XPS and magnetization studies of Sr-v-borate glasses

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OUTLINE

- Amorphous materials
- Introduction to the XPS technique
- Desirability for Magnetization & XPS Studies
- XPS of Sr-V-borate 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 (As_2Te_3)
- Insulating glasses (oxide glasses) but TM oxide glasses are Semicond.

Oxide glasses have technological applications such as:

- Optical fibers (Si, Ge)
- Ionic conductors (Alkali-Si or Alkali-Ge)
- Semiconductors (Fe-B, Cu-Si, V-Ge)
- Glass Ceramics (Mg-Al-Si, Mg-P-Si)

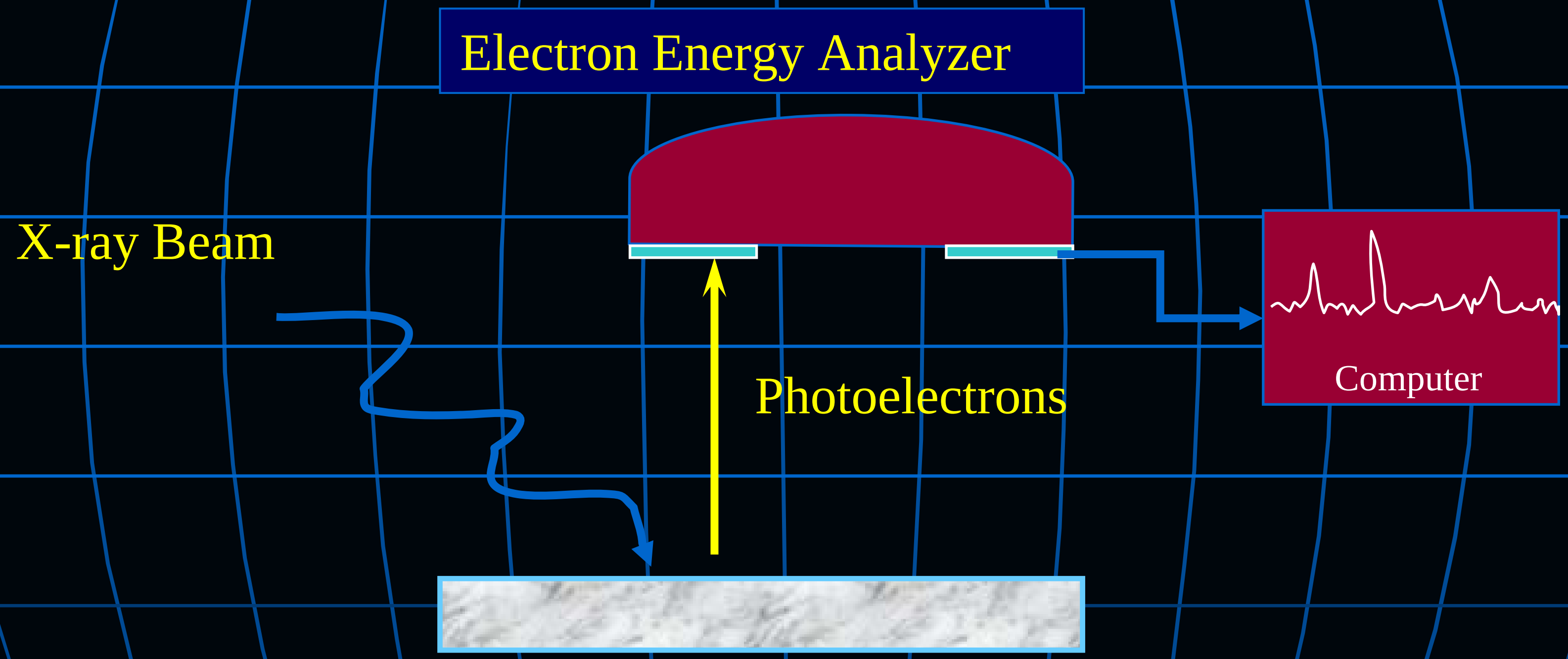
Methods of preparation

- 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 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)

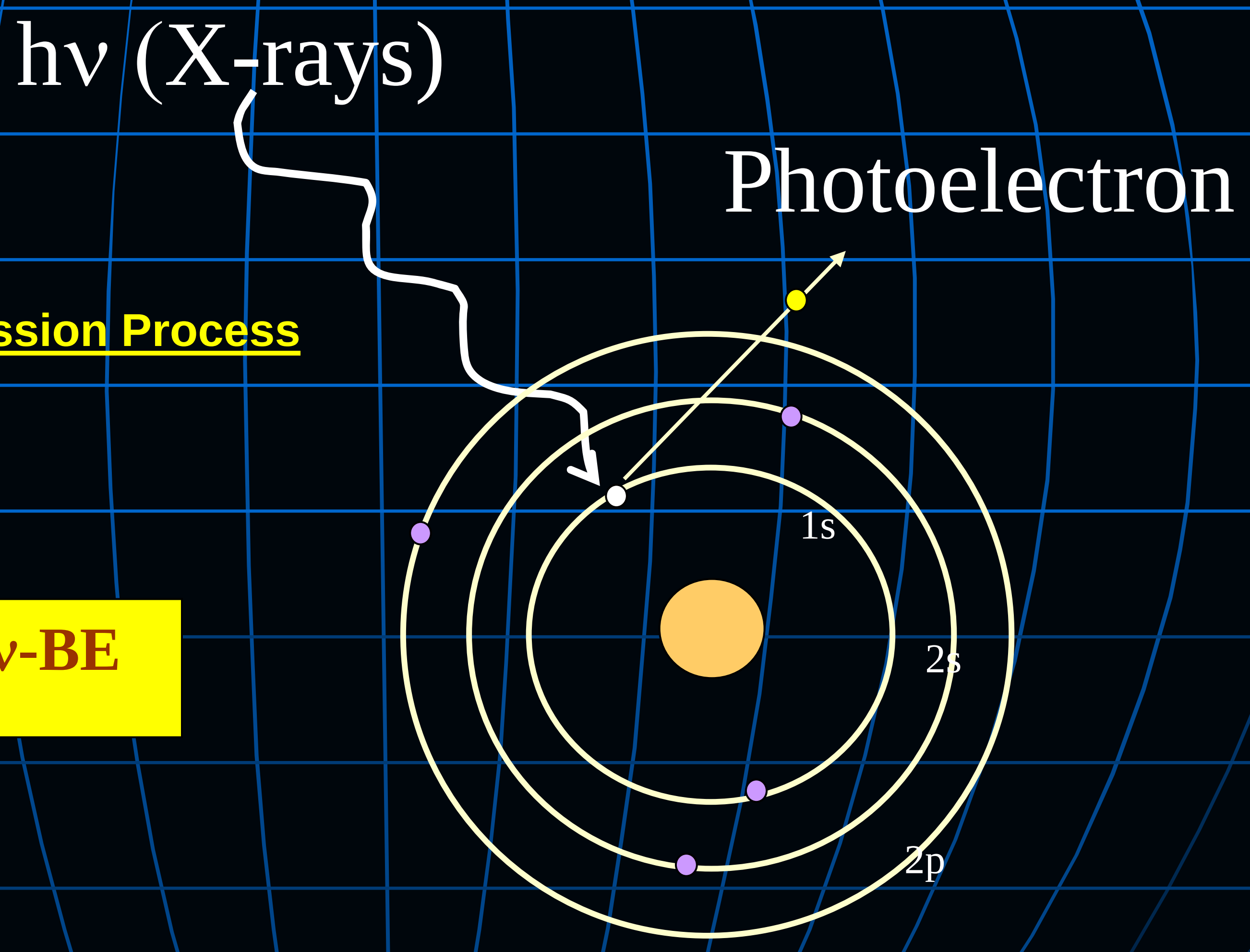
X-Ray Photoelectron Spectroscopy (XPS)



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

Basic aspects of XPS

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



Photoelectron emission Process

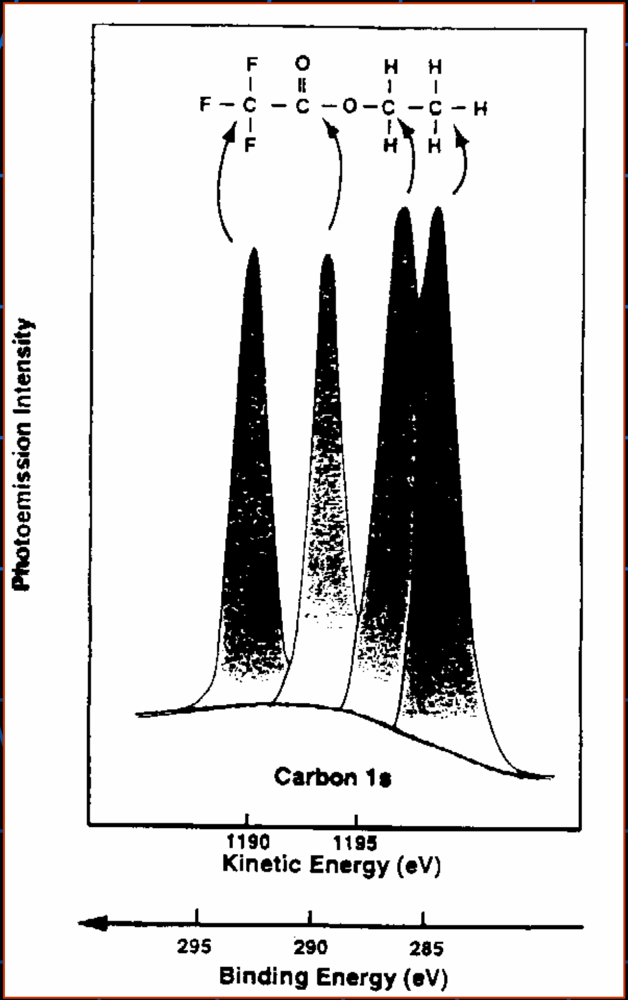
$$KE_{photoelectron} = h\nu - BE$$

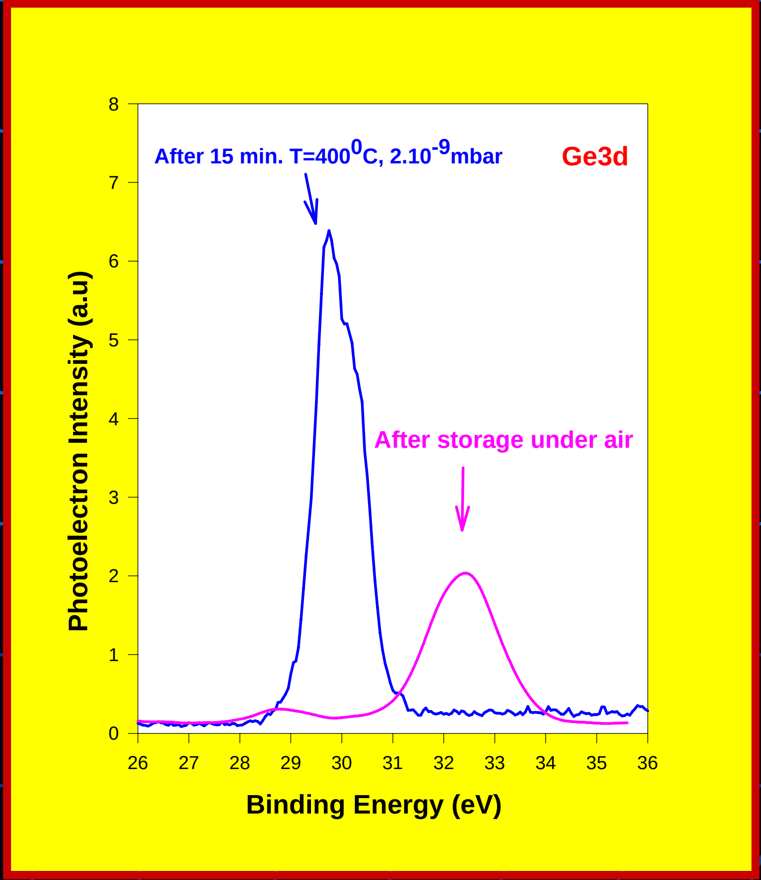
Chemical and structural effects

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) Investigate the magnetic properties of V ions in Sr-V-borate glasses.

(ii) Find the redox state(s) of V ions using both XPS and magnetic measurements.

(iii) Study the structural role of V & Sr in these materials

Glass system investigated

$$\mathbf{(V_2O_5)_z(SrO)_{0.2}(B_2O_3)_{0.8-z}}$$

z = ***0.4, 0.5, 0.6, 0.7, 0.8***

Experimental details

Sample preparation

Stoichiometric amounts of V_2O_5, SrO and B_2O_3 were melted in Alumina crucibles at ~ 1100 ºC for two hours.

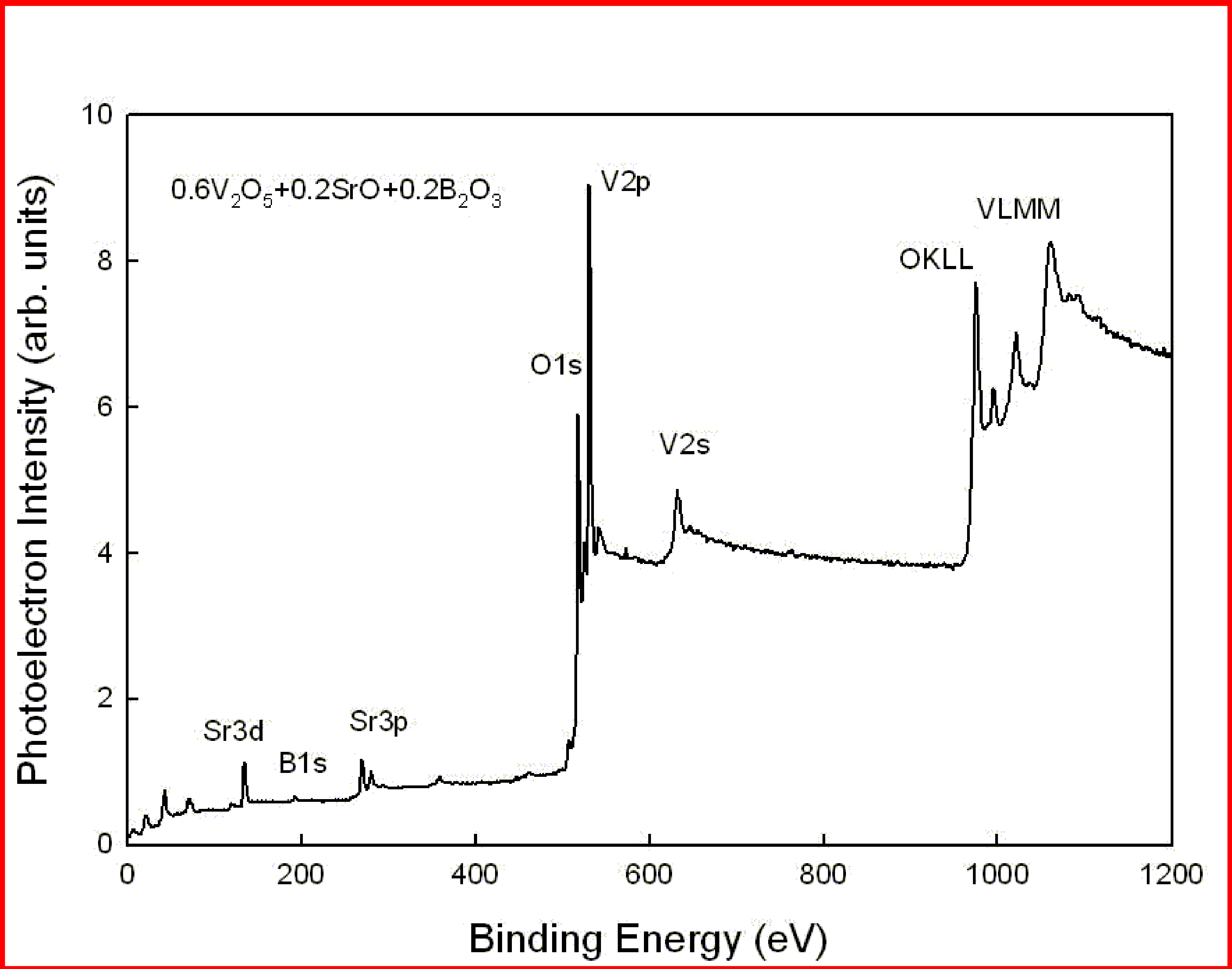
Chemical composition was determined by ICP.

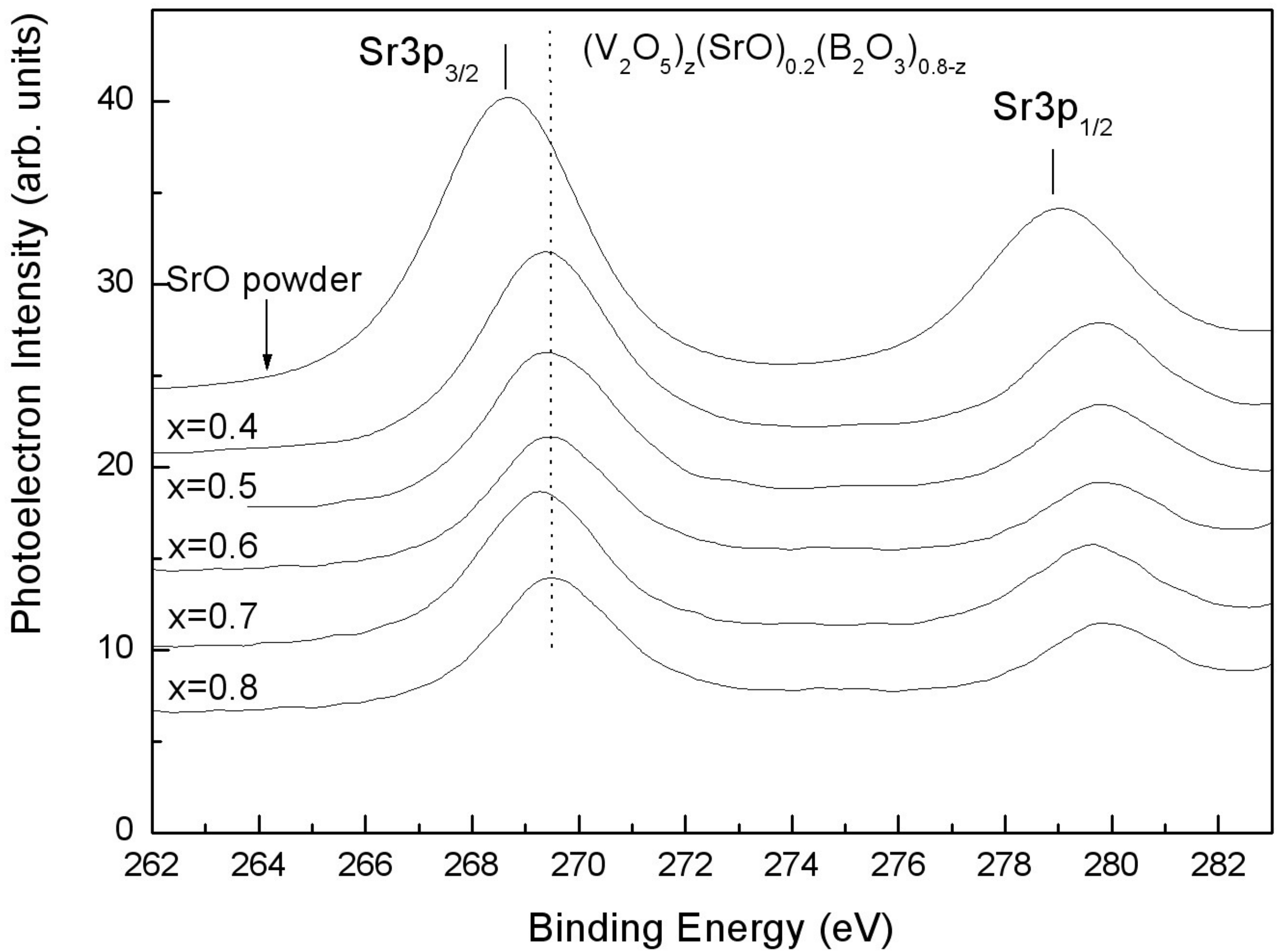
Magnetic data

M vs. T data were recorded using a SQUID magnetometer in a magnetic field of 5000 Oe over a temperature range of 5 K to 300 K. Accuracy ~ ±3%.

XPS measurements

High resolution V 2p, O 1s, Sr 3p, and B 1s 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%.


0.6V2O5+0.2SrO+0.2B2O3
V2p
VLMM
OKLL
O1s
V2s
Sr3d
B1s
Sr3p
Photoelectron Intensity (arb. units)
Binding Energy (eV)
0
2
4
6
8
10
0
200
400
600
800
1000
1200

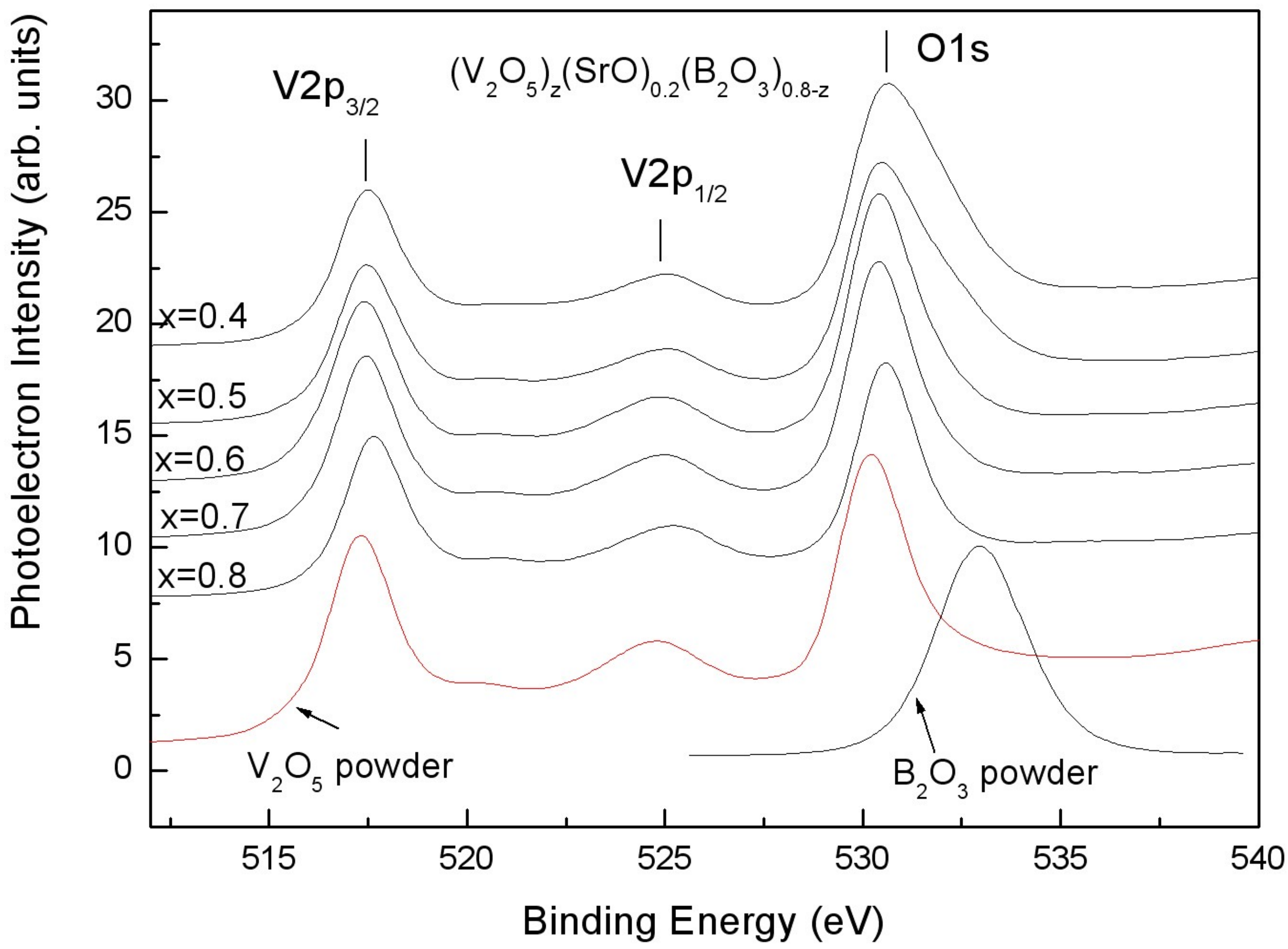


Sr3p3/2
(V2O5)z(SrO)0.2(B2O3)0.8-z
Sr3p1/2
SrO powder
x=0.4
x=0.5
x=0.6
x=0.7
x=0.8
Photoelectron Intensity (arb. units)
Binding Energy (eV)
0
10
20
30
40
262
264
266
268
270
272
274
276
278
280
282

- Sr 3p spectra have the same B.E. for all samples.

- Shifted by 0.6 eV towards higher B.E. in comparison to their vaues in SrO powder.

- This shift arises from a change in the molecular environment.

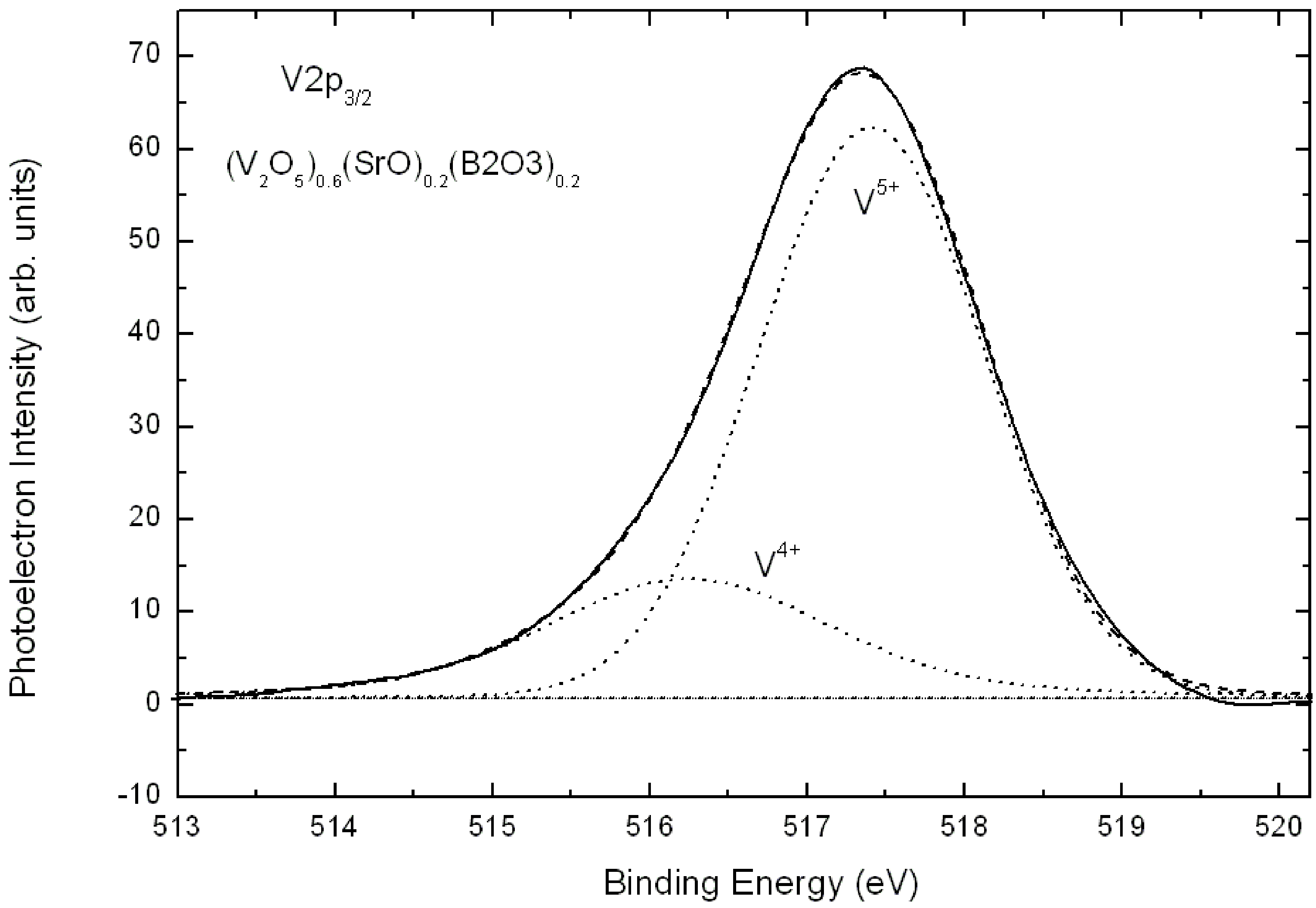


Photoelectron Intensity (arb. units)
Binding Energy (eV)
V2p3/2
V2p1/2
O1s
(V2O5)z(SrO)0.2(B2O3)0.8-z
x=0.4
x=0.5
x=0.6
x=0.7
x=0.8
V2O5 powder
B2O3 powder
0
5
10
15
20
25
30
515
520
525
530
535
540

V 2p spectra

. the 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.
- More than 90% of the V is found to be in the V^{5+} state in these glass samples.



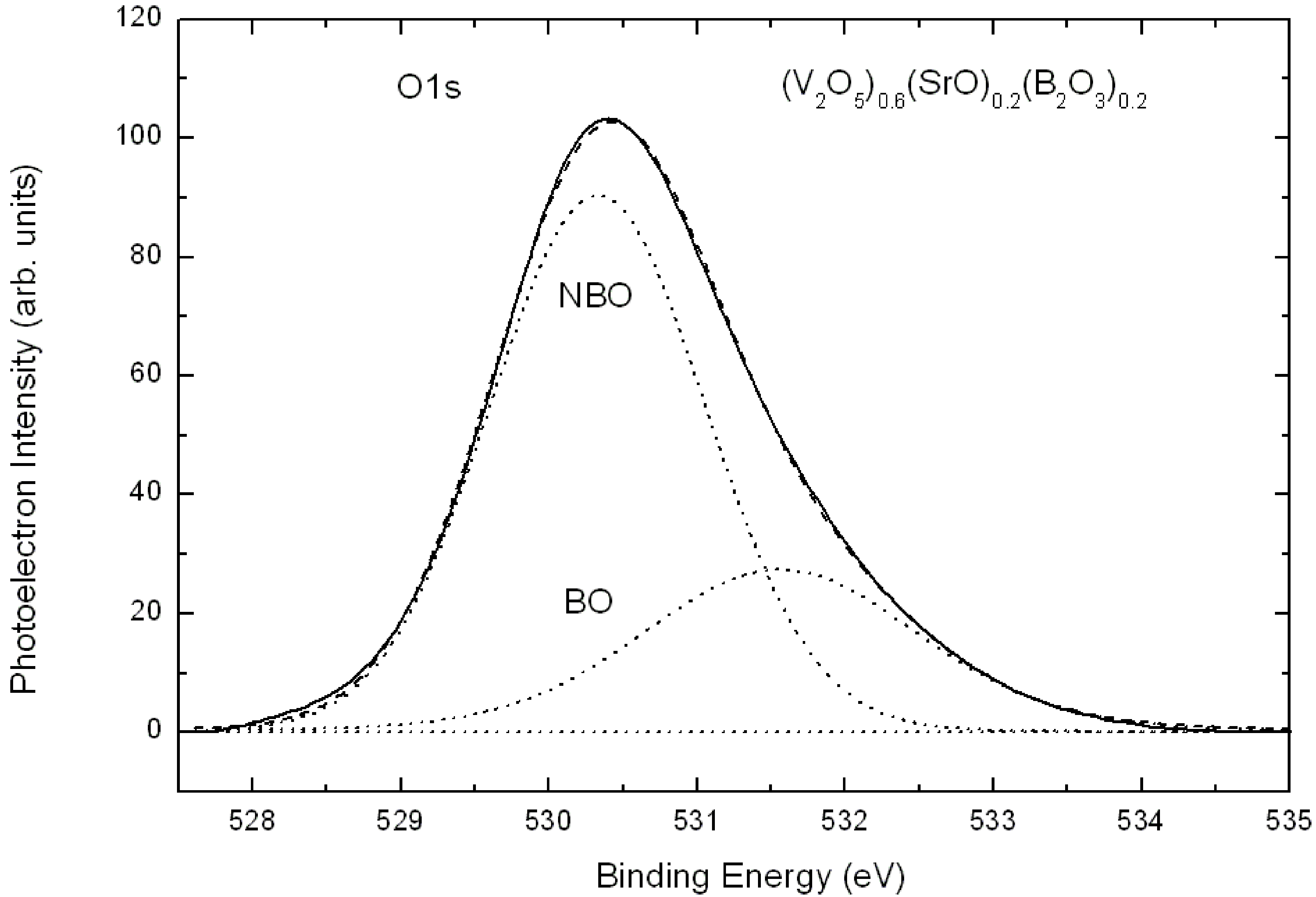
V2p3/2
(V2O5)0.6(SrO)0.2(B2O3)0.2
V5+
V4+
Photoelectron Intensity (arb. units)
Binding Energy (eV)
70
60
50
40
30
20
10
0
-10
513
514
515
516
517
518
519
520

O 1s spectra

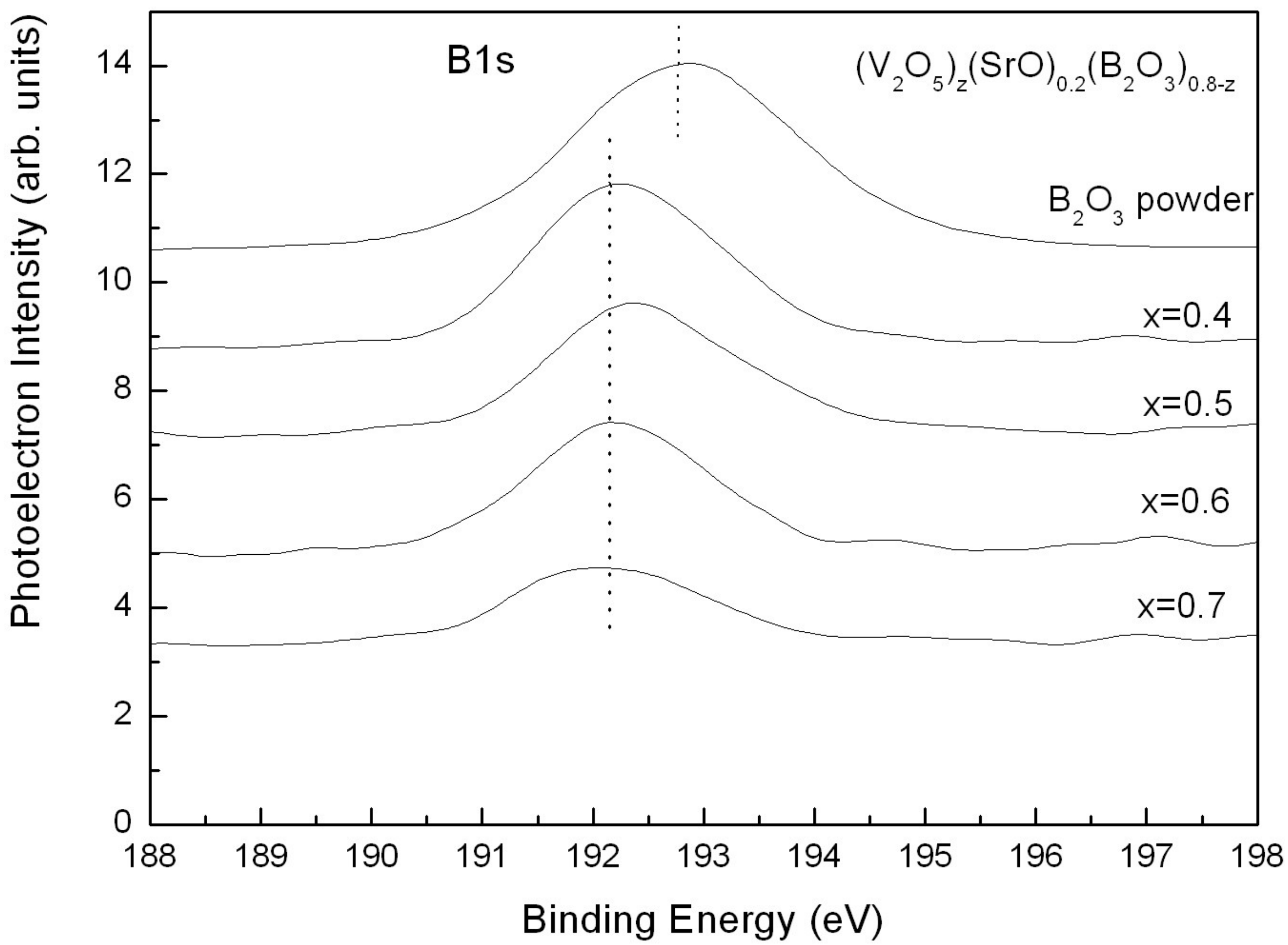
- V-O-V,V-O-B, B-O-B: bridging oxygen (BO)
- V-O-Sr, Sr-O-Sr, V = O non-bridging oxygen

$$(V_2O_5)_x\ (SrO)_y\ (B_2O_3)_z$$

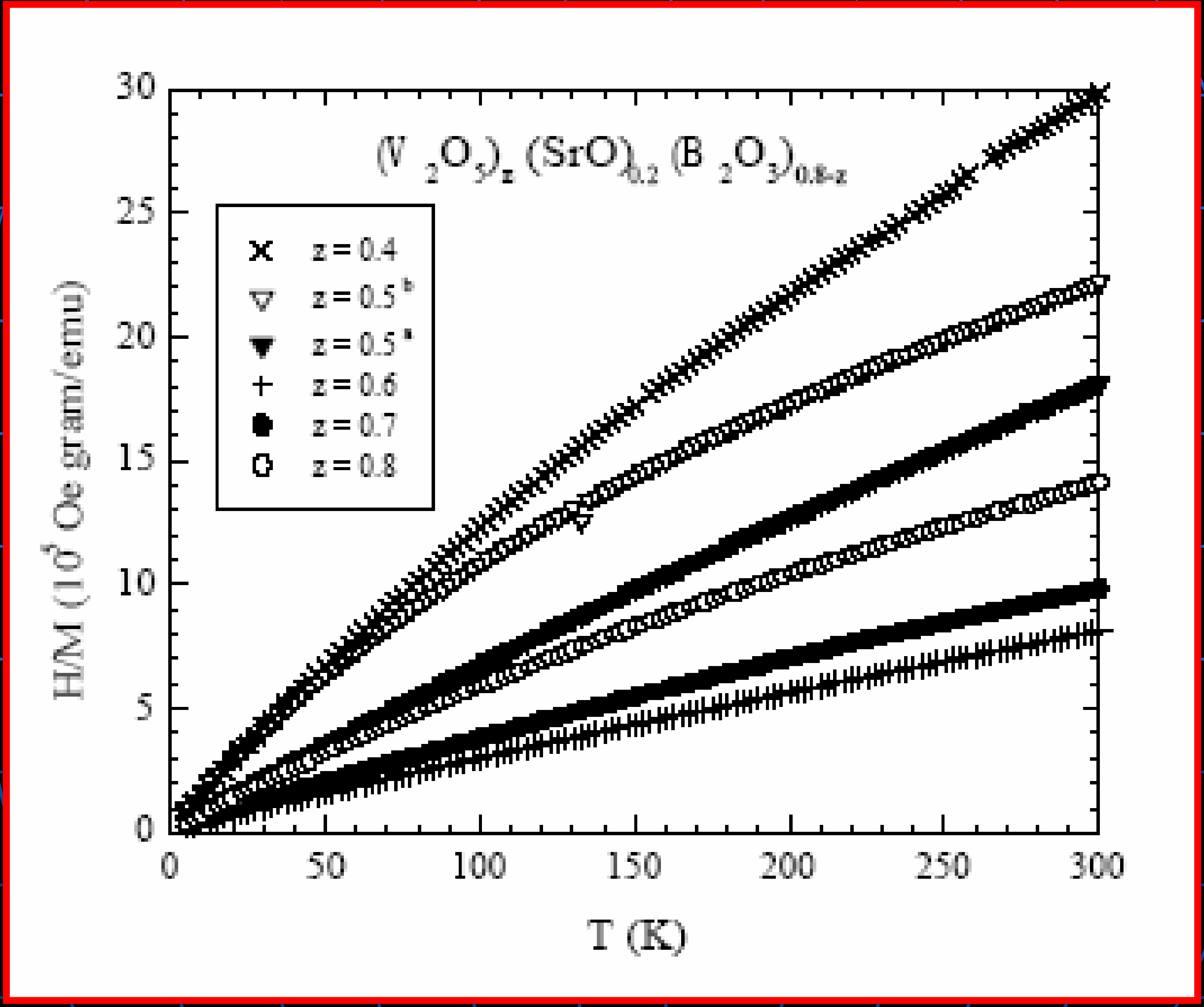
- NBO/TO = (4x+2y)/(5x+y+3z)
- NBO/TO 57-85%
  - Good agreement between calculated and measured.



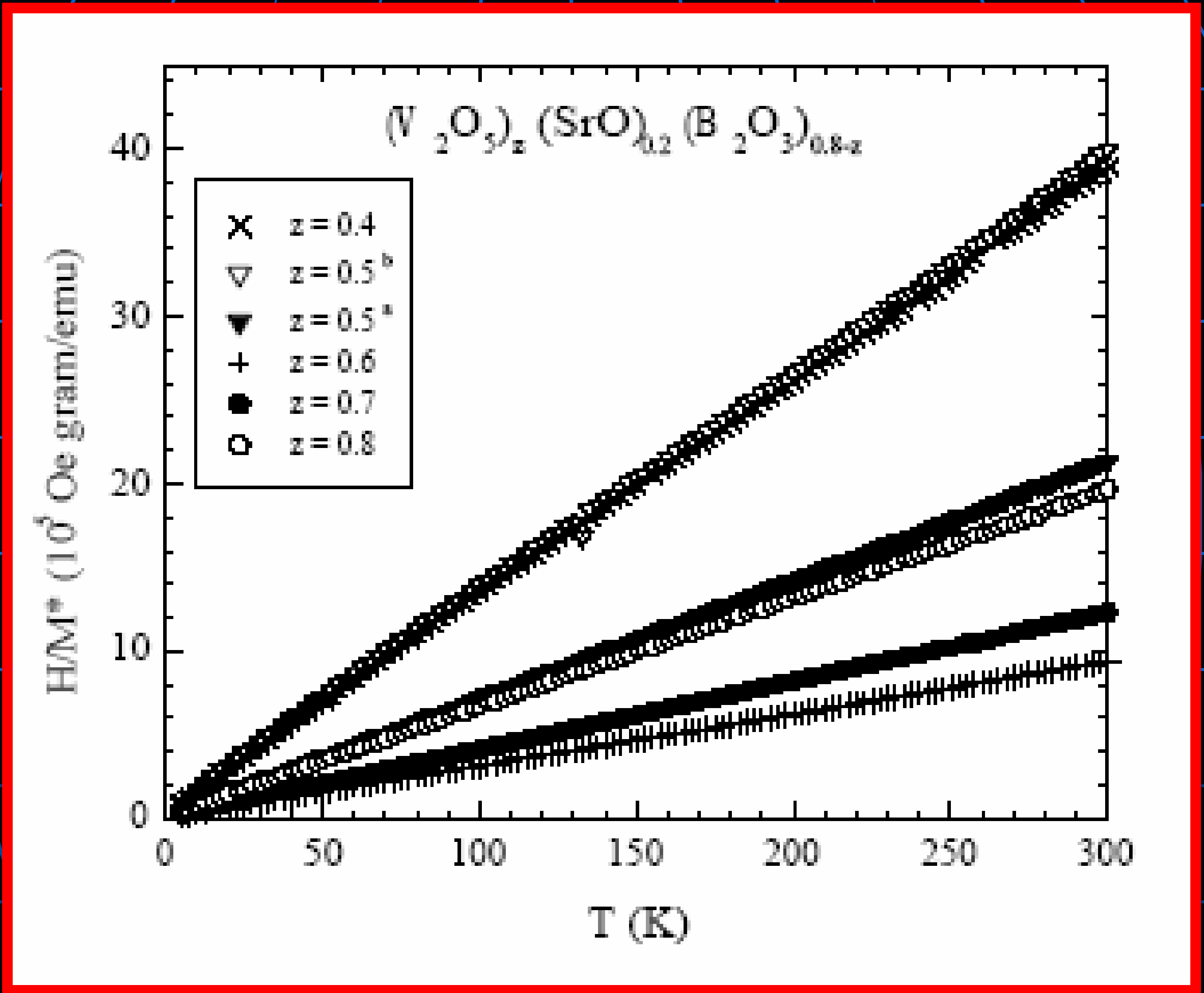
O1s
$(V_2O_5)_{0.6}(SrO)_{0.2}(B_2O_3)_{0.2}$
NBO
BO
Photoelectron Intensity (arb. units)
Binding Energy (eV)
120
100
80
60
40
20
0
528
529
530
531
532
533
534
535



B1s
$(V_2O_5)_z(SrO)_{0.2}(B_2O_3)_{0.8-z}$
B_2O_3 powder
x=0.4
x=0.5
x=0.6
x=0.7
Photoelectron Intensity (arb. units)
Binding Energy (eV)
0
2
4
6
8
10
12
14
188
189
190
191
192
193
194
195
196
197
198



$(V_2O_5)_z (SrO)_{0.2} (B_2O_3)_{0.8-z}$
z = 0.4
z = 0.5 b
z = 0.5 a
z = 0.6
z = 0.7
z = 0.8
H/M (10^3 Oe gram/emu)
T (K)
0
5
10
15
20
25
30
0
50
100
150
200
250
300



$(V_2O_5)_z (SrO)_{0.2} (B_2O_3)_{0.8-z}$
z = 0.4
z = 0.5 [b]
z = 0.5 [a]
z = 0.6
z = 0.7
z = 0.8
H/M* (10[3] Oe gram/emu)
T (K)
0
10
20
30
40
0
50
100
150
200
250
300

Magnetization Results

TABLE Compositions and magnetic characterization parameters for the vanadate glasses.

	Batch	Actual V_2O_5	Actual SrO	Actual B_2O_3	$(M/H)_{const}$ $\left(\frac{10^{-7}\,\text{emu}}{\text{g Oe}}\right)$	C $\left(\frac{10^{-4}\,\text{emu K}}{\text{g Oe}}\right)$	θ (K)	V^{4+}/V
$(SrO)_x(V_2O_5)_{1-x}$	x = 0.5	0.488	0.511	-	0.700	0.533	-0.91	0.0206
	x = 0.4	0.591	0.409	-	1.17	0.700	0.03	0.0236
	x = 0.3	0.692	0.308	-	1.55	0.955	-0.05	0.0289
	x = 0.2	0.792	0.208	-	2.00	1.54	-2.85	0.0427
$(V_2O_5)_{0.5}(SrO)_{0.5-y}(B_2O_3)_y$	y = 0.1	0.498	0.415	0.087	0.670	0.603	-0.07	0.0225
	y = 0.2	0.483	0.299	0.218	0.630	0.731	0.42	0.0270
	y = 0.3[a]	0.516	0.214	0.270	0.850	1.41	-1.38	0.0489
	y = 0.3[b]	0.486	0.192	0.322	2.00	0.771	-5.65	0.0276
	y = 0.4	0.539	0.112	0.347	1.76	0.617	-7.41	0.0204
$(V_2O_5)_z(SrO)_{0.2}(B_2O_3)_{0.8-z}$	z = 0.4	0.434	0.220	0.346	0.950	0.734	-1.88	0.0283
	z = 0.5[b]	0.486	0.192	0.322	2.00	0.771	-5.65	0.0276
	z = 0.5[a]	0.516	0.214	0.270	0.850	1.41	-1.38	0.0489
	z = 0.6	0.613	0.209	0.178	2.00	3.24	-2.64	0.1007
	z = 0.7	0.701	0.209	0.091	1.67	2.47	-1.94	0.0721
	z = 0.8	0.792	0.208	0.000	2.00	1.54	-2.85	0.0427

[a,b] – Refers to two samples with the same nominal composition.

Conclusion

✓*The XPS analysis of V 2p core level indicates that more than 90% V ions exist in the V5^{+} state only*

✓*The magnetization studies also suggests that V ions are mainly in the V^{5+} valence state and behave antiferromagnetically*

✓*The strength of the interaction increases with increase in vanadium concentration*

Thank you