

Density and Glass Transition Temperature Study of Low-Alkali Content Vanadate Glasses

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Abstract

The densities, glass transition temperatures, and recrystallization temperatures were determined for a series of rapidly cooled low alkali-containing vanadate glasses. The alkalis studied include lithium, sodium, potassium, rubidium, and cesium. The physical property data indicate significant structural changes in the range $R = 0.1$ to 0.25 , where R is the molar ratio of alkali oxide to vanadium pentoxide. The changes in density and T_g are consistent with a coordination change of the vanadium upwards from four. The glasses in the sodium and potassium vanadate systems maintain a small stability of about $15\text{-}20^\circ\text{C}$ for these compositions. Laser ionization time-of-flight mass spectroscopy indicates chain-like structures in vanadia, these structures may be a source for property anomalies observed in the glasses as alkali oxide modifies vanadia.

1. Introduction

The goals of this paper are three-fold: (1) to report densities, glass transition temperatures (T_g), and recrystallization temperatures (T_x) of alkali vanadate glasses; (2) to discuss the trends and differences between the various alkali vanadate glass systems; and (3) to propose possible structural changes to explain the property trends found in the alkali vanadate glass system.

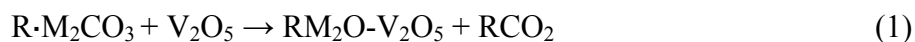
The glasses are compositionally described by $RM_2O \cdot V_2O_5$, where R is the ratio of alkali oxide to vanadium pentoxide and M is an alkali metal. The alkali metals studied include lithium, sodium, potassium, rubidium, and cesium.

Little is known about the structure of these glasses. Hoppe^{1,2} proposes that glassy vanadium pentoxide consists of V^{5+} ions with five bridging oxygen atoms. As alkali or alkaline-earth is added to the glass, bridging oxygens are replaced by non-bridging oxygens. This model predicts that for alkali vanadate glasses, at $R=1$ all V^{5+} ions would be surrounded by 4 bridging oxygens and 1 non-bridging oxygen. In addition, available spectroscopic evidence asserts that the presence of V^{4+} and other lower vanadate oxidation state ions are minimal. For example, this model has been supported by x-ray and neutron diffraction data collected by Hoppe. In Hoppe's two recent studies of alkali-earth and zinc vanadate glasses, he found that these glasses contained a mixture of VO_5 and VO_4 subunits, with the addition of alkali-earth or zinc increasing the number of VO_4 units and decreasing the number of VO_5 units^{1,2}. In addition structural studies of the alkali-earth vanadate glasses have been performed using IR³ and NMR⁴.

2. Experimental Procedure

Process of Making Glass

Alkali vanadate glasses were made by combining alkali carbonate with vanadium pentoxide according to reaction (1) below, in which R is the ratio of alkali oxide to vanadium pentoxide:



The well-mixed samples were placed into an electric muffle furnace set to 850 °C for 15-20 minutes depending on composition. Weight loss measurements were in excellent agreement with complete evolution of carbon dioxide. Glass formation required rapidly cooling the samples and we employed roller quenching. The resulting glass was transparent and purple in color.

Thermal Measurements

A Perkin-Elmer DSC-7 operating at 40 °C/min was used to determine the glass transition temperature (T_g) and recrystallization temperatures (T_x) of the alkali vanadate glasses. The onset method was employed and the error was estimated at $\pm 4^\circ\text{C}$ for both T_g and T_x .

Density Measurements

Densities were found using a Quantachrome MircoPycnometer or Ultrapycnometer employing He gas. To ensure consistency, high purity aluminum was used as a reference density and equal volumes of aluminum to sample were run before and after the sample run. The

estimated absolute error for these densities was determined to be $\pm 1\%$ while the relative error is estimated to be $\pm 0.3\%$.

Laser Ionization Time-of-flight Mass Spectroscopy Measurements (LITOF-MS)

The LITOF-MS spectrum was obtained using a Comstock reflectron with a conical source region and delayed pulse extraction. (DPE). The DPE along with the ion mirror gave a resolution of $M/\Delta M > 1000$. The laser used was a low power nitrogen laser ($\lambda = 337.1$ nm, 150 $\mu\text{J}/\text{pulse}$, 10 Hz, < 4 ns temporal duration pulse). The instrument yielded spectra whose systematic mass error was smaller than 0.2 amu. Two hundred pulses were averaged for each spectrum. The program ISOPRO[®] was used to simulate the isotopic distribution for each cluster resulting in unambiguous molecular identification.

3. Results

Tables 1 and 2 present the densities and molar volumes collected for the alkali vanadate system. The densities for the lithium vanadate system were taken from the study done by Lewis et al.⁵. Figure 1 displays the densities for the alkali vanadate glasses. Table 3 and figure 2 present the T_g values collected for the alkali vanadate system. These data are in good agreement with an earlier study from this group⁶. Table 4 reports the collected T_x , crystallization temperatures, for the sodium and potassium glasses. Plotted in figure 3 is the stability, ΔT , defined by $\Delta T = (T_x - T_g)$, as a function of R for these two systems.

Table 1
Alkali Vanadate Densities in g/cm^3 ($\pm 1\%$)

R	Lithium ¹	Sodium	Potassium	Rubidium	Cesium
0.00	2.96	2.94	2.94	2.94	2.94
0.10	2.94	2.98	2.92	3.01	3.11
0.15	-	3.07	-	-	-
0.20	2.93	3.21	2.95	3.09	3.24
0.25	-	3.14	2.99	-	-
0.30	2.95	3.04	2.92	3.17	3.34
0.40	2.94	2.95	2.87	3.19	3.45
0.50	2.92	2.92	2.82	3.19	3.49

Table 2
Alkali Vanadate Molar Volumes in cm³/mol ($\pm 1\%$)

R	Lithium ¹	Sodium	Potassium	Rubidium	Cesium
0.00	61.4	61.9	61.9	61.9	61.9
0.10	57.2	57.5	59.5	60.5	61.4
0.15	-	54.2	-	-	-
0.20	53.4	50.4	56.7	59.1	61.3
0.25	-	50.3	55.1	-	-
0.30	49.8	50.7	55.3	57.8	61.4
0.40	47.1	50.0	54.6	57.4	61.1
0.50	44.9	48.6	54.2	57.5	61.6

Table 3
Alkali Vanadate Glass Transition Temperatures in °C ($\pm 4^\circ\text{C}$)

R	Lithium ²	Sodium	Potassium	Rubidium	Cesium
0.00	209	212	212	212	212
0.10	210	216	215	212	210
0.15	-	216	-	-	-
0.20	205	213	211	207	204
0.25	-	211	208	-	-
0.30	202	206	206	203	198
0.40	200	200	200	195	185
0.50	-	194	186	176	160

Table 4
T_x Temperatures of Alkali Vanadate Glasses in °C ($\pm 4^\circ\text{C}$)

R	Sodium	Potassium
0.00	227	227
0.10	235	230
0.15	233	-
0.20	230	226
0.25	227	224
0.30	221	222
0.40	215	215
0.50	211	208

4. Discussion

In the densities of the sodium and potassium vanadate glasses there is a distinctive maximum around R=0.20-0.25, most noticeable in the sodium system, see figure 1. In the rubidium and cesium systems the densities are level around R=0.40. No maximum in the density is seen in the lithium vanadate system, which suggests that it is structurally different than the heavier alkali vanadate systems.

In the transition temperature data (figure 2) all of the alkali vanadate systems maximize in transition temperatures around R=0.10-0.20 with the heavier alkali dropping more quickly as R

continues to increase. The T_x for the sodium and potassium systems closely follow the T_g s so ΔT is nearly constant (figure 3). This suggests that these glasses are uniformly unstable over the studied composition range.

A Simple Density Model

In a simple density model of ideal mixing where the volumes are additive we would expect the density of alkali vanadate glasses to uniformly change from that of vitreous vanadium pentoxide ($R=0$) to the density of the alkali oxide as R increases. These densities are 2.96 g/cc for glassy vanadium pentoxide¹, 2.013 g/cc for lithium oxide⁸, 2.27 g/cc for sodium oxide⁸, 2.32 g/cc for potassium oxide⁸, 3.72 g/cc for rubidium oxide⁸ and 4.25 g/cc for cesium oxide⁸. However, the data collected does not follow this trend. We observe a peak in density in the $R=0.20-0.25$ range for both the sodium and potassium vanadate glasses, see Table 1 and figure 1. In the rubidium and cesium systems we see a leveling in density around $R=0.40-0.50$. If we calculate the densities predicted by this simple model, and then calculate the difference between the actual density and the predicted density we obtain the results displayed in figure 4. We see that the sodium, potassium, rubidium, and to some extent the cesium system have maxima in deviation between the model and experimental densities. The R values where this difference peak exists seems to move to higher R as the alkali increase in size, with sodium having the earliest peak at $R=0.20$ and cesium having a last peak at $R=0.40$. This similarity between these four systems and the large peaks in the sodium and potassium densities suggests some common structural modification. Two possible structural modifications are described in the next section along with predicted structural data that would be evident in such modifications, but first we examine the structures of various crystalline vanadium oxides.

Vanadium Oxide Structures

The structures of crystalline vanadium oxides have been well studied in the past. According to a study by Zavalij⁷ there are three subunits and five coordination polyhedra which vanadium oxides can form in the +3, +4 and +5 oxidation states. The first of these subunits is VO_5 which is trigonal bipyramidal or square pyramid in shape. Structural studies by Zavalij and Whittingham⁷ show one or two short V-O double bonds of length 1.55-1.75 Å, with the remaining V-O bonds being long single bonds of length 1.9-2.1 Å. The VO_4 units are tetrahedral in shape, with four V-O bonds of length 1.6-1.8 Å. The VO_6 unit is octahedral in shape, either distorted or regular depending on the presence or lack of a double bonded oxygen. In the distorted octahedral coordination the most distinguishing feature is a long $V\cdots O$ bond with length between 2.1 and 2.6 Å. The regular octahedral has only been seen in vanadium oxides with vanadium in an oxidation state of 3+ and is unlikely to form in the alkali vanadate glass system.

Proposed structural modifications

One structural modification that would explain the density maxima at low R values is that a higher conformation of vanadium is forming in these composition regions. This would be similar to the structural changes seen in the alkali germanates and alkali borate glasses. Past studies^{3,4} have shown that vitreous vanadium pentoxide glass has a structure formed by VO_4 and VO_5 units linked by corners with a vanadium coordination number of 4.8 ± 0.2 .⁵ Since the

densities increase while alkali is added up to the maximum around $R=0.25$ we would expect a coordination change, either converting VO_4 to VO_5 or, more likely, VO_5 to VO_6 . Beyond this density peak VO_6 units are predicted to convert rapidly to VO_5 with varying numbers of non-bridging oxygens per vanadium. It is noted that the observed increase in T_g in the low alkali regime is consistent with an increase in the connectiveness of the network. Another possible structural modification to the initial vitreous vanadium pentoxide glass would be a change in the chain structure. As stated above vitreous vanadium pentoxide consists of corner-linked VO_4 and VO_5 units. Using only VO_5 units with a square pyramidal shape, Zavalij and Whittingham⁷ found no less than 6 different chains that can form. These chains can be seen in figure 5. Of these, 3 are corner linked, two edge linked and the final chain is a mixture of both corner and edge sharing. The presence of these chains can be found by measuring the repeat distance, which for vanadium oxides is the distance between vanadium atoms. For crystals these data would be straightforward to interpret, but in glass there is no long range order so the chains would not be neatly formed into sheets but rather would be random.

Evidence for these chains is present in laser ionization time-of-flight mass spectroscopy data presented in figure 6 for vitreous V_2O_5 . In this figure we see chain fragments that increase in mass in steps of VO_2 or VO_3 to form the sequence $\text{VO}_3 \rightarrow \text{V}_2\text{O}_5 \rightarrow \text{V}_3\text{O}_7 \rightarrow \text{V}_3\text{O}_8 \rightarrow \text{V}_4\text{O}_{10} \rightarrow \text{V}_5\text{O}_{13}$. This is in contrast to the borates where there is evidence of superstructural units in the TOF data⁹.

The fact that vanadium oxides can form both corner and edge links could lead to changes in the short range glass structure and cannot be overlooked as a possible source of structural change.

5. Conclusions

The densities of the sodium and potassium vanadate system show maxima near $R=0.20-0.25$. The rubidium vanadate glass system appears to have a leveling in density around $R=0.40$. These changes in these systems suggest a still unknown structural change in these systems but two possible changes are proposed in this paper. One change involves an increase in the coordination of vanadium, the other change would involve a change in polyhedra linking. ^{51}V NMR and Raman studies are currently in progress to elucidate the nature of the property anomalies. The density maximum is not seen in the lithium system, suggesting that this system is somehow different than the other four systems and does not have the above structural change. All alkali vanadate systems show maximal transition temperature at $R=0.10$, with the heavier alkali dropping faster in temperature past this composition. The T_x temperatures for the glasses closely follow the T_g values for the sodium and potassium systems.

6. Acknowledgments

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7. References

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Figure captions

Figure 1: Densities of alkali vanadate glasses as a function of R, the molar ratio of alkali oxide to vanadium pentoxide. The curves are meant to be guides to the eye.

Figure 2: Glass transition temperatures for alkali vanadate glasses as a function of R, the molar ratio of alkali oxide to vanadium pentoxide. The curves are meant to be guides to the eye.

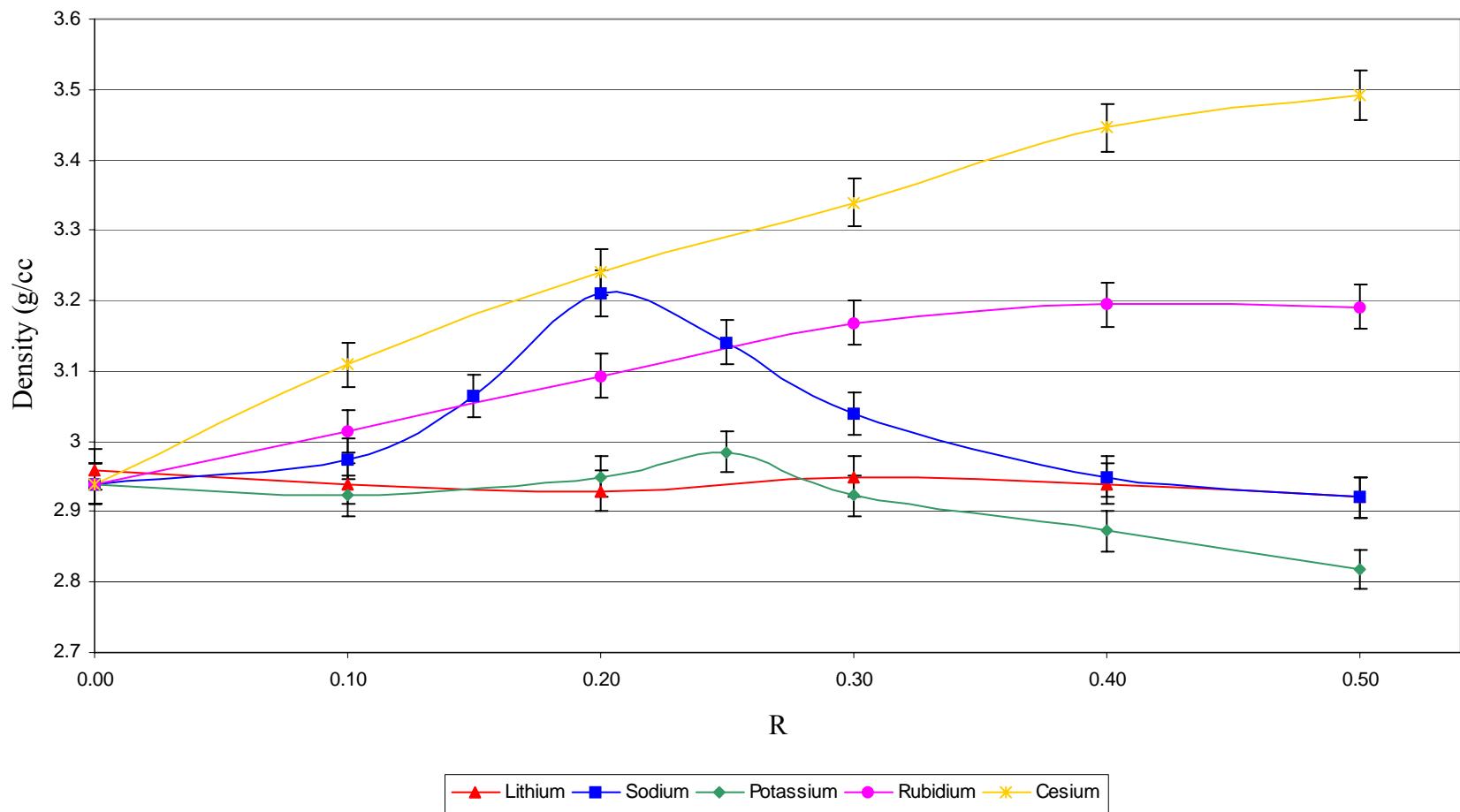
Figure 3: Stability temperatures ($T_x - T_g$) from sodium and potassium vanadate glasses as a function of R, the molar ratio of alkali oxide to vanadium pentoxide. The lines are meant to be guides to the eye.

Figure 4: Deviations of the densities of alkali vanadate glasses from a simple mixing model. R is the molar ratio of alkali oxide to vanadium pentoxide. The curves are meant to be guides to the eye.

Figure 5: Sample chaining structures of vanadium oxides taken from Zavalij and Whittingham⁷.

Figure 6: Negative ion mass spectrum of glassy vanadium pentoxide using laser ionization time-of-flight mass spectroscopy (LITOF-MS).

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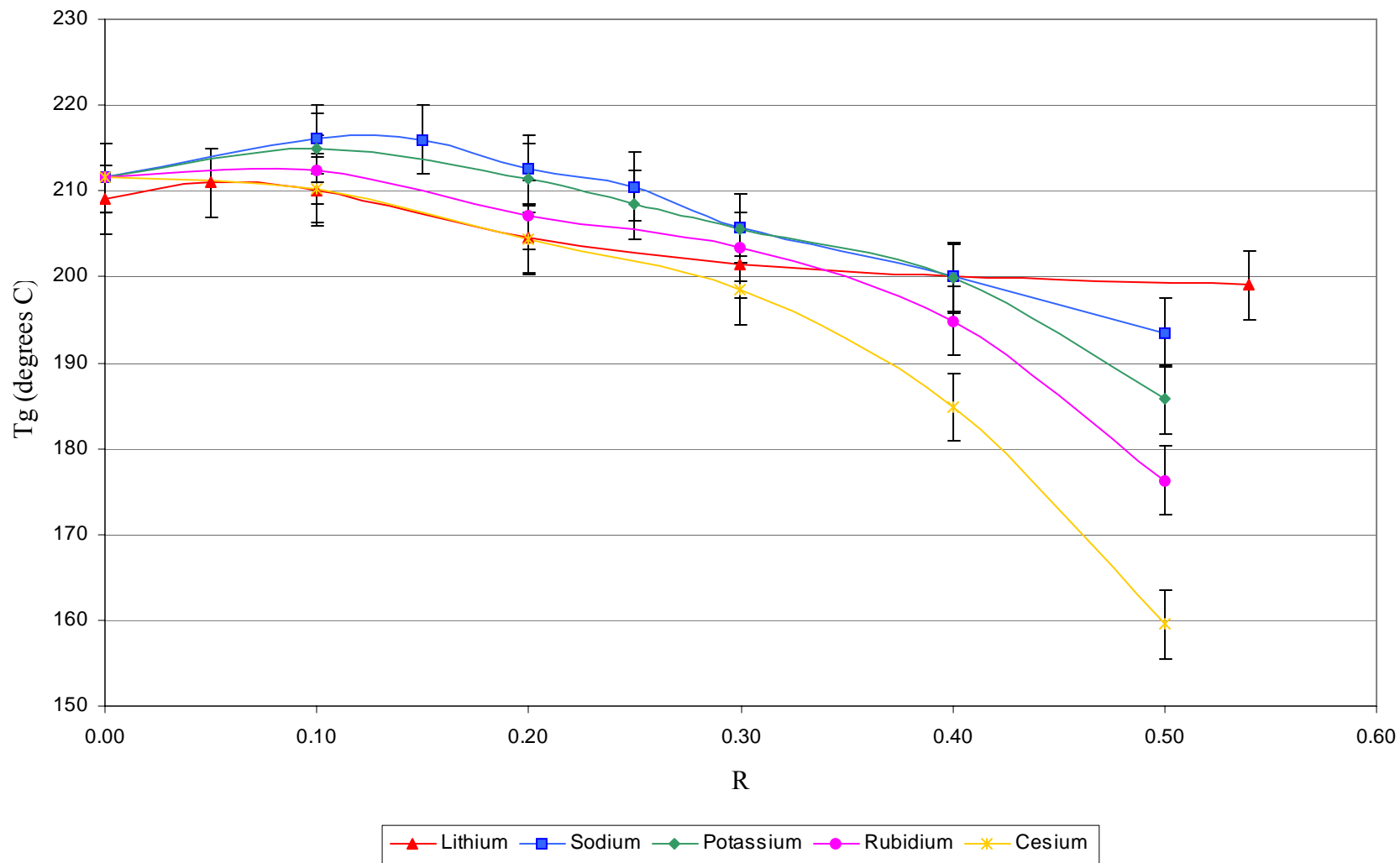


Figure 2: Glass transition temperatures for alkali vanadate glasses as a function of R, the molar ratio of alkali oxide to vanadium pentoxide. The curves are meant to be guides to the eye.

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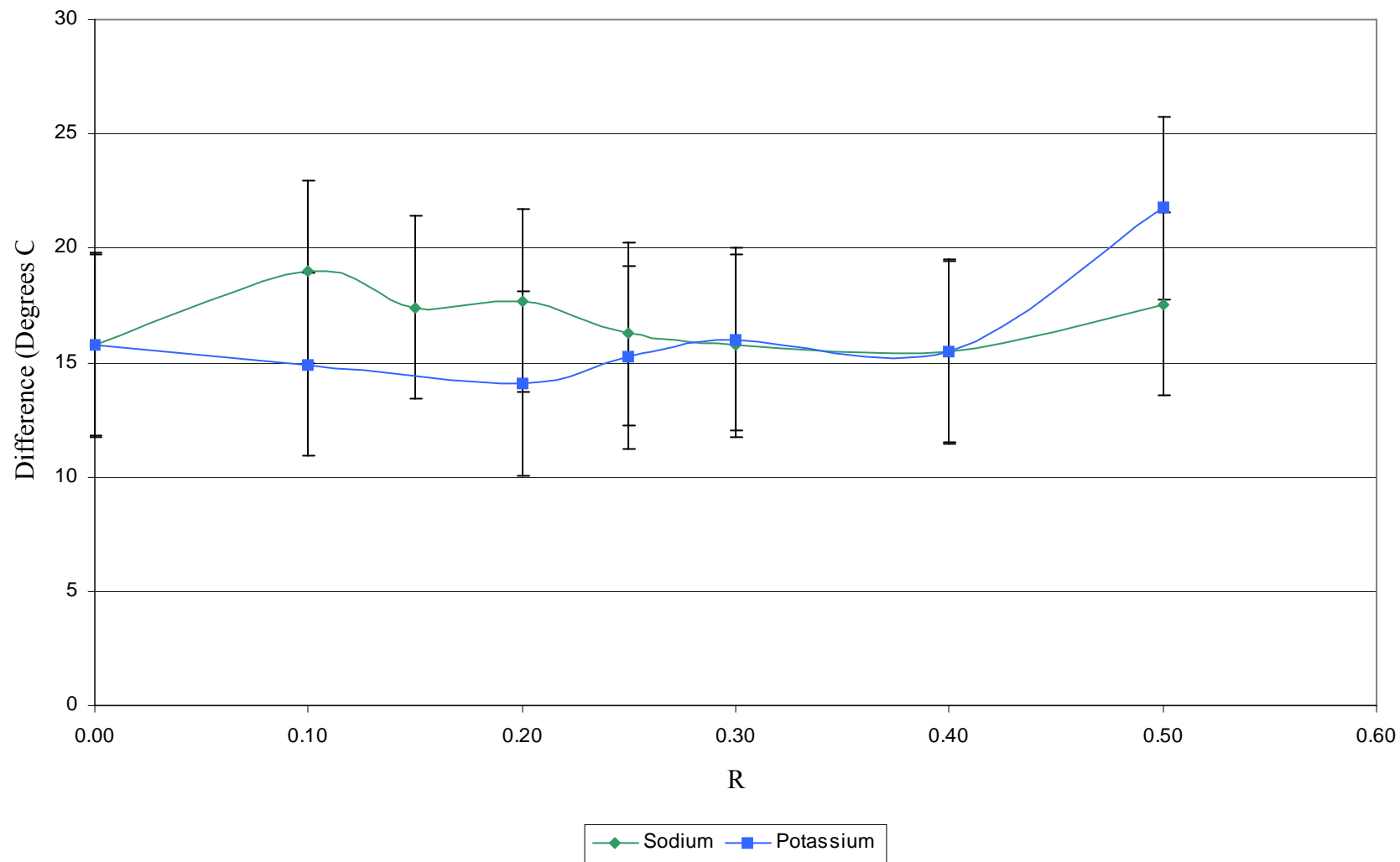


Figure 4: Deviations of the densities of alkali vanadate glasses from a simple mixing model. R is the molar ratio of alkali oxide to vanadium pentoxide. The curves are guides to the eyes.

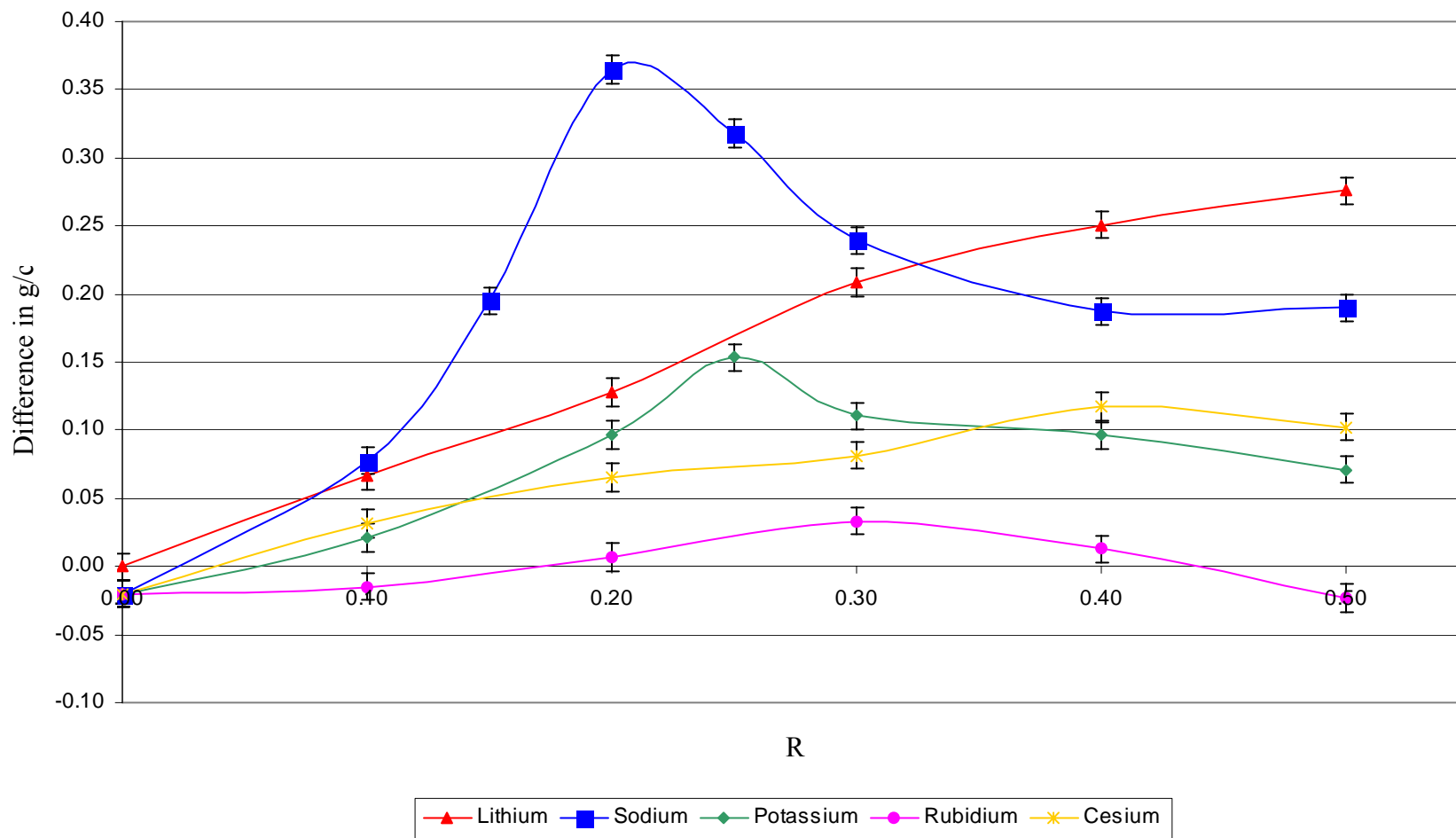


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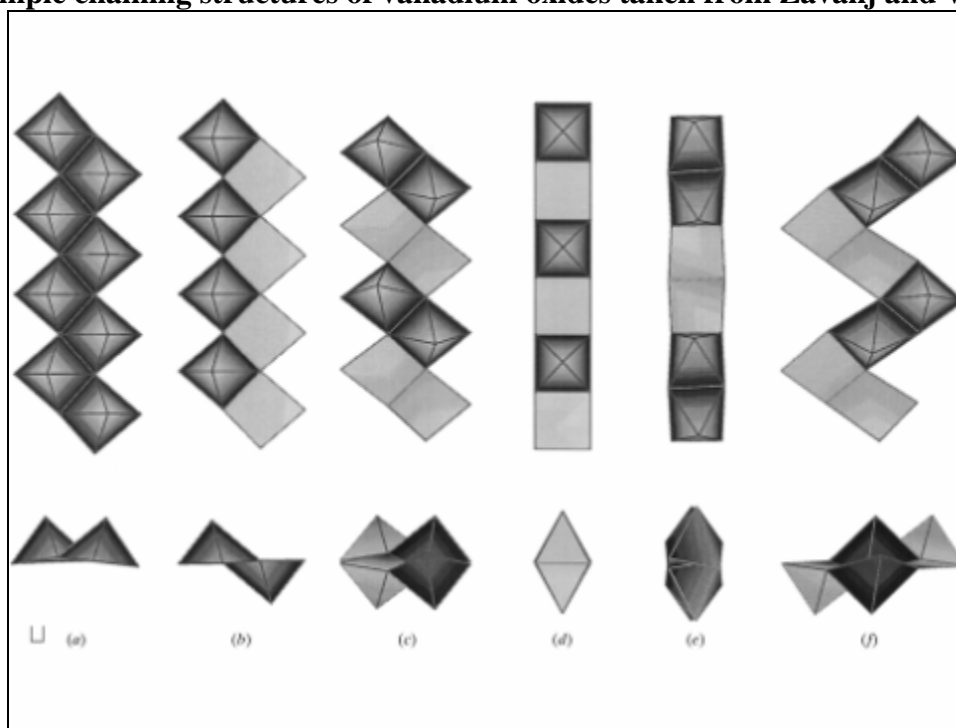


Figure 6: Negative ion mass spectrum of glassy vanadium pentoxide using laser ionization time-of-flight mass spectrscopy (LITOF-MS).

