Density, Volume, and Packing: Part 2
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Lecture 3 of Glass Properties Course

Some Definitions

- x = molar fraction of alkali or alkaline-earth oxide (or any modifying oxide)
- $1-x$ = molar fraction of glass former

- $R = x/(1-x)$ This is the compositional parameter of choice in developing structural models for borates.
- $J = x/(1-x)$ for silicates and germanates

Short Ranges B and Si Structures

Short-range borate units,

$$R = \frac{molar\ \%\ MO}{molar\ \%\ B_2O_3}$$

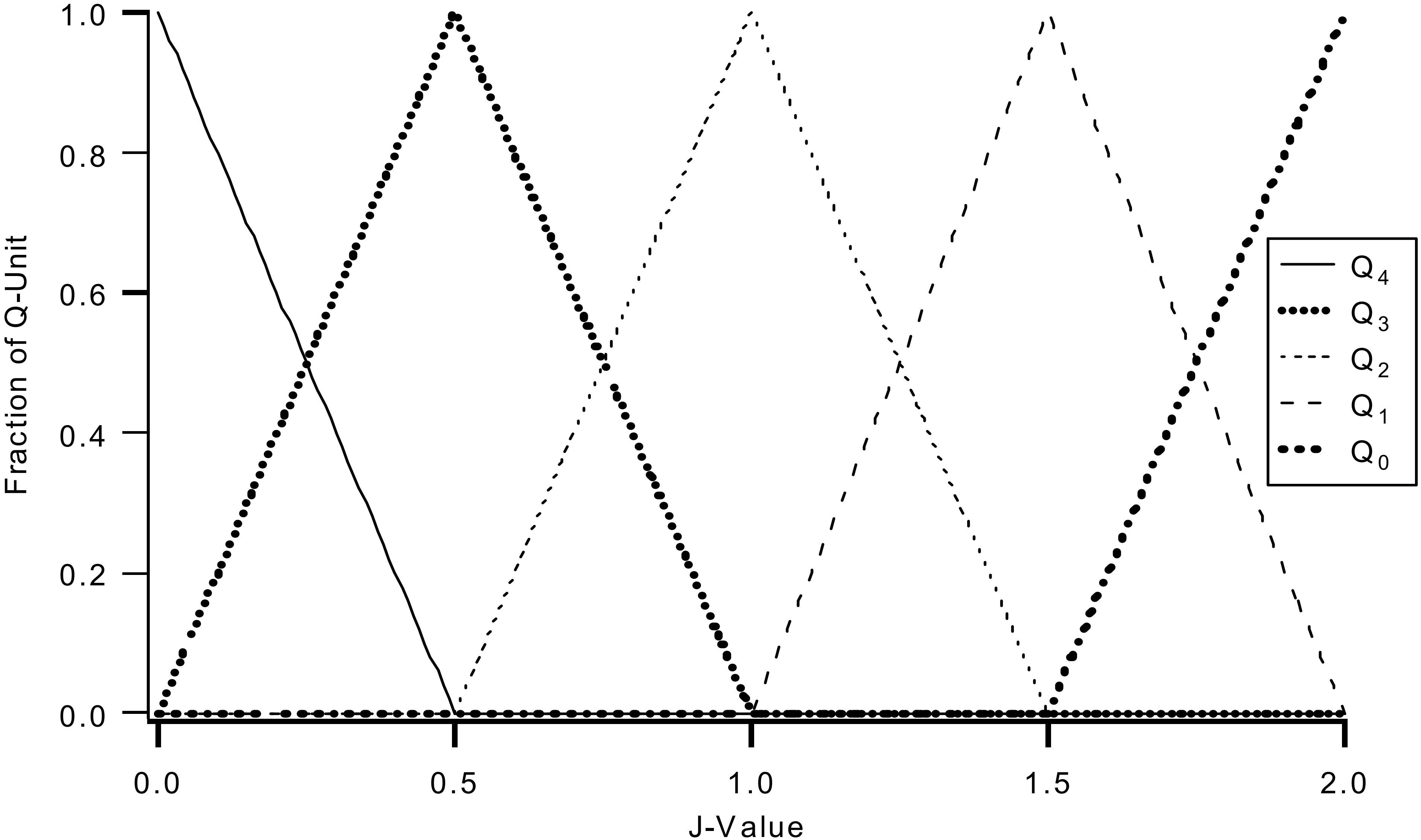
F_i unit	Structure	R value
F_1	trigonal boron with three bridging oxygen	0·0
F_2	tetrahedral boron with four bridging oxygen	1·0
F_3	trigonal boron with two bridging oxygen (one NBO)	1·0
F_4	trigonal boron with one bridging oxygen (two NBOs)	2·0
F_5	trigonal boron with no bridging oxygen (three NBOs)	3·0

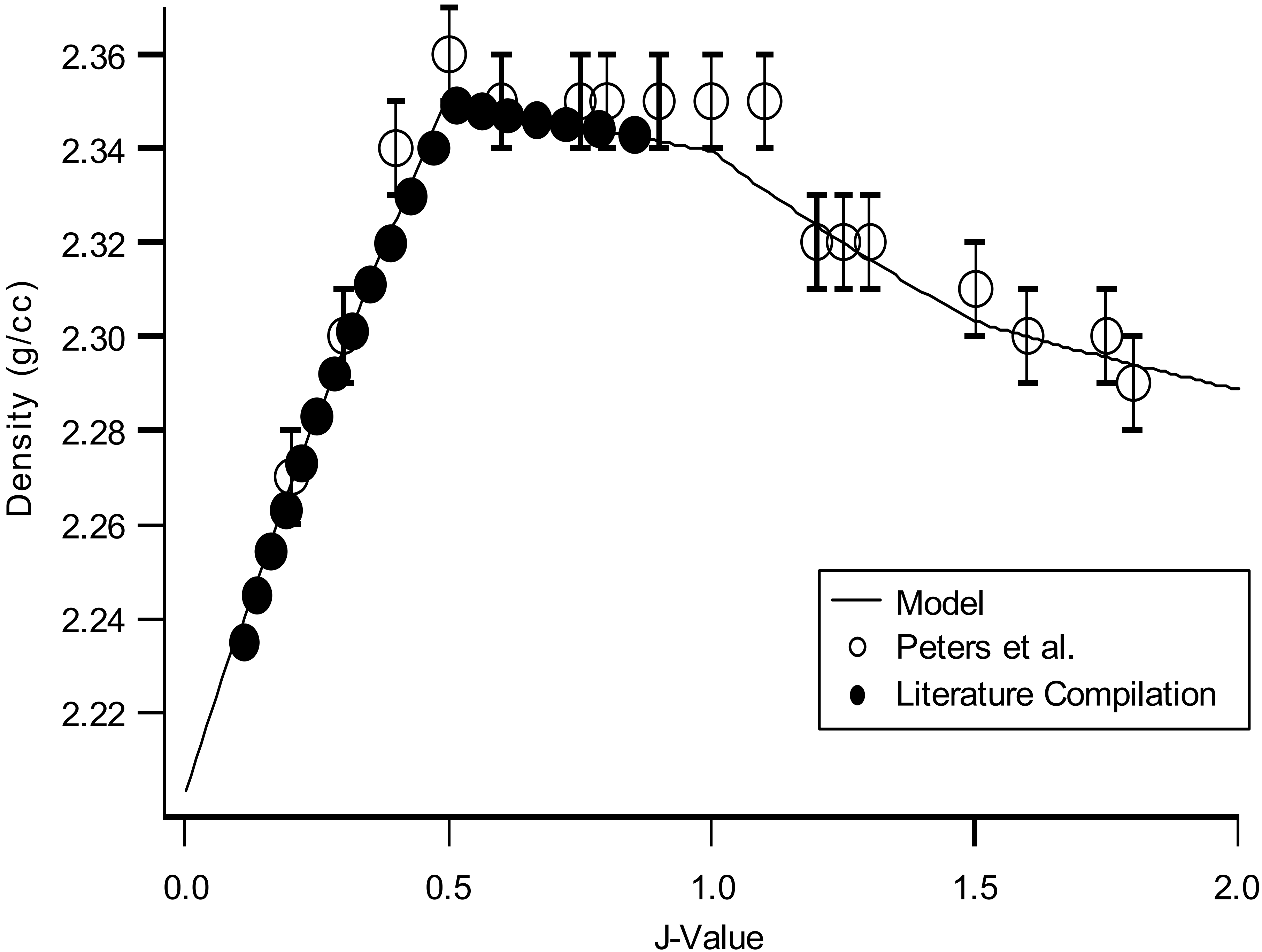
Short-range silicate units,

$$J = \frac{molar\ \%\ MO}{molar\ \%\ SiO_2}$$

Q_i unit	Structure	J value
Q_4	tetrahedral silica with four bridging oxygen	0·0
Q_3	tetrahedral silica with three bridging oxygen (one NBO)	0·5
Q_2	tetrahedral silica with two bridging oxygen (two NBOs)	1·0
Q_1	tetrahedral silica with one bridging oxygen (three NBOs)	1·5
Q_0	tetrahedral silica with no bridging oxygen (four NBOs)	2·0

Lever Rule Model for Silicates





Density (g/cc)
2.36
2.34
2.32
2.30
2.28
2.26
2.24
2.22
0.0
0.5
1.0
1.5
2.0
J-Value
Model
Peters et al.
Literature Compilation

Method of Least Squares

- Take $(\rho_{mod} - \rho_{exp})^2$ for each data point
- Add up all terms
- Vary volumes until a least sum is found.
- Volumes include empty space.

- ρ_{mod} **= $\Sigma M/(f_i V_i)$**

Example: Li-Silicates

- $V_{Q4} = 1.00$
- $V_{Q3} = 1.17$
- $V_{Q2} = 1.41$
- $V_{Q1} = 1.69$
- $V_{Q0} = 1.95$

- $V_{Q4}(J = 0)$ defined to be 1.
- The J = 0 glass is silicon dioxide with density of 2.205 g/cc

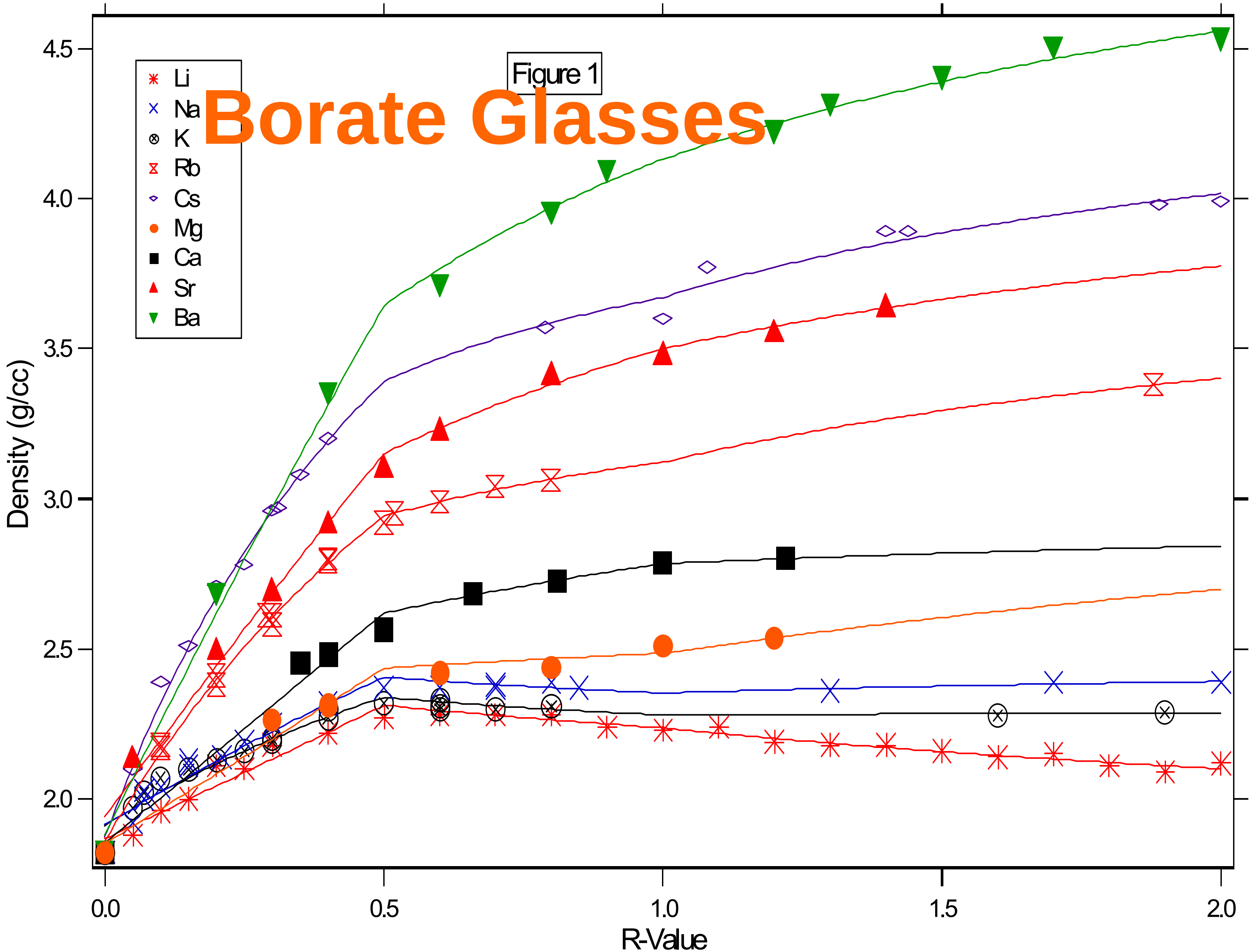


Figure 1
Borate Glasses
Li
Na
K
Rb
Cs
Mg
Ca
Sr
Ba
Density (g/cc)
4.5
4.0
3.5
3.0
2.5
2.0
0.0
0.5
1.0
1.5
2.0
R-Value

Borate Structural Model

- $R < 0.5$
- $F_1 = 1-R$, $F_2 = R$

- $0.5 < R < 1.0$
- $F_1 = 1-R$, $F_2 = -(1/3)R + 2/3$, $F_3 = +(4/3)R - 2/3$

- $1.0 < R < 2.0$
- $F_2 = -(1/3)R + 2/3$, $F_3 = -(2/3)R + 4/3$, $F_4 = R-1$

Another Example: Li-Borates

- $V_1 = 0.98$
- $V_2 = 0.91$
- $V_3 = 1.37$
- $V_4 = 1.66$
- $V_5 = 1.95$

- $V_1(R = 0)$ is defined to be 1.
- The R = 0 glass is boron oxide with density of 1.823 g/cc

	Barium	Calcium
V_{f1}	0·96	0·99
V_{f2}	1·16	0·96
V_{f3}	1·54	1·29
V_{f4}	2·16	1·68
V_{Q4}	1·44	1·43
V_{Q3}	1.92	1.72
V_{Q2}	2.54	2.09

Li and Ca Silicates

- Li | Ca
- $V_{Q4} = 1.00$ | $V_{Q4} = 1.00$
- $V_{Q3} = 1.17$ | $V_{Q3} = 1.20$
- $V_{Q2} = 1.41$ | $V_{Q2} = 1.46$

- $V_{Q4}(J = 0)$ defined to be 1.
- The J = 0 glass is silicon dioxide with density of 2.205 g/cc

Silicates

System	*Unit*	*Least squares volumes*	*Packing fraction*
Li	Q_4	1·00	0·33
	Q_3	1·17	0·38
	Q_2	1·41	0·41
	Q_1	1·67	0·42
	Q_0	1·92	0·43
Na	Q_4	1·00	0·33
	Q_3	1·34	0·42
	Q_2	1·74	0·46
	Q_1	2·17	0·48
	Q_0	2·63	0·49
K	Q_4	0·99	0·33
	Q_3	1·58	0·52
	Q_2	2·27	0·58
	Q_1	2·97	0·61
Rb	Q_4	1·00	0·33
	Q_3	1·72	0·53
	Q_2	2·63	0·57
	Q_1	3·53	0·59
Cs	Q_4	0·98	0·33
	Q_3	1·96	0·56
	Q_2	2·90	0·64
	Q_1	4·25	0·62

Densities of Barium Borate Glasses

- R = x/(1-x)		Density (g/cc)
- 0·0		1·82
- 0·2		2·68
- 0·2		2·66
- 0·4		3·35
- 0·4		3·29
- 0·6		3·71
- 0·6		3·68
- 0·8		3·95
- 0·8		3·90
- 0·9		4·09
- 1·2		4·22
- 1·3		4·31
- 1·5		4·40
- 1·7		4·50
- 2·0		4·53

Use these data and the borate model to find the four borate volumes. Note this model might not yield exactly the volumes given before.

- **Volumes and packing fractions of borate short-range order groups. The volumes are reported relative to the volume of the BO1.5 unit in B2O3 glass. Packing fractions were determined from the density derived volumes and Shannon radii[i],[iii].**

System	Unit	Least Squares Volumes	Packing Fraction
Li	f1	0.98	0.34
	f2	0.94	0.65
	f3	1.28	0.39
	f4	1.61	0.41
Na	f1	0.95	0.35
	f2	1.24	0.62
	f3	1.58	0.41
	f4	2.12	0.46
K	f1	0.95	0.35
	f2	1.66	0.69
	f3	1.99	0.52

System	Unit	Least Squares Volumes	Packing Fraction
Mg	f1	0.98	0.34
	f2	0.95	0.63
	f3	1.26	0.39
	f4	1.46	0.44
Ca	f1	0.98	0.34
	f2	0.95	0.71
	f3	1.28	0.44
	f4	1.66	0.48
Sr	f1	0.94	0.36
	f2	1.08	0.68
	f3	1.41	0.45
	f4	1.92	0.48
Ba	f1	0.97	0.35
	f2	1.13	0.73
	f3	1.55	0.47
	f4	2.16	0.51

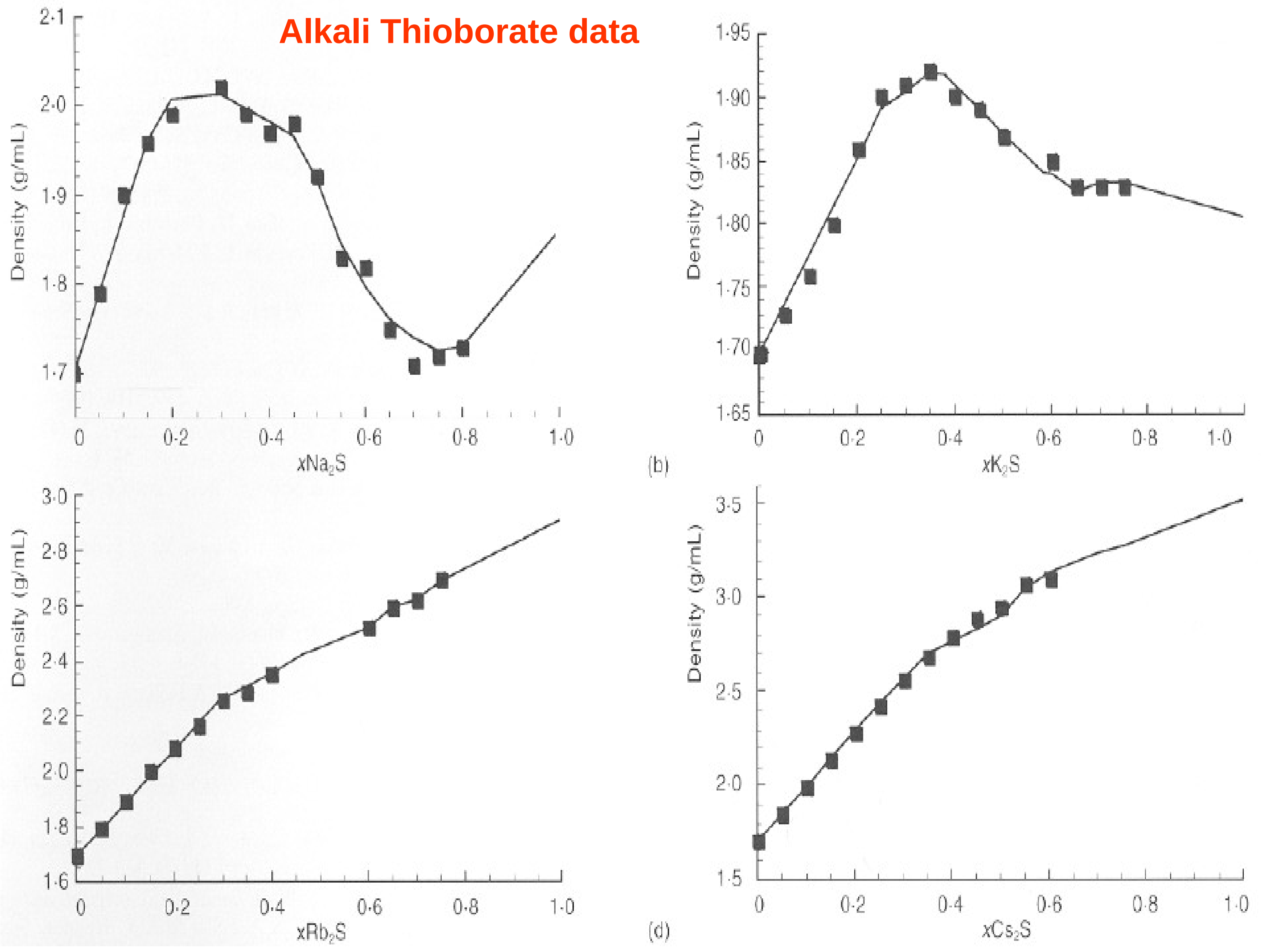
- Volumes and packing fractions of silicates short-range order groups. The volumes are reported relative to the volume of the Q4 unit in SiO2 glass. Packing fractions were determined from the density derived volumes and Shannon radii4,23.

System	Unit	Least Squares Volumes	Packing Fraction
Li	Q4	1.00	0.33
	Q3	1.17	0.38
	Q2	1.41	0.41
	Q1	1.67	0.42
	Q0	1.92	0.43
Na	Q4	1.00	0.33
	Q3	1.34	0.42
	Q2	1.74	0.46
	Q1	2.17	0.48
	Q0	2.63	0.49
K	Q4	0.99	0.33
	Q3	1.58	0.52
	Q2	2.27	0.58
	Q1	2.97	0.61
Rb	Q4	1.00	0.33
	Q3	1.72	0.53
	Q2	2.63	0.57
	Q1	3.53	0.59
Cs	Q4	0.98	0.33
	Q3	1.96	0.56
	Q2	2.90	0.64
	Q1	4.25	0.62

Alkali Thioborates

- Data from Prof. Steve Martin
- x $M_2S.(1-x)B_2S_3$ glasses
- Unusual F2 behavior

Alkali Thioborate data



- **Volumes and packing fractions of thioborate short-range order groups. The volumes are reported relative to the volume of the BS1.5 unit in B2S3 glass.**

System	Unit	Least Squares Volumes	Corresponding Oxide Volume (compared with volume of BO1.5 unit in B2O3 glass.)
Na	f1	1.00	0.95
	f2	1.37	1.24
	f3	1.51	1.58
	f5	2.95	2.66*
K	f1	1.00	0.95
	f2	1.65	1.66
	f3	1.78	1.99
	f5	3.53	3.91*
Rb	f1	1.00	0.98
	f2	1.79	1.92
	f3	1.97	2.27
	f5	3.90	4.55*
Cs	f1	1.00	0.97
	f2	1.83	2.28
	f3	2.14	2.62
	f5	4.46	5.64*

*extrapolated

Molar Volume

- Molar Volume = Molar Mass/density

It is the volume per mole glass.

It eliminates mass from the density and uses equal number of particles for comparison purposes.

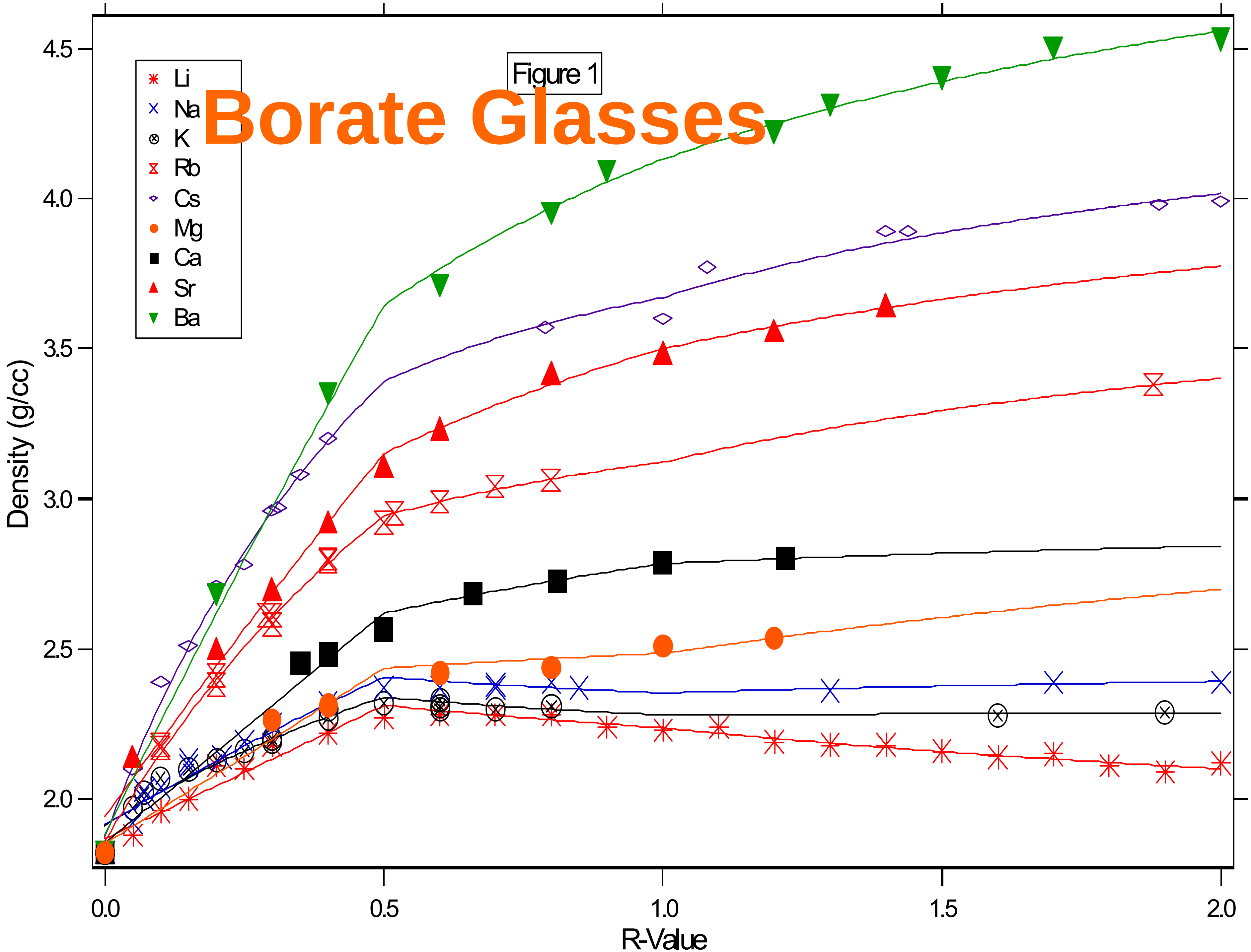
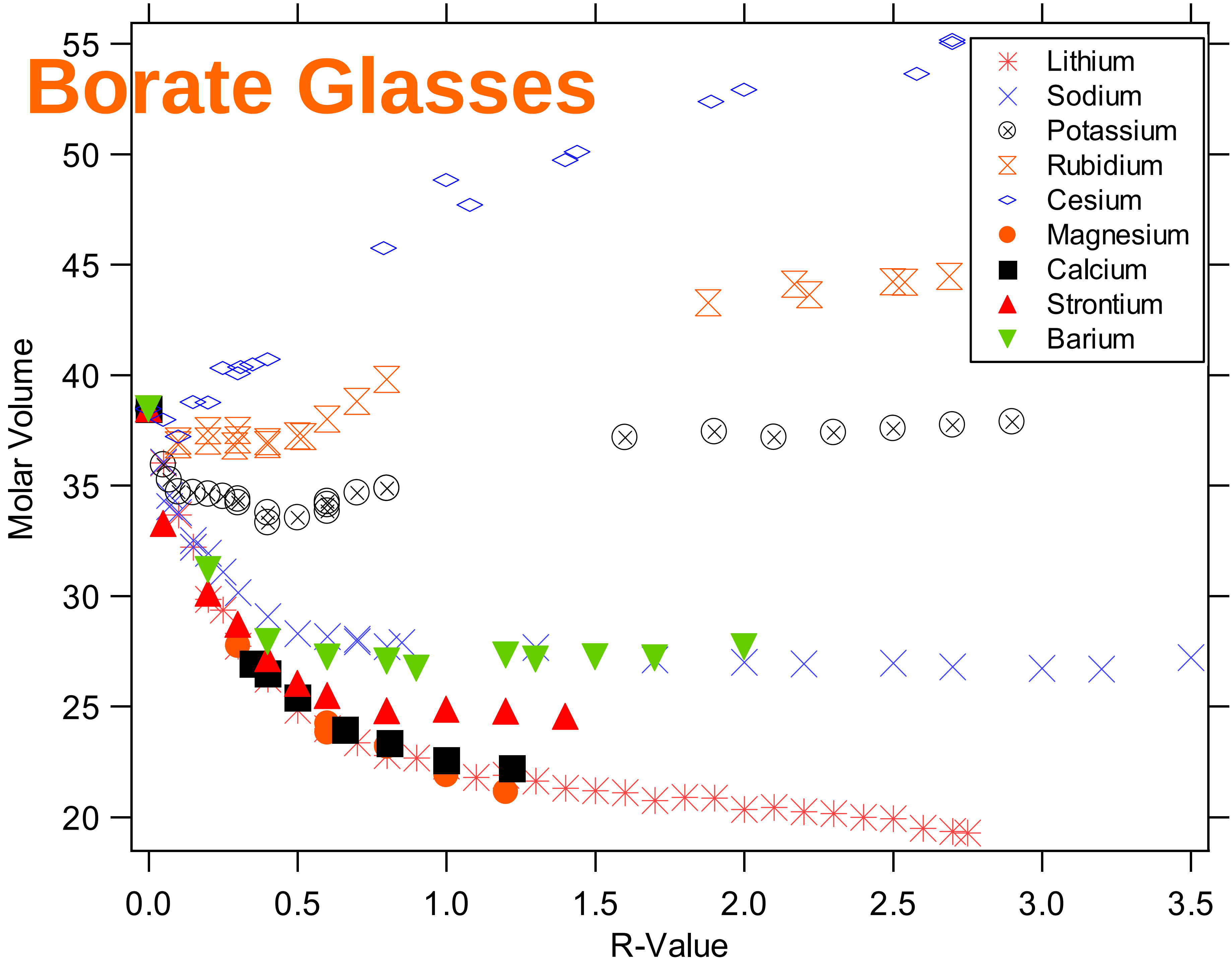
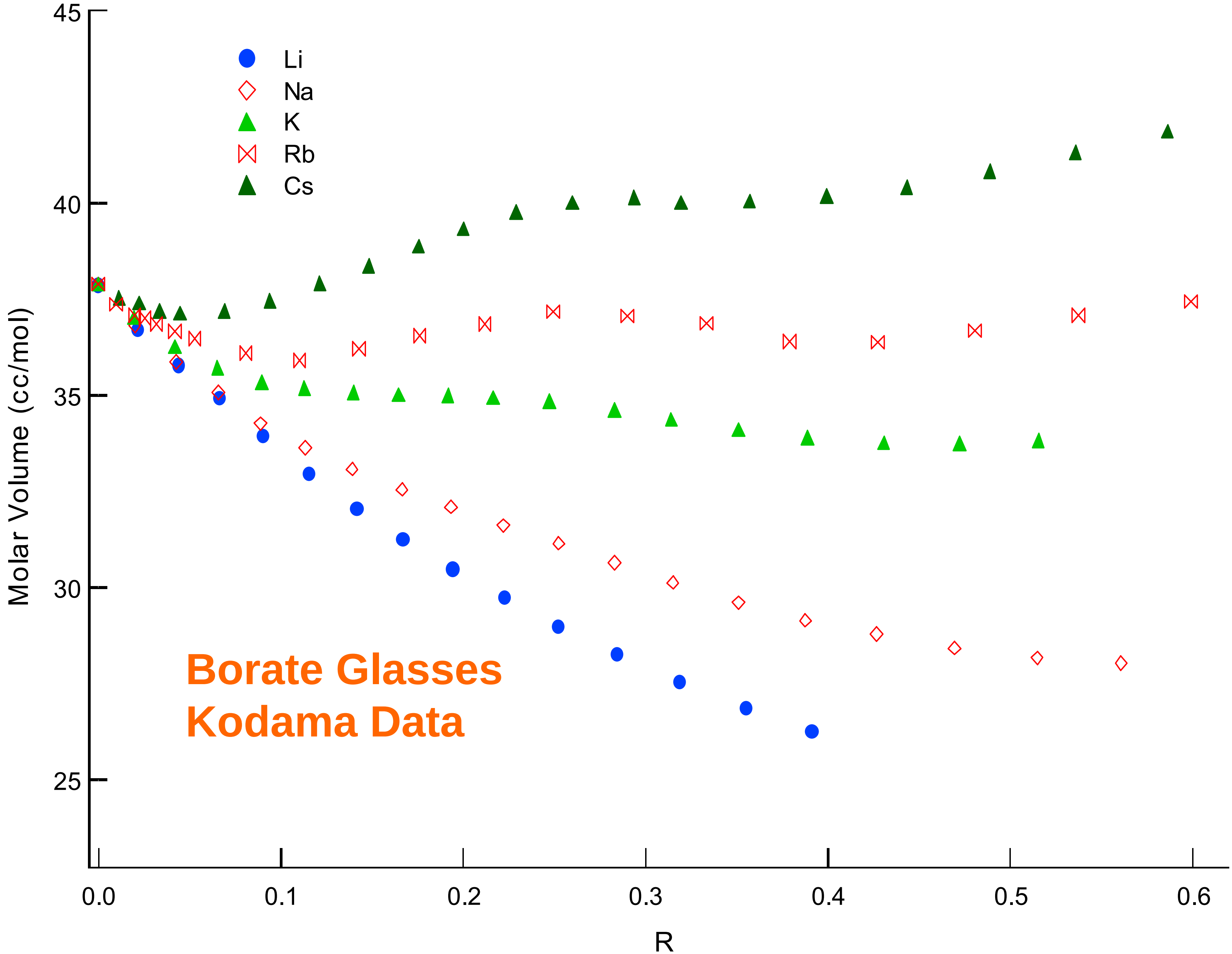


Figure 1
Borate Glasses
Li
Na
K
Rb
Cs
Mg
Ca
Sr
Ba
Density (g/cc)
R-Value
4.5
4.0
3.5
3.0
2.5
2.0
0.0
0.5
1.0
1.5
2.0



Borate Glasses
Molar Volume
R-Value
55
50
45
40
35
30
25
20
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
Lithium
Sodium
Potassium
Rubidium
Cesium
Magnesium
Calcium
Strontium
Barium

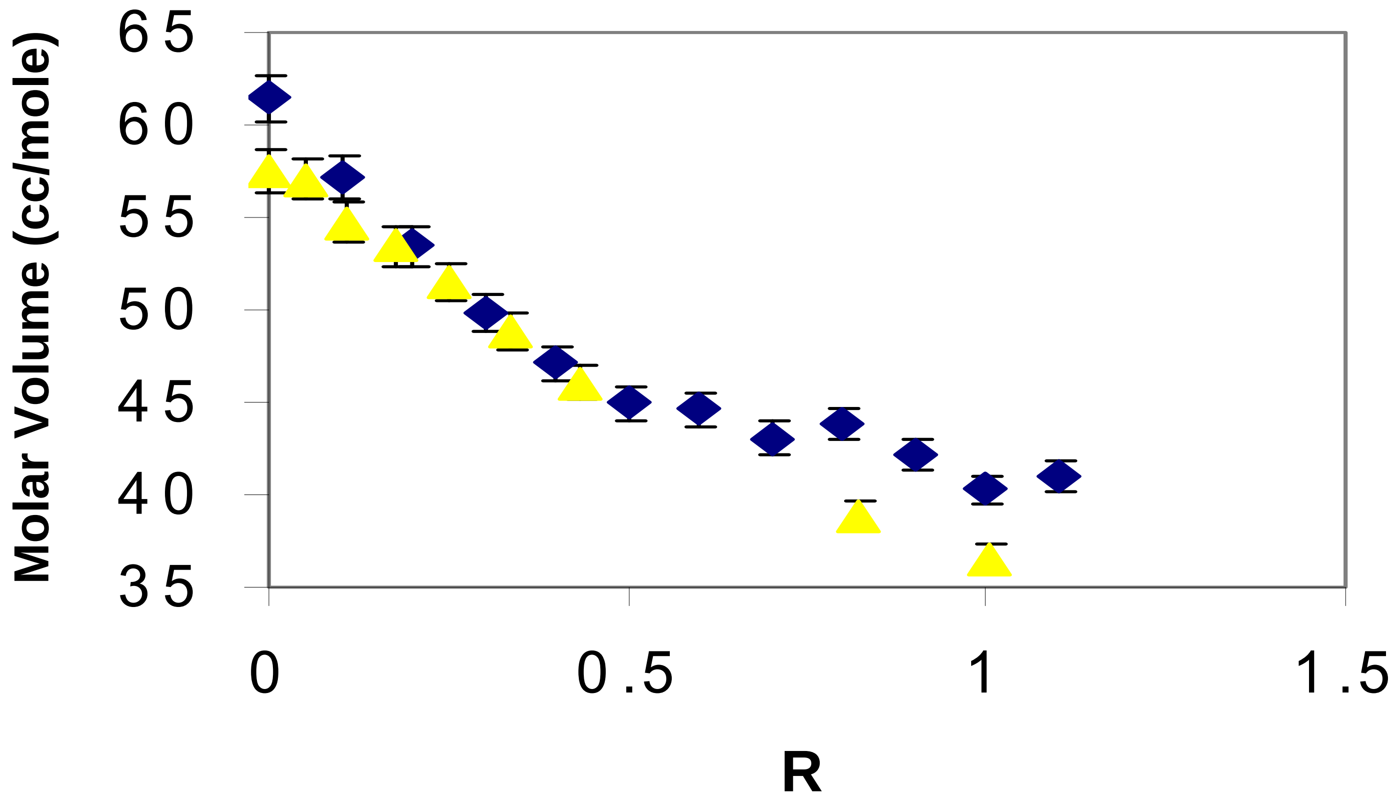


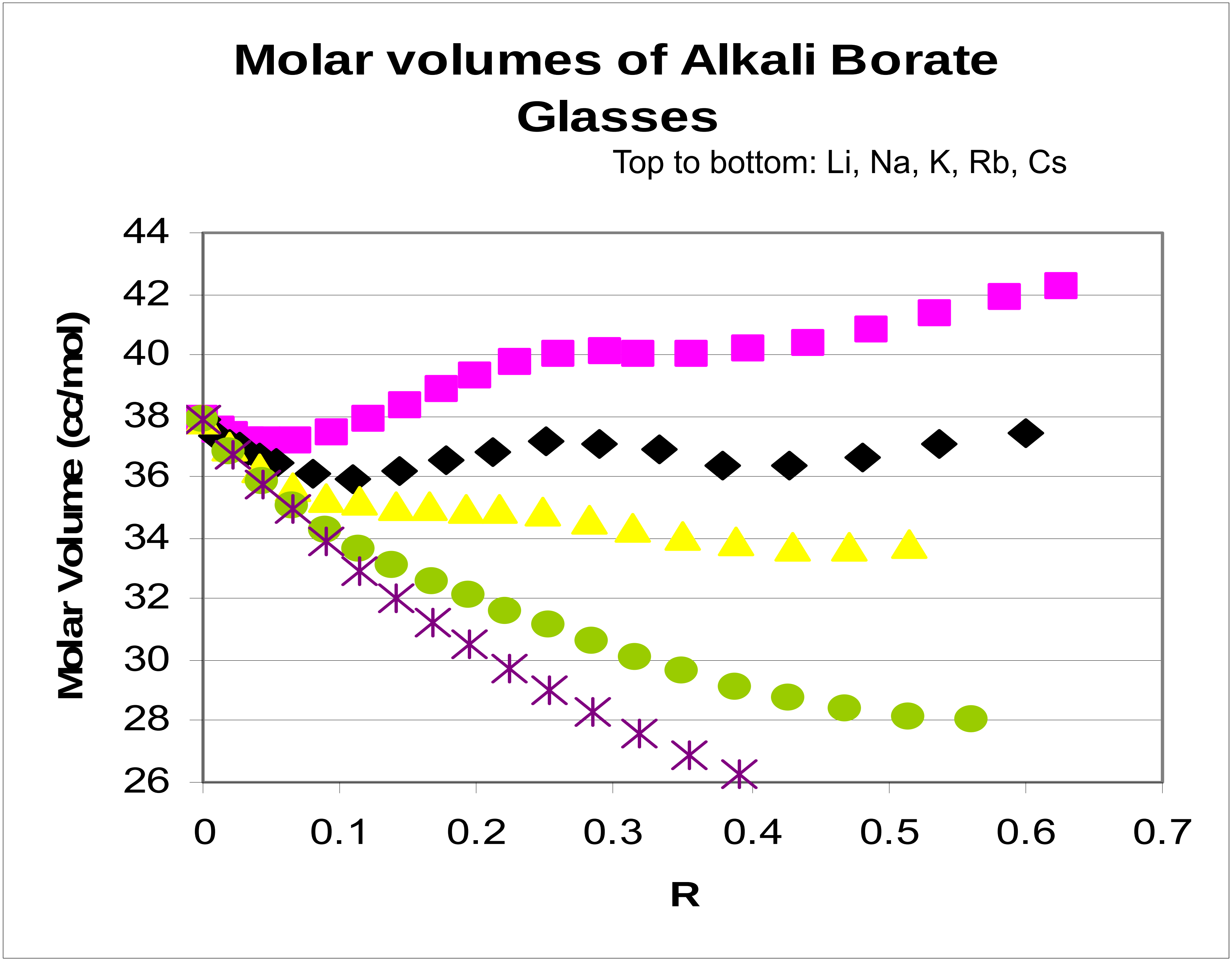
Li
Na
K
Rb
Cs
Borate Glasses
Kodama Data
Molar Volume (cc/mol)
R
45
40
35
30
25
0.0
0.1
0.2
0.3
0.4
0.5
0.6

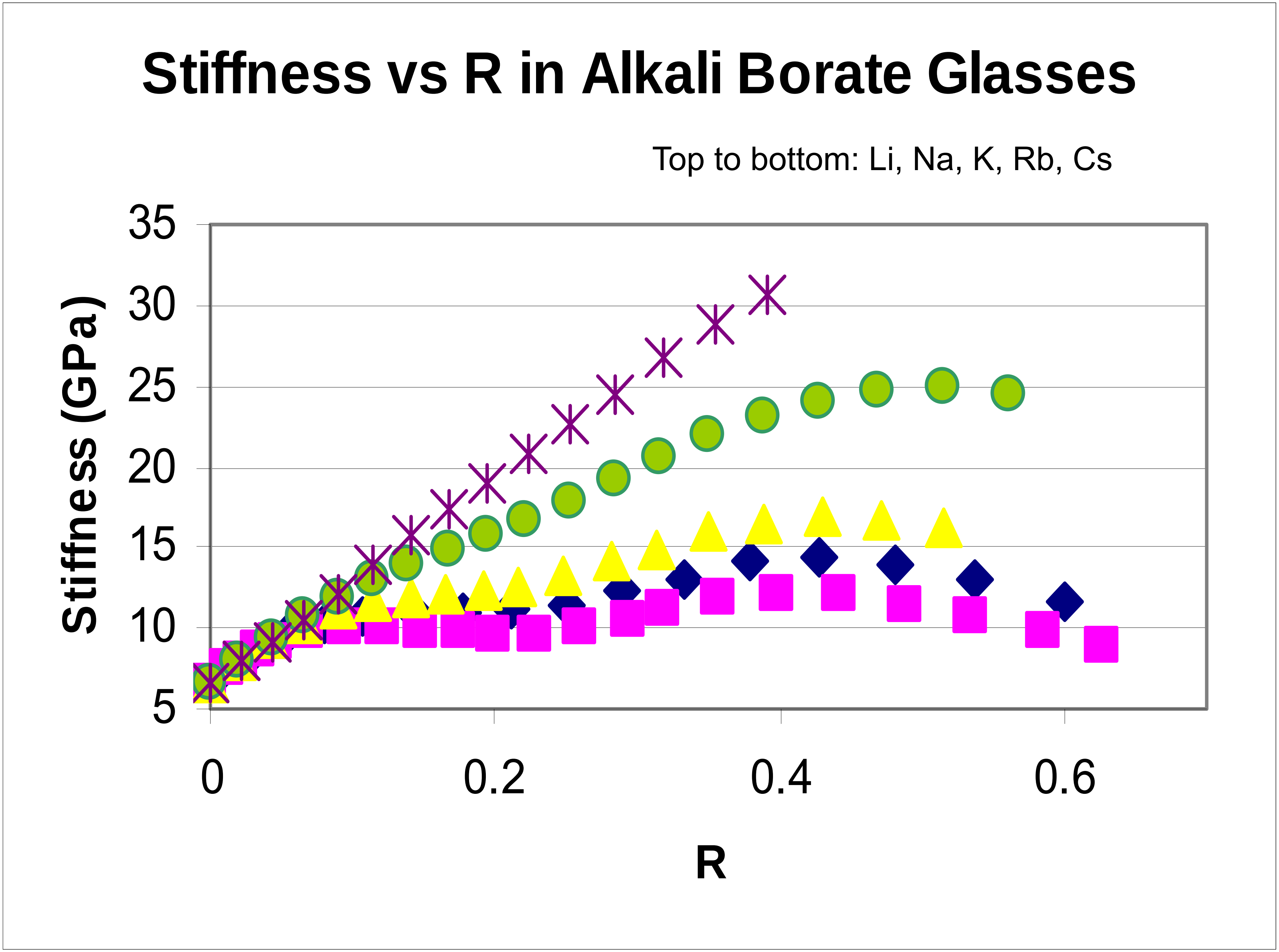
Problem:

- Calculate the molar volumes of the barium borates given before. You will need atomic masses. Also, remember that the data are given in terms of R and there are R+1 moles of glassy materials. You could also use x to do the calculation.

Li-Vanadate (yellow) Molar Volumes campared with Li-Phosphates (black)

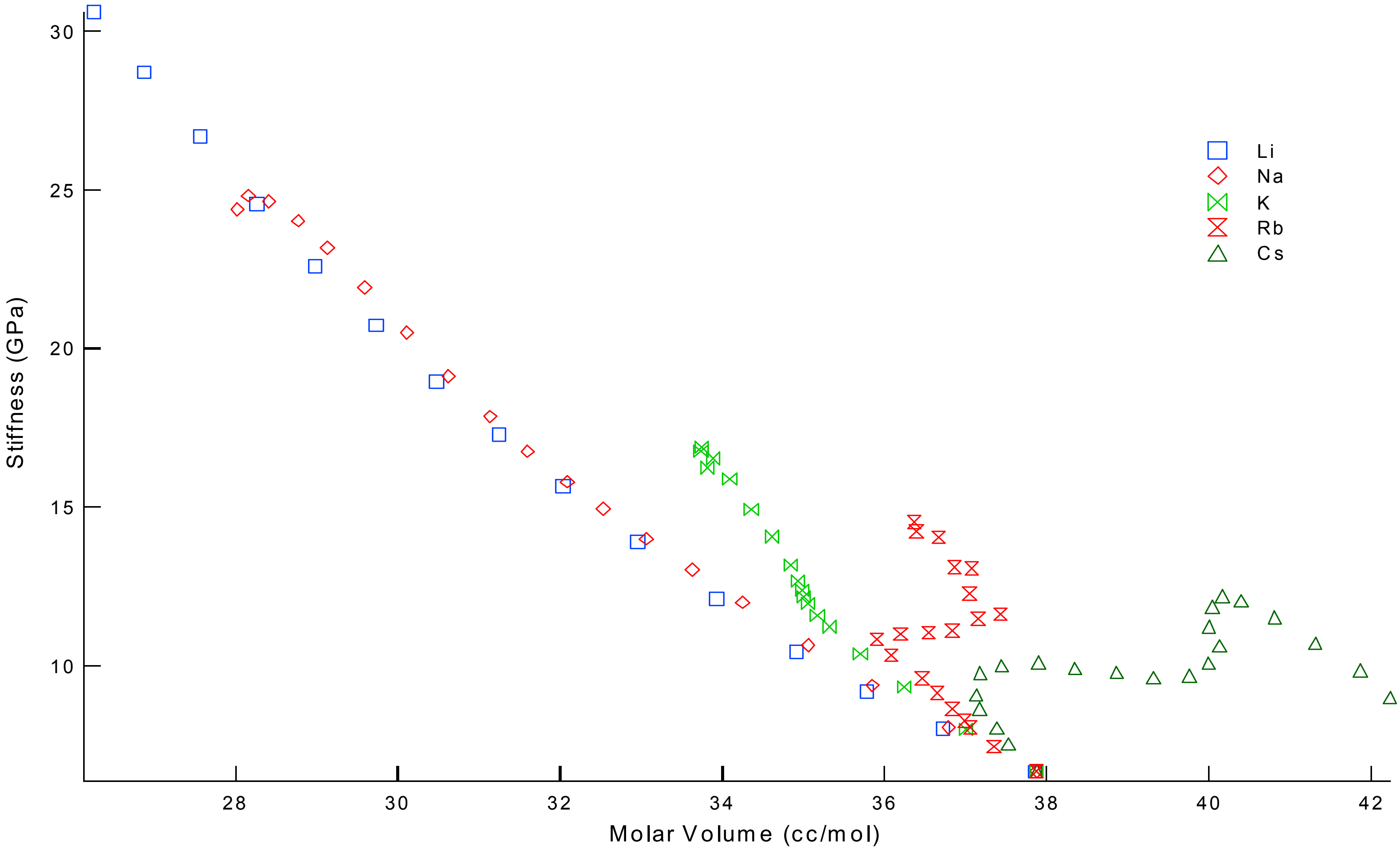


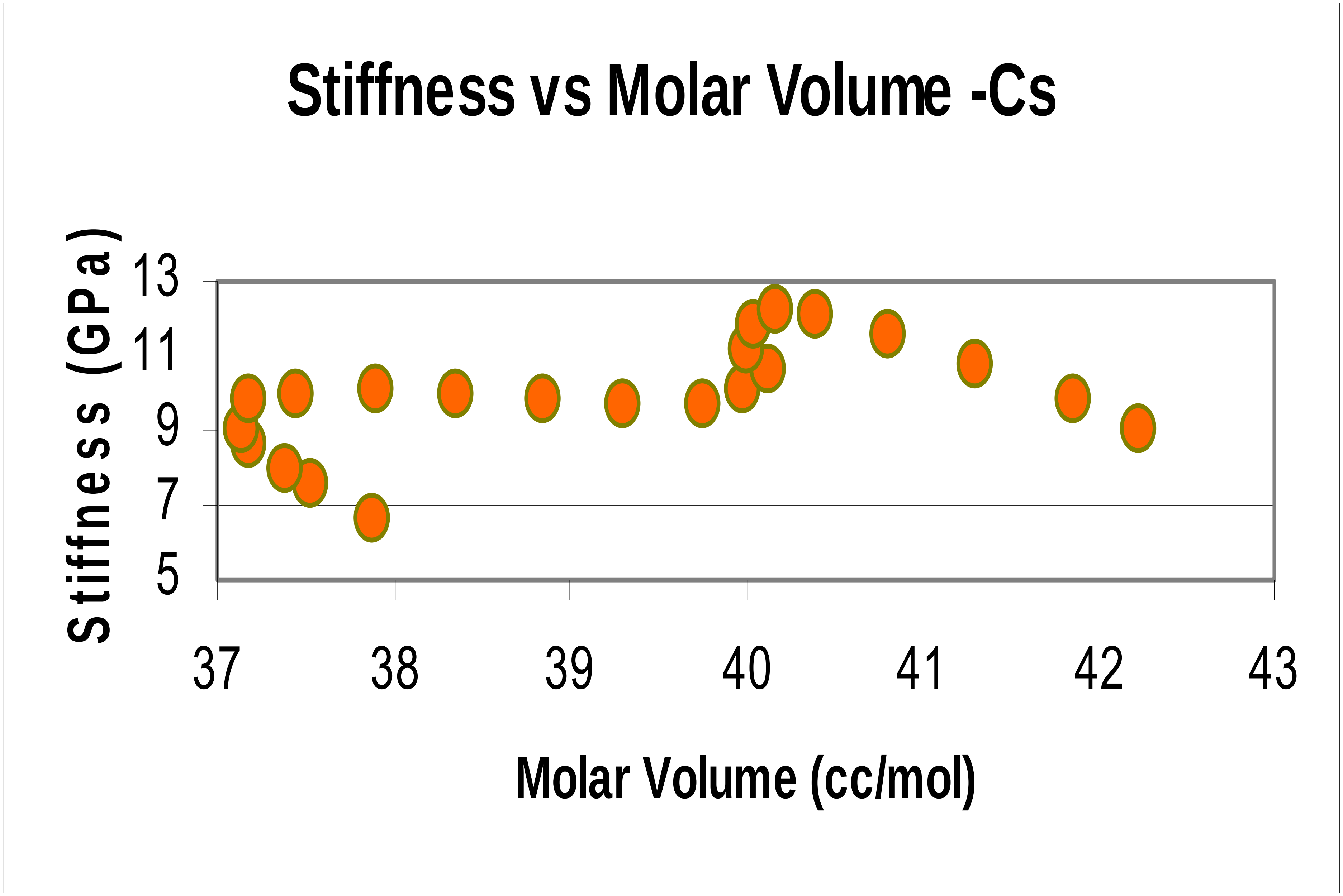

Molar volumes of Alkali Borate Glasses
Top to bottom: Li, Na, K, Rb, Cs
Molar Volume (cc/mol)
44
42
40
38
36
34
32
30
28
26
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
R

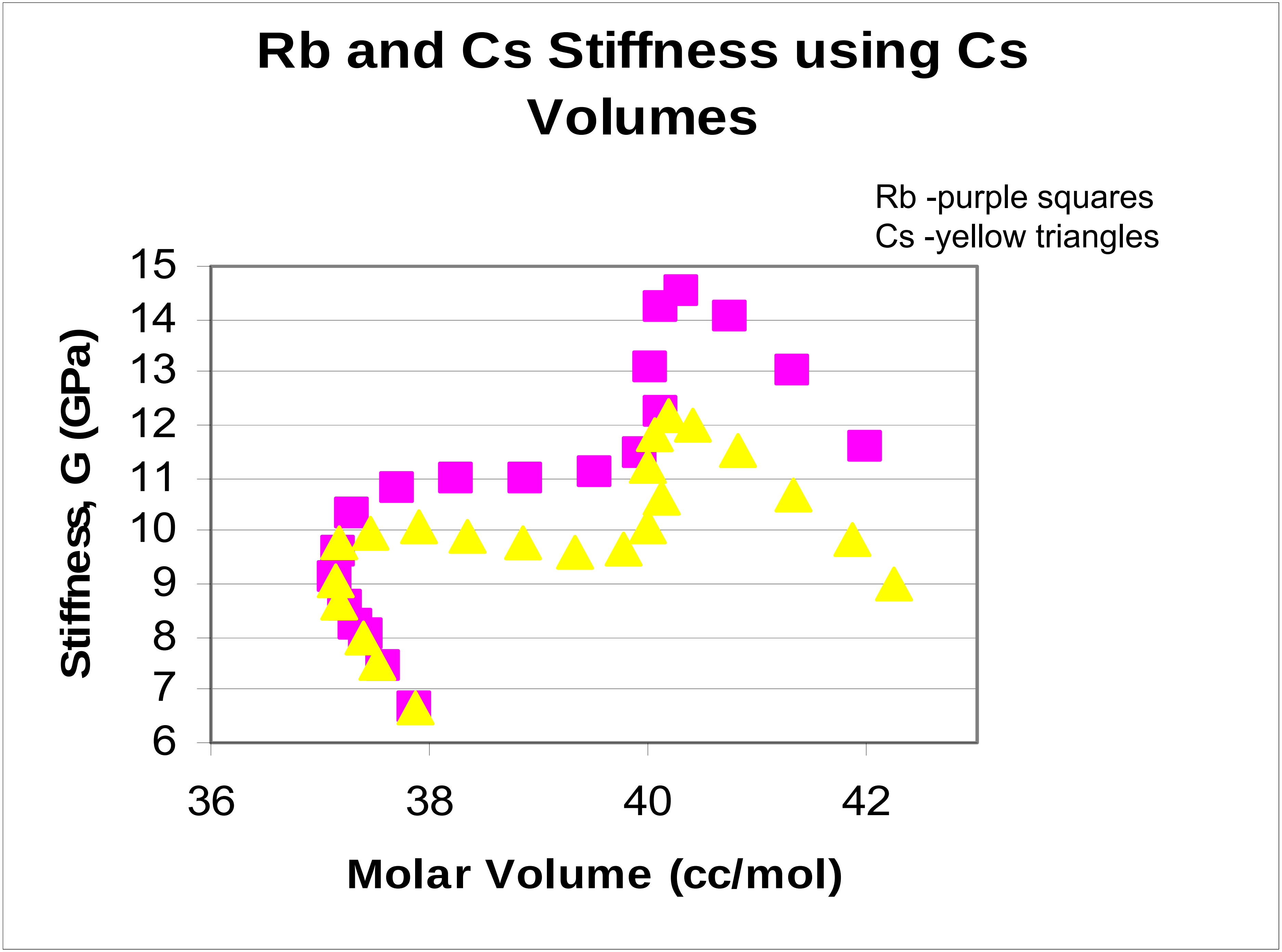


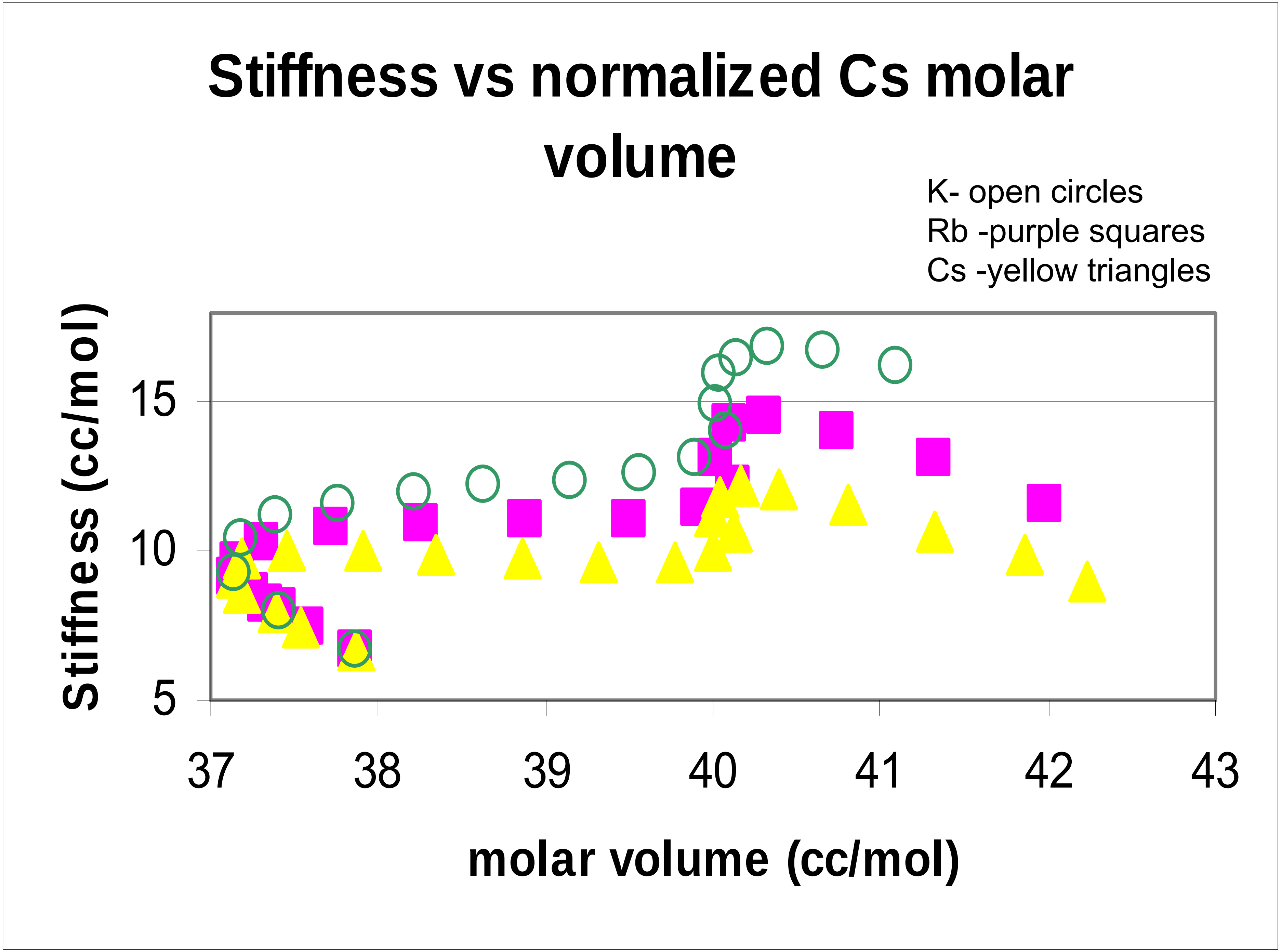
Stiffness vs R in Alkali Borate Glasses
Top to bottom: Li, Na, K, Rb, Cs
Stiffness (GPa)
35
30
25
20
15
10
5
0
0.2
0.4
0.6
R

Stiffness of Borates vs Molar Volume




Stiffness vs Molar Volume -Cs
Stiffness (GPa)
13
11
9
7
5
37
38
39
40
41
42
43
Molar Volume (cc/mol)


Rb and Cs Stiffness using Cs Volumes
Rb -purple squares
Cs -yellow triangles
Stiffness, G (GPa)
15
14
13
12
11
10
9
8
7
6
36
38
40
42
Molar Volume (cc/mol)



Stiffness vs normalized Cs molar volume
K- open circles
Rb -purple squares
Cs -yellow triangles
Stiffness (cc/mol)
15
10
5
37
38
39
40
41
42
43
molar volume (cc/mol)

Differential Changes in Unit Volumes

- To begin the calculation, we define the glass density in terms of its dimensionless mass relative to pure borate glass (R=0), *m'*(*R*), and its dimensionless volume relative to pure borate glass, *v'*(*R*):

$$\rho(R) = \frac{m(R)}{v(R)} = \frac{m'(R)}{v'(R)} \cdot \rho(0),$$

$$v'(R) = \frac{m'(R)}{\rho(R)} \cdot \rho(0),$$

$$v'(R_1) = f_1(R_1)\cdot v_1 + f_2(R_1)\cdot v_2$$
$$v'(R_2) = f_1(R_2)\cdot v_1 + f_2(R_2)\cdot v_2,$$

Implies:

$$f_1(R_1)\cdot v_1 + f_2(R_1)\cdot v_2 = \frac{m'(R_1)}{\rho(R_1)}\cdot \rho(0)$$

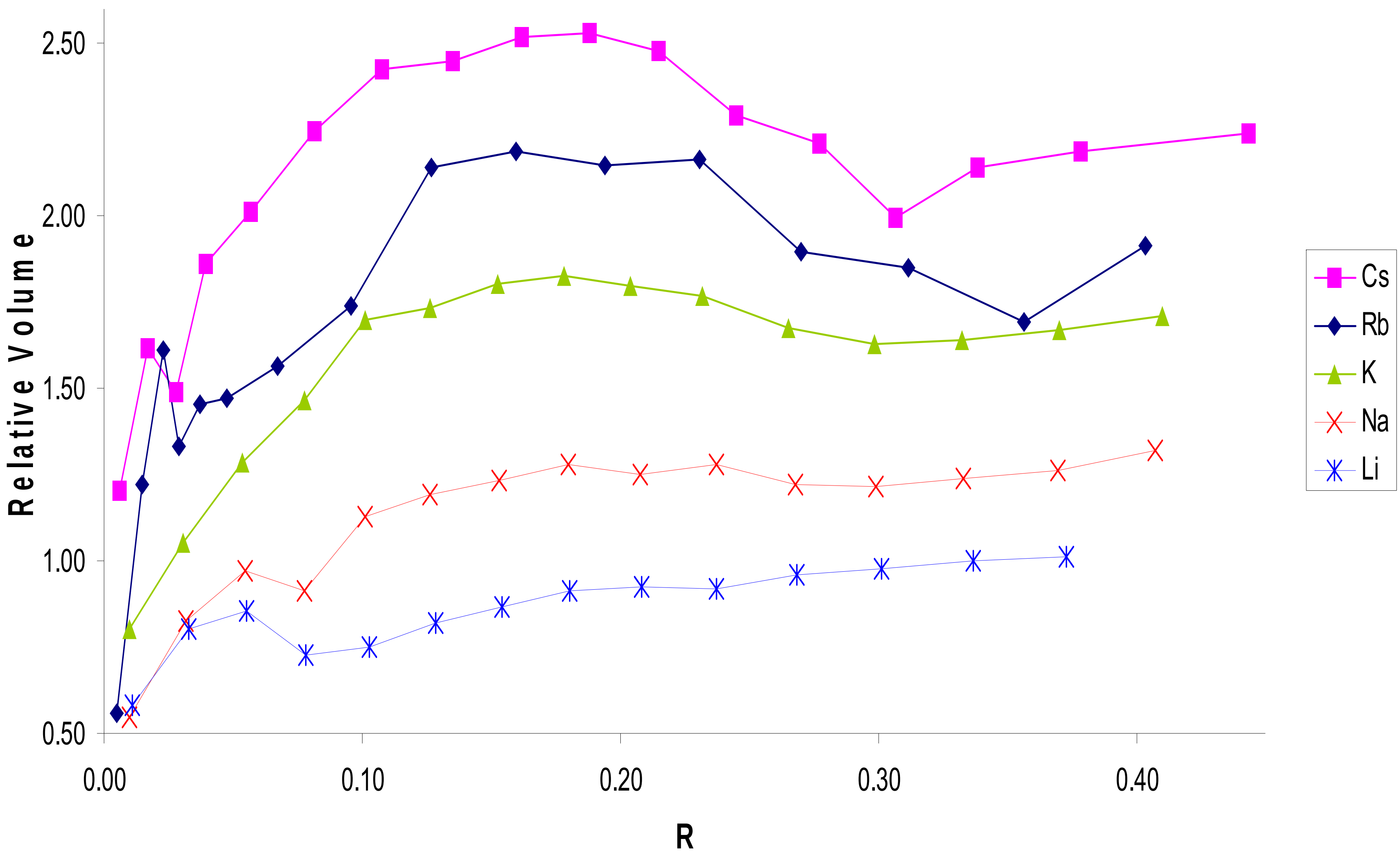
$$f_1(R_2)\cdot v_1 + f_2(R_2)\cdot v_2 = \frac{m'(R_2)}{\rho(R_2)}\cdot \rho(0).$$

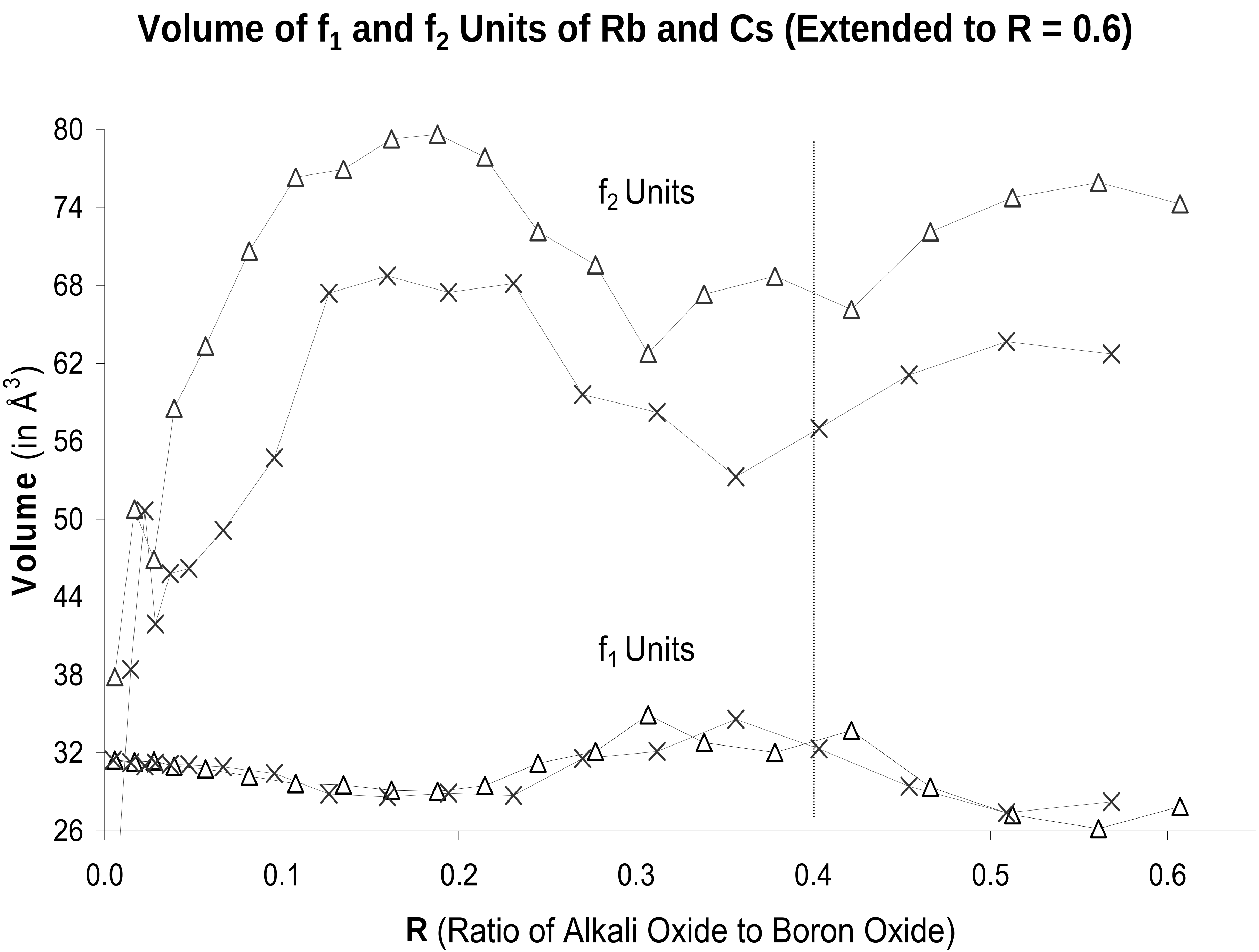
$$f_1(R_1)\cdot v_1 + f_2(R_1)\cdot v_2 = \frac{m'(R_1)}{\rho(R_1)}\cdot\rho(0)$$

$$f_1(R_2)\cdot v_1 + f_2(R_2)\cdot v_2 = \frac{m'(R_2)}{\rho(R_2)}\cdot\rho(0).$$

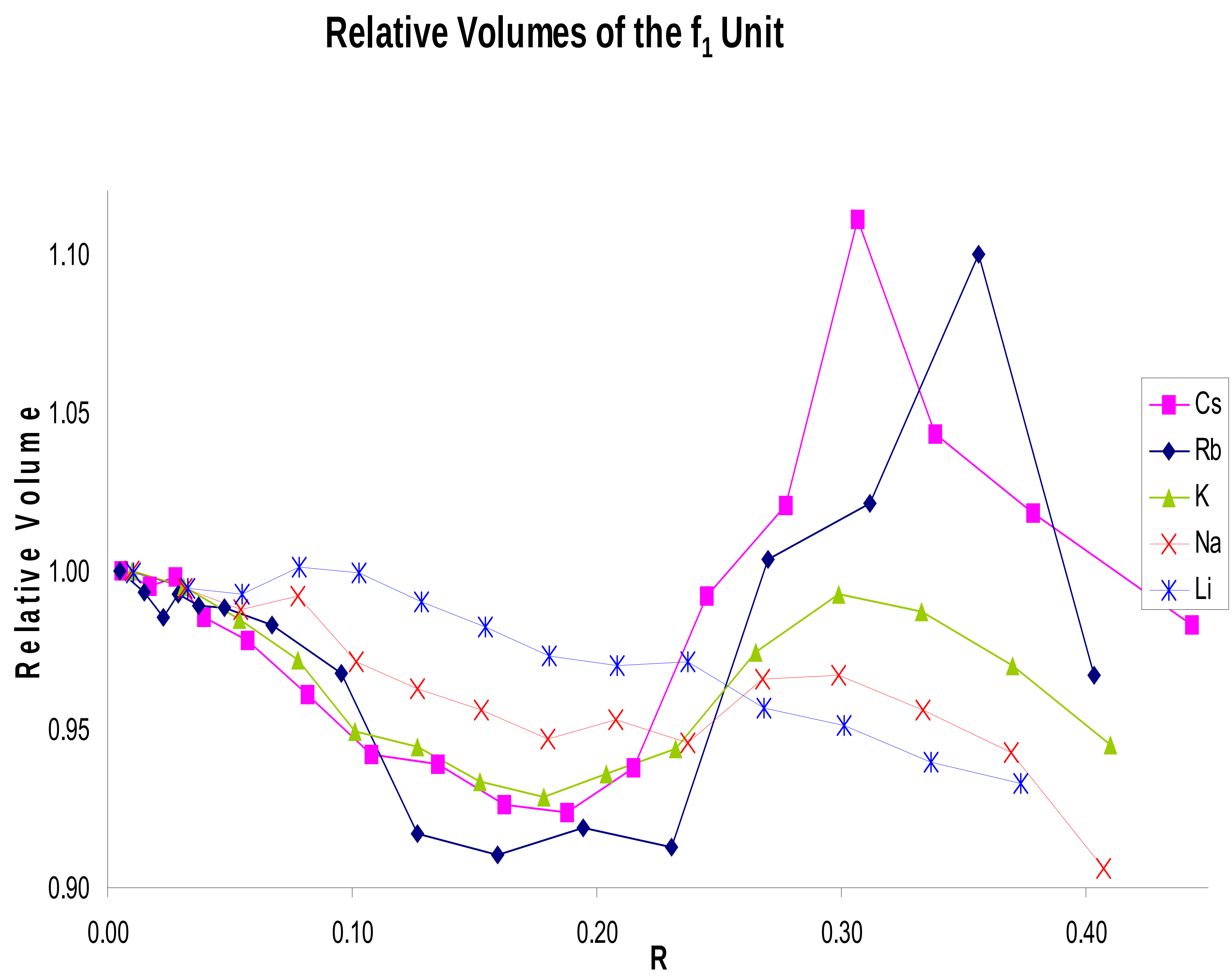
- Solve for v_1 and v_2 simultaneously and assign it to $R = (R_1 + R_2)/2$
- This is accurate if R_1 and R_2 are close to each other; in Kodama's data this condition is met.

Relative Volumes of the f_2 Unit

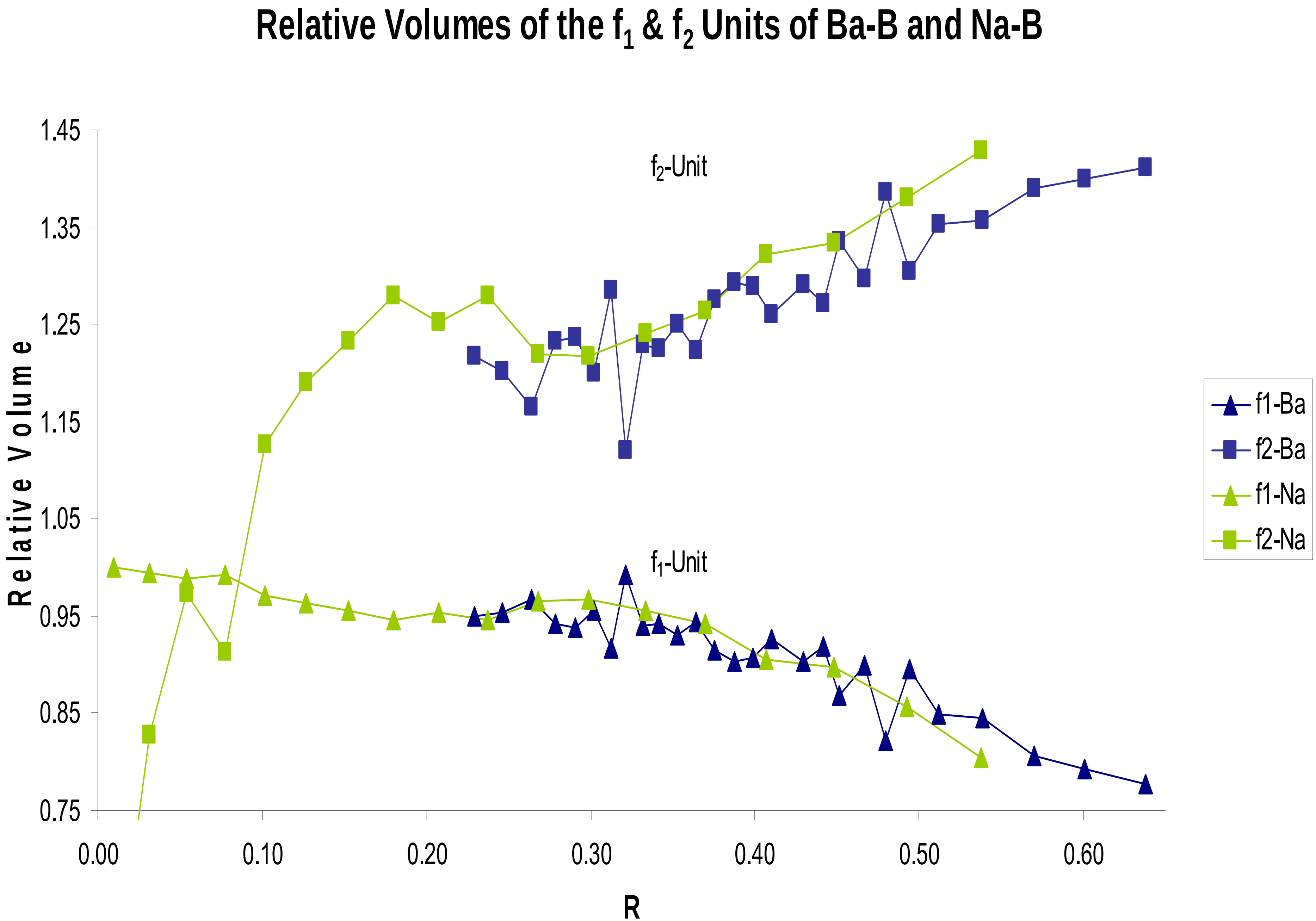




Volume of f_1 and f_2 Units of Rb and Cs (Extended to R = 0.6)
f_2 Units
f_1 Units
80
74
68
62
56
50
44
38
32
26
Volume (in $Å^3$)
0.0
0.1
0.2
0.3
0.4
0.5
0.6
R (Ratio of Alkali Oxide to Boron Oxide)



Relative Volumes of the f_1 Unit
Relative Volume
R
1.10
1.05
1.00
0.95
0.90
0.00
0.10
0.20
0.30
0.40
Cs
Rb
K
Na
Li

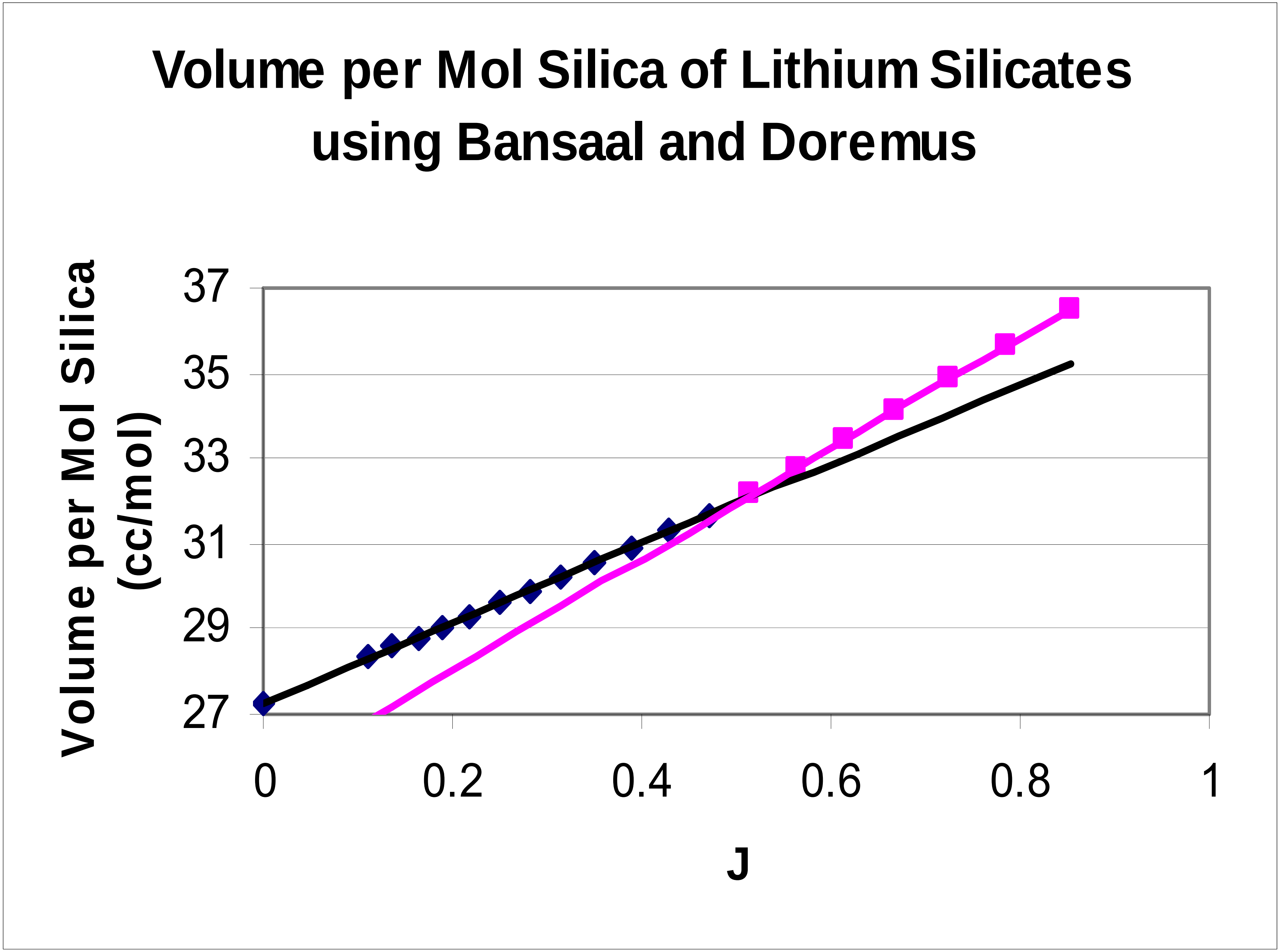


Relative Volumes of the f1 & f2 Units of Ba-B and Na-B
f2-Unit
f1-Unit
Relative Volume
R
1.45
1.35
1.25
1.15
1.05
0.95
0.85
0.75
0.00
0.10
0.20
0.30
0.40
0.50
0.60
f1-Ba
f2-Ba
f1-Na
f2-Na

The Volume per Mole Glass Former

- Volume per mole glass former = Mass ($JM_2O.SiO_2$)/density

It is the volume per mole glass former and R moles of modifier.

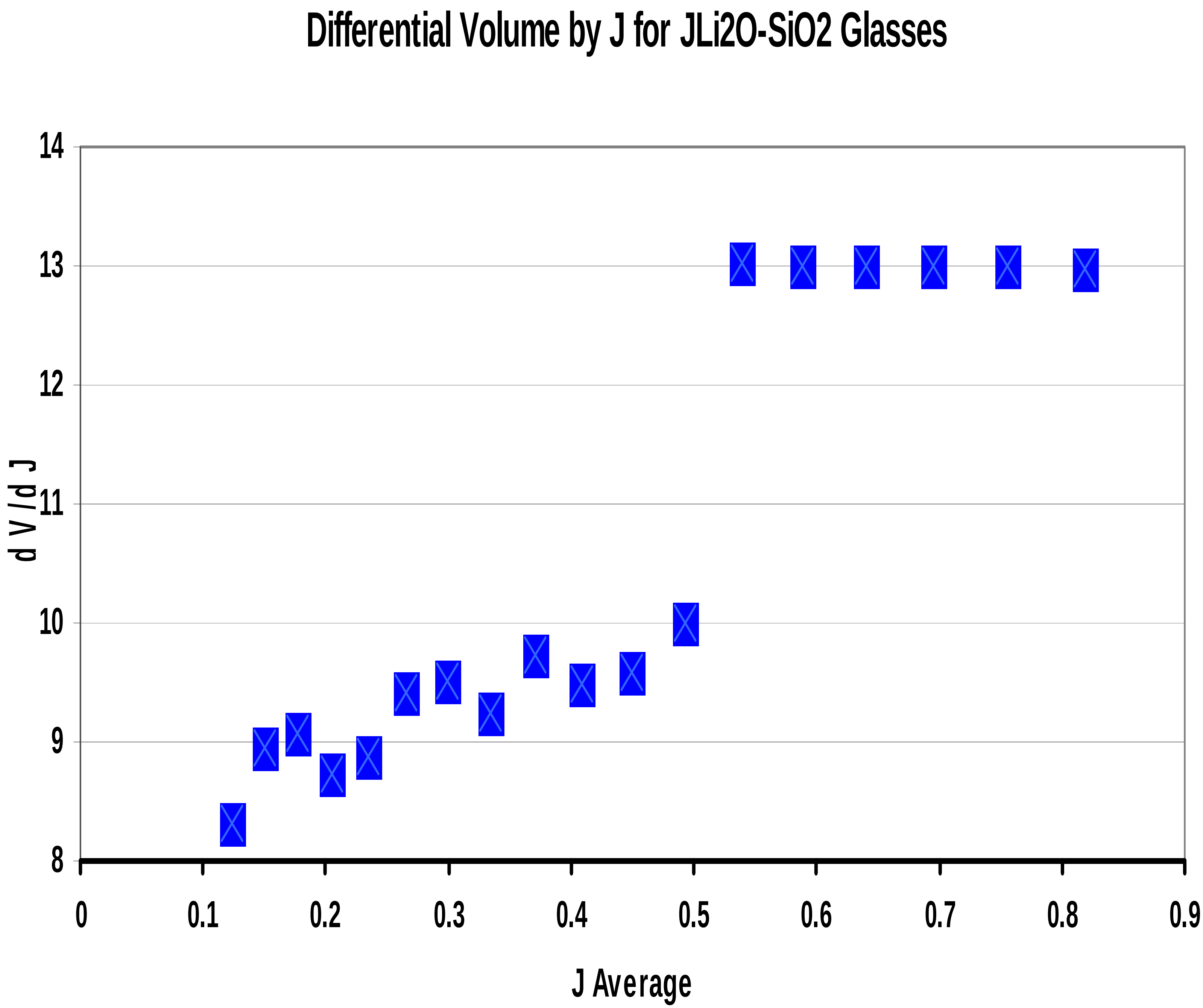


Volume per Mol Silica of Lithium Silicates using Bansaal and Doremus
Volume per Mol Silica (cc/mol)
37
35
33
31
29
27
0
0.2
0.4
0.6
0.8
1
J

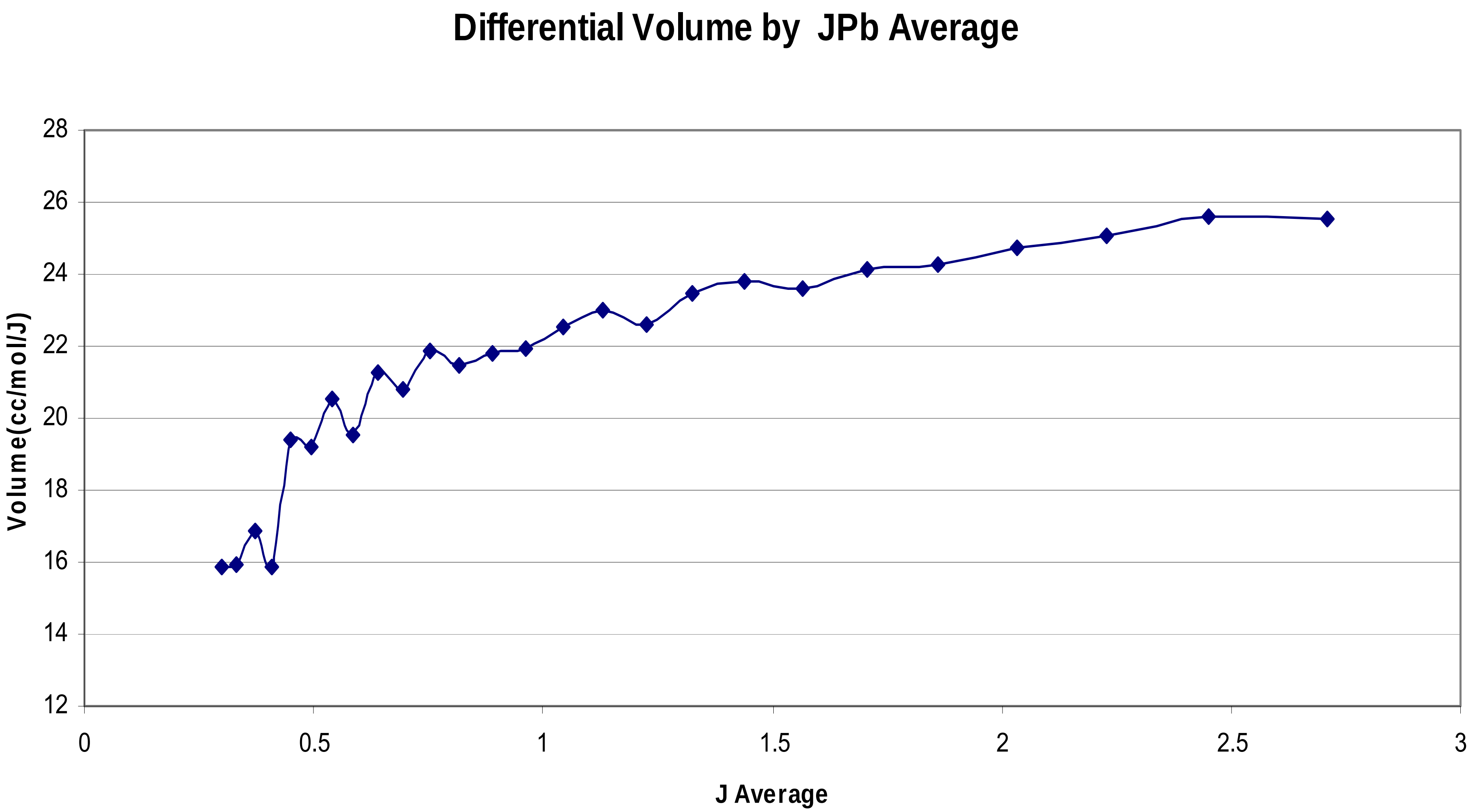
The Volume per Mole Glass Former

- Why is there a trend linear?

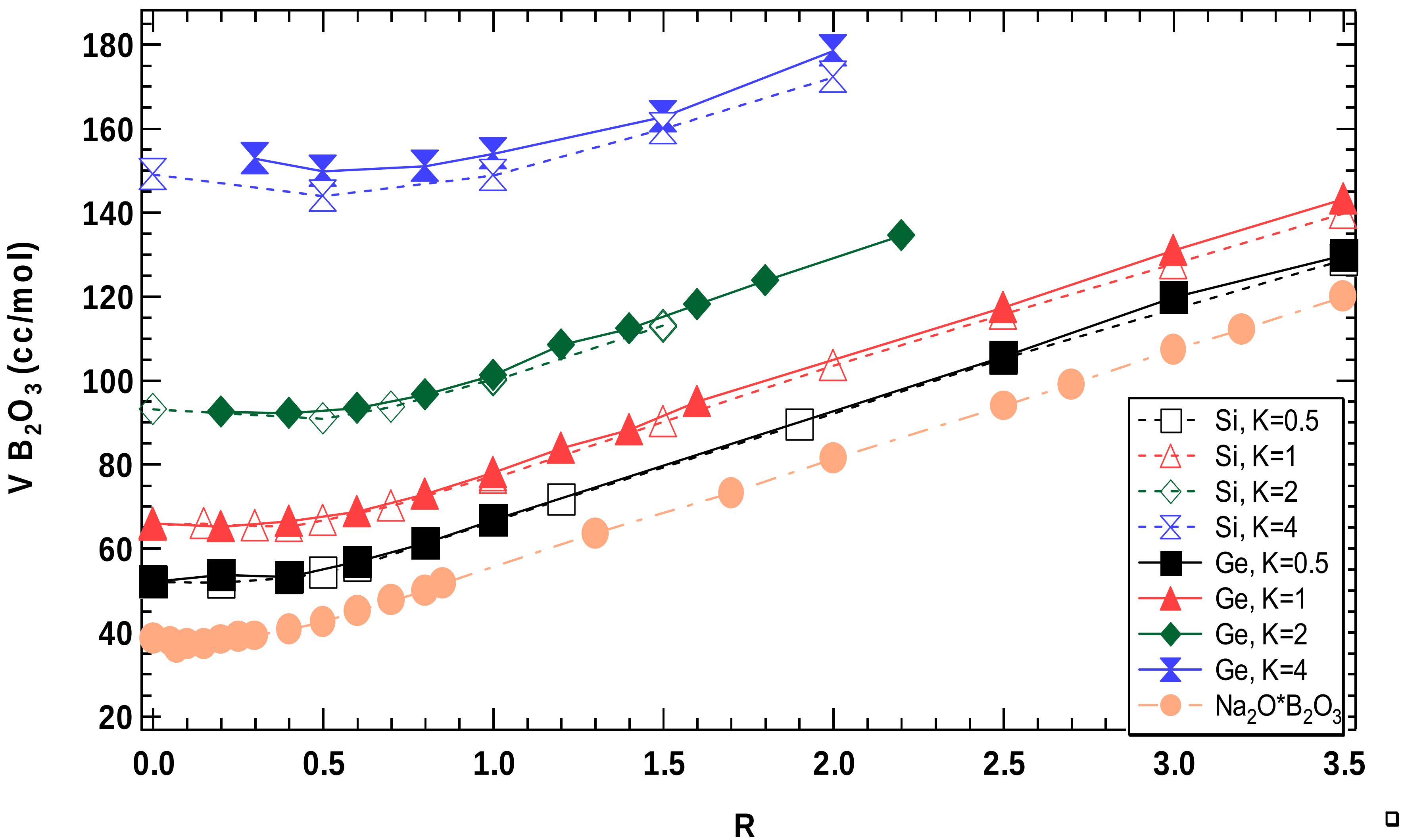
- $JM_2O.SiO_2 \rightarrow \quad (1\text{-}2J)Q_4 + 2JQ_3$ **J<0.5**
- So slope of volume curve is the additional volume needed to form Q_3 at the expense of Q_4. This is proportional to J.

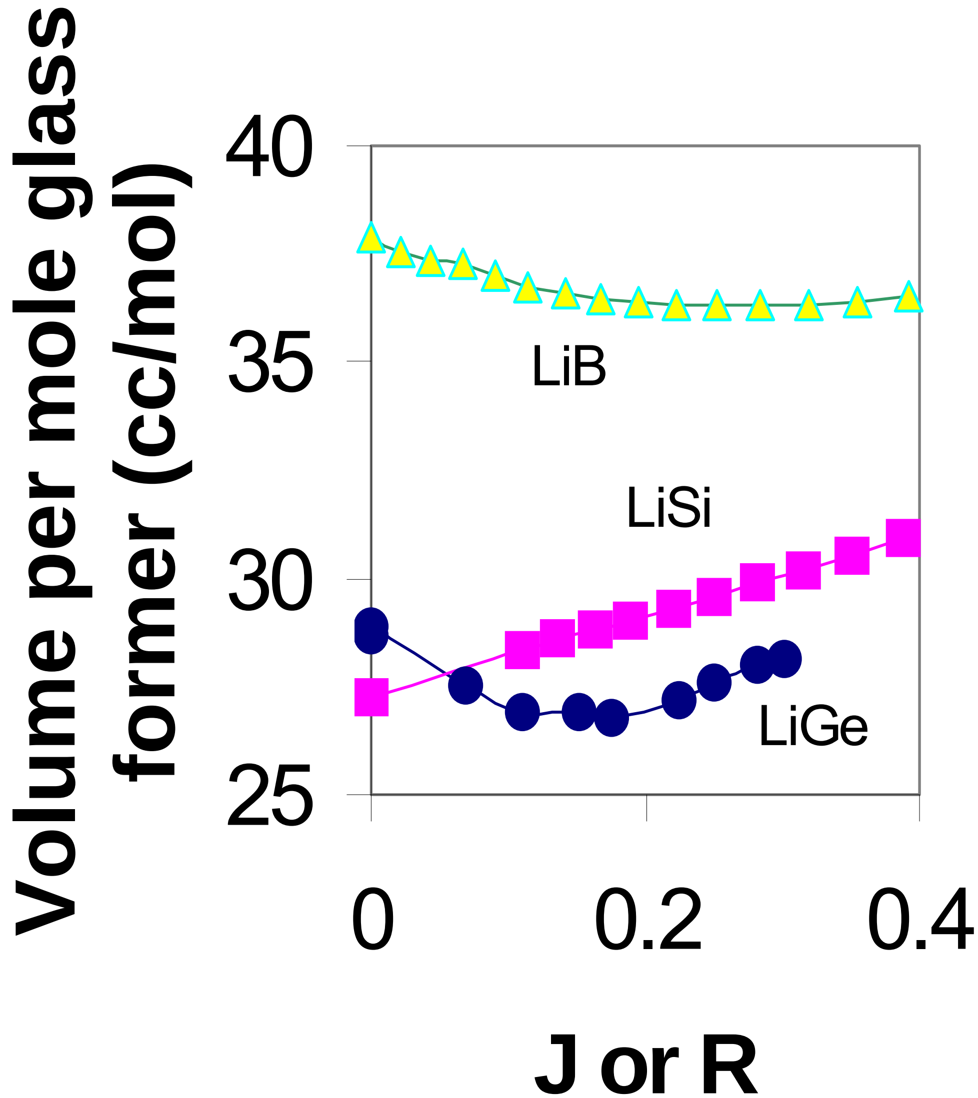

Differential Volume by J for JLi2O-SiO2 Glasses
d V /d J
14
13
12
11
10
9
8
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
J Average

Lead Silicate System: Bansaal and Doremus Data



Sodium Borogermanates Volumes per Mol B_2O_3 Compared to Sodium Borosilicates





Volume per mole glass former (cc/mol)
40
35
30
25
LiB
LiSi
LiGe
0
0.2
0.4
J or R

Problem

- For the barium borate data provided earlier plot the volume per mol boron oxide as a function of R.
- How do you interpret the result?

Lecture 2 ends here

Packing in Glass

- We will now examine the packing fractions obtained in glasses. This will provide a dimensionless parameter that displays some universal trends.
- We will need a good knowledge of the ionic radii. This will be provided next.

$$pf = \frac{\frac{4}{3}\pi \sum r_i^{3} N_i}{V_f}$$