JOURNAL OF SOLID STATE CHEMISTRY 76, 407–411 (1988)

BRIEF COMMUNICATIONS

A Raman Spectral Study of Hydrated Niobium Phosphate ($NbPO_5$) Phases*

G. T. STRANFORD AND R. A. CONDRATE, SR.

New York State College of Ceramics, Alfred University,
Alfred, New York 14802

Received March 15, 1988; in revised form June 6, 1988

Raman spectra were measured for a hydrated $NbPO_5$ phase after heating at various temperatures. Analyses of the spectra suggest that hydrogen phosphate groups were present in the materials heated at the lower temperatures (25, 105, and 195°C), consistent with earlier infrared spectral studies. Interlamellar water could be detected in the samples that were unheated or heated in this investigation below 1000°C which form Nb–O bonds with Nb ions in the layers, replacing the van der Waal Nb–O bonds between layers.

Introduction

The hydrated phases of $NbPO_5$ are polyfunctional cation exchangers of moderate acidity (*1, 2*). One functional group contains water molecules coordinated to niobium, while the other group contains HPO_4^{2-} ions. These groups operate at different levels of acidity. The exchange capacity of the as-precipitated compounds decreases as the degree of hydration is reduced.

The solid hydrated $NbPO_5$ phases are formed by precipitation in the presence of excess phosphoric acid from a solution prepared with niobium pentoxide (*3*). The resulting air-dried precipitate is a trihydrate material. Its infrared spectrum indicates a material containing PO_4 tetrahedra. When $NbPO_5 \cdot 3H_2O$ is heated between 85 and 105°C, two weakly bonded water molecules are lost. The only change observed in the infrared spectrum is a decrease in the intensity of the water bands (*4, 5*). The X-ray powder diffraction patterns indicate little change in the *a*- and *b*-axis parameters for the crystalline phases during dehydration, which suggests that the hydrated crystalline phases possess a layered structure. Since the structures of the crystalline materials are capable of one-dimensional intracrystalline swelling along the *c*-axis, water molecules can be included between the layers (*4, 5*). This study will present the Raman spectral/structural changes that occur during the heat treatment of hydrated $NbPO_5$.

Experimental

Hydrated $NbPO_5$ phases were prepared by a method involving fusion of Nb_2O_5 with potassium pyrosulfate. For example, 2 g of

---

* Based on thesis submitted by G. T. Stranford for a Ph.D. degree in Ceramics at Alfred University.

0022-4596/88 $3.00

Nb_2O_5 were fused with 10 g of potassium pyrosulfate. After cooling, the fused mass was leached with boiling distilled water, dried, dissolved in a 4% oxalic acid solution with the aid of heat, and then filtered to remove the insoluble matter. This solution was placed on a steam bath, and then a mixture of distilled water, 10 ml 15.8 M HNO_3, and 10 ml 14.8 M H_3PO_4 was added. After a few minutes, 1 g of $KBrO_3$ was added, and the resulting precipitate was digested on the steam bath for 1 h, filtered, washed with large amounts of water, and dried in air. The resulting precipitate was a crystalline hydrate of $NbPO_5$. Powders prepared by the above-mentioned method were calcined at 25, 105, 195, 450, 750, and 1000°C. Powders were sealed after heat treatment in capillary tubes for Raman spectral measurement. Raman spectra were measured with a Spex Model 1401 spectrometer and a CRL Model CR3 argon ion laser using 90° optics and both the blue and the green laser lines.

Analysis of the X-ray powder diffraction pattern for the powder calcined at 1000°C indicated that α-$NbPO_5$ was the only phase present in the powder. Wet chemical analysis indicated that its Nb_2O_5 content was 65 wt% while its P_2O_5 content was 34.6 wt%. The theoretically predicted amounts are 65.19 and 34.81 wt%, respectively. The water contents (H_2O wt%) which were determined by thermogravimetric analyses were 19.3% at 25°C, 12.1% at 105°C, 3.2% at 195°C, 1.8% at 450°C, 1.0% at 750°C, and 0.0% at 1000°C. Broad peaks were observed in the X-ray powder diffraction patterns of the powders calcined at temperatures below 450°C, which probably indicated that the crystallite sizes are small. Such small crystals would be expected to develop at lower heat treatment temperatures. An alternate interpretation is that some of the broadness might develop due to stacking faults in crystals with respect to layer structures. Only the 001 diffraction peak significantly shifted with temperature. The 001 d-spacing was observed at 8.066 Å for the as-precipitated phase. The c-axis length decreased with increasing temperature, and was 4.514 Å for the material calcined at 1000°C. On the other hand, the a and the b parameters are 6.484 Å for the as-precipitated sample and 6.382 Å for α-$NbPO_5$. Thus, the water of hydration was incorporated between the layers formed by the ab-plane of α-$NbPO_5$. Trace emission spectrographic analysis indicated that the trace element impurity contents were below 0.1 wt%.

Results

The Raman spectra measured for hydrated $NbPO_5$ phases after different stages of dehydration are illustrated in Fig. 1. Emphasis will be placed mainly upon the interpretation of the Nb–O and P–O stretching vibrations. The band locations and assignments of the various Raman bands for the various investigated hydrated materials are listed in Table I.

TABLE I

BAND LOCATIONS (cm^{-1}) AND EMPIRICAL BAND ASSIGNMENTS FOR VARIOUS HYDRATED AND ANHYDROUS $NbPO_5$ PHASES

25°C	105°C	195°C	450°C	750°C	1000°C	Assignments
				1113	1113	ν(P–O)
				1014	1014	
984	987	987	984	984	984	
945	936	936				
			813	800	800	ν(Nb=O)
672	672	672				ν(Nb–O) and δ(O–P–O)
				612	612	
517	517	517				
			458	458	458	δ(O–P–O) and δ(O–Nb–O)
437	437	437				
404	404	404				
			376	376	376	
			284	288	288	
			263	267		
239	246	246	239	239		
				200	200	
175	188	188	177	177	177	
				160	160	
136	136	136				
				111	111	

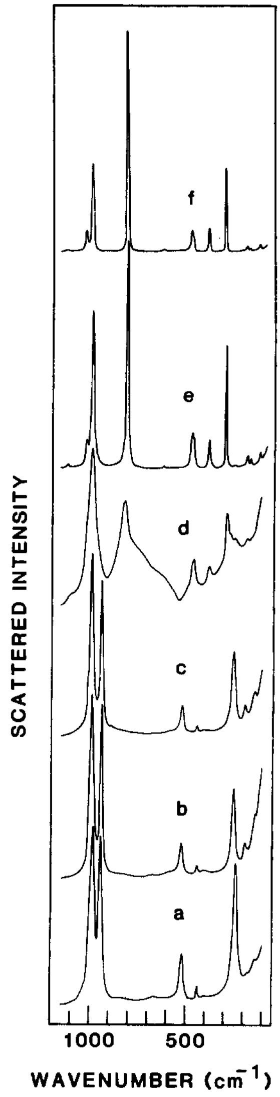

FIG. 1. Raman spectra for various hydrated $NbPO_5$ phases heated at different temperatures: (a) 25°C, (b) 105°C, (c) 195°C, (d) 450°C, (e) 750°C, and (d) 1000°C.

The crystal structure of α-$NbPO_5$ is based upon layers containing corner-shared distorted NbO_6 octahedra. The distorted octahedral arrangement around the niobium ion is explained in terms of the ion being too small to form regular octahedrally coordinated oxide units but not small enough to be restricted to tetrahedrally coordinated sites (*6*). The Nb–O bonds along the *c*-axis (perpendicular to the layer planes) are displaced to give one shortened and one elongated Nb–O bond around each octahedrally coordinated niobium ion. The ions associated with the elongated Nb–O bonds involve van der Waal types of interaction between each other. The four equatorial Nb–O bonds in the layer around each niobium ion possess equal lengths. The four corresponding equatorial oxygens are shared with four different PO_4 groups. NbO_6 and PO_4 groups alternate in the layer. The elongated van der Waal Nb–O bonds provide the major bonding between the above-mentioned layers that contain the niobate and phosphate groups (*6*). In the hydrated phases, the Nb–O–Nb linkages along the *c*-axis are broken by water molecules incorporated between the layers (*4*, *5*). NMR spectroscopic analysis, which is consistent with the infrared spectoscopic analysis, suggests that one of these water molecules is bonded directly to a niobium ion and directly replaces the elongated van der Waal Nb–O bond while another water molecule is located between PO_4 groups of adjacent layers. An additional water molecule with greater mobility was observed in the as-precipitated phase (*7*).

Spectra e and f of Fig. 1, which correspond to α-$NbPO_5$, are characterized by a very strong bond at 800 cm^{-1}. This band has been assigned for α-$NbPO_5$ to the stretching mode of the short Nb═O bond using normal coordinate analysis (*8*). This assignment is consistent with those of McConnell *et al.* (*9*). The lack of a corresponding band in spectra a, b, and c, which correspond to hydrated phases, suggests the presence of disordered NbO_6 octahedra (*9*). Spectra d contains a broadband at 813 cm^{-1} which can be assigned to the stretching mode of the Nb═O bond, indicating that the regular layered structure of α-$NbPO_5$ has started to form at this level of hydration. Displacement of this band to higher wavenumber suggests a shorter

Nb=O bond in this hydrated phase when the elongated Nb–O bond is being replaced by a Nb–O bond involving the interlamellar water. The intensity of this band for the hydrated material decreases relative to the intensity of the other Raman bands. A similar trend was observed for the hydrated phases of α-VSO_5 (*10*).

Normal coordinate analysis for α-$NbPO_5$ indicates that the bands between 580 and 630 cm^{-1} in both the infrared and Raman spectra mainly involve stretching modes of the Nb–O equatorial bonds. A shifting of these bands or the appearance of new bands is observed in the spectra for the hydrated phases. These spectral changes are the result of changes in the NbO_6-site symmetry or Nb–O bonding or vibrational coupling from the replacement of elongated Nb–O bonds between layers by Nb–O bonds involving water molecules in the layer.

The bands between 980 and 1115 cm^{-1} for α-$NbPO_5$ mainly involve the stretching vibrations of the PO_4 tetrahedra (*8*). Some shifting of these bands is expected in the hydrated phases, probably as a result of the water molecules incorporated between the layers close to phosphate groups, interacting with them. A band is observed at 2920 cm^{-1} in the infrared spectrum for the hydrated phases, which suggests the pressence of an HPO_4 group (*1, 2, 11, 12*). Also, a very strong and a strong Raman band are observed at ca. 985 and 940 cm^{-1}, respectively, in spectra a, b, and c for the hydrated phases, similarly to the Raman bands at 983 and 946 cm^{-1} for $CaHPO_4$. Also, $CaHPO_4 \cdot 2H_2O$ possesses a very strong Raman band at 984 cm^{-1} (*11*). Since X-ray powder diffraction data seem to indicate that the *ab*-plane of α-$NbPO_5$ is intact in the hydrated phases, complete breakage of all the Nb–O–P linkages in the layer seems unlikely. Therefore, the hydrogen phosphate groups possibly arise from the chemical interaction of water with P–O bonds dangling at the surfaces of the crystallites. Since the crystallite sizes are extremely small, enough surface area is available to allow the formation of a significant number of hydrogen phosphate units which can be detected by infrared spectroscopy. The shifting of the P–O stretching vibrations in the Raman spectra for the hydrated phases with respect to those of α-$NbPO_5$ is consistent with this observation. The Raman spectrum for the hydrated sample heated to 450°C, which contains broadbands, is beginning to look like the Raman spectrum for α-$NbPO_5$. This observation, which suggests that the hydrogen phosphate groups are almost completely removed at 450°C in our heat treatment procedure, is consistent with proton NMR data. The NMR spectra indicate that most of the interlamellar water is removed below 200°C. However, a single line is observed in the NMR spectrum for hydrated $NbPO_5$ heated to 280°C, which is associated with OH groups that were formed during synthesis (*7*).

The bands below 460 cm^{-1} can be assigned to O–P–O and O–Nb–O bending vibrations, many of which should be coupled (*8*). The most significant differences between the hydrated phases heated at lower temperatures and the α-$NbPO_5$ phase in this region of the spectra involve the band shifts and splittings observed between 240 and 460 cm^{-1}. These shifts can be related to the presence of hydrogen phosphate groups in the hydrated phases since very little change is observed with respect to Raman bands for α-$NbPO_5$ when only interlamellar water molecules are removed by heating the hydrated materials in this study at 450°C and higher temperatures. The Raman bands for the hydrated materials heated at lower temperatures also relate to Raman bands that occur at similar band locations for $CaHPO_4$ (*11*).

Thus, for the hydrated $NbPO_5$ phases, Raman spectroscopy appears to be more sensitive to the local site symmetry effects in the *ab*-plane than X-ray powder diffraction analysis. While the diffraction patterns for the hydrated phases indicate that the *ab*-planes of the anhydrous phase are established in the precipitated powder, vibrational spectroscopic techniques suggest that hydrogen phosphate groups are present in the materials with higher water contents, altering the local PO_4–site symmetries.

References

1. G. I. Deulin, R. B. Dushin, and V. N. Krylov, *Inorg. Mater.* (*Engl. Transl.*) **16**(4), 478 (1980).
2. G. I. Deulin, R. B. Dushin, V. N. Krylov, V. G. Pitalev, A. A. Pospelov, and V. G. Chukhlantsev, *J. Appl. Chem. USSR* (*Engl. Transl.*) **53**(3), 371 (1980).
3. R. B. Hahn, *J. Amer. Chem. Soc.* **73,** 5091 (1951).
4. G. I. Deulin, R. B. Dushin, and V. N. Krylov, *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **24**(9), 1291 (1979.
5. N. G. Chernorukov, N. P. Egorov, and I. R. Mochalara, *Russ. J. Inorg. Chem.* (*Engl. Transl.*) **23**(11), 1627 (1978).
6. J. M. Longo and P. Kierkegaard, *Acta Chem. Scand.* **20**(1), 71 (1966).
7. S. Bruque, M. Martinez-Lara, L. Moreno-Real, A. Jimenez-Lopez, B. Casa, E. Ruiz-Hitzky, and J. Samz, *Inorg. Chem.* **26,** 847 (1987).
8. G. T. Stranford and R. A. Condrate, Sr., *J. Solid State Chem.* **52,** 248 (1984).
9. A. A. McConnell, J. S. Anderson, and C. N. R. Rao, *Spectrochim. Acta A* **32,** 1067 (1976).
10. G. T. Stranford and R. A. Condrate. Sr., *J. Solid State Chem.* **56,** 394 (1985).
11. F. S. Casciani and R. A. Condrate, Sr., *in* "Proceedings of the 2nd Int. Congr. on Phosphorus Compounds" (C. Eon, Ed.), pp. 175–190, Paris (1980).
12. N. G. Chernorukov, N. P. Egrov, and T. A. Galanova, *Inorg. Mater.* (*Engl. Transl.*) **17**(2), 328 (1981).