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Solid-State Synthesis, Structure, and Vibrational Spectra of $NaGdP_2O_7$*

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$NaGdP_2O_7$ was synthesized by the solid-state reaction of Gd_2O_3 with Na_2CO_3 and $4(NH_4)_2HPO_4$ at 650°C. The X-ray powder diffraction data of $NaGdP_2O_7$ was indexed in the orthorhombic system with the approximate unit cell dimensions of $a = 12.44$, $b = 15.00$, and $c = 15.87$ Å and the space group is $Pmm2$. Analysis of the vibrations of the $P_2O_7^{4-}$ ion according to C_{2v} symmetry and approximate band assignments for IR spectra are also reported in this work. The P–O–P band was found to be nonlinear, and some coincidences in the infrared and Raman spectra suggest that the most probable space group is noncentrosymmetric. © 1993 Academic Press, Inc.

Introduction

Work performed by Konak and Kizilyalli (*1, 2*) showed the importance of lanthanide double diphosphates as ceramic materials. Quite recently, Kizilyalli (*3*) prepared $HGdP_2O_7 \cdot nH_2O$ from sodium diphosphate and an acidic solution of gadolinium chloride. Giesbrecht and Perrier (*4*) claimed to have obtained $NaCeP_2O_7 \cdot 4.5H_2O$ by adding sodium diphosphate solution to a solution of cerium(III) chloride. The same method was applied for the preparation of $NaGdP_2O_7 \cdot 4.5H_2O$ in our laboratory. However, after correction for loss of water at 700°C, the chemical analysis of the prepared product showed that it contained only 0.11% Na_2O, whereas the theoretical percentage of Na_2O should be 8.71. This work indicated that compounds obtained by the use of this method and which were previously believed to be alkaline lanthanide diphosphates were in fact hydrogen lanthanide diphosphates retaining some alkali metal. It was established that it was impossible to introduce sodium in a diphosphate precipitated at about pH 1–2. As had been demonstrated earlier (*5*), the amount of Na_2O introduced was 1.17% at pH 4.6. It is not convenient to work at a pH higher than 4.6 because the precipitation of gadolinium hydroxide will interfere.

Some double diphosphates of rare earths have been synthesized by several researchers (*4, 6, 7*). Tananaev *et al.* (*8*) reported the preparation of some rare earth alkali double diphosphates through solution reactions and gave some complex X-ray powder diffraction patterns in the case of $LiLaP_2O_7$, $KLaP_2O_7$, and α- and β-$NaLaP_2O_7$ (J.C.P.D.S. Nos. 21-502, 21-651, 21-1131, and 21-1133). They were not indexed. Investigation of $NaGdP_2O_7$ and solid-state methods of preparation have not been reported in the literature.

Because of the failure to prepare $NaGdP_2O_7$ in solution, the following solid-solid reaction was attempted:

(i) $Gd_2O_3 + 4(NH_4)_2HPO_4 + Na_2CO_3 \rightarrow 2NaGdP_2O_7 + CO_2 + 6H_2O + 8NH_3$.

The X-ray powder diffraction patterns of

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several products prepared under different conditions, in air, showed the formation of a new phase in addition to $GdPO_4$. It therefore appeared necessary to investigate this reaction very carefully. In the course of these investigations, two other solid-state reactions were also studied:

(ii) $Gd_2O_3 + P_2O_5 + Na_2CO_3 \rightarrow 2NaGdP_2O_7 + CO_2$,

(iii) $GdPO_4 + NaPO_3 \rightarrow NaGdP_2O_7$.

For the third reaction, pure $GdPO_4$ also has to be prepared and X-ray powder diffraction has to be recorded and compared with the published data (Ref. (*9*) and J.C.P.D.S. No. 32-386) since it does not exist as a commercial product.

In light of all these experiments, a solid-state method of preparation was suggested for this new compound, and an attempt was made to determine its structure by X-ray powder diffraction and to identify the new compound through its vibrational spectra.

Experimental

Materials and Instrumentation

The chemicals used were reagent grade Gd_2O_3 (99.9% pure, Fluka), Na_2CO_3, P_2O_5, $NaPO_3$, and $(NH_4)_2HPO_4$ (Merck). $GdPO_4$ was prepared in the laboratory by the method of Buyers *et al.* (*10*).

Spectroscopic grade KBr was used as a pellet material and for Perkin–Elmer 1430 ratio recording; an FTIR (Nicolet and Hitachi Model 270-30) spectrophotometer was employed to record infrared spectra. Far-IR data were recorded with PE pellets and an IFF/113V Bruker spectrometer. For Raman spectra, Spect./1877 equipment with a triple monochromator, in combination with PSD and an argon ion laser (515 nm) was used. A Philips diffractometer with a PW 1050/25 goniometer and CuK_α radiation was used for taking X-ray powder diffraction patterns.

The purity of $GdPO_4$ was confirmed through X-ray powder diffraction and IR methods which were in close agreement with our previous work (*9*) and the vibrational modes described by Hezel and Ross (*11*).

Chemical Analysis of the Products

The method described by Vogel (*12*) was adopted with several modifications to determine the percentages of gadolinium and phosphorus.

Reaction of $Gd_2O_3 + Na_2CO_3 + 4(NH_4)_2HPO_4$. Na_2CO_3 and $(NH_4)_2HPO_4$ were dried at 80°C to constant weight. $(NH_4)_2HPO_4$, Gd_2O_3, and Na_2CO_3 were weighed separately and ground together in an agate mortar, then the mixture was weighed and was put in a porcelain crucible for heating. The reactions were carried out in air at several temperatures ranging from 500 to 1000°C using variable time intervals. Different reactant compositions were also tried using the same temperature.

Reaction of $GdPO_4 + NaPO_3$. The reaction was carried out at 500 to 1000°C for several time intervals.

Reaction of $Gd_2O_3 + Na_2CO_3 + 2P_2O_5$. Utmost care was taken in weighing and grinding the samples to avoid absorption of water. The optimum temperature range was found to be around 550–650°C.

Results and Discussion

X-Ray Powder Diffraction Results of the Reaction Products Obtained from $GdPO_4 + NaPO_3$ *Solid-State Reactions*

This reaction was performed at 250, 500, 600, and 700°C for about 8 hr. It was found that no appreciable reaction took place at 250°C. In the X-ray powder data of the product, synthesized at 500°C, some strong undefined lines were observed (together with $GdPO_4$ and $NaPO_3$), resembling those of $NaLaP_2O_7$ (J.C.P.D.S. Nos. 21-1131 and 21-1133). The product was assumed to be $NaGdP_2O_7$. For the 600°C product, intensities of the unidentified lines in the X-ray powder pattern increased and those of $GdPO_4$ and

$NaPO_3$ were quite weak. At 700°C the product which was predicted to be $NaGdP_2O_7$ decomposed into $GdPO_4$ + $NaPO_3$, but since $NaPO_3$ melted at this temperature and became amorphous, its lines did not appear in the pattern. X-ray diffraction data of $NaPO_3$ used in this reaction were recorded also (after heating at 600°C) for comparison purposes.

X-Ray Powder Diffraction Results of the Reaction Products Obtained from Gd_2O_3 + Na_2CO_3 + $2P_2O_5$ Solid-State Reactions

The experiment was performed at 600°C since it was observed that after several initial experiments this was the optimum temperature for the formation of the desired product. The X-ray powder pattern was quite complicated, but the product presumed to be $NaGdP_2O_7$ was again observed together with $GdPO_4$ and a double phosphate, X-phase, reported by Sungur (*13*) and Kizilyalli (*14*), which resembled $Na_3Gd(PO_4)_2$.

X-Ray Powder Diffraction Results of the Reaction Products Obtained from Gd_2O_3 + Na_2CO_3 + $4(NH_4)_2HPO_4$ Solid-State Reactions

First the mixture was heated at 650°C for 3 hr in air. The calcined sample was repowdered and heated again at the same temperature for 4 hr, followed by an additional repowdering. This procedure was repeated several times to obtain a more homogeneous sample. Powder X-ray diffraction studies indicated that the product was essentially a single phase. The reactions were repeated and reproducible results were obtained. Some lines of $GdPO_4$ and $(NaPO_3)_3$ seem to be present in the X-ray data, but their intensities were not consistent with the reported data for $GdPO_4$ (J.C.P.D.S. No. 32-386) and the $NaPO_3$ pattern obtained at 600°C. This powder data, which are given in Table I, were indexed in the orthorhombic system, and the approximate lattice constants were found to be a = 12.44, b = 15.00, and c = 15.87 Å. The space group was $Pmm2$.

The weight loss during the reaction was also studied and it was observed that in a period of about 3 hr the experimental and theoretical losses agreed quite well. They were calculated on the basis of the following reaction:

$$Gd_2O_3 + Na_2CO_3 + 4(NH_4)_2HPO_4 \rightarrow 2NaGdP_2O_7 + 8NH_3 + CO_2 + 6H_2O.$$

The average weight percentages of Gd, P, and Na obtained through the analysis of the three products (which were prepared separately) and theoretical results for $NaGdP_2O_7$ are given in Table II.

These results proved that the product is essentially $NaGdP_2O_7$, but it is probable that some $GdPO_4$ or $NaPO_3$ may be present in small amounts, which explains the discrepancies between the theoretical and analytical results.

IR Studies

Corbridge and others (*15–18*) examined the spectra of a number of diphosphate salts and found strong characteristic absorptions from 950–910 and 670–735 cm^{-1}.

C_{2v} symmetry and a bent bridge eclipsed orientation of the two PO_3 groups through the P–O–P bridge of the $P_2O_7^{4-}$ ion was supported by Palmer (*18*) and MacArthur and Beevers (*19*). The number of normal modes of vibrations is 21, but only 17 are IR active (*20*), hence the number could be increased both by the appearance of combinations and overtones. In a few cases, such as the study of Savoie and Giguere (*21*) on Cl_2O_7, all 21 modes are described and assigned.

Most of the work carried out on molecules of the X_2Y_7 type involves approximate assignments; that is, the modes are simply classified as $V_{as}PO_3$, V_sPO_3, V_{as} OPO, V_s OPO, δ PO_2, and δ POP, which are terminal and bridge stretching and bending frequencies (*22–26*).

The crystallographic investigations of

TABLE I

X-RAY POWDER DIFFRACTION DATA OF $NaGdP_2O_7$

Orthorhombic: a = 12.44, b = 15.00, and c = 15.87Å S.G. $Pmm2$ Rad. CuK_α			
I/I_0	$d_{obs.}$	$d_{calc.}$	hkl
9	12.19	12.44	100
9	10.98	10.90	011
10	9.46	9.58	110
11	8.19	8.20	111
6	7.94	7.94	002
10	7.48	7.50	020
5	7.08	7.02	012
5	6.81	6.78	021
5	6.46	6.42	120
100	6.22	6.22	200
5	5.80	5.79	201
5	5.75	5.75	210
5	5.46	5.44	022
6	5.29	5.29	003
18	5.00	5.00	030,013
28	4.77	4.77	031,220
5[a]	4.57	4.58	221
5	4.32	4.32	023
50	4.21	4.23	032
18	4.162	4.147	300
10[a]	4.086	4.086	123,222
37[a]	3.978	3.967	004,310
16	3.909	3.897	230,213
8	3.845	3.835	014
3	3.794	3.785	231,104
14	3.730	3.751	040
13	3.655	3.650	041,114
10	3.580	3.591	140
1	3.507	3.507	024,141
12	3.482	3.488	133
66	3.277	3.271	142
50	3.209	3.212	240
84	3.175	3.174	005
78	3.153	3.146	241
42	3.110	3.110	400
31[a]	3.063	3.060	043
18[a]	3.015	3.015	134
18[a]	2.997	3.000	050
—	—	2.961	332
20	2.954		—
—	—	2.948	051
16[a]	2.917	2.917	150
12	2.885	2.873	420
14[a]	2.803	2.806	052
18	2.734	2.733	333
5	2.710	2.703	250
4	2.640	2.645	006,430
45	2.608	2.610	053,431,016
26	2.589	2.588	106
25[a]	2.552	2.554	153,116
20	2.501	2.500	060
10	2.491	2.488	500,334
10	2.433	2.433	206,350
18[a]	2.387	2.389	325,062
7[a]	2.326	2.327	424
13[a]	2.276	2.277	344
12	2.268	2.267	007
12	2.242	2.242	017
27	2.218	2.222	405
16	2.194	2.197	415
12	2.178	2.180	055,443
8	2.154	2.156	523
11[a]	2.138	2.139	127,326
68[a]	2.0745	2.0734	600
5[a]	2.0490	2.0492	444,227
14	2.0149	2.0148	406
10	1.9955	1.9971	416
31	1.9725	1.9722	317
12	1.9509	1.9486	460
25	1.9407	1.9403	047
14	1.8769	1.8754	080
27	1.8614	1.8618	632
14	1.7890	1.7892	308,356
6	1.7776	1.7772	700,318
11	1.7664	1.7661	701
13	1.6980	1.6987	381

TABLE I—*Continued*

[a] Matching $GdPO_4$ lines.

some diphosphates proved that the diphosphate ion is nonlinear. The terminal and bridging bonds are unequal in length and the two PO_3 groups are imperfectly staggered. This being the case, the symmetry is either C_s or C_1, and in both cases all 21 vibrations are both IR and Raman active. A normal coordinate analysis of C_s or C_1 was found

TABLE II

EXPERIMENTAL AND THEORETICAL WEIGHT PERCENTAGES FOR $NaGdP_2O_7$

	%Na	%Gd	%P	P/Gd
Theoretical	6.49	44.44	17.49	2.00
Experimental	6.02	42.81	16.83	2.02

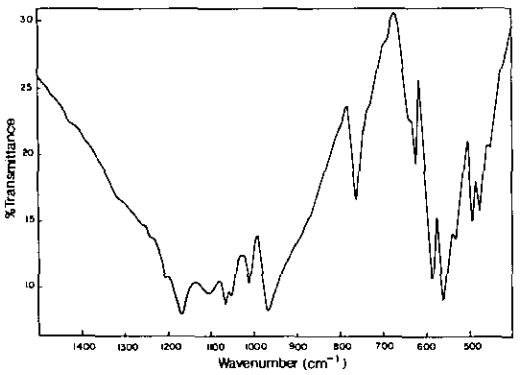

FIG. 1. IR spectrum of $NaGdP_2O_7$ in the region 1500–400 cm^{-1}.

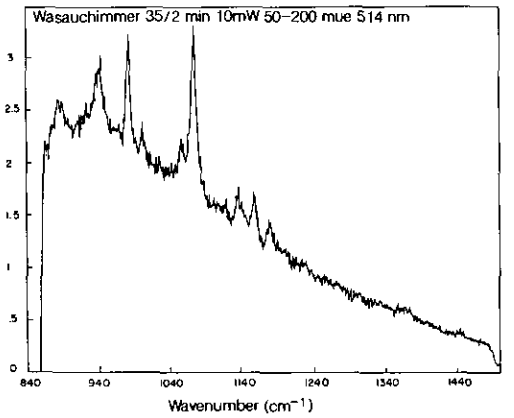

FIG. 3. Raman spectrum of $NaGdP_2O_7$ in the region 1440–840 cm^{-1}.

to be difficult to compute since there was a large number of force constants which would need to be estimated. Therefore a D_3, D_{3h}) and D_{3d} model was considered by Mooney *et al.* (*27*). This would give a general picture of vibrational assignments and it would be possible to predict the effects of lower symmetry (*20*).

On the other hand, the IR and Raman spectra of monoclinic α-$Mg_2P_2O_7$, β-$Mg_2P_2O_7$, and α-$Ca_2P_2O_7$, orthorhombic α-$Sr_2P_2O_7$ and α-$Ba_2P_2O_7$, and triclinic $Ca_2P_2O_9 \cdot 2H_2O$ were predicted using the C_{2v} free ion group symmetry species (*28–30*). Cubic SiP_2O_7 was reported earlier (*31*). Recently, infrared, and Raman spectra of cubic and monoclinic SiP_2O_7 were measured and interpreted by Chakraborty *et al.* (*32*) using coordinate analysis.

The infrared and Raman spectra of the product obtained in this research and predicted to be $NaGdP_2O_7$ are given in Figs. 1–4. The large number of infrared bands observed (more than 17) support the assumption of distorted C_{2v} symmetry. In Table III the distribution of modes among symmetry classes for the $P_2O_7^{4-}$ ion were determined on the basis of Cornilsen's discussions on $Ca_2P_2O_7$, $Mg_2P_2O_7$, and $Sr_2P_2O_7$ (*29*), and Walrafen's calculations (*26*) for the C_{2v} free ion group symmetry.

Infrared spectra obtained in this work indicate a peak at 1200 cm^{-1} which was considered of a_2 type by Simon and Wagner

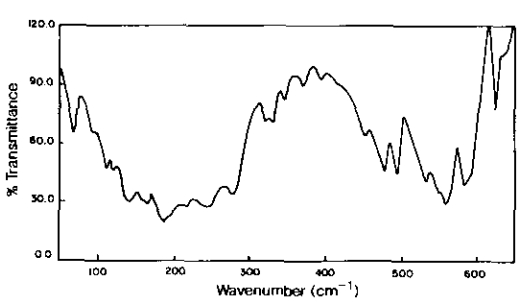

FIG. 2. IR spectrum of $NaGDP_2O_7$ in the region 50–650 cm^{-1}.

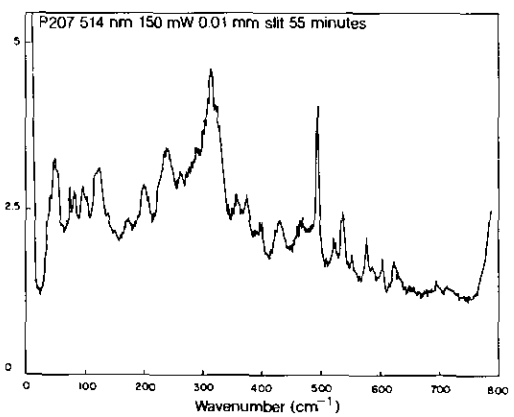

FIG. 4. Raman spectrum of $NaGdP_2O_7$ in the region 800–50 cm^{-1}.

TABLE III

BAND ASSIGNMENTS FOR $NaGdP_2O_7$ (cm^{-1}) [S. G. *Pmm2*]

IR	Intensity[a]	Approximate assignments	Intensity	Raman
1205	W		M	1181
1167	S		M	1160
—		V_{as} PO_3	M	1137
1110	M		W	1120
1067	M		S	1075
1050	M	V_s PO_3	M	1056
1010	S	V_{as} PO_3	M	1002
996	S	V_{as} POP	S	981
—			M,S	940
—		Combination	M	884
765	S	V_s POP	S	775
670	W	Combination band		—
625	S		M	623
—			M	603
585	S		M,S	576
559	S		M	551
531	W		M,S	536
—		δ PO_2 terminal bending	M	522
492	W		S	494
478	S			—
455	M		M	469
431	W		M	431
392	M		M	400
369	M		M	375
342	M		M	356
329	M	δ POP bridge bending	S	329
318	M		S	315
278	S	Gd–O stretching (*32*)	M	275
243	S		S	239
218	W			—
197	S	External lattice modes	M,S	201
188	M			—
162	M		M	173
157	S			—
118	M		S	121
112				—
91	W		M	96
69	S	Torsional mode (*33*)	M	70

[a] W, weak; M, medium; S, strong.

(*25*). It should be IR inactive; so, it is concluded that some slight deviations from C_{2v} symmetry exists in $NaGdP_2O_7$. Such deviations result in a structure of C_2 symmetry where infrared-forbidden $4A_2$ become IR active, so all 21 vibrations were observed.

Examination of Table III shows that there are some coincidences in infrared and Raman spectra, which suggests that the most probable space group is noncentrosymmetric (*29*). X-ray data also gave a noncentrosymmetric space group, which is *Pmm2*. The bridge frequencies V_s POP and V_{as} POP are (ii) type as given by Ross (*33*) where V_a is about 200 cm^{-1} greater than V_s (966 cm^{-1} ~ 765 + 200 cm^{-1}) and δ POP bridge bending (329–318) is around 1/3 to 1/2 of V_s (765/2 or 3 × 382–282 cm^{-1}). This

suggests that the bridge is nonlinear (*33*), since as the bridge becomes more nearly linear the separation between frequencies increasing such as in Si–O–Si (*34*).

The infrared and Raman bands observed are in good agreement with the reported values for diphosphate compounds of divalent and tetravalent cations such as α-$Mg_2P_2O_7$ (*28*), α-$Ca_2P_2O_7$ (*29*), or SiP_2O_7 (*32*), although their space groups are not the same. Especially for α-$Sr_2P_2O_7$, a noncentrosymmetric orthorhombic structure is reported (*29*).

Conclusion

$NaGdP_2O_7$ was synthesized through the following solid-state reaction at 650°C:

$$Gd_2O_3 + Na_2CO_3 + 4(NH_4)_2HPO_4 \rightarrow 2NaGdP_2O_7 + 8NH_3 + 6H_2O + CO_2.$$

Over 650°C it decomposes into $GdPO_4$ + $NaPO_3$ · $NaGdP_2O_7$ dissolves by boiling in dilute nitric acid solution. The undissolved part was found to be $GdPO_4$ (around 5%). The X-ray powder diffraction data reported by Tananaev *et al.* (*6*) for $NaLaP_2O_7$ have some common reflections with the data of $NaGdP_2O_7$, but it appears that the two structures are not isostructural. On the other hand, the $NaLaP_2O_7$ prepared in our laboratory is isostructural with $NaGdP_2O_7$. The findings of investigations on double pyrophosphates of lanthanum and other rare earths will be published later.

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