XPS STUDY OF VANADIUM PHOSPHATE GLASSES

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Motivations

▪Transition metal doped oxide glasses continue to be of scientific interest due to their semiconducting properties and the corresponding potential applicability to electronic devices.

▪ The structure of vanadate glasses remains a subject of interest because there is no clear picture as to the exact nature of the oxygen polyhedra surrounding the vanadium atoms.

Objectives

Use the XPS technique to investigate:

• Structural role of V_2O_5 in phosphate glasses

•Identify BO atoms and NBO atoms

•Identify the presence of the valence states of V ions in these glasses

Glasses composition

$(V_2O_5)_x$-$(P_2O_5)_{1-x}$ $\quad 0.30 \leq x \leq 0.60$

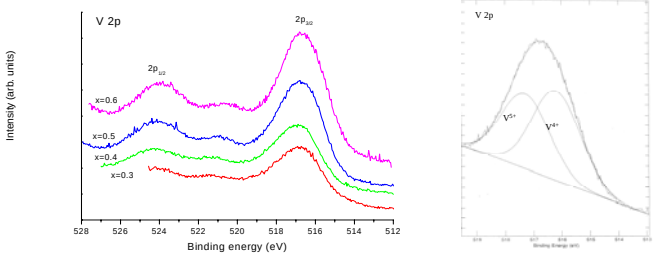
Sample preparation

•Stoichiometric amounts of V_2O_5 and P_2O_5 were melted in alumina crucibles between 1000-1100 °C depending on the composition for one hour

•XPS measurements were performed on glass rods fractured in UHV (~ 10^{-10} mbar). Core level spectra of V 2p, O 1s and P 2p were recorded and analyzed

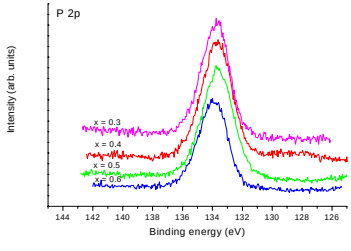
Results and Discussion

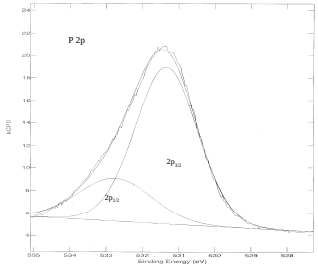
V 2p Core Level Spectra



An asymmetry is observed on the lower binding energy side of the V $2p_{3/2}$ core level spectra which is indicative of V existing in more than one oxidation state. Hence, each V $2p_{3/2}$ spectrum was fitted to two Lorentzian-Guassian peaks with the lower binding energy corresponding to V^{4+} and the higher binding energy peaks to V^{5+}. The ratio V^{4+}/V_{total} shows that more than 70 % of V ions in the V4+ state for samples with x = 0.30-0.50 and 56 % for the glass with x = 0.60.

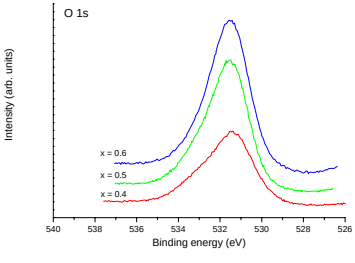
P 2p Core level Spectra

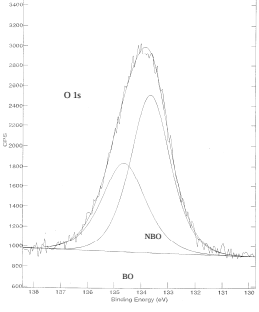




XPS indicates that the BE of the P 2p does not vary much with an increase in V_2O_5 content. An asymmetry is observed in the P 2p spectra and so fitting of the P 2p was done with two contributions corresponding to P $2p_{3/2}$ and P $2p_{1/2}$

O 1s Core level Spectra





The asymmetry observed in the O 1s spectra is a result of two contributions, one from BO atoms and the other from NBO atoms. From the fitting of the O 1s spectra to two Lorentzian -Gaussian peaks, the ratios BO/O_{total} was calculated and found to decrease from 0.426 to 0.188 with an increase in the vanadium content from 0.30 to 0.60.

x	V $2p_{3/2}$ (1) FWHM [area]	V$2p_{3/2}$(2) FWHM [area]	V4+/Vtotal	P 2p(1) FWHM [area]	P 2p(2) FWHM [area]	(1)/(2)	O1s (1) FWHM [area]	O1s (2) FWHM [area]	BO/O_{total} (±0.030)
0.3	516.28 2.00 3738.18	517.56 2.00 1611.68	0.699	133.35 2.00 2273.79	134.39 2.00 1111.82	0.672	431.27 2.10	532.46 2.43	0.426 0.410
0.4	516.24 2.04 3960.96	517.61 2.00 1396.62	0.739	133.61 2.10 2075.96	134.57 1.90 1360.82	0.604	531.10 2.10 18026.8	532.79 2.43 8328.4	0.316
0.5	516.07 2.00 7751.12	517.32 2.00 3276.62	0.7028	133.66 1.80 3074.29	134.65 1.99 1924.83	0.615	531.34 2.10 30461.6	532.75 2.43 8538.45	0.219
0.6	516.19 2.00 3703.51	517.29 2.00 2955.13	0.556	133.65 1.90 1504.01	134.55 2.10 669.624	0.692	531.49 2.10 19283.8	532.93 2.43 4472.81	0.188

Conclusions

The results are summarized as follows

(i) V exists in both V^{4+} & V^{5+} oxidation states and the ratios V^{4+}/V_{total} indicate that more than 70% of V ions are in the V^{4+} state for samples with x = 0.30 – 0.50 and 56 % for the glass with x = 0.60.

(ii) From the ratios BO/O_{total} it is concluded that V plays the role of a network modifier rather than a glass former as reported in other vanadate glasses.

(iii) Using the peak areas the resulting ratios of P $2p_{3/2}$ /P $2p_{1/2}$ were on the average 65 % close to the theoretical value of 67 %.