

Structural Investigation of Vanadium – Sodium Metaphosphate Glasses

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The structure of the glass forming system $(V_2O_5)_x - (Na_2O \cdot P_2O_5)_{(1-x)}$ ($x = 0-0.4$), has been investigated using Raman spectroscopy. The stretching vibrations of various phosphate groups, connected to phosphorus or vanadium atoms, have been assigned. Variation of the composition leads to structural changes where the sodium metaphosphate -P–O–P-chains break and then reconnect with the oxovanadium units forming a -V–O–P-network structure.

Key words: Vanadium; Phosphates; Vanadium Glass; Raman Spectroscopy; Metaphosphates.

1. Introduction

The ternary systems $P_2O_5-V_2O_5-AO_n$ ($A =$ alkali, alkaline earth metal) form a series of compounds and amorphous solids at different compositions. In these systems the vanadium coordinated polyhedra (octahedra, square pyramids, trigonal bipyramids and tetrahedra) are characterized by none, one or two V–O terminal bonds and can be either isolated or connected into more complicated structural arrangements [1, 2]. The phosphorous coordination in these solids is four-fold forming PO_4 groups which, depending on the composition, are linked together in pairs, chains, rings or cages. The size and valence of the nearest neighbor cations (A) and the length of the phosphate linkages determine the geometric parameters and distortions of the PO_4 groups.

The determination of structure of amorphous solids is a difficult task and usually requires a combination of experimental techniques. Thus for the glasses formed in the $P_2O_5-V_2O_5$ system, neutron diffraction [3], EXAFS [4], XANES [5], and Mössbauer spectroscopy [6] has shown the presence of VO_4 and/or VO_5 and PO_4 units which are connected to each other via oxygen bridges to form a three dimensional network.

Raman spectroscopy can also supply useful information on amorphous materials [7, 8]. The measured vibrational modes of the amorphous solid can be correlated to

the coordination number and bonding of the structural units formed. In many cases bridging and terminal vibrations can be distinguished, thus obtaining additional short range structural information on the material.

The present paper deals with the structural properties of $(V_2O_5)_x - (Na_2O \cdot P_2O_5)_{(1-x)}$ glasses, where the values of x varies from zero (i.e. pure $NaPO_3$) to 0.4. Raman spectroscopy is used to determine the different metal oxygen vibrational frequencies and to correlate them to the vibrational frequencies and to correlate them to the local structure of vanadium and phosphorous atoms. The systematic changes of the vibrational frequencies with variation of composition gives information on the structural modifications of the sodium phosphate “network” upon addition of vanadium (V) oxide.

2. Experimental

Vanadium pentoxide (V_2O_5) was purchased from Cerac Pure 99.9% and used as obtained. Trimetaphosphate (trisodium salt) (Sigma 98%) was dried under vacuum. All materials were handled in a nitrogen atmosphere glove box with a water content less than 1 ppm.

The dry $(NaPO_3)_3$ and V_2O_5 were mixed in an agate mortar with an pestle and loaded into quartz cells (6 mm o.d., 4 mm i.d.) which were evacuated and sealed under

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~0.4 atm of O₂ in order to prevent autoreduction of V(V) to V(IV) at high temperatures. For the preparation of the glasses, the cells were heated in a furnace at ~700 °C for 3 h, and the metal phosphate melts were then quenched in a water bath. All the glasses prepared as described above were transparent but highly colored (dark red-brown).

A T-64000 Raman spectroscopy system from Jobin-Yvon was used. The spectra were excited by a linearly polarized monochromatic radiation at 488, 514.5, and 647.1 nm (power 100–200 mW) produced by a Spectra Physics laser (model 2018-RMIR). The excitation beam was directed towards the microscope plano-achromatic objective 10X and was focused onto the sample with the use of a beam splitter and the microscope objective. The Raman scattered radiation was collected in backscattering geometry by the same microscope objective and passed through the beam splitter which was focused on the slit (100 μm) of a double subtractive monochromator. This geometry was used in order to eliminate the problems arising from the strong absorption of the laser line by the vanadium (V) samples.

One polarization configuration was used by means of the polarization of the incident – scattered light, namely VV (vertical–vertical). The detection device was a charge-coupled-device (CCD) operating at 140 K. The resolution was ~3 cm⁻¹. The UV/vis electronic absorption spectrum was recorded with a Hitachi U3000 spectrophotometer.

3. Results and Discussion

The UV/vis electronic absorption spectrum of a glassy film of vanadium-sodium metaphosphate mixture, poor in vanadium content, is presented in Figure 1. The tail of the broad charge transfer band of vanadium (V) [9] is extended until ~700 nm. It seems that there are no impurities of vanadium (IV) or (III) in the glass, since there is no absorption peak in the 600–800 nm region [10, 11], where a maximum for these oxidation states is expected. Back-scattered Raman spectra were measured with different excitation laser lines (488, 514.5 and 647.1 nm). The best signal to noise ratio was obtained with the 647.1 nm laser line which was absorbed least by the samples (see Fig. 1).

Figure 2 presents the room-temperature Raman spectra of the (V₂O₅)_x–(Na₂O · P₂O₅)_(1-x) (where $x = 0$ –0.4) glassy mixtures. The molar ratio of phosphorous to sodium was always 1 (metaphosphate stoichiometry), and the P/V molar ratio changed from 15 to 1.5.

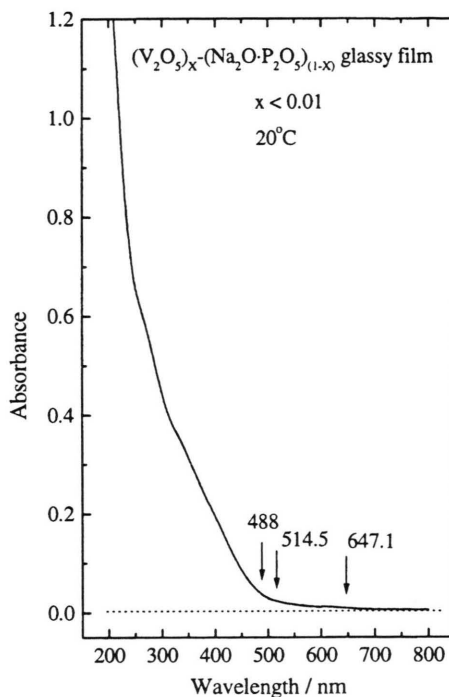


Fig. 1. UV/vis spectrum of a vanadium–sodium metaphosphate glassy film.

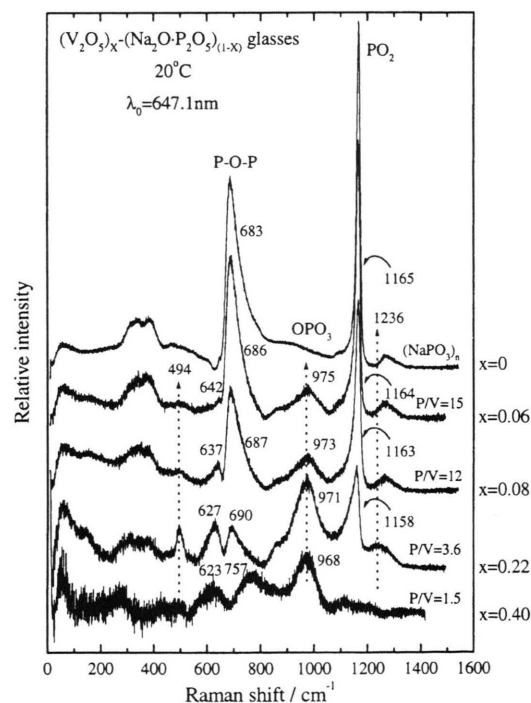


Fig. 2. Raman spectra of vanadium–sodium metaphosphate glasses.

The main characteristics of the Raman spectra of the metaphosphate composition are the two strong, polarized bands, which are assigned to the symmetric bridging stretching vibrations (ν_s) of the $-P-O-P-$ units along the chains at $\sim 685\text{ cm}^{-1}$, and the terminal $P-O$ stretching vibrations of the PO_2 units at $\sim 1160\text{ cm}^{-1}$ [12].

Upon addition of vanadium pentoxide to sodium metaphosphate the following spectra changes are observed with increasing x :

- the relative intensity of the ~ 685 and $\sim 1160\text{ cm}^{-1}$ bands decreases and disappears when the P/V ratio reaches 1.5 ($x = 0.4$),
- the $\nu_s(\text{POP})$ and $\nu_s(\text{PO}_2)$ bands shift to higher and to lower frequencies, respectively (Fig. 3),
- new bands appear, as shown in Table 1, which dominate the spectra at low P/V ratios.

The first two observations indicate the break ('depolymerization') of the sodium metaphosphate network. As the chains become shorter, electrons are released from the bridging bonds ($-P-O-P-$) and localized to the terminal ones (PO_2). Thus the bridging bonds become stronger and their vibrational frequency increases, while the terminal bonds are weakened and their vibrational frequency decreases (Fig. 3).

The third observation indicates the formation of new species in the glass. The bands at $968\text{--}975$ and $623\text{--}642$ appear to increase their relative intensity in a parallel way. These bands are assigned to the formation of PO_4 "tetrahedral" units bridged through one oxygen to vanadium ($-V-O-PO_3$). For the "free" $[PO_4]^{3-}$ tetrahedra the $P-O_{(\text{terminal})}$ stretching frequency is $\nu_1 = 938\text{ cm}^{-1}$ [13]. Bridging an oxygen distorts the tetrahedron and furthermore shifts the terminal frequency to higher energies. Thus the band in the $968\text{--}975\text{ cm}^{-1}$ region is assigned to the $P-O_{(\text{terminal})}$ frequency of the bridged PO_4 unit while the band in the $623\text{--}642\text{ cm}^{-1}$ region is assigned to the $-V-O-P-$ bridging vibration.

The spectra with the highest vanadium concentration studied ($x = 0.4$) show a relatively strong band at 757 cm^{-1} . This band is assigned to the $-V-O-V-$ bridging vibration which arises by connecting neighboring VO_x polyhedra through oxygen in the glass. For the "free" $[VO_4]^{3-}$ units the stretching frequency $\nu_1 = 826\text{ cm}^{-1}$ [13] is, as expected, at higher energies than the 757 cm^{-1} bridging frequency.

It is well known that the structure of sodium metaphosphate consists of chains having infinite length [14]. These chains interact with each other via Na atoms. The coordination number of Na is about 5 [15, 16]. It appears

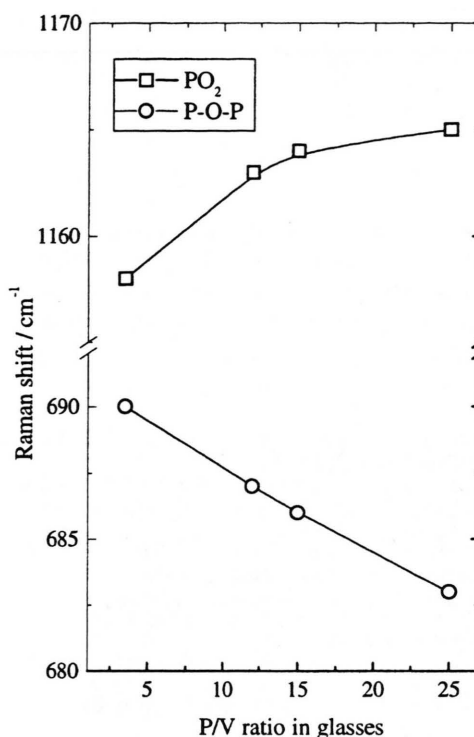


Fig. 3. Raman shift of the two symmetric stretching vibrations of the sodium metaphosphate chains upon the addition of vanadium pentoxide, at the glassy state.

Table 1. Main bands (cm^{-1}) of the $(V_2O_5)_x-(Na_2O \cdot P_2O_4)_{(1-x)}$ glasses and assignments.^a

Wavenumber/ cm^{-1}	Assignment
1158–1165 (s)	$\nu_s(\text{PO}_2)$
968–975 (s)	$\nu_1(\text{PO}_4)$
757 (m, br)	$\nu(-V-O-V-)$
690–683 (s)	$\nu_s(-P-O-P-)$
623–642 (m)	$\nu(-V-O-P-)$
350–500 (w, br)	Bending modes

^a Abbreviations: s: strong; m: medium; w: weak; br: broad.

that the introduction of vanadium oxide (which is also a glass forming material like phosphorus pentoxide) into the metaphosphate 'matrix' results in the formation of VO_x polyhedral units, which disrupt the phosphate chains and connect the shorter parts, forming a network structure. The basic units of this network are phosphate chains of short length, VO_x monomeric or polymeric units and new PO_4 groups connected with oxygen bridges to vanadium polyhedra. As the concentration of vana-

dium increases, the VO_x polyhedra are connected to each other with oxygen bridges, giving rise to a new vibration that appears at 757 cm^{-1} .

Conclusions

Raman spectroscopy was used to investigate the structural modifications of vanadium–sodium metaphosphate glasses. It is argued that the addition of vanadium to metaphosphate structure results in the ‘depolymerization’ of

the phosphate chains and the formation of a -V–O–P- ‘network’ which has a higher dimensionality. The stretching frequencies of the different units has been recorded and assigned to specific vibrations.

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