XPS studies of vanadium-phosphate glasses

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OUTLINE

- Amorphous materials
- Introduction to the XPS technique
- Desirability for XPS Studies
- XPS of v-phosphate glasses
- Results/Discussion
- Conclusion

Amorphous materials

- **Without form/no periodicity**
- **Not-crystalline**
- **Have short range order rather than long range order**

Glass form a particular class of amorphous materials

Types of glasses

- Metallic glasses/spin glasses (CuMn, FeMn)
- Semiconducting glasses can be generally devided into two groups:

  i) Chalcogenide glasses (As_2Te_3, GeSe, As_2Se_3, GeSeTe)

  ii) Oxide glasses containing TM ions
- Insulating glasses (Other oxide glasses)

Phosphate glasses have technological applications such as:

- Have a very high transmission in the ultraviolet region.
- Suitable materials for high power lasers because of low thermo-optical coefficient and large emission.
- Most biocompatible glasses are also based on phosphate glasses, used for bone repair etc.
- Alkali-alumino-phosphate glasses indicate the possibility of connection with organic polymers.

Applications continued

- V_2O_5,B_2O_3 and phosphate glasses containing mono-valent cations like Li+ and/or Ag+ have applications as solid electrolytes in electrochemical devices such as batteries, chemical sensors, storage devices and smart windows because of their high ionic conductivity.
- TM oxide glasses have applications as optical and electrical memory switching devices, making solid state devices and optical fibre.
- TeO_2 based glasses have both optical and electrical applications.

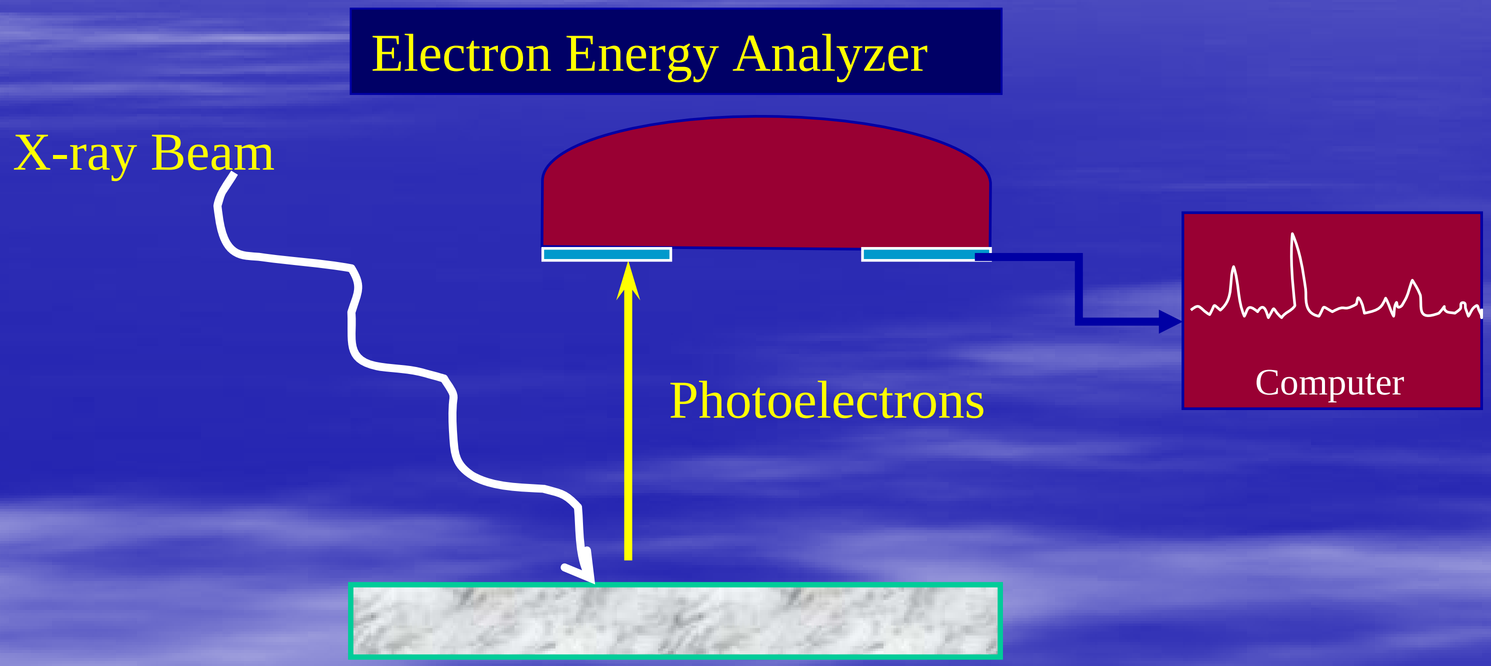
Methods of preparation

- Cooling from the melt
- Condensation from vapor
- Pressure quenching
- Solution hydrolysis
- Anodization
- Bombardment of crystals by high-energy particles or by shock waves

Role of different oxides in glasses

- SiO_2, P_2O_5, GeO_2, B_2O_3 , are called **network formers** (these oxides readily form a glass)
- Al_2O_3, TiO_2, MgO, TeO2, V2O5 are called **intermediate** (can substitute for network formers but do not form glasses on their own)
- Na_2O, LiO_2, K_2O are called **network modifiers** (disrupt the glass network)

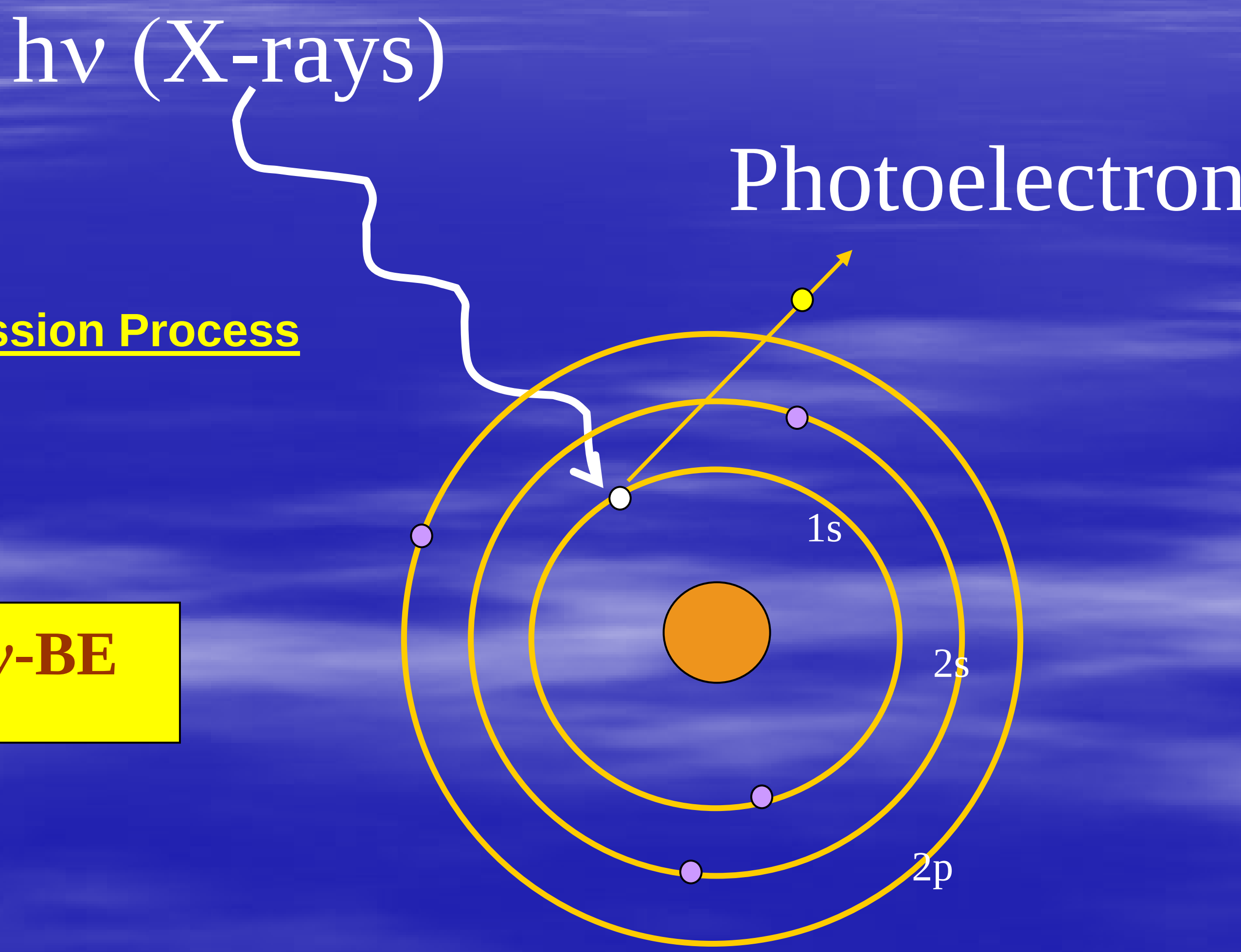
X-Ray Photoelectron Spectroscopy (XPS)



$$E_k = h\nu - E_b - \Phi$$

Basic aspects of XPS

XPS is a <u>surface</u> analytical technique (top 0.5-5 nm) that is widely used for material surface characterization.



Photoelectron emission Process

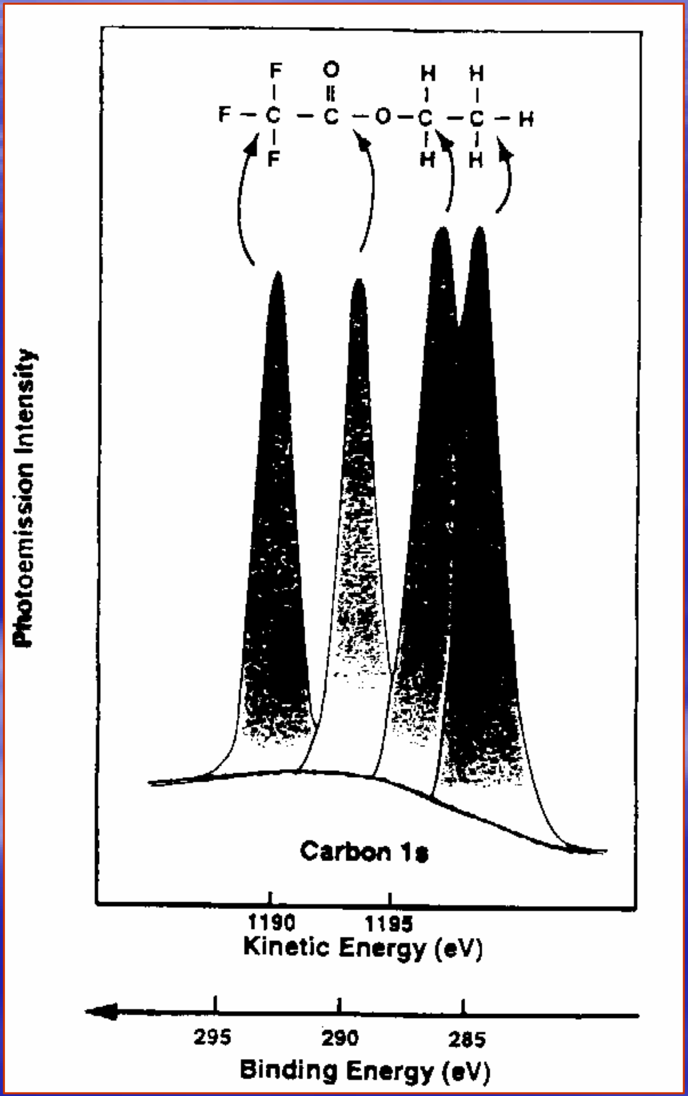
$$KE_{photoelectron} = h\nu\text{-}BE$$

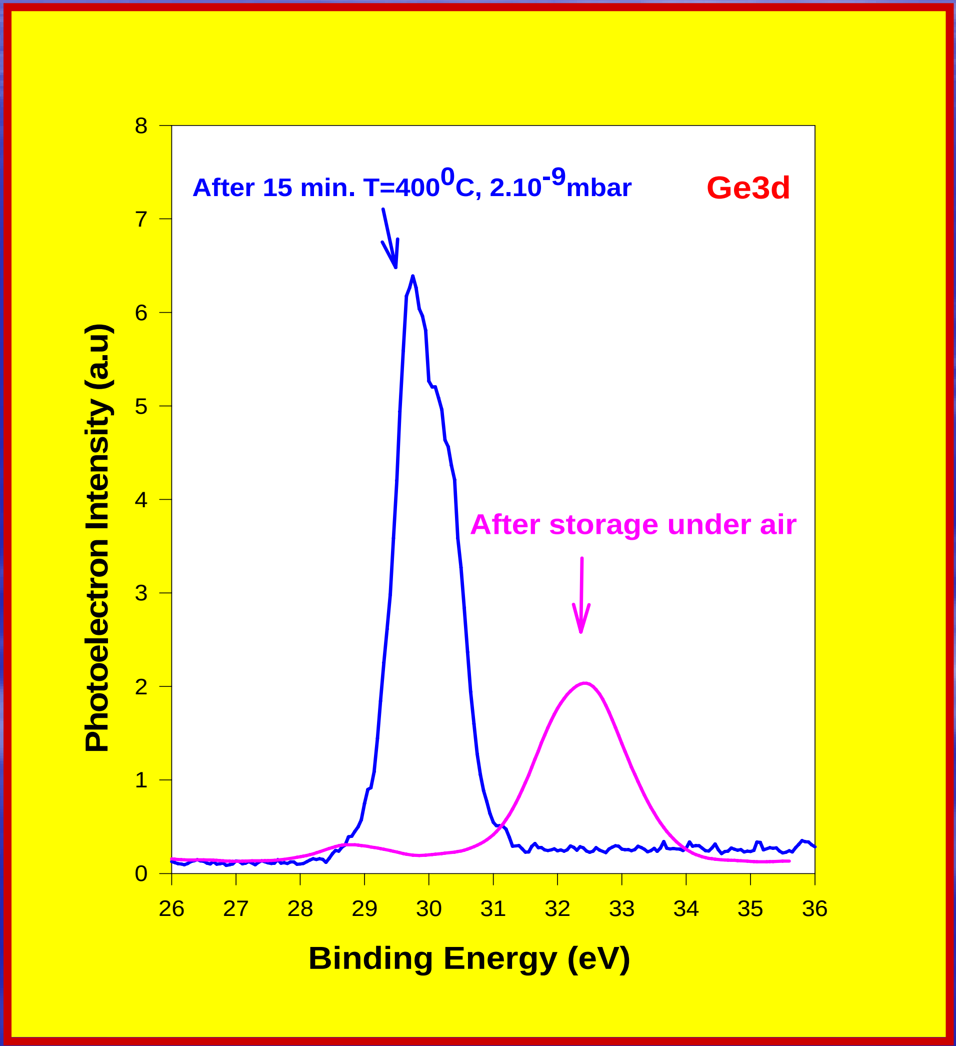
Chemical and structural effects

BE of photoelectron sensitive to:

- Type of atoms
- The oxidation state of the atom
- Local chemical environment

X-ray photoelectron spectroscopy (XPS) showing chemical shift





Objectives

(i) Find the redox state(s) of V ions using XPS

(ii) Finding BO/O $_{total}$

(iii) Study the structural role of V in these glasses

Glass system investigated

$$(V_2O_5)_x\ (P_2O_5)_{1-x}$$

x = 0.3, 0.4, 0.5, 0.6

Experimental details

Sample preparation

-Stoichiometric amounts of $V_2O_5$and P_2O_5 were melted in Alumina crucibles at ~ 1100 ^oC for two hours.
-Oxidation & reduction reactions in a glass melt depend on several factors and so the glasses were prepared under similar conditions to minimize the effect

Chemical composition was determined by ICP.

XPS measurements

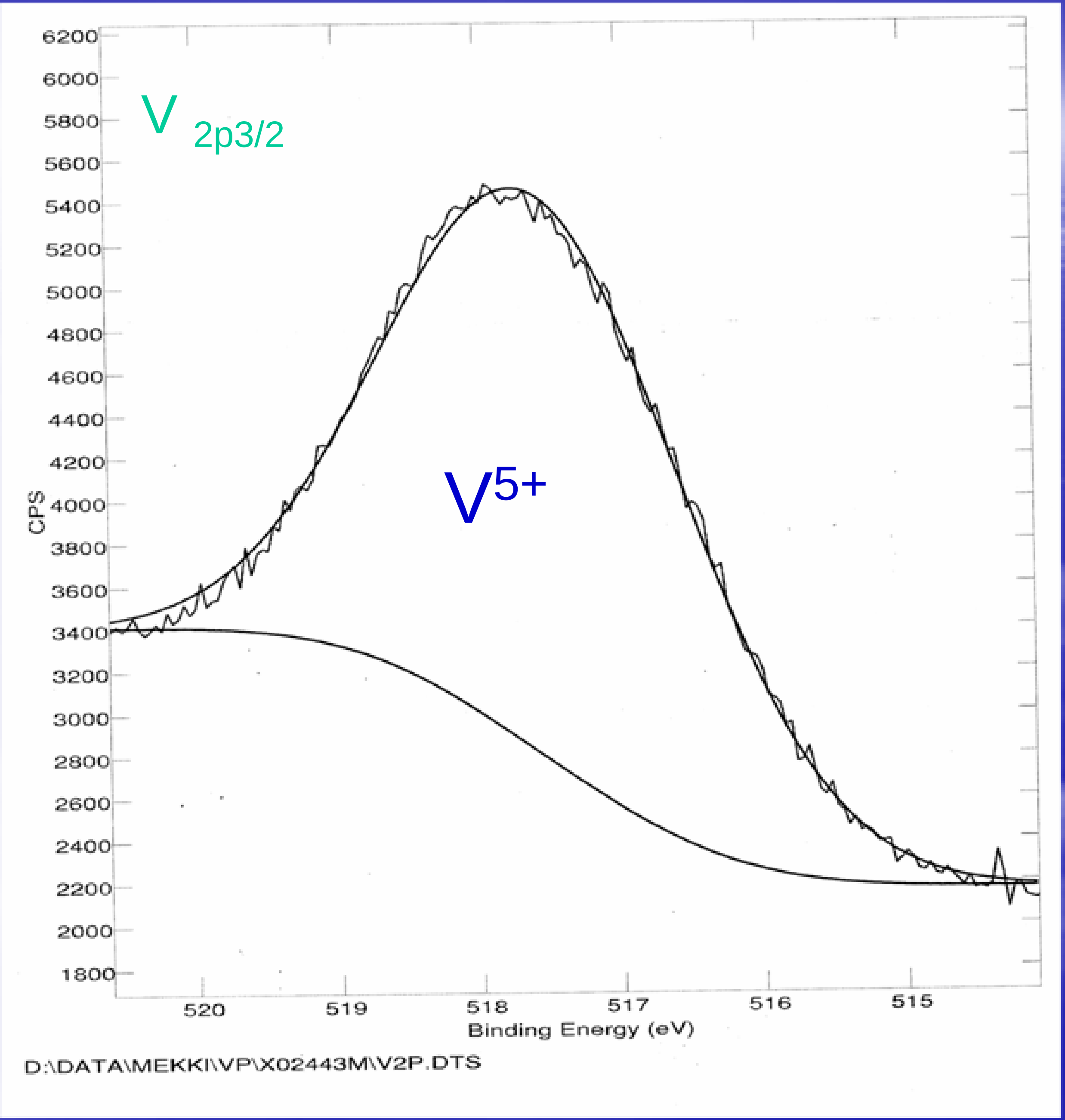
High resolution V 2p, O 1s, and P 2p core level spectra were obtained Using an Al Kα X-ray source on a VG ESCALAB Mk II. Glass rods were Fractured in UHV (~ 10^{-10} mbar). The C 1s was a reference level. Accuracy in the quantitative analysis ~ ± 5%.

ICP measurements

	Nominal		Analysed	
x	P_2O_5	V_2O_5	P_2O_5	V_2O_5
0.30	0.70	0.30	0. 64	0.36
0.40	0.60	0.40	0.61	0.39
0.50	0.50	0.50	0.54	0.46
0.60	0.40	0.60	0.46	0.54

V 2p spectra

- Usually V $2p_{3/2}$ spectra for the glass samples are sufficiently broaden such that two peaks are fitted to the data.
- These peaks are associated with the presence of V^{5+} and V^{4+} and the relative area under each peak reflects the relative amount of each ion.
- Here in this study the spectra could be fitted to only one peak, V^{5+}, so V is found to be in the V^{5+} state in these glass samples.

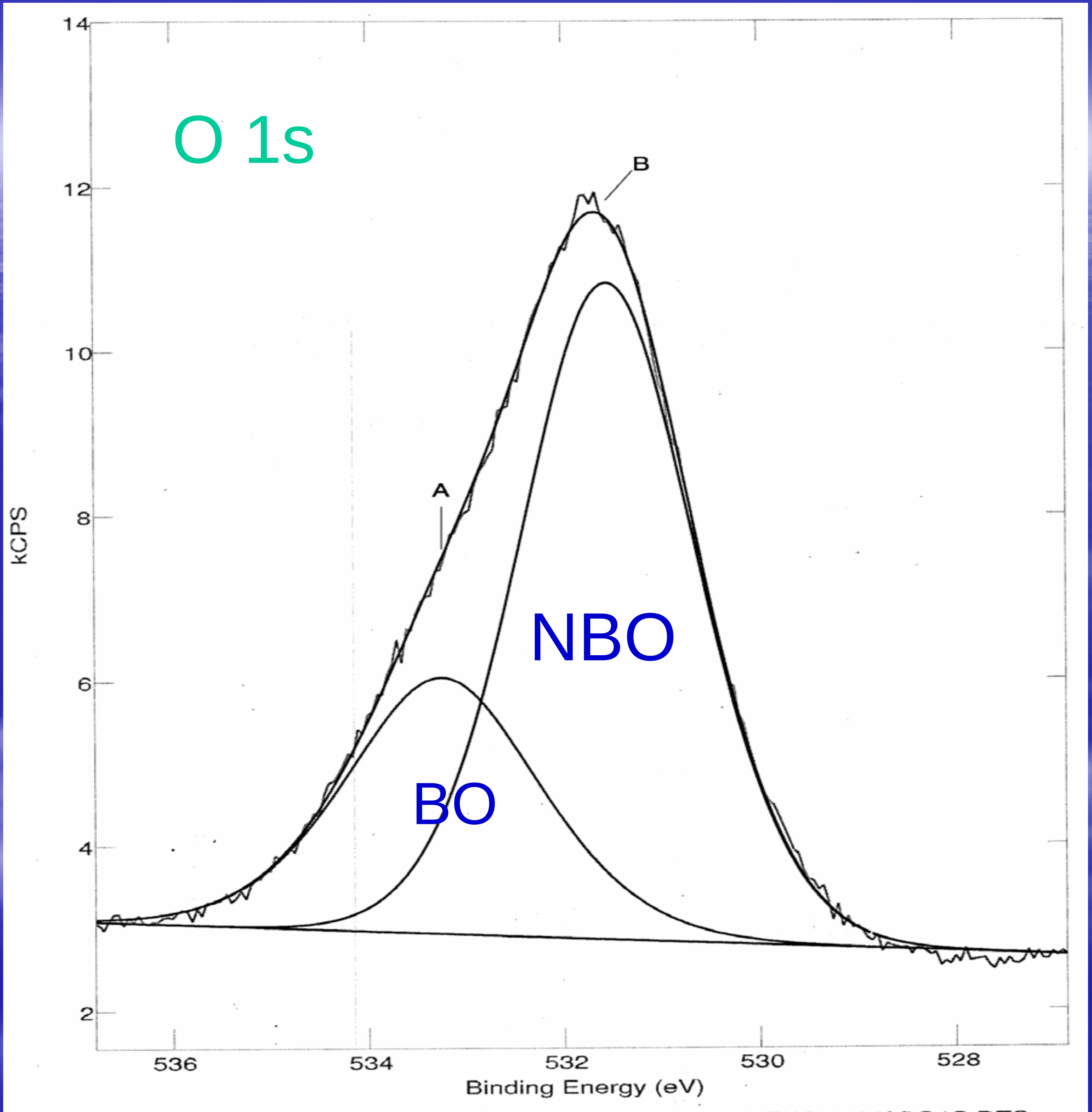

V 2p3/2
V5+
CPS
6200
6000
5800
5600
5400
5200
5000
4800
4600
4400
4200
4000
3800
3600
3400
3200
3000
2800
2600
2400
2200
2000
1800
520
519
518
517
516
515
Binding Energy (eV)
D:\DATA\MEKKI\VP\X02443M\V2P.DTS

O 1s spectra

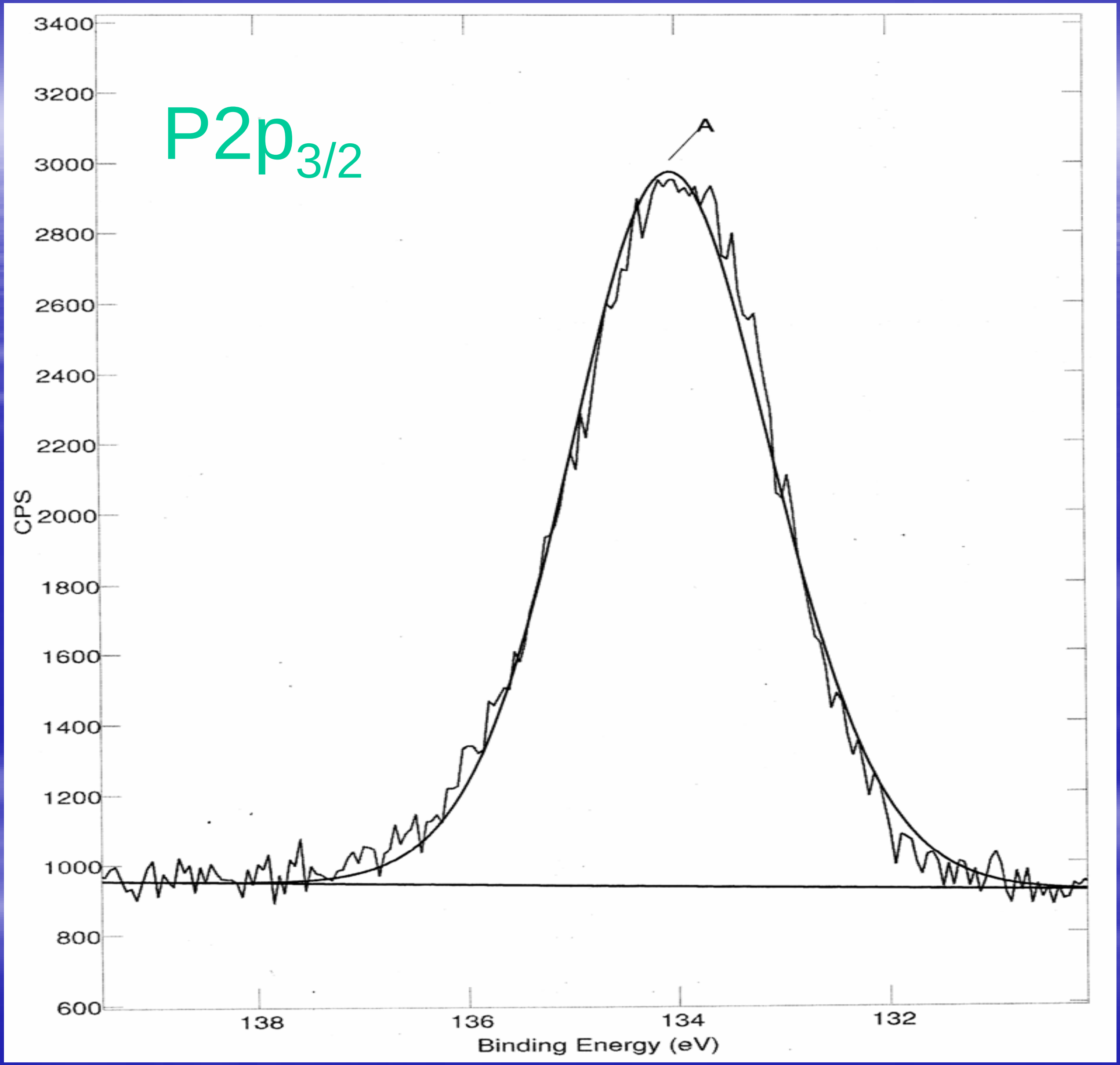
- V-O-V,V-O-P, P-O-P: bridging oxygen (BO)
- V = O, P=O: non-bridging oxygen

$$(V_2O_5)_x\ (P_2O_5)_{1-x}$$

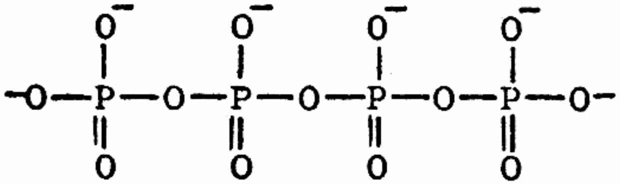
- BO/TO = 42, 30, 22, 19 % for x = 0.3,0.4, 0.5 & 0.6, respectively
- NBO/TO 58-80%

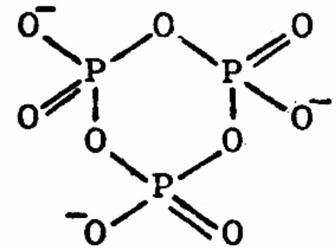


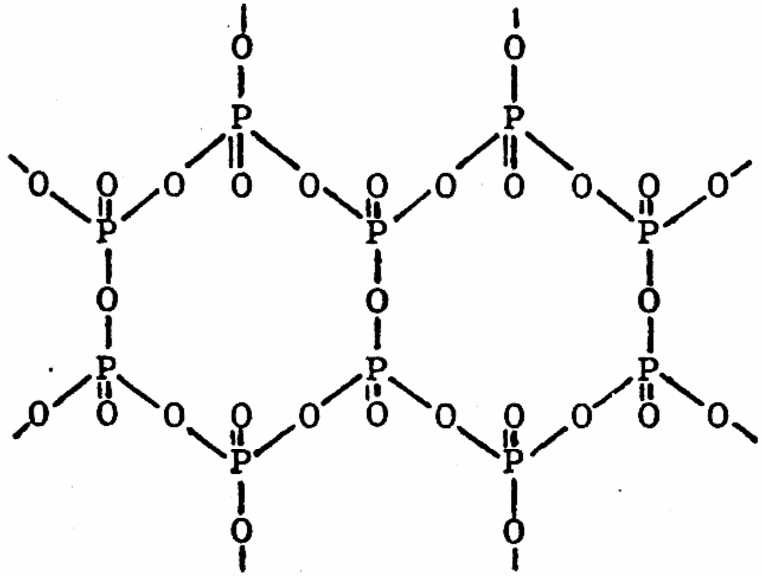
O 1s
B
A
NBO
BO
kCPS
14
12
10
8
6
4
2
536
534
532
530
528
Binding Energy (eV)


P2p3/2
A
CPS
3400
3200
3000
2800
2600
2400
2200
2000
1800
1600
1400
1200
1000
800
600
138
136
134
132
Binding Energy (eV)

x	V $2p_{3/2}$ FWHM	P 2p FWHM	O1s (A) FWHM	O1s (B) FWHM	BO/O_{total} (±0.030)
0.3	516.56 2.17	133.65 2.41	532.46 2.43	531.27 2.10	0.427
0.4	517.32 2.55	134.39 2.45	533.24 2.43	531.54 2.19	0.298
0.5	517.2 2.46	134.04 2.35	533.00 2.40	531.39 2.01	0.217
0.6	517.55 2.47	133.95 2.30	533.03 2.43	531.53 2.10	0.193







Condensed phosphates can conveniently be divided into three major groups :

(a)	Linear Polyphosphates	$P_nO_{3n+1}^{(n+2)-}$	chains
(b)	Metaphosphates	$P_nO_{3n}^{n-}$	rings
(c)	Ultraphosphates	$P_nO_{3n+m}^{(n+2m)-}$	cages, sheets, 3-D structures

Three main structural groups for phosphates

Linear phosphates: *$R = P/M \leq 2$ &*

$R^* = O/P > 3$

Metaphosphates: $R = P/M = 2$ &

$R^* = O/P = 3$

Ultraphosphates: $R = P/M > 2$ &

$R^* = O/P < 3$

Ratios of phosphorous to metal ($R = P/M \leq 2$) and oxygen to phosphorous ($R^* = O/P > 3$) suggest that these phosphate glasses probably exist as linear chains.

Conclusion

✓*The XPS analysis of V 2p core level indicates that almost all V ions exist in the $V5^+$ state only*

✓*The XPS analysis of O 1s core level indicates that both BO & NBO exist in these glasses [BO/O total varies from 42-19% for V =0.3-0.6*

✓*The study shows that vanadium plays, in these glasses, the role of a network modifier rather than a glass former as reported in other vanadate glasses.*

✓

Thank you