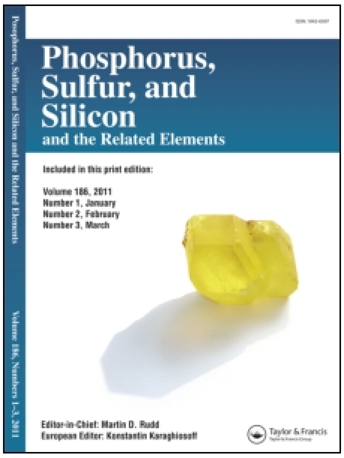

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Synthesis of Sodium Neodymium Diphosphate, $NaNdP_2O_7$, and Its Powder XRD Data and IR Spectra

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Synthesis of Sodium Neodymium Diphosphate, $NaNdP_2O_7$, and Its Powder XRD Data and IR Spectra

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$NaNdP_2O_7$ was synthesized by the solution reaction of $NdCl_3$ with $Na_4P_2O_7$ and heated the precipitate at 650°C for 6–7 h. The X-ray powder diffraction data of this compound was indexed in the orthorhombic system with the refined unit-cell parameters of $a = 12.579(7)$, $b = 15.10(1)$, and $c = 16.03(1)$Å, which were in good agreement with the reported data of $NaGdP_2O_7$. It was found that $NaLnP_2O_7$ compounds (Ln: La, Eu, Gd, and Y) cannot be synthesized by this method, but $NaCeP_2O_7$ has been prepared as an amorphous product. The IR spectra of $NaNdP_2O_7$ also agreed with the IR data of $NaGdP_2O_7$ with the presence of $P_2O_7^{4-}$ vibrational modes.

Keywords Diphosphate; infrared spectra; Neodymium; sodium neodymium diphosphate; X-ray diffraction (XRD)

INTRODUCTION

Phosphates of the rare earth elements are very important in chemistry and technology because of their main form of their occurrence in nature.

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Giesbrecht and Perrier[1] claimed to have obtained $NaCeP_2O_7 \cdot 4.5H_2O$ by adding a sodium diphosphate solution to a solution of cerium(III) chloride, without mentioning the pH of the solution. Kızılyallı[2] applied the same method for the preparation of $NaGdP_2O_7 \cdot 4.5H_2O$; however, the chemical analysis of the product heated at 700°C showed that it contained only 0.11% of Na_2O, whereas the theoretical percentage of Na_2O in $NaGdP_2O_7$ is 8.71%. Therefore, it was concluded that this compound was, in fact, hydrogen gadolinium diphosphate retaining some alkali metal as an impurity, as also suggested by X-ray powder diffraction and IR data. The single crystal structure of this compound has been reported.[3] Most recently, acid rare earth phosphates have been prepared by using the same method in which the solution of sodium diphosphate and the acidic solution of the rare-earth chloride were mixed.[4]

Some mixed diphosphates of rare earths have been synthesized by several researchers.[1,5,6] Tannanaev, Kuznetsov, and Vasil'eva[7] reported the preparation of some rare earth alkali double diphosphates through solution reactions and complex X-ray powder diffraction patterns in the case of $LiLaP_2O_7$, $KLaP_2O_7$, and α- and β-$NaLaP_2O_7$, without indexing. Later, Anisimova, Trunov, and Chudinova[8] prepared mixed diphosphates of the type $NaLnP_2O_7$ ($Ln =$ La, ... Lu) by using Ln_2O_3 and vitreous $NaPO_3$, and annealing the mixed powders for 50 h. According to the crystal–chemical parameters of the products obtained, $NaNdP_2O_7$ and $NaGdP_2O_7$ were indexed in a monoclinic system, whereas $NaCeP_2O_7$ was in the orthorhombic system. They also found that when the mixed diphosphate is heated at 790°C, it decomposed in the solid phase as shown in the following reaction;

$$NaNdP_2O_7(\text{cryst.}) \rightarrow NdPO_4(\text{cryst.}) + NaPO_3(\text{amorph}) \tag{1}$$

But they have not studied the IR spectra of these compounds.

Quite recently, $NaGdP_2O_7$ has been prepared using the following solid-state reactions by Kizilyalli and Darras;[9]

$$\begin{aligned} Gd_2O_3 + 4(NH_4)_2HPO_4 + Na_2CO_3 &\rightarrow 2NaGdP_2O_7 + CO_2 \\ &\quad + 8NH_3 + 6H_2O \\ Gd_2O_3 + 2P_2O_5 + Na_2CO_3 &\rightarrow 2NaGdP_2O_7 + CO_2 \\ GdPO_4 + NaPO_3 &\rightarrow NaGdP_2O_7 \end{aligned} \tag{2}$$

In these reactions, to avoid the decomposition of $NaGdP_2O_7$, utmost care was taken and the temperature was kept around 650°C. The X-ray diffraction (XRD) powder data is indexed in the orthorhombic system with the approximate unit cell dimentions of $a = 12.44$, $b = 15.00$, and c = 15.87 Å, and the space group was found to be Pmm2. Analysis of the vibrations of the $P_2O_7^{4-}$ ion, according to C_{2v} symmetry and band assignments for IR and Raman spectra, also were reported. The P-O-P band was found to be nonlinear; coincidences in the IR and Raman spectra suggested that the most probable space group is noncentrosymmetric.

In this study, we aimed to search the possibility of preparation of the $NaLnP_2O_7$ compounds (Ln: La, Ce, Nd, Eu, Gd, and Y) using a new method. This was accomplished by adding a solution of $Na_4P_2O_7$ to the solution of $LnCl_3$, and then sintering the precipitate for a short reaction period. By using this new method, only $NaNdP_2O_7$ could been obtained and was found to crystallize in the orthorhombic system. In the same way, we seamingly obtained $NaCeP_2O_7$ as an amorphous product. But the other rare earth mixed diphosphates could not be synthesized by this solution method.

EXPERIMENTAL

Chemicals and Instrumentations

The chemicals that we used were reagent grade Ln_2O_3, $CeCl_3.6H_2O$ (99.9% pure, Fluka), and $Na_4P_2O_7$ (Merck).

Spectroscopic grade KBr was used as a pellet material; a Nicolet 510 Fourier Transform Infrared Spectrophotometer was employed to record infrared spectra using transmission mode.

X-ray diffraction patterns of the powder specimens and heat treated at different temperatures were recorded on a conventional Philips Diffractometer with PW 1050/25 goniometer and CuK_α radiation. NaCl was used as an external standard. Indexing of the XRD pattern was accomplished by a program developed in our laboratory and checked by a Huber diffractometer program. The least-square refinement procedure of the unit cell parameters was done by the Huber program.

Procedure

To each of 2 25-mL portions of 0.09M $LnCl_3$, which was obtained by the dissolution of Ln_2O_3 in dilute HCl solution (Ln: La, Nd, Gd, Eu, and Y) and adjusted to pH = 1–2, 25 mL of 0.09M $Na_4P_2O_7$ solutions, were added with stirring. Stirring was continued for 6 h. The gelatinous precipitate then was filtered and dried under vacuum at 130°C. The X-ray powder diffraction patterns of the products that were obtained were amorphous. Further heatings were done at 650, 700, and 750°C for about 6–7 h.

The method outlined above also was used for the preparation of the cerium compound by using $CeCl_3 \cdot 6H_2O$ and $Na_4P_2O_7$ solutions.

RESULTS AND DISCUSSION

The following reaction was predicted to take place in solution:

$$LnCl_3(aq) + Na_4P_2O_7(aq) \rightarrow NaLnP_2O_7 \cdot xH_2O(s) + 3Na^+(aq) + 3Cl^-(aq) \quad (3)$$

X-Ray Powder Diffraction Studies

The X-ray powder diffraction patterns of the precipitates that were dried in vacuum at 130°C indicated that an amorphous compound was obtained for each rare earth element. In an effort to isolate an anhydrous crystalline compound, the six products dried in vacuum were heated at 650, 700, and 750°C under the same conditions and for the same time. These treatments gave crystalline and anhydrous compounds, except for the Ce compound, which was amorphous. These results are outlined below.

Nd-compound

Examination of the X-ray powder data of the Nd compound heated at 650°C and showed that the product essentially was a single phase. Some diffraction lines of $NdPO_4$ and $NaPO_3$ seemed to be present in the X-ray pattern, but their intensities were not consistent with the literature data. The powder data given in Figure 1 and Table I were similar to those of $NaGdP_2O_7$.[9] Therefore, it is believed that the primary phase

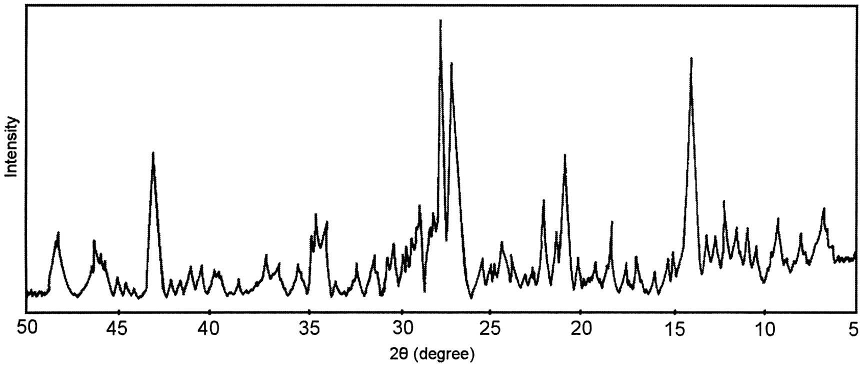

FIGURE 1 X-ray powder diffraction pattern of $NaNdP_2O_7$.

TABLE I X-Ray Powder Diffraction Data of $NaNdP_2O_7$. Orthorhombic: $a = 12.579(7)$, $b = 15.10(1)$, and $c = 16.03(1)$ Å. Rad. CuK_α

I/I_o	d_{obs}	d_{calc}	hkl
26	12.54	12.56	100
21	10.94	10.98	11
29	9.57	9.65	110
11	8.28	8.27	111
27	8.07	8.00	2
22	7.60	7.55	20
34	7.25	7.07	12
21	6.90	6.82	21
21	6.56	6.47	120
88	6.28	6.28	200
18	5.86	5.84	201
13	5.79	5.80	210
13	5.54	5.49	22
20	5.24	5.33	3
20	5.02	5.03	30
32	4.84	4.83	220
15*	4.67	4.67	130
18	4.37	4.36	23
69	4.24	4.26	32
21	4.162	4.152	222
12*	4.114	4.115	123
39*	4.035	4.033	310
12	3.927	3.925	213
14	3.895	3.910	311
11	3.831	3.812	231
14	3.754	3.772	40
24	3.663	3.660	320
11	3.596	3.579	223
12	3.541	3.524	141
14	3.500	3.513	133
87	3.280	3.293	142
100	3.198	3.201	5
53	3.157	3.154	331
42	3.132	3.131	34
45*	3.077	3.073	410
19*	3.039	3.038	134
18*	3.028	3.018	50
13	2.991	2.985	332
14	2.957	2.947	25
26*	2.937	2.934	150
16	2.903	2.892	304
28*	2.831	2.824	52
18	2.763	2.755	152
11	2.667	2.663	430

(Continued on next page)

TABLE I X-Ray Powder Diffraction Data of $NaNdP_2O_7$. Orthorhombic: a = 12.579(7), b = 15.10(1), and c = 16.03(1) Å. Rad. CuK_α *(Continued)*

I/I_o	d_{obs}	d_{calc}	hkl
46	2.625	2.627	431
49	2.613	2.609	106
38*	2.579	2.571	153
20	2.520	2.511	500
20	2.455	2.448	350
26*	2.411	2.409	54
9*	2.348	2.341	352
16*	2.292	2.295	344
18	2.284	2.283	522
26	2.239	2.238	163
25	2.202	2.196	55
13	2.173	2.175	450
13*	2.156	2.148	425
72*	2.098	2.092	600
7*	2.0659	2.0662	444
12	2.0324	2.0326	406
15	2.0123	2.0007	612
17	1.9893	1.9832	18
41	1.9636	1.9626	460
19	1.9529	1.9480	461
44	1.8861	1.8845	436
38	1.8787	1.8764	552

*Matching $NdPO_4$ lines.

was $NaNdP_2O_7$. It was indexed in the orthorhombic system and the refined lattice parameters were found to be a = 12.579(7), b = 15.10(1), and c = 16.03(1) Å (Table I), which were in good agreement with the unit-cell parameters of $NaGdP_2O_7$, so the two compounds were proved to be isostructural. The X-ray powder diffraction studies of the same material heated at 700°C indicated that the product was still $NaNdP_2O_7$ with the same x-ray data that was obtained at 650°C. When the experiment was performed at 750°C, the product, $NaNdP_2O_7$, started to decompose into $NdPO_4$ and $NaPO_3$. But since $NaPO_3$ melts at this temperature and becomes amorphous, its diffraction lines did not appear in the X-ray pattern. Only $NaNdP_2O_7$ and $NdPO_4$ lines were observed in the X-ray data at 750°C.

Gd-Compound

By investigating the XRD data of the Gd compound that were heated at 650, 700, and 750°C, the diffraction lines belonging to $GdPO_4$,[10] $HGdP_2O_7$,[2] and $Gd_4(P_2O_7)_3$[11] compounds appeared. When the compound obtained at 750°C was reheated at 900°C, $Gd_2P_4O_{13}$ was observed as a product, which was previously reported.[12,13]

In the case of La and Eu, similar observations were obtained for heat treatments at 650, 700, and 750°C.

Y-compound

In the X-ray diffraction patterns of the Y compound that were heated at 650, 700, and 750°C, only YPO_4 diffraction lines were observed.

Ce-compound

In the case of Ce compound, no crystalline phase could be obtained at all studied temperatures.

Infrared Spectroscopy Studies

The IR spectra of a number of diphosphate salts have been examined in the literature[14–19] and it has been found that their strong characteristic absorption bands appeared in the region of 950–910 and 670–735 cm^{-1}. C_{2v} symmetry and a bent bridge eclipsed the orientation of the two PO_3 groups through a P—O—P bridge of the $P_2O_7^{4-}$ ion, which was supported by Palmer.[17]

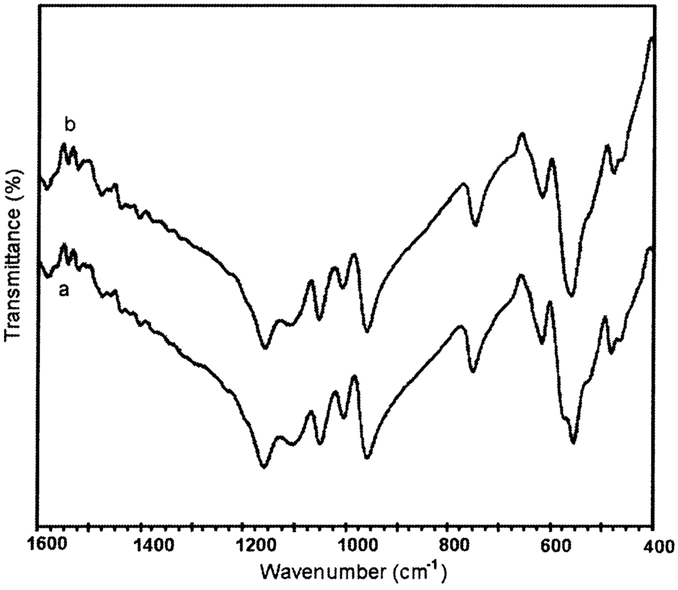

FIGURE 2 (a) Infrared spectrum of $NaNdP_2O_7$. (b) The IR spectrum observed for heat-treated products of Ce at 650°C.

The number of normal modes of vibrations is 21, but only 17 are IR active,[20] the number of vibrational modes could be increased by both the appearance of combinations and overtones.

On the other hand, the IR and Raman spectra of monoclinic α- and β-$Mg_2P_2O_7$, α-$Ca_2P_2O_7$, orthorhombic α-$Sr_2P_2O_7$, and α-$Ba_2P_2O_7$ and triclinic $Ca_2P_2O_7.2H_2O$ were predicted using the C_{2v} free ion-group symmetry species.[21–23]

Recently, the infrared and Raman spectra of orthorhombic $NaGdP_2O_7$ were interpreted by Kizilyalli and Darras. They assigned the vibrational bands for $NaGdP_2O_7$ on the basis of Cornilsen's discussions on $Ca_2P_2O_7$, $Mg_2P_2O_7$, and $Sr_2P_2O_7$,[22] and on Walrafen's calculations[24] for the C_{2v} free ion-group symmetry. Later, the vibrational spectra of $M^ILnP_2O_7$ ($M^I =$ Rb, Cs; Ln = rare earth) have been studied using factor group analysis.[25–26]

The infrared spectrum of the product that was obtained and predicted to be $NaNdP_2O_7$, which was found to be isostructural with $NaGdP_2O_7$,[9] is given in Figure 2(a). Examination of the IR data in Table II indicated that there was a good agreement with the reported values for $NaGdP_2O_7$.[9]

The IR spectra observed for the heat-treated products of Ce at 650, 700, and 750°C were similar to that of $NaNdP_2O_7$. The IR spectrum of the Ce compound that were obtained at 650°C is shown in Figure 2(b).

TABLE II The Approximate Vibrational Band Assignments for $NaNdP_2O_7$

ν(cm^{-1})	Approximate assignments
1232	$\nu_{as}(PO_3)$
1196	$\nu_{as}(PO_3)$
1157	$\nu_{as}(PO_3)$
1104	$\nu_{as}(PO_3)$
1051	$\nu_s(PO_3)$
1010	$\nu_{as}(PO_3)$
960	$\nu_{as}(POP)$
754	$\nu_s(POP)$
631	$\delta(PO_2)$ terminal bending
622	$\delta(PO_2)$ terminal bending
575	$\delta(PO_2)$ terminal bending
558	$\delta(PO_2)$ terminal bending
528	$\delta(PO_2)$ terminal bending
486	$\delta(PO_2)$ terminal bending
469	$\delta(PO_2)$ terminal bending

CONCLUSION

The preparation of $NaNdP_2O_7$ has been reported by Anisimova, Trunov, and Chudinova[8] using a mixture of $NaPO_3$: Nd_2O_3 with the molar ratio of $NaPO_3$:$Nd_2O_3 = 19{:}1$. Then, they annealed the powders for 50 h at 550–580°C and indexed the obtained product in the monoclinic system with the cell parameters of $a = 12.613$, $b = 8.538$, $c = 5.267$ Å, and $\beta = 90.79$°C.

In this work, a new method for the synthesis of $NaNdP_2O_7$ was achieved through a solution reaction by mixing the appropriate amounts of $NdCl_3$ and $Na_4P_2O_7$ solutions, and, subsequently, heating the amorphous product at 650°C for 6–7 h.

Examination of the powder diffraction data of $NaNdP_2O_7$ prepared in this study showed that this compound is isostructural with $NaGdP_2O_7$ synthesized through a solid-state reaction by Kızılyallı and Darras.[9] The X-ray powder pattern of the product was found to be orthorhombic with the refined unit-cell parameters of $a = 12.579(7)$, $b = 15.10(1)$, and $c = 16.03(1)$Å, and the IR spectra of $NaNdP_2O_7$ agreed with the previous data for $NaGdP_2O_7$.

We were unable to obtain other sodium lanthanide mixed diphosphates through the method described above. Even though it was not possible to crystallize the Ce-compound, IR data suggest that $NaCeP_2O_7$ actually was obtained.

On the other hand, $NaLaP_2O_7$,[27] prepared through solid-state reactions in our laboratory, was found to be isostructural with $NaNdP_2O_7$. Further details will be published later.

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