JOURNAL OF SOLID STATE CHEMISTRY 120, 275–278 (1995)

Solid-State Synthesis, X-Ray Powder Diffraction, and IR Data of Na_2GdOPO_4

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Received May 3, 1995; in revised form June 26, 1995; accepted July 19, 1995

Na_2GdOPO_4, sodium gadolinium oxyphosphate, was prepared by the solid state reaction of Gd_2O_3 + $Na_4P_2O_7$ and its X-ray powder diffraction data was studied. The compound prepared at 1200°C showed the presence of two polymorphs which are orthorhombic and pseudoorthorohombic (monoclinic). The refined unit cell parameters were found to be a = 13.074(6), b = 10.637(5), c = 6.469(3) Å for the orthorhombic form. The X-ray powder data and the cell parameters were quite similar to that of $RbTiOPO_4$. The IR spectra of the compound is identical to that of M^ITiOPO_4 (M^I = K, Rb, Tl) except for three Ti–O vibrations. © 1995 Academic Press, Inc.

INTRODUCTION

A great number of oxyphosphates have been reported in the literature. A series of materials of $MOPO_4$ stoichiometry were characterized before (1–7). Some of these materials possess layered structures that are useful for catalytic, electronic, or ion exchange applications. The K_2O–Sb_2O_5–P_2O_5 system was recently investigated (8, 9) within a research program devoted to compounds likely to exhibit fast alcali ion mobility. Oxyphosphates of the type $MOPO_4$ in the Ta_2O_5–P_2O_5 system have been studied by Hahn (10), Heider (11), and Rakhmalutin *et al.* (12) who reported a $TaOPO_4$ compound with a complicated X-ray pattern. Levin and Roth (1) have shown that the unit cell is monoclinic with $a = 11.272, b = 5.281, c = 6.621$ Å and $\beta = 90.13°$.

The Nb_2O_5–P_2O_5 system has also been studied by many scientists. Levin and Roth (1) have reinvestigated the entire system and written a comprehensive review. At a 1:1 composition and preparation temperatures above 1250°C, $NbOPO_4$ is found to be isostructural with monoclinic $TaOPO_4$. However, when prepared below 1250°C, $NbOPO_4$ is tetragonal and isostructural with $MoOPO_4$ (2, 10, 13).

On the other hand, the single-crystal X-ray study of $SbOPO_4$ also indicates a monoclinic symmetry, but it is not isomorphous with the Nb and Ta system since its space group is $C2/c$ and a = 6.791, b = 8.033, c = 7.046 Å and β = 115.90° (14).

M^ITiOPO_4 (M^I = K, Rb, Tl) (15) was obtained at 1000°C by the use of the following reaction:

$$1/2M_2CO_3 + (NH_4)_2HPO_4 + TiO_2 \rightarrow MTiOPO_4 + 2NH_3 + 1/2CO_2 + 3/2H_2O.$$

The unit cell parameters of $KTiOPO_4$ (KTP) are reported as a = 12.814, b = 10.616, c = 6.404 Å and space group is reported as $Pnma$ or $Pn2_1a$ (15, 16). The short distance between Ti and the independent O atom causes a distortion of TiO_4 octahedra. KTP is a relatively new nonlinear optical material. It is increasingly used commercially for second harmonic generation and is a promising material for frequency doubling of laser radiation (17–19). On the other hand Bamberger and Cavin (20) reported the existence of $NaOTiO_4$ and $Na_4(TiO)(PO_4)_2$, but only powder diffraction data was given in this work.

Before this work (21) there was no study related to oxyphosphates of rare earths and alkaline metals of the type $M^I_2LnOPO_4$.

In the present research, the following solid state reaction was used to obtain Na_2GdOPO_4:

$$Gd_2O_3 + Na_4P_2O_7 \rightarrow 2Na_2GdOPO_4.$$

EXPERIMENTAL DETAILS

The chemicals used were commercial Gd_2O_3 (99.9% pure, obtained from Fluka) and $Na_4P_2O_7$ (Merck). The solid state reactions were carried out in platinum or silica crucibles. A Philips diffractometer with a PW 1050/25 goniometer and Cu$K\alpha$ radiation was used for X-ray powder diffraction studies. The experimental XRD data have been corrected using internal standard methods and refined using least-squares and computer indexing techniques supplied from Huber Company (Germany). The IR absorp-

[1] Based on a thesis submitted by A. Uztetik-Amour for the Ph.D. degree in chemistry.

0022-4596/95 $12.00

tion spectra of the products were obtained using a Nicolet 510 FT-IR spectrophotometer. The mixtures were sintered at several temperatures in the range 600–1200°C for different time intervals. The products were subjected to X-ray diffraction analysis after each sintering process.

RESULTS AND DISCUSSION

XRD Studies

In the XRD patterns of the reaction products synthesized at 600, 700, and 800°C, lines resembling those of $Na_4P_2O_7$ and unreacted Gd_2O_3 were observed.

As the reaction proceeded at 900 and 1000°C, α-$Na_3Gd(PO_4)_2$ (22), $GdPO_4$ (23), Gd_3PO_7 (24, 25), Na_3PO_4 (26), Gd_2O_3, and Na_2O (JCPDS) Card No. 23-528) lines appeared.

In the X-ray diffraction data of the product obtained at 1100°C, α-$Na_3Gd(PO_4)_2$, Gd_2O_3, and Na_2O were still present but the other compounds disappeared, showing that the following reaction had taken place:

$$2Na_4P_2O_7 + 2Gd_2O_3 \rightarrow 2Na_3Gd(PO_4)_2 + Gd_2O_3 + Na_2O.$$

At 1200°C, $2Na_3Gd(PO_4)_2$, Gd_2O_3, and Na_2O reacted, resulting in a new product not reported in the literature, which was presumed to be Na_2GdOPO_4. Weak β-$Na_3Gd(PO_4)_2$ lines (27) were also present in the X-ray powder diffraction pattern. Since there was no weight loss during the solid state reaction and the product was not pure, the chemical analysis of it was found to be unnecessary. The crystal symmetry of this new compound was found to be orthorhombic with the refined cell parameters of a = 13.074(6), b = 10.637(5), and c = 6.469(3) Å. The powder data of this compound together with β-$Na_3Gd(PO_4)_2$ is given in Table 1.

TABLE 1
X-Ray Powder Data for Orthorhombic Na_2GdOPO_4 (a = 13.074(6), b = 10.637(5), c = 6.469(3) Å)

d_{obs} (Å)	d_{calc} (Å)	I/I_0	$h\ k\ l$	Remarks	I/I_0 of β-$Na_3Gd(PO_4)_2$ (Ref. (24))
13.07	13.07	14	1 0 0		
10.54	10.64	23	0 1 0		
9.05	—	5	—	β-$Na_3Gd(PO_4)_2$	5
8.24	8.25	15	1 1 0		
6.96	—	5	—	β-$Na_3Gd(PO_4)_2$	10
6.53	6.54	31	2 0 0		
6.33	—	5	—	β-$Na_3Gd(PO_4)_2$	50
4.60[a]	4.60	40	2 0 1	β-$Na_3Gd(PO_4)_2$	70
4.20	4.22	14	2 1 1		
4.18	—	5	—	β-$Na_3Gd(PO_4)_2$	30
4.13	4.12	15	2 2 0		
3.83	—	20	—	β-$Na_3Gd(PO_4)_2$	50
3.54	3.55	9	0 3 0		
3.48[a]	3.48	17	2 2 1	β-$Na_3Gd(PO_4)_2$	2
3.42	3.42	16	3 1 1		
3.233	3.235	10	0 0 2		
3.148	3.140	74	1 0 2		
3.109	3.109	100	0 3 1		
2.816[a]	2.813	26	4 1 1	β-$Na_3Gd(PO_4)_2$	30
2.784[a]	2.785	62	4 2 0	β-$Na_3Gd(PO_4)_2$	30
2.703	2.704	21	1 2 2		
2.658[a]	2.659	75	0 4 0	β-$Na_3Gd(PO_4)_2$	100
2.609	2.606	15	1 4 0		
2.521	2.523	10	3 1 2		
2.404	2.403	10	4 3 0		
2.304[a]	2.302	9	2 4 1	β-$Na_3Gd(PO_4)_2$	5
2.206	2.206	11	5 2 1		
2.112	2.110	10	4 2 2		
2.085[a]	2.086	16	1 1 3	β-$Na_3Gd(PO_4)_2$	10
1.9128[a]	1.9110	38	2 2 3	β-$Na_3Gd(PO_4)_2$	10
1.8581	1.8564	16	6 3 0		
1.7390[a]	1.7392	16	4 4 2	β-$Na_3Gd(PO_4)_2$	5
1.6835[a]	1.6854	18	6 4 0	β-$Na_3Gd(PO_4)_2$	5
1.6738	1.6749	20	0 4 3		
1.6517[a]	1.6502	11	5 5 0	β-$Na_3Gd(PO_4)_2$	5
1.6335	1.6342	17	8 0 0		

[a] Matching β-$Na_3Gd(PO_4)_2$ lines.

Examination of Table 1 revealed that there is a close relation between the $M^{I}TiOPO_4$-type of orthorhombic compounds (M^{I} = K, Rb, Tl) (15) and Na_2GdOPO_4, but the space group $Pna2_1$ reported for these compounds was not observed in this study, since in $0kl$ indices $k + l = 2n + 1$, in $h00$ indices $h = 2n + 1$, and in $0k0$ indices $k = 2n + 1$. So they do not seem to be isostructural. This may be due to distorted GdO_6 octahedra in which Gd^{+3} ions are displaced from the centers of the octahedra and slightly distorted PO_4 tetrahedra, which are coupled at the vertices, as reported by Kugel *et al.* for $KTiOPO_4$ (27). The X-ray powder diffraction data of $RbTiOPO_4$ and $KTiOPO_4$ (15) also did not fit the space group $Pna2_1$ since they contain indices such as 101, 301, and 501. On the other hand, in Na_2GdOPO_4, Na should be in different positions. Another important observation is that the calculated d-spacings for $RbTiOPO_4$ are the similar to those observed for Na_2GdOPO_4. Investigation of the hkl values showed that for 001 indices only 002 is present where l is equal to $2n$ and this is also a line of β-$Na_3Gd(PO_4)_2$. So the space group could be probably $Pmm2$ (no condition) which has the same site symmetry C_1 with the space group $Pna2_1$. Chahboun *et al.* (29) studied β-$NbPO_5$ and β-$TaPO_5$ by X-ray diffraction and high-resolution electron microscopy. They characterized different supercells based on an orthorhombic subcell. These supercells have unit cell dimensions corresponding to a doubling of c or/and a parameters.

After 11 hr of heating at 1200°C, the orthorhombic symmetry changed to the monoclinic system. The d-spacings of this product were found to be very similar to those of the $La_2Te_3O_9$ compound reported in JCPDS Card No. 22-376. If $La_2Te_3O_9$ is written as $La_2TeO(TeO_4)_2$, where Te

is in the oxidation state of +4, then it could be thought as an oxytellurate which may be isomorphous with oxyphosphates.

IR Studies

The IR vibrational spectra of α- and β- VPO_5 phases with space groups $P4/n$ and $Pnma$ were investigated by Bhargave *et al.* (30). Stranford *et al.* (31) studied the normal coordinate analysis of VSO_5, VPO_5, and $VMoO_5$ phases with the same layered tetragonal crystal structure. Infrared and Raman spectra of monoclinic β-$TaPO_5$ and β-$NbPO_5$ were reported and factor group analysis was performed to show that the most probable space group is $P2_1$ (31). It was stated that bands above 950 cm^{-1} are characteristic of the stretching modes of PO_4 units. Vibrational spectra of hydrated $NbOPO_4$ and $TaOPO_4$ phases was also reported by Stranford *et al.* (5, 33). The IR spectra of tetragonal and monoclinic α- and β-$WOPO_4$ phases were investigated by Baran *et al.* (4). On the other hand, Kugel *et al.* (28) studied the spectra of orthorhombic $KTiOPO_4$ by Raman (R) and IR reflectivity spectroscopy. The IR spectra of $KTiOPO_4$, which was studied by Jacco (34), showed significant symmetry lowering, consistent with the distorted tetrahedral structure for phosphate ions.

The tetrahedral PO_4 ion with Td symmetry has four internal modes of vibration, ν_1 = 938 cm^{-1} (R), ν_2 = 420 cm^{-1} (R), ν_3 = 1017 cm^{-1} (IR, R), and ν_4 = 567 cm^{-1} (IR, R). Generally the antisymmetric stretching modes are found between 1290 and 1050 cm^{-1} and the symmetric modes between 1050 and 900 cm^{-1}. Husson (9) stated that the highest frequency observed is due to antisymmetric stretching involving the terminal bond, a bond between a phosphorus atom and a so-called unshared oxygen atom or the shortest bond. For example in $KTiOPO_4$ ν_{as}P–O was observed at around 1135 cm^{-1}.

The IR spectrum of the orthorhombic compound Na_2GdOPO_4 is given in Fig. 1a. The broad band between 1250 and 850 cm^{-1} is resolved into six peaks associated with the ν_3, which is fundamental for the PO_4 groups. These peaks are at 1138, 1099, 1031, 984, 956, and 945 cm^{-1}. The ν_1 vibration also lies within this region. In this research, it appeared at 926 and 906 cm^{-1}. Agrawal and White (35) stated that the number of peaks resolved in the P–O stretching region should be a rough measure of the number of PO_4 groups that are crystallographically distinct if there are no additional peaks due to correlation field splitting or nonequivalent sites. In the case of KTP this argument seems to hold true since the known structure data reveals two distinct PO_4 groups and the spectrum shows six resolved peaks for ν_3. In this work, for the same reason, ν_1 (which becomes IR active because of the lowering of symmetry) split into two bands. The remaining peaks in the region between 660 and 350 cm^{-1} are ascribed to the

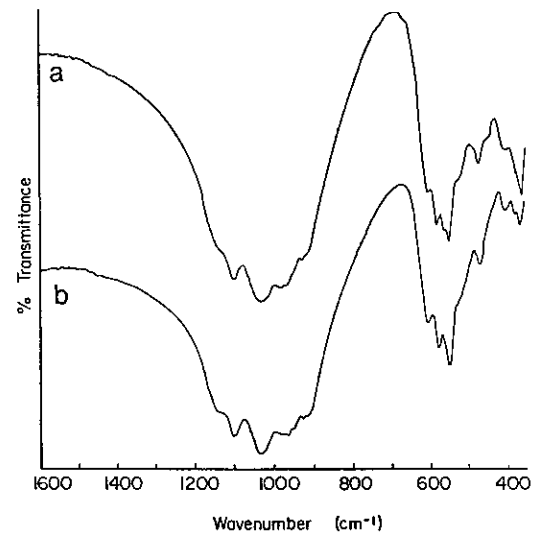

FIG. 1. IR spectra of (a) orthorhombic Na_2GdOPO_4 and (b) the product heated at 1200°C.

splitting of the degenerate ν_4 and ν_2 modes. As is indicated by the factor group analysis scheme for the PO_4 ion given by Jacco (34), the number of peaks is higher than in the free PO_4. This is due to the slight deformation of the PO_4 tetrahedra occupying two crystallographic sites of site symmetry C_1. Only 17 bands were observed instead of 21 with respect to factor group C_{2v} which showed that the site symmetry analysis is enough to explain the data (34). With the existing IR spectrophotometer, bands below 350 cm^{-1} were not observed which belong to the ν_2 deformation vibration O–P–O coupled with Gd–O stretching or O–Gd–O bending frequencies (36, 37). The band assignments for Na_2GdOPO_4 are listed in Table 2. The assignments were made on the basis of previous literature results for oxyphosphates (4, 5, 28, 30, 34) and double phosphates of sodium and gadolinium (38).

The IR spectrum of the product heated at 1200°C for 11 hr was about the same as the orthorhombic form. The IR spectrum of this product is shown in Fig. 1b.

TABLE 2
IR Band Locations and Empirical Assignments for Na_2GdOPO_4

Assignments	Band (cm^{-1})	
ν_3 (F_2)	1136, 1099, 1034, 982, 965, 945	ν_{as} and ν_s (P–O)
ν_1 (A_1)	926, 909	Stretching modes
ν_4 (F_2)	604, 579, 560, 548, 523, 470	δ (O–P–O)
ν_2 (E)	406, 381, 367	Deformation modes

CONCLUSION

A polycrystalline sample of Na_2GdOPO_4 was obtained through the solid state reaction of $Gd_2O_3 + Na_4P_2O_7 \rightarrow 2Na_2GdOPO_4$ at 1200°C. It was characterized by its IR and X-ray powder diffraction data, which resembles that of KTP and $RbTiOPO_4$. The powder pattern was indexed and the unit cell parameters were found to be similar to those of M^ITiOPO_4-type compounds, but the space group may not be the same. After prolonged heating the product showed another polymorph, probably having the monoclinic symmetry. The IR spectra of both products are about the same as those of M^ITiOPO_4-type compounds except for the Ti–O bands in the latter. A comparison of X-ray diffraction and IR results showed that Na_2GdOPO_4 structure should be closely related to the structure of M^ITiOPO_4-type compounds. This should be confirmed by single-crystal analysis.

ACKNOWLEDGMENT

This work was supported by METU-AFP No. 93-01-03-05. The authors also acknowledge the Volkswagen Foundation for their support for installing a computerized X-ray powder diffractometer (Huber) in METU, Chemistry Department, where the calculations of refined parameters were possible through its software program.

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