

A Vibrational Spectral Study of Hydrated Tantalum Phosphate (TaPO₅) Phases*

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Infrared and Raman spectra were measured for various hydrated tantalum phosphate (TaPO₅) materials after dehydration at various temperatures, and the spectral differences were interpreted on the basis of structure. The structural nature of water along with protonated phosphate and TaO₆ groups in the amorphous hydrated materials was discussed. © 1990 Academic Press, Inc.

Introduction

Earlier investigations have looked at the dehydration of $ABO_5 \cdot nH_2O$, where A and B represent either Nb and P or V and S, using both infrared and Raman spectroscopy (1-4). The final products in these studies were α - ABO_5 phases which possessed layered structures. In contrast, complete dehydration of the currently prepared TaPO₅ · nH_2O materials generates a final crystalline product with a three-dimensional network structure. This study investigates the structural changes that occur during various stages of heat treatment of the latter hydrate material, using both infrared and Raman spectroscopy.

Experimental

The hydrated tantalum phosphate (TaPO₅) materials were formed using a

method that was described earlier by Hahn (5). Tantalum pentoxide was fused with potassium hydroxide in a zirconium crucible using a 1 : 4 weight ratio. After cooling, the fused mass was dissolved in distilled water, allowed to settle for several hours, and filtered to remove the insoluble matter. The solution was placed on a steam bath, and then a mixture of 14.8 M H₃PO₄, 15.8 M HNO₃, and water was added. This mixture contained enough H₃PO₄ to generate a 75 mol% excess of P₂O₅ along with an equal molar amount of HNO₃. A precipitate formed immediately which was digested on the steam bath for one hour, centrifuged, filtered, washed with an acetone-water mixture, and finally dried in air. Several different precipitates were formed by this method, and heated to 25, 105, 300, 700, 850, and 1000°C (+/- 10°C) so that samples with varying degrees of hydration could be investigated. Heat treatment at 1000° completely generates the crystalline form of TaPO₅ which is isostructural to β -NbPO₅.

Single crystals of TaPO₅ were formed by

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using a method that was described earlier by Longo *et al.* (6). Tantalum pentoxide was mixed with a 10:1 weight excess of KH_2PO_4 , placed in a platinum crucible, and heated at low heat on a burner to remove the water. The material was melted at 900°C for 16 hr, cooled, and then leached with boiling water. After drying, the material was placed in a furnace at 1225°C ($\pm 10^\circ\text{C}$) for 12 hr. When the crucible was removed, single crystals of $\beta\text{-TaPO}_5$ were deposited on its inside surface.

Powders that were treated at various temperatures were sealed in capillary tubes for Raman spectral measurements. Their 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 green laser lines. Infrared spectra were measured for the powdered samples with a Perkin-Elmer Model 621 infrared spectrometer using an air purging device and the KBr pellet technique.

Results

In contrast to hydrated VSO_5 and NbPO_5 phases, the hydrated TaPO_5 phases that were prepared in this investigation were amorphous with respect to X-ray diffraction data. Similarly to hydrated NbPO_5 phases, hydrated TaPO_5 phases could only be formed in this investigation by initial precipitation of the materials from an aqueous solution. The dehydration of $\text{TaPO}_5 \cdot x\text{H}_2\text{O}$ is essentially complete at 850°C with the completed formation of crystalline $\beta\text{-TaPO}_5$ occurring at ca. 900°C .

The infrared and Raman spectra of the precipitated powders that are heated to various temperatures in the $25\text{--}1000^\circ\text{C}$ range are illustrated in Figs. 1 and 2, respectively. Their band locations and assignments are listed in Table I. In contrast to those of hydrated NbPO_5 and VSO_5 , the infrared and Raman bands for hydrated TaPO_5 are very broad, which are characteristic of

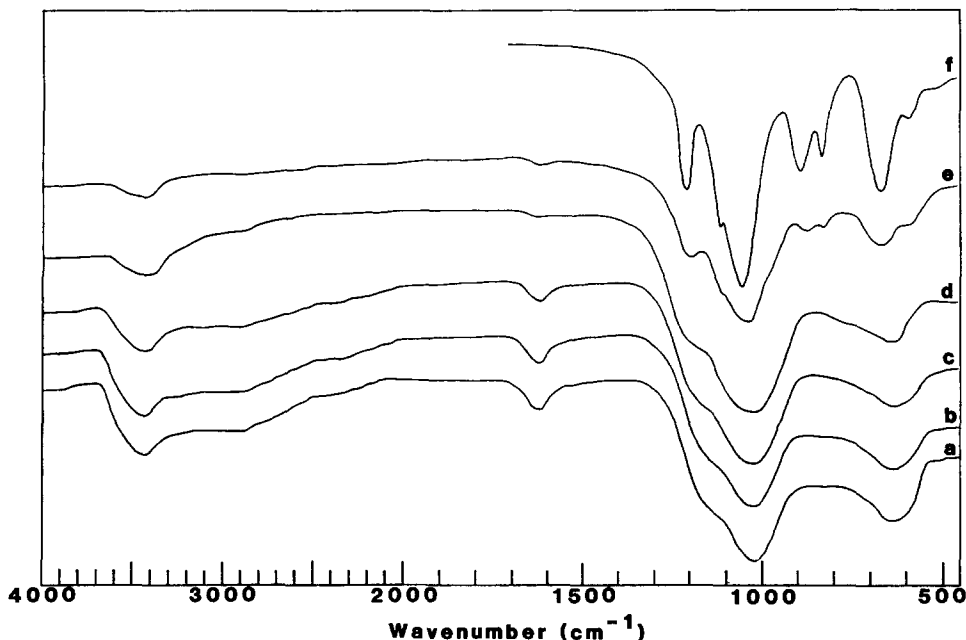


FIG. 1. Infrared spectra of hydrated tantalum phosphate after heat treatment at various temperatures. (a) 25°C , (b) 105°C , (c) 300°C , (d) 700°C , (e) 850°C , and (f) 1000°C .

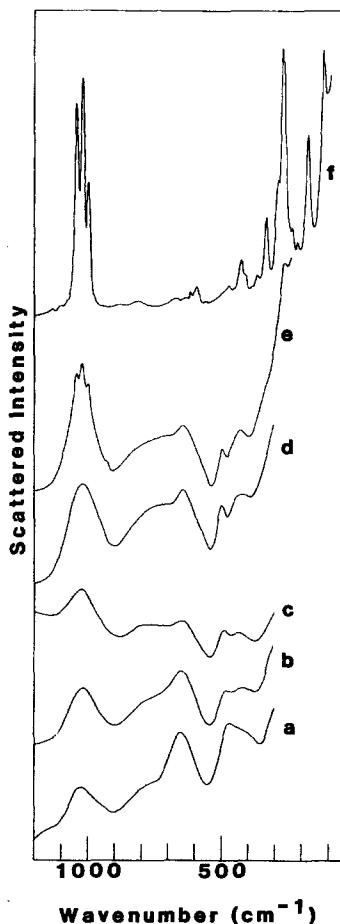


FIG. 2. Raman spectra of hydrated tantalum phosphate after heat treatment at various temperatures. (a) 25°C, (b) 105°C, (c) 300°C, (d) 700°C, (e) 850°C, and (f) 1000°C.

amorphous materials (1-4). Few dramatic changes are seen in the vibrational spectra until crystallization begins at ca. 850°C.

The infrared bands for O-H stretching modes occur between 2000 and 3600 cm^{-1} , while those for the H-O-H bending mode occurs at 1625 cm^{-1} . The very broad infrared bands occurring around 3000 cm^{-1} indicate the presence of HPO_4 groups (2, 7, 8). The broadness of the bands for the O-H stretching modes suggests that hydrogen bonding involving OH bonds occurs in the

material's structure. As expected, the intensities of such bands decrease with increasing heat treatment temperature, indicating a decrease in the concentration of water molecules and/or OH units in the material.

The intense infrared band at 1016 cm^{-1} and the intense Raman band at 1025 cm^{-1} for the precipitated phase can be assigned to P-O stretching modes involving PO_4 tetrahedra. The broadness of these bands and the shoulder on the high wavenumber side of the infrared band indicate that the PO_4 units are highly distorted from tetrahedral symmetry in the hydrated phases. Such distortion could be due to protonated PO_4 units in the structure. The infrared band gradually shifts to higher wavenumbers as the material is dehydrated and is split into three strong bands involving P-O stretching modes upon crystallization. On the other hand, the Raman band at 1025 cm^{-1} shifts to lower wavenumber as the water content decreases. This band splits into three intense bands at 1039, 1018, and 966 cm^{-1} along with a weak band at 927 cm^{-1} upon heat treatment at 850°C. The latter weak Raman band is probably due to the distortion of the symmetry of PO_4 tetrahedra because it disappears when the sample is heat treated to 1000°C. This band might be due to a P-OH stretching mode. In an earlier study, Casciani and Condrate observed a Raman band in this region for brushite ($\text{CaHPO}_4 \cdot 2\text{H}_2\text{O}$) which contained only isolated HPO_4^{2-} ions (9).

Two bands appear in the infrared spectrum between 825 and 885 cm^{-1} when the sample is heated to 850°C. These infrared bands can be assigned to the Ta-O stretching modes of the TaO_6 octahedra (10, 11). Related Raman bands are observed at 810 and 882 cm^{-1} for the sample that was heated to 1000°C.

The Raman spectra for the hydrates possess broad bands between 725 and 825 cm^{-1} . These Raman bands possibly correspond to

The bands observed between 200 and 500 cm^{-1} can be assigned to various O–P–O and O–Ta–O bending modes while the bands observed at 176 and 118 cm^{-1} for samples heated to 1000°C can involve torsional or other complex vibrational modes. The broad bands for the bending modes in the Raman spectra of the hydrated materials suggest that a wide range in O–P–O and O–Ta–O angles exists in the amorphous materials because of the inclusion of water into the structure or the protonation of phosphate and TaO_6 groups.

The similarities in the vibrational spectra for the powders heated below 700°C indicate that little structural change is taking place in the network for this amorphous material in this heating range. The thermogravimetric analysis (TGA) curve (see Fig. 3) indicates three separate weight loss steps. The first step involves a gradual weight loss up to 670°C. This weight change corresponds to the loss of weakly bonded water molecules in the material. The next weight loss step occurs between 670 and 860°C, and corresponds to the loss from the amorphous network of ca. one mole of water per mole of TaPO_5 formula units, probably due to the dehydration of protonated

oxide units. $\beta\text{-TaPO}_5$ is essentially formed by 900°C, and further weight loss (step 3) probably corresponds to the vaporization of the sample, mainly involving volatilization of P_2O_5 . The similarities in the vibrational spectra of samples dehydrated in this study at temperatures below 700°C confirm that the only major change below this temperature is the loss of weakly bonded water molecules which have very little effect upon the bonding in the network structure of the material. However, the water loss generated between 700 and 850°C plays an important role in the bonding associated with the amorphous network of the material because significant changes are observed in the vibrational spectra in this temperature range. As noted earlier, the most noticeable changes occur for the bands assigned to modes involving the Ta–O and Ta–OH bonds.

There are significant differences between the Raman spectra of NbPO_5 and TaPO_5 . These differences can be explained on the basis of the differences in the structures of the end products from dehydration of the two different types of hydrated material. The hydrated NbPO_5 decomposes to form $\alpha\text{-NbPO}_5$ which possesses a layered struc-

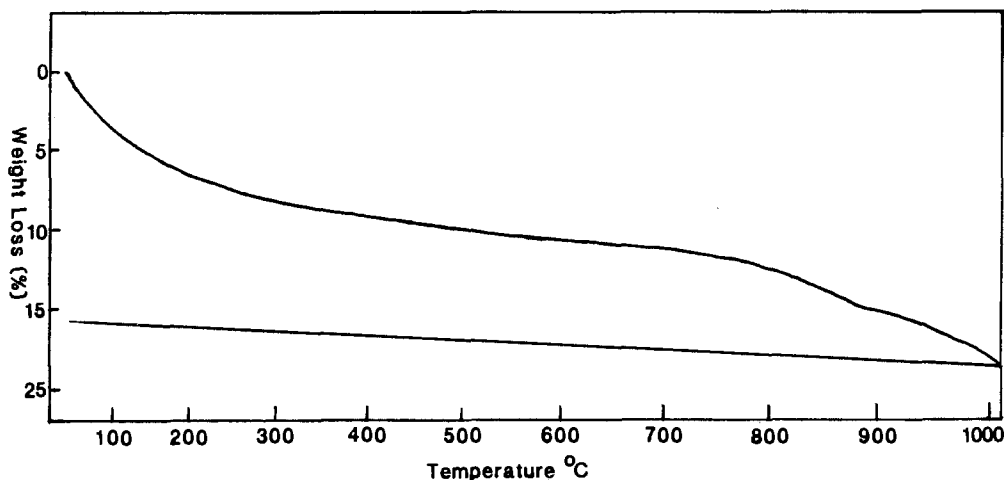


FIG. 3. Thermogravimetric (TGA) curve for hydrated tantalum phosphate.

ture. This layered structure is already present in the last dehydrated crystalline phase ($\text{NbPO}_5 \cdot \text{H}_2\text{O}$) that is formed before complete dehydration. In this latter case, the remaining H_2O molecules are located between the layers in the crystalline structure. On the other hand, the dehydration of $\text{TaPO}_5 \cdot x\text{H}_2\text{O}$ results in the formation of $\beta\text{-TaPO}_5$ which does not possess a layered structure. In the hydrated TaPO_5 phases, water molecules can be occluded in the structure during synthesis. These water molecules can distort various structural units as well as cause the formation of Ta-OH and P-OH bonds in the network structure. The amorphous nature of hydrated TaPO_5 is probably due to the random inclusion of water molecules into its network structure which causes a nonperiodic orientation of PO_4 and TaO_6 units with respect to each other. Also, the presence of protonated phosphate and TaO_6 groups can cause in the amorphous materials the break down of the periodicity in the solid state structure.

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