text{Ln,An})_2(\text{PO}_4)_3$

Compounds of this type have been reported by Tananaev *et al.* where Ln is Pr, Sm, or Yb [12]. The compounds were prepared by dehydrating the corresponding heptahydrates which, in turn, were obtained

by precipitation from solution of LnCl_3 or $\text{Ln}(\text{NO}_3)_3$ with Na_3PO_4 [13].

Although listings of X-ray diffraction intensities and 'd' values are given, no identification of the structures is reported. According to the authors [12], air dried salts were 'semiamorphous', and when dehydrated at 600 °C they became crystalline; when heated to 1000 °C the same lines were present in the X-ray diffraction patterns as in those heated to 600 °C, but the intensities were different. Thus, it was proposed that 'two high temperature modifications' exist in compounds heated up to 1000 °C. Tananaev *et al.* concluded that, when heated to 1000 °C, the double phosphates do not decompose into simple orthophosphates (LnPO_4 and Na_3PO_4) because mechanical mixtures of those two orthophosphates heated to 1000 °C yield X-ray diffraction patterns different from those of the double compounds of type II. No indication is given whether such diffraction patterns are those of the single orthophosphates or of double compounds of type I, although as will be shown below we believe that they should have been of the latter type.

Kryukova *et al.* [14] have reported lattice parameters for Na- and K-double phosphates (type II) of Ce, Pr and Nd. The compounds were prepared by addition of the tenfold stoichiometric excess (over Ln) of an ammoniacal solution of Na_2HPO_4 or K_2HPO_4 at 70 °C to a $\text{Ln}(\text{NO}_3)_3$ solution. The amorphous precipitates were dried at 180 °C and held in molten NaCl or KCl, probably at 800 °C. A second preparative method consisted of heating to 1200 °C a mixture of lanthanide oxide and alkali metal phosphate in the presence of B_2O_3 , followed by extraction of the boron compounds by boiling the solids in water. X-ray diffraction results were used to verify that the compounds obtained by the two methods were identical. Kryukova *et al.* [15], in an extension of the above reported work, prepared compounds of type II of Sm, Eu and Gd with Na or K using the methods described above. The compounds were found to be isomorphous with those of Ce, Pr and Nd, and were indexed as trigonal.

While studying the interaction of CeO_2 or CeCl_3 with zirconium phosphate in alkali metal chloride melts at 700 °C, Kryukova *et al.* [16] found that the corresponding Na- and K-compounds of type II were formed; consequently, their X-ray diffraction patterns were obtained. A comparison of the Na-compound's pattern with that of $\text{Na}_3\text{Sm}_2(\text{PO}_4)_3$ obtained by Tananaev *et al.* [12] shows a very close resemblance, but this is not so with the patterns of either of the two forms of $\text{Na}_3\text{Pr}_2(\text{PO}_4)_3$ [12].

Kazantsev *et al.* [17] have recently reported on the preparation of Am and Cm-compounds containing Na or K. The preparation was based on the addition of AnCl_3 and M_3PO_4 to molten MCl at 820 °C, a method similar to that used by

Skiba *et al.* [8] for preparing their unidentified plutonium phases.

A plot of the unit cell volume for the above lanthanide compounds [14, 15], and some analogs of actinides [17], as a function of effective ionic radii [11] is shown in Fig. 2. It can be seen that an empirical linear correlation similar to that found for compounds of type I in Fig. 1 is not so clearly evident in Fig. 2. Furthermore, and perhaps more important, the type II compounds reported by Kryukova [14, 15] do not show a significant change in the unit cell volume when changing from Na to K, the only exception being the Ce-compounds. This behavior, and the fact that compounds of type II were not observed either by Kizilyalli *et al.* when reacting LnPO_4 directly with varying amounts of Na_3PO_4 at temperatures up to 1000 °C [1], or by Bamberger *et al.* [3] who, by means of eqn. 4, obtained $\text{Na}_3\text{Ce}(\text{PO}_4)_2$ and CePO_4 , made us suspicious of the existence of compounds of type II in general.

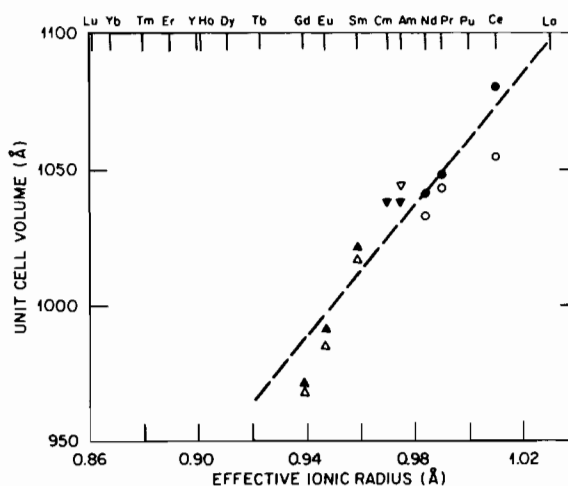


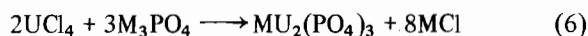
Fig. 2. Unit cell volume, in Å^3 of $\text{M}_3(\text{Ln},\text{An})_2(\text{PO}_4)_3$ vs. effective ionic radii for coordination number 6 from [11]. \circ Na-Ln compounds from [14], \bullet K-Ln compounds from [14], \triangle Na-Ln compounds from [15], \blacktriangle K-Ln compounds from [15], ∇ Na-An compounds from [17], \blacktriangledown K-An compounds from [17].

Type III. $\text{M}(\text{An})_2(\text{PO}_4)_3$

Compounds of this type have been prepared by Matkovic *et al.* [18] by reacting metal dioxides with any of the acidic or neutral alkali metal phosphates in the presence of B_2O_3 at 1200 °C. The compounds, $\text{M} = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$ and $\text{An} = \text{Th}$ or $\text{M} = \text{Li}, \text{Na}$ and $\text{An} = \text{U}$, have been identified as having a monoclinic structure, and their lattice parameters are given. Thorium in the compound $\text{KTh}_2(\text{PO}_4)_3$, which was studied the most extensively, was concluded to be nine coordinated.

Nectoux and Tabuteau [19] have recently prepared $\text{NaNp}_2(\text{PO}_4)_3$ by reaction of NpO_2 , Na_3PO_4 and $(\text{NH}_4)_2\text{HPO}_4$ at 750–800 °C. The intensities and 'd' values are listed. These have been used to calculate lattice parameters based on a monoclinic structure and Np was considered to be nine coordinated, similarly to the Th-compounds [18].

Kryukova *et al.* [20] reported in 1981 the preparation of U(IV) and U(VI) containing double phosphates, the former by means of the reaction



(where M is either Na or K) performed in molten alkali metal chlorides at 820 °C. The authors state that equilibration time at constant temperature affects the structure and color but not the stoichiometry of the solid formed. The solids are identified as phases I and II and their diffraction patterns are given. The fact that the temperature remained constant suggests that probably one of the solids (phase I, short contact time) was not an equilibrium phase. Some resemblance between the diffraction patterns of $\text{NaU}_2(\text{PO}_4)_3$, phases I and II, with those of $\text{NaNp}_2(\text{PO}_4)_3$ [19] can be detected; however, one would have expected a much closer agreement.

In earlier work (1977) Kryukova *et al.* [21] also reported the synthesis and diffraction patterns of Na- and $\text{KU}_2(\text{PO}_4)_3$ by reacting UO_2 with ZrP_2O_7 in melts of NaCl or KCl at 700 °C in an argon atmosphere. Not much resemblance can be detected among the diffraction patterns of $\text{NaU}_2(\text{PO}_4)_3$ with that synthesized in 1977 [21] and those of material synthesized in 1981 [20]. However, the X-ray patterns of the $\text{NaU}_2(\text{PO}_4)_3$ synthesized earlier [21] and of $\text{NaNp}_2(\text{PO}_4)_3$ [19] show sufficient resemblance to suggest that they are analogous compounds.

Skiba *et al.* [22] report on the synthesis of $\text{NaPu}_2(\text{PO}_4)_3$ prepared by reaction of PuO_2 with NaH_2PO_4 in molten B_2O_3 for 16 hours at 1200 °C without specifying the nature of the gaseous environment (vacuum, air, *etc.*). The solid reaction product was treated with boiling 10% HCl solution. The structure of the resulting solid was assigned to the orthorhombic system, and a listing of intensities and 'd' values was provided. The plutonium content was analyzed to be 56.7 wt.%, which is not in close agreement with the calculated value of 60.82 wt.% of ^{239}Pu .

A comparison of the diffraction pattern of $\text{NaPu}_2(\text{PO}_4)_3$ [22] with those of $\text{NaU}_2(\text{PO}_4)_3$ [20, 21] and those of $\text{NaNp}_2(\text{PO}_4)_3$ [19] again fails to show any of the expected resemblance. Unless the presence of sodium confers a significant stability to the Pu(IV) phosphate structure, the results obtained by Skiba *et al.* [22] may be suspect, because our work [23] and Bjorklund's [24] with ternary plutonium phosphates indicate that at temperatures above 1000 °C only Pu(III)-phosphates are stable.

The lattice parameters of $\text{NaNp}_2(\text{PO}_4)_3$ [19] seem to be in good agreement with those of analogous compounds of Th and U measured by Matkovic [18].

Experimental and Discussion

Rare earth oxides and fluorides from commercial sources (99+% purity) were used without further purification; PuO_2 was obtained from ORNL's Isotope Sales; all the other reagents were of analytical grade purity. The preparation of specific rare earth phosphates is described below as needed. Platinum boats were used to contain the various mixtures of phosphates. Reactions with plutonium were done in a silica system connected to a Model #741 Beckman Oxygen Analyzer and argon was used as carrier gas. X-ray powder diffraction patterns, using Cu-K α radiation, were obtained with Debye-Scherrer cameras. Absorption spectra were recorded with a specially designed spectrophotometer described elsewhere [25]. Raman spectra were recorded with a Ramanor HG-2S spectrometer using the 514.5 or 457.9 nm argon-ion laser lines for excitation [26–28].

Experiments Performed to clarify Discrepancies in the Literature

Because neither Kizilyalli *et al.* [1] nor Bamberger *et al.* [3] had heated their reagents to temperatures as high (1200 °C) as some of the other investigators, we mixed PrPO_4^* and Na_3PO_4 (1:1 and 2:1 molar ratios) by grinding and heated the mixtures for 16 hours at 1225 °C. The products were examined by Raman spectroscopy and X-ray diffraction and were found to consist, respectively, of pure $\text{Na}_3\text{Pr}(\text{PO}_4)_2$, similar to that reported by Mayer [5], and a mixture $\text{Na}_3\text{Pr}(\text{PO}_4)_2$ with PrPO_4 . In order to confirm this further, we obtained the Raman spectra of mechanical mixtures of PrPO_4 with $\text{Na}_3\text{Pr}(\text{PO}_4)_2$ and found that they were the same as those obtained from the product of the reaction of $2\text{PrPO}_4 + \text{Na}_3\text{PO}_4$ at 1225 °C. These Raman spectra are shown in Fig. 3. Similar results were obtained with cerium compounds, except that some small amounts of CeO_2 were formed as found in [3].

Quaternary compounds of type I, $\text{Na}_3\text{Ln}(\text{PO}_4)_2$, of the rare earths La to Gd were prepared by reaction of the corresponding oxides with $\text{Na}_4\text{P}_2\text{O}_7$. Their Raman spectra and selected X-ray diffraction patterns confirmed their identity. Attempts to prepare analogous compounds of Y and Tb to Lu revealed that such compounds may exhibit polymorphism and/or even form together with additional phases of a dif-

*Prepared by means of: $\text{PrF}_3 + \text{BPO}_4 \rightarrow \text{PrPO}_4 + \text{BF}_3$.

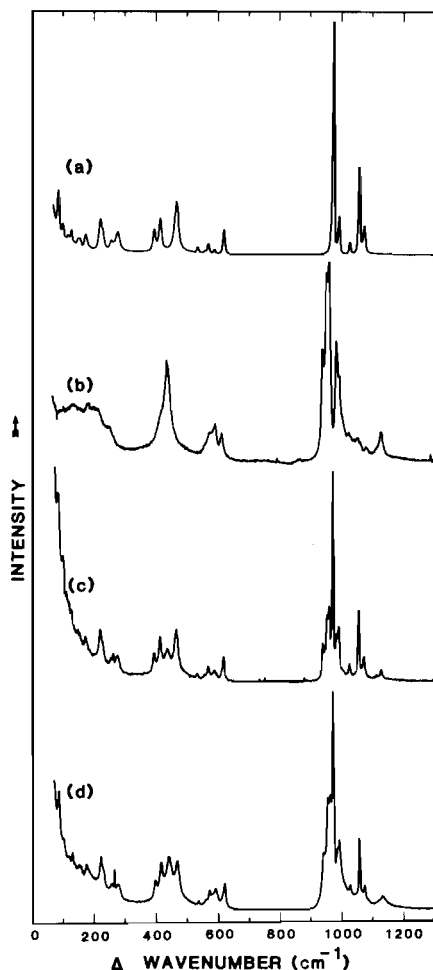


Fig. 3. Raman spectra, with 514.5 nm excitation, of: (a) PrPO_4 , (b) $\text{Na}_3\text{Pr}(\text{PO}_4)_2$ made by heating to 1225 °C $\text{Na}_3\text{PO}_4 + \text{PrPO}_4$ and also $\text{Pr}_6\text{O}_{11} + 9\text{Na}_4\text{P}_2\text{O}_7$, (c) Mechanical mixture of a + b, (d) Product of heating to 1225 °C a mixture of $2\text{PrPO}_4 + \text{Na}_3\text{PO}_4$.

ferent stoichiometry. Elucidation of the latter continues and will be reported at a later time.

Additionally, we sought to replicate the experiments of Skiba *et al.* [8] and Kryukova *et al.* [16], which had in common the use of alkali metal chlorides as fluxes. Skiba *et al.* [8] did not specify the amount of NaCl, while Kryukova *et al.* [16] mention a "six to seven fold excess" of NaCl–KCl, which we interpreted to be with respect to the lanthanide element. In one experiment resembling Skiba's, we substituted NdF_3 for PuCl_3 and used the ratios $\text{Na}_3\text{PO}_4:\text{NdF}_3 = 2$ and $\text{NaCl}:\text{NdF}_3 = 16$. The mixture was heated to 900 °C for about 20 minutes plus 2 minutes at 1200 °C. After extraction with warm water, the solids remaining were dried at 75 °C under vacuum and examined by Raman spectroscopy. The product was identified as $\text{Na}_3\text{Nd}(\text{PO}_4)_2$. In another experiment, NdF_3 was reacted with 3.3 Na_3PO_4

in KCl-NaCl ($\text{Cl}^-/\text{Nd} = 7$) for 4 hours at 700 °C. After washing with water, the resulting solid was identified by Raman spectroscopy as pure $\text{Na}_3\text{Nd}(\text{PO}_4)_2$.

Kryukova *et al.* made seemingly conflicting statements [16] about reactions with CeO_2 in which no interaction was observed with Na_3PO_4 in a KCl-NaCl melt at 700 °C, while later on it is indicated that the reaction with CeO_2 goes to completion "only under the condition that the CeO_2 is formed in the chloride melt from CeCl_3 ". We duplicated the above experiment and found that no reaction had occurred. The water insoluble residue was pure CeO_2 . Thus, we interpret Kryukova's and our results as an indication that the CeO_2 used was unreactive because of its small surface area, possibly a result of its being heated to a high temperature. The important conclusion from this set of experiments is that we found no evidence for the synthesis of compounds of type (II), $\text{Na}_3\text{Ln}_2(\text{PO}_4)_3$.

Because we have indications that $\text{Pu}(\text{IV})$ is not stable toward thermal reduction in the presence of phosphate at 1200 °C [23], we sought to simulate the experiment of Skiba *et al.* [22] by replacing $\text{Pu}(\text{IV})$ by $\text{Ce}(\text{IV})$ for experimental convenience. This preparative method was also used by Matkovic *et al.* [18] for preparing $\text{MAn}_2(\text{PO}_4)_3$ and by Kryukova *et al.* [14, 15] for preparing their $\text{M}_3\text{Ln}_2(\text{PO}_4)_3$ compounds. Thus, CeO_2 was reacted with NaH_2PO_4 at two molar ratios Ce/PO_4 , 1:3.7 and 1:7.5, in excess B_2O_3 (molar ratio $\text{B}_2\text{O}_3/\text{CeO}_2 = 24$) at 1200 °C for about 16 hours. The solids were extracted with warm 10% HCl solution (to reproduce conditions used in [22]) and dried under vacuum at 80 °C. Raman spectra of the solids revealed, surprisingly, that they consisted of pure monoclinic CePO_4 . Because Kizilyalli [1] indicated that the compounds $\text{Na}_3\text{Ln}(\text{PO}_4)_2$ are dissolved by dilute mineral acids, we sought to verify this for the conditions (boiling in 10% HCl) used by Skiba [22] for removing the boron compounds. It was found that $\text{Na}_3\text{Pr}(\text{PO}_4)_2$ and $\text{Na}_3\text{Ce}(\text{PO}_4)_2$, pure or mixed with CeO_2 , all dissolved rapidly; only the latter left a residue of CeO_2 . Because this finding suggests that Skiba's residue may not represent all the products formed in their preparation, we decided to repeat the preparation with cerium and extract the solids with boiling water instead of 10% HCl solution. The residue was examined by X-ray diffraction and Raman spectroscopy and again was identified as monoclinic CePO_4 . This identification was considered sufficient because we had established earlier [26–28] that Raman spectroscopy is one of the best techniques for identifying and analyzing rare earth phosphate mixtures. With this new knowledge, we compared the X-ray diffraction patterns of compounds of type II, ref. [12] for lanthanides and ref. [17] for actinides, with the patterns corresponding to the pure $\text{Ln}_2\text{An}(\text{PO}_4)_3$

orthophosphates available in the literature, including data by Kuznetsov *et al.* [29], and with those of compounds of type I reported in [1] and [5]. From this comparison we may conclude that the compounds of type II, $\text{Na}_3(\text{Ln},\text{An})_2(\text{PO}_4)_3$, reported in refs. [12, 17] and phases I and II reported in [8], consist essentially of $(\text{Ln},\text{An})\text{PO}_4$ as a major phase with possibly the corresponding quaternary compounds of type I as a minor phase. We were not able, however, to offer an alternative stoichiometry for the compound identified as $\text{NaPu}_2(\text{PO}_4)_3$ (type III) by Skiba [22] which gives a diffraction pattern different from the Th, U and Np analogs.

Synthesis and Characterization of $\text{Na}_3\text{Pu}(\text{PO}_4)_2$

A mixture of PuO_2 and Na_2HPO_4 was heated at 1050°C for 16 hours under flowing N_2 . O_2 evolution was observed, but only qualitatively, because the amount of PuO_2 used was too small (0.14 mMol). The solid product was amorphous by X-ray diffraction. It was then annealed at 800°C for 16 hours in a stream of Ar-4% H_2 , the latter to insure complete plutonium reduction. The solid was examined by Raman spectroscopy and its spectrum compared to that of water-extracted $\text{Na}_3\text{Pr}(\text{PO}_4)_2$ used as a reference and prepared by the following reactions

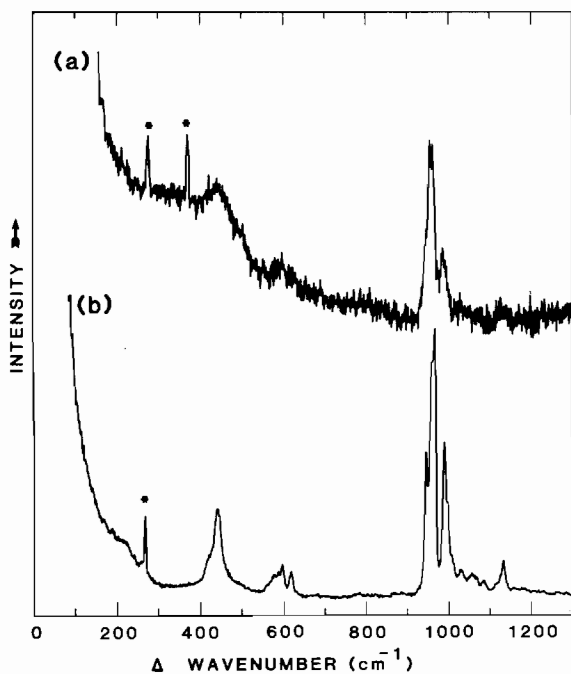


Fig. 4. Raman spectra of (a) $\text{Na}_3\text{Pu}(\text{PO}_4)_2$ and of (b) $\text{Na}_3\text{Pr}(\text{PO}_4)_2$. Both compounds were obtained by reaction of, respectively, PuO_2 and Pr_6O_{11} with Na_2HPO_4 and washed with warm water. Excitation: (a) 457.9 nm, (b) 514.5 nm; * = laser plasma lines.

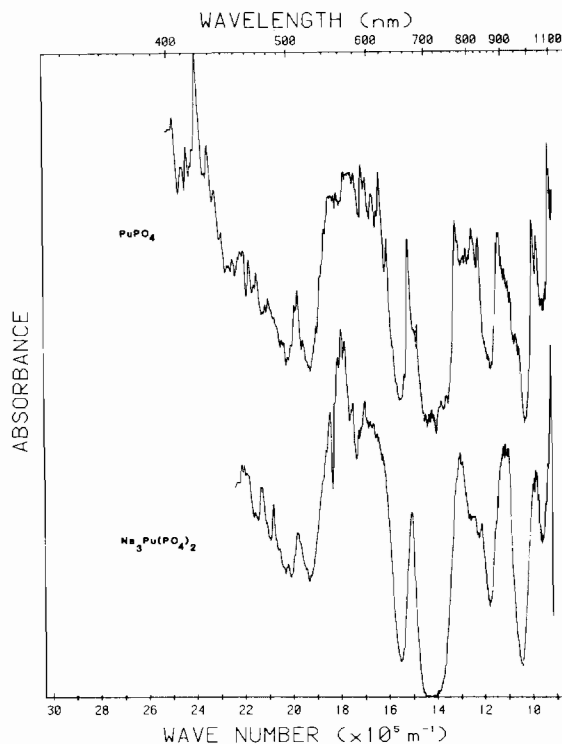
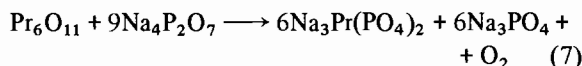
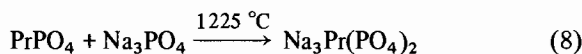


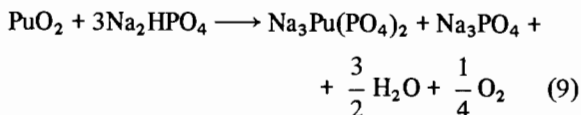
Fig. 5. Absorption spectra of PuPO_4 and $\text{Na}_3\text{Pu}(\text{PO}_4)_2$.



performed under flowing N_2 to 1080°C and



The Raman spectra of the $\text{Na}_3\text{Pr}(\text{PO}_4)_2$ obtained matched that reported in [4] for $\text{Na}_3\text{Nd}(\text{PO}_4)_2$ within the slight shift in peaks expected for such closely related elements; an exception is one medium intensity peak present in our preparation at 442 cm^{-1} (Fig. 4). The Raman spectrum of the plutonium compound also showed the presence of $\text{Na}_4\text{P}_2\text{O}_7$; this reagent and the Na_3PO_4 formed in the reaction were removed by extraction with warm water. The Raman spectrum of the washed solid is shown in Fig. 4, and the absorption spectrum, together with that of PuPO_4 [23], is shown in Fig. 5. A very strong similarity between the two spectra can be observed; this provides strong evidence that the oxidation state of the plutonium in the double phosphate is (III). Because PuPO_4 and $\text{Na}_3\text{Pu}(\text{PO}_4)_2$ have different crystal structures, their absorption spectra also indicate that the valence of plutonium, (III), is the dominating factor in the spectra rather than their crystal structure. The above results together with its diffraction pattern proved that the solid consisted of $\text{Na}_3\text{Pu}(\text{PO}_4)_2$ and that its formation can be represented by:



The diffraction patterns of the $\text{Na}_3\text{Pu}(\text{PO}_4)_2$ could be indexed in either the orthorhombic or tetragonal systems with similar uncertainties in their respective lattice parameters. Since no choice of structure can be made at this time, values for both systems are reported here:

$$\text{Orthorhombic } a_0 = 5.344(4), b_0 = 18.53(1), c_0 = 13.98(2) \text{ \AA}$$

$$\text{Tetragonal } a_0 = 13.08(3), c_0 = 10.69(2) \text{ \AA}$$

These values, together with those for our $\text{Na}_3\text{Pr}(\text{PO}_4)_2$, are included in Fig. 1. A comparison of the diffraction pattern of our $\text{Na}_3\text{Pu}(\text{PO}_4)_2$ with that of phase III of Skiba *et al.* [8] confirmed that phase III consists of $\text{Na}_3\text{Pu}(\text{PO}_4)_2$. We had suspected this from a prior comparison of diffraction patterns of phase III and of $\text{Na}_3\text{Ln}(\text{PO}_4)_2$ [2]. This is further confirmed by comparison of its theoretical plutonium content (48.0 wt.%) with that found by the Russian authors, 47.0 wt.%.

Conclusions

It is very likely that the discrepancies found in the literature regarding double phosphates of alkali metals and rare earths of different stoichiometries resulted from relying only on a single identification technique such as X-ray diffraction without taking into account its limitations of sensitivity. The lack of chemical analysis and/or a complementary technique to examine the solids after treatments such as boiling in 10% HCl may have compounded the identification problem.

From examination of literature data we conclude that many, if not all, of the preparations identified as having the stoichiometry $\text{Na}_3\text{Ln}_2(\text{PO}_4)_3$ consist mainly of LnPO_4 with minor amounts of $\text{Na}_3\text{Ln}(\text{PO}_4)_2$. This would also explain the negligible effect of replacing Na by K observed in the alleged compounds of type II, shown in Fig. 2.

Additionally, our experiments replicating those in the literature for preparing $\text{Na}_3\text{Ln}_2(\text{PO}_4)_3$ confirmed that the products were LnPO_4 . Based on the above and on the lack of experimental confirmation of the existence of compounds of type II reported in [12, 14–17], these compounds have to be regarded at least as highly questionable.

The compound $\text{Na}_3\text{Pu}(\text{PO}_4)_2$ has been synthesized and characterized by X-ray diffraction. Its Raman spectrum, which verifies its identity, and its absorption spectrum are reported for the first time.

From a practical point of view, it can be concluded that the formation of alkali metal-containing double phosphates should be avoided in nuclear waste management schemes because of their appreciable solubility in water and high solubility in dilute mineral acids. Furthermore, because of the complex composition of nuclear wastes, the formation of alkali metal-containing double phosphates can occur in ceramic forms other than monazite. Such findings have been reported recently; in attempts to convert to titanates an acid waste stream containing phosphate (from TBP degradation) and Gd (added as neutron poison), the presence of $\text{Na}_3\text{Gd}(\text{PO}_4)_2$ in the resulting solids was shown [30].

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