DC Conductivity studies of Sr-V-B glasses

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OUTLINE

- Amorphous materials
- Desirability for Magnetization & XPS Studies
- XPS & Magnetization Results of Sr-V-borate glasses
- Desirability for DC conductivity studies
- Description of the proposed research
- Theory
- Conclusion/Expectations

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)

Techniques used

- XPS (Previous project)
- Magnetization (previous project)
- DC conductivity (New project as a continuation of the previous work)

Objectives (Previous Project)

(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

(iv) Study electrical conductivity to further understand the mechanism of electrical properties. (New Project)

Glass systems investigated

$$[(V_2O_5)_x\ (SrO)_{1-x}]$$

$$[(V_2O_5)_{0.5}(SrO)_{0.5-y}(B_2O_3)_y]$$

and $[(V_2O_5)_x(SrO)_{0.2}(B_2O_3)_{0.8-x}$

Experimental details

Sample preparation

Stoichiometric amounts of V_2O_5, SrO and B_2O_3 were melted in Alumina crucibles at ~ 1100 °C 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%.

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

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

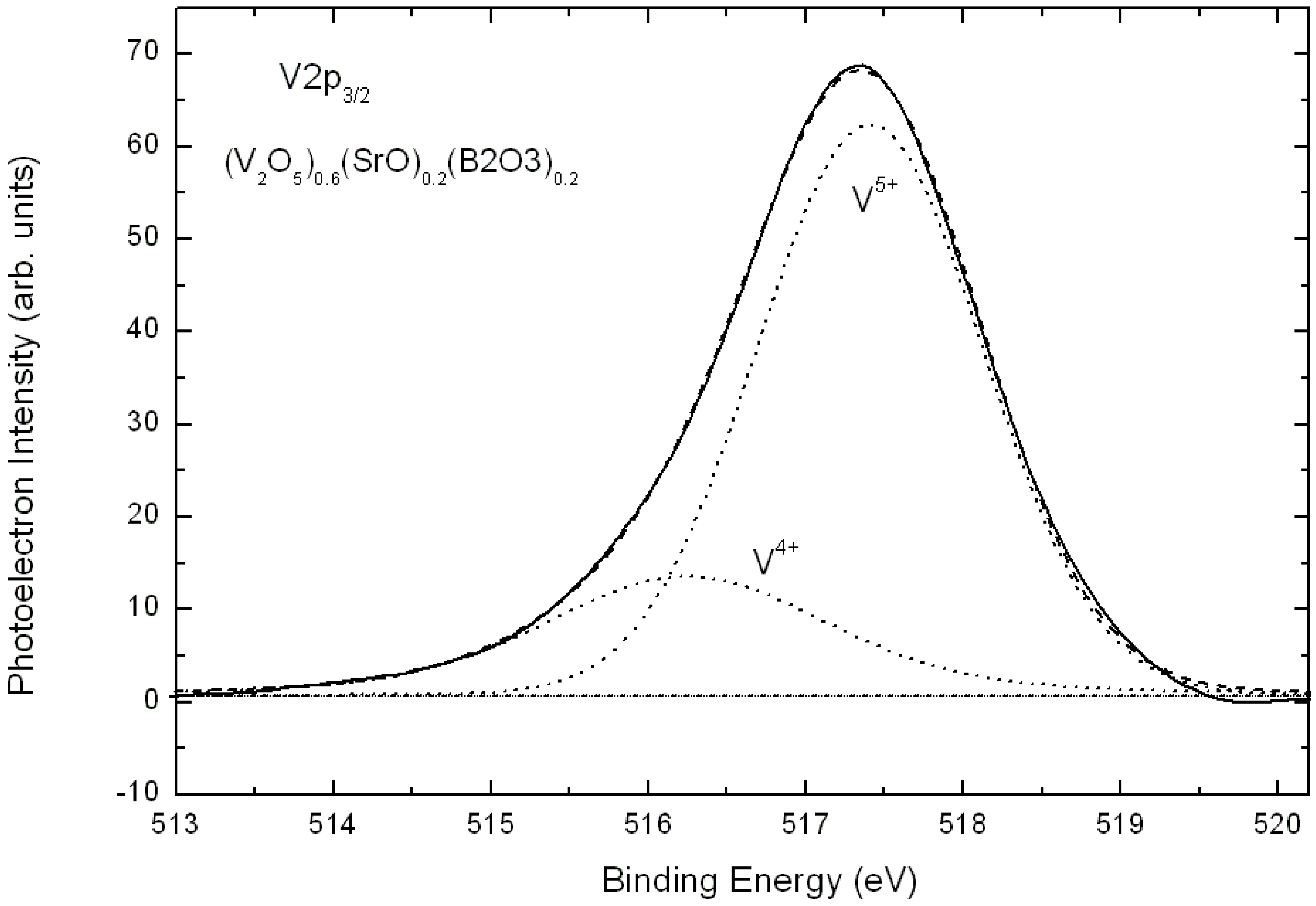
- This shift arises from a change in the molecular environment.

V 2p spectra

. 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.


V2p$_{3/2}$
$(V_2O_5)_{0.6}(SrO)_{0.2}(B2O3)_{0.2}$
V^{5+}
V^{4+}
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

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

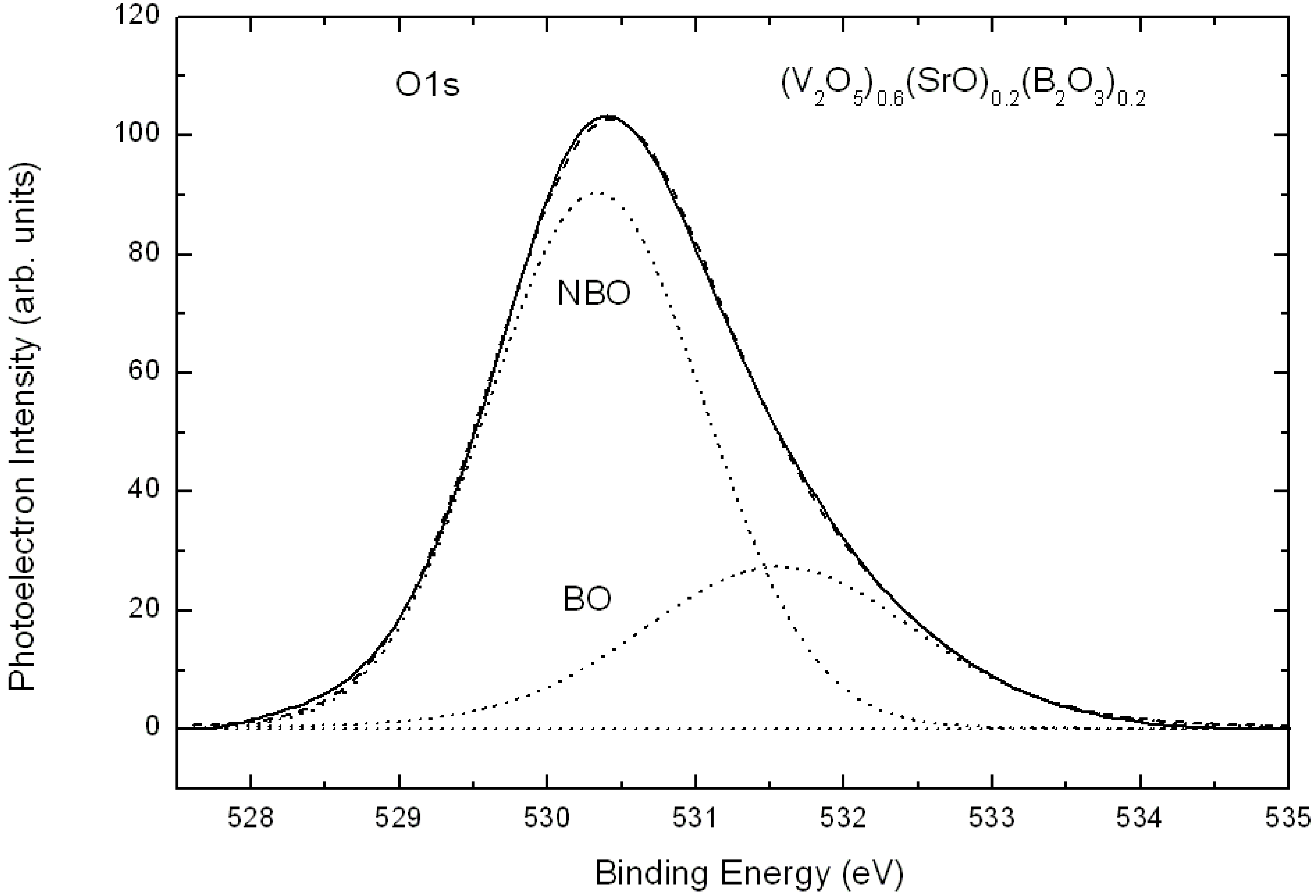
- NBO/TO = $(4x+2y)/(5x+y+3z)$

- NBO/TO 57-85%

  - Good agreement between calculated and measured.

NBO/Total

Series	**z ,y ,x**	**(0.030±) $_{total}$O/NBO** ***[1Equation]**
I	= x0.2 0.3 =x 0.4 =x 0.5 =x	*0.857 0.851 *0.895 0.844 *0.941 1.000 *1.000 1.000
II	0.1 =y 0.2 =y 0.3 =y 0.4 =y	0.875 0.810 0.765 0.792 0.667 0.612 0.579 0.536
III	0.4 =z 0.5 =z 0.6 =z 0.7 =z 0.8 =z	0.588 0.572 0.667 0.612 0.737 0.731 0.780 0.771 0.857 851..0


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

Magnetization Data

The Temperature independent term from two contributions:

i) Diamagnetic from core ions in the glass matrix

ii) Temperature-independent paramagnetic contribution from V_2O_5 (~$5x10^{-7}$emu/Oe g V_2O_5)

The temperature-independent term can be either positive or negative depending on the relative size of these two contributions

-In these glasses it is positive as V_2O_5 contribution dominates

-In V-Na-Silicate glasses the diamagnetic contribution dominates so the term (M/H)background is negative

- V_2O_5 contribution increases with an increase in the V_2O_5 content

Magnetization Data

Curie-Weiss formula is adequate:

Magnetic ions appear to be interacting

Still in the low field limit ($\mu H << kT$)

$M/H = C/(T-\theta)$

Analysis based on three fitting parameters

$M/H = (M/H)_{background} + C/(T-\theta)$; M/H vs T will give $(M/H)_{background}$

$M^*/H = M/H - (M/H)_{background} = C/(T-\theta)$

H/M^* vs T, least square fitting gives C & θ

Finally we use the three fitting parameters in the

$M/H = (M/H)_{background} + C/(T-\theta)$ equation and compare the fit to the measured M/H.

$(M/H)_{background}$ is positive, θ values negative, antiferromagnetic Interactions between the V^{4+} ions.

Magnetization Results

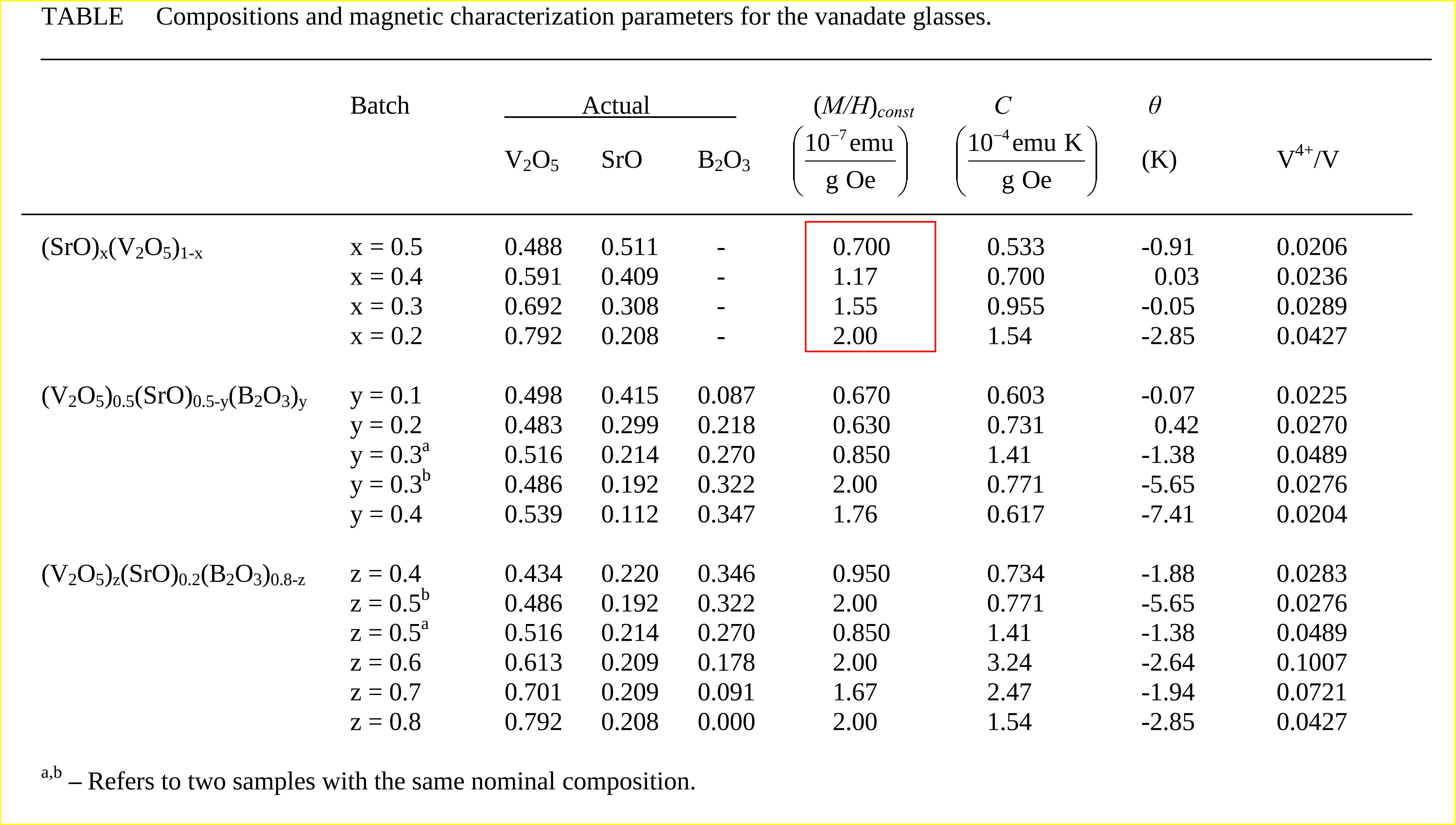


TABLE Compositions and magnetic characterization parameters for the vanadate glasses.

	Batch	Actual			$(M/H)_{const}$	C	θ	
		V_2O_5	SrO	B_2O_3	$\left(\frac{10^{-7}\,\text{emu}}{\text{g Oe}}\right)$	$\left(\frac{10^{-4}\,\text{emu K}}{\text{g Oe}}\right)$	(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.

Magnetization Results

1. The Ratio V^{4+} / V_{total} consistent with XPS findings

2. The negative values for θ in the range of -0.2 - -4.2 K indicate a weak 2 antiferromagnetic interaction between the V4+ ions

3. These small values are not surprising since θ is proportional to:

a) the # of neighboring magnetic ions (negligible for these low V4+ concentration)

b) as well as the strength of the magnetic interaction.

DC electrical conductivity

- Continuation of our previous work (XPS & Magnetization)
- To understand the nature of the mechanism of DC conductivity
- To develop a correlation between the composition, microstructure & DC conductivity in these glasses.

DC conductivity

- Two types of conductivities:

i)Ionic conductivity (higher temp. region)

ii)Electronic conductivity (lower temp.region)

- ionic conductivity is a thermally activated process: mobile ions jump from a potential well to the next due to thermal motion. The vibrating ions have a finite and equal probability of surrounding the potential barrier and moving to the adjacent pot.well.

Ionic conductivity continued

- Resistivity ρ is given by

$$\rho = \rho_o \exp(W/K_B T)$$

ρ_o = constant = $6K_B T/fsd^2q^2N$

f =frequency of the ions

d =average distance between holes

q = ionic charge, N = # mobile ions

W = activation energy

S =# of holes

Example of ionic and electronic conduction

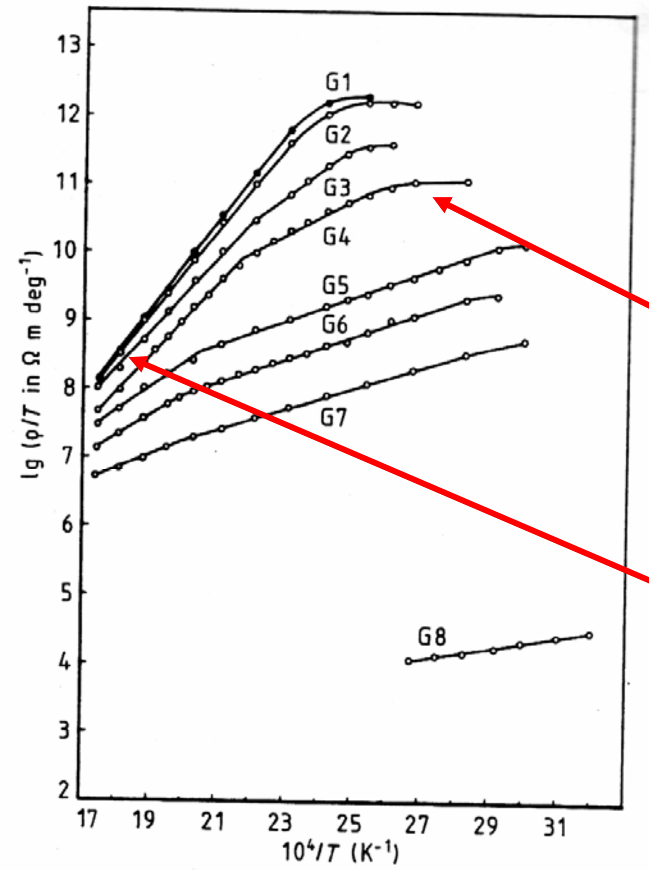


Figure 1. Resistivity–temperature dependence of glasses G1–G8.

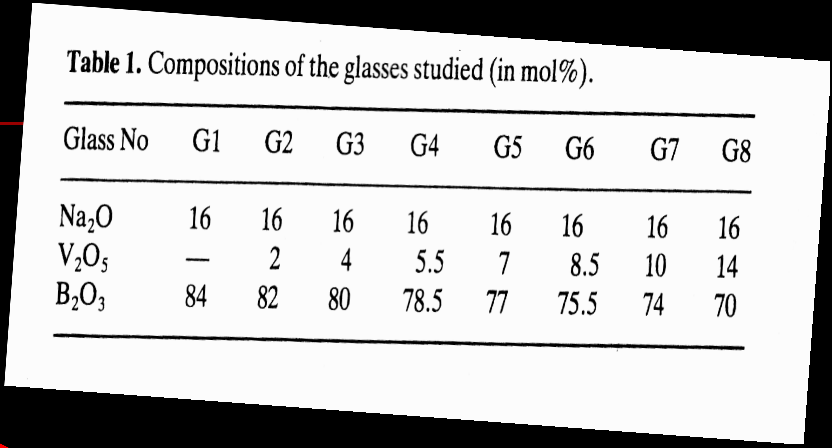


Table 1. Compositions of the glasses studied (in mol%).

Glass No	G1	G2	G3	G4	G5	G6	G7	G8
Na_2O	16	16	16	16	16	16	16	16
V_2O_5	—	2	4	5.5	7	8.5	10	14
B_2O_3	84	82	80	78.5	77	75.5	74	70

electronic

ionic

Procedure

- Disc- shaped samples
- Polished
- Evaporation of Gold electrodes
- Measure I vs V in the temperature range 293-473 K
- Analysis of the data will be carried out as follows

DC conductivity

- Electronic conduction by small polaron hopping process (through the hopping of an unpaired electrons from V^{4+} site to V^{5+} site..)
- Depends on the ratio of V^{4+}/V^{5+}
- Analysis of the conductivity as follows:

DC Electrical Conductivity Theory

$$\sigma(T) = A\ (T)\ e^{-\beta W(T)}, \quad (1)$$

Where:

W is the activation energy

T is the temperature,

$\beta^{-1} = k_B T$, k_B is the Boltzmann constant,

and A(T) and W(T) are assumed to be slowly varying functions of the temperature. Usually analysis of the conduction curve by Arrhenius plot calculates the slope, or

$W'(T)/k_B^{-1}$ where

DC conductivity continued

$$W'(T) = -\partial \ln \sigma/\partial\beta \qquad (2)$$

$$= W(T) - \partial/\partial\beta \ln[A(T)] + \beta\, \partial/\partial\beta[W(T)] \qquad (3)$$

$$= W$$

for A and W to be temperature independent, the slope should be constant, yielding directly the activation energy, W.

DC conductivity continued

- In general case, W'(T) does not

permit A and W to be uniquely determined.

- Often, however, models of electrical transport place additional constraints on the functions A(T) and W(T), and with these constraints we can determine both A(T) and W(T) from σ(T). We illustrate this with two model examples.

Model1-Variable range hopping

- Assuming $N(E) = N_0 (E-E_F)^p$,Hamilton has shown that

$\sigma(T) = \sigma(o) \exp(-BT^{-[(p+1)/(p+4)]})$,

Where $0 < p < \infty$ (5)

Equation (3) yields the function

$W'(T) = Bk_B [(p+1)/(p+4)] T^{3/(p+4)}$.

(6)

The constants B and p can be determined from the intercept and slope on a log W' versus log T plot.

Brief explanation

- Mott (1968): At low temperatures the most frequent hopping process would not be to a nearest neighbor.
- Within a range R of a given site the density of states per unit energy range is, near E_F,

  $(4\pi/3)R^3N(E_F)$

The energy $\Delta E = 1/[(4\pi/3)R^3N(E_F)]$

continued

- But hopping over a large distance involves tunneling and the probability will contain a factor exp(-2αR), 1/α =decay length of the localized wave function.
- There will be an optimum hopping distance R,for which $\exp(-2\alpha R)\exp(-\Delta E / k_B T)$ is a maximum or $2\alpha R + 1/(4\pi/3)R^3 N(E_F)$ is minimum ----> $R = [1/8\pi N(E)\ \alpha k_B T]^4$

Continued..

- $\sigma(T) = A \exp(-B/T^n)$,

  $B = 2(3/2\pi)^{1/4}[\alpha^3/k_B N(E_F)$

Continued

- As a check on the validity of this model, according to Mott the energy W'(T) must satisfy

$W'(T) < 2^{p/(p+4)} K_B T.$ (7)

Model 2-Conduction by small polarons

- Schnakenberg has analysed the hopping energy W of small polarons at temperatures above $\Theta_D/4$, where Θ_D is the Debye temperature of the optical phonons of the solid, and he deduced the following high temperature relation:

$$W(T) = W_H \left[\{\tanh(\Theta_D/4T)/(\Theta_D/4T)\}\right] + W_D/2 \qquad (8)$$

Continued

- W_D and W_H are two constants, called disorder energy and small polaron hopping energy, respectively.
- W_D between the initial and final sites due to variations in the local distributions of the TM ions.
- W_D 0.09 eV, $W_H = 0.35$ eV
- Using Eqn.(3) again, we find

$$W'(T) = W_H \operatorname{sech}^2 (\Theta_D/4T) + W_D/2 \qquad (9)$$

Continued

- W_H, W_D and Θ_D are determined in two steps:

i) First we assume $W_D = 0$, and expand $\mathrm{sech}^2(\Theta_D/4T)$. Eqn(9) becomes

$W'(T) = W_H\,[1 - (\Theta_D/4T)^2 + \ldots.]$ (10)

A plot of $W'(T)$ vs T^{-2} yield a straight

Line with intercept W_H and slope $W_H(\Theta_D/4T)^2$ Θ_D is found here.

Continued

ii) The data is then replotted as W' versus $\text{sech}^2(\Theta_D/4T)$ using Θ_D values

determined in the preceding step. A straight line should yield

Intercept = $W_D/2$ and

Slope = W_H

The hopping energy W(T) may then be determined using eq.(8).

Expectations

✓ ***We hope to achieve the following:***

i) Dependence of σ(T) **on V^{4+} / V_{total}**

ii) *Dependence of σ(T)* on BO / O_{total}

iii) V_2O_5 plays the role of a glass modifier or glass former and its concentration dependence.

Thank you