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Role of Crystal Field in Mixed Alkali Metal Effect: Electron Paramagnetic Resonance Study of Mixed Alkali Metal Oxyfluoro Vanadate Glasses

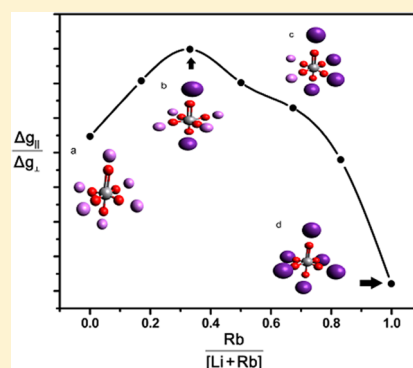
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S Supporting Information

ABSTRACT: The mixed alkali metal effect is a long-standing problem in glasses. Electron paramagnetic resonance (EPR) is used by several researchers to study the mixed alkali metal effect, but a detailed analysis of the nearest neighbor environment of the glass former using spin-Hamiltonian parameters was elusive. In this study we have prepared a series of vanadate glasses having general formula (mol %) 40 V₂O₅–30BaF₂–(30 – *x*)LiF–*x*RbF with *x* = 5, 10, 15, 20, 25, and 30. Spin-Hamiltonian parameters of V⁴⁺ ions were extracted by simulating and fitting to the experimental spectra using EasySpin. From the analysis of these parameters it is observed that the replacement of lithium ions by rubidium ions follows a “preferential substitution model”. Using this proposed model, we were able to account for the observed variation in the ratio of the *g* parameter, which goes through a maximum. This reflects an asymmetric to symmetric changeover of the alkali metal ion environment around the vanadium site. Further, this model also accounts for the variation in oxidation state of vanadium ion, which was confirmed from the variation in signal intensity of EPR spectra.



1. INTRODUCTION

Glasses, because of the inherent nonperiodic arrangement of their constituent units, always pose a challenge in understanding their behavior. The mixed alkali metal effect (MAE) is one such example. It is now an established fact that some of the physical properties of glasses that contain two alkali metal elements show a nonlinear behavior when one alkali metal is gradually replaced by another. The properties related to ion dynamics, viz., ionic conductivity, dielectric behavior, etc., are the most affected ones. This effect is termed the MAE.¹ The effect is more pronounced if the difference in the atomic radii of the two alkali metals is large.² There is no universally accepted model for explaining the MAE in glasses.

Electron paramagnetic resonance (EPR) is a powerful local probe for the study of paramagnetic species present in solids. EPR spin-Hamiltonian parameter “*g*” in particular is sensitive to the local environment around a paramagnetic species. The variation in the *g* parameter is attributed to the variation in crystal field, which in turn is a measure of change in the local environment.

EPR has been successfully employed in glass research.^{3,4} Sands⁵ was the first to analyze EPR spectra of glasses by considering them to be equivalent to powder spectra using an axially symmetric spin-Hamiltonian. This method is well accepted and widely used to analyze the EPR spectra of glasses.

MAE has been investigated using EPR as a tool to observe the variation in spin-Hamiltonian parameters with various

paramagnetic species such as Cu²⁺,^{6,7} Mn²⁺,^{8,9} and Fe³⁺.^{10,11} as EPR probes. But none of these reports give a detailed analysis of the mechanism for such a variation of the local environment.

Vanadium (nuclear spin *I* = 7/2) gives a rich hyperfine spectra and is one of the well-studied paramagnetic species through EPR. Vanadium has four oxidation states, viz., V²⁺, V³⁺, V⁴⁺, and V⁵⁺. As a glass constituent, at lower concentrations, vanadium pentoxide (V₂O₅) enters the glass matrix as a modifier, whereas at higher concentrations it acts as a glass former.¹² In glasses, vanadium usually enters as either V⁴⁺ or V⁵⁺,¹³ of which V⁴⁺ is EPR active. When MAE is investigated using EPR, there are reports in which vanadium has been used as a probe,^{14,15} but a complete analysis of alkali metal substitution based on the “*g*” parameters was hitherto not attempted. Even in a recent communication this aspect is looked down upon.¹⁶ In this communication we intend to study the effect of mixed alkali metal on the local environment of V₂O₅ using EPR as a tool.

2. EXPERIMENTAL SECTION

2.1. Glass Sample Preparation and Basic Characterization. Glass samples with varying amounts of lithium (Li)

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fluoride and rubidium (Rb) fluoride were prepared by usual melt quenching method. V_2O_5 was used as a major component in these glasses, which can be summarized using the general formula (in mol %); $40 V_2O_5-30BaF_2-(30-x)LiF-xRbF$ with $x = 5, 10, 15, 20, 25$, and 30 . All the samples were melted at ~ 973 K and quenched between two brass plates. T_g was determined by differential scanning calorimetry with 10 K/min as heating rate. The temperature precision was ± 0.05 K. The samples were annealed at a temperature 30 K below their glass transition temperature T_g . The largest chunk of samples was used for density measurement. Densities of these glass samples were measured following Archimedes' principle, using xylene (density = 0.86 g/cm³) as an immersion liquid. The densities reported here are to an accuracy of ± 0.01 g/cm³. Table 1 summarizes the starting material used (in mol %) and some of the basic properties.

Table 1. Glass Composition, Glass Transition Temperature, and Glass Density

Sl no.	batch code	glass content (mol %)				T_g (± 0.05 K)	density (± 0.01 g/cm ³)	$n[V]$ (cm ⁻³ 10^{20})
		V_2O_5	BaF_2	LiF	RbF			
1	VBL	40	30	30	0	267.25	3.68	1.332
2	VBLR1	40	30	25	5	263.78	3.64	1.281
3	VBLR2	40	30	20	10	264.39	3.61	1.235
4	VBLR3	40	30	15	15	262.41	3.68	1.223
5	VBLR4	40	30	10	20	261.16	3.57	1.155
6	VBLR5	40	30	5	25	260.61	3.66	1.156
7	VBR	40	30	0	30	254.29	3.45	1.062

2.2. EPR of Samples and Use of EasySpin. EPR spectra of the glass samples were recorded on a Bruker EMX spectrometer operating in X band frequency (~ 9.39 GHz) with a field modulation frequency of 100 kHz. The magnetic field was swept with a width of 450 mT, keeping 380 mT as the center field. With a resolution of 4096 points the experimental error involved in the measurement was ± 0.05 mT. "g" values were determined with an accuracy of ± 0.0002 . EPR spectra of annealed and unannealed glass samples were identical except for a slight increase in the S/N in the case of annealed samples. Samples used to obtain the EPR spectra were weighed. The intensity of the EPR spectra was normalized by dividing spectral intensity by the respective weight of the sample.

The EPR spectra were simulated and fitted to the experimental data using EasySpin,¹⁷ which is a MATLAB toolbox meant for this. We used the procedure explained by Muncaster and Parke¹⁸ to obtain the first guess of the spin-Hamiltonian values. EasySpin ver4.5.0 running in MATLAB

7.11 was used to obtain refined values. An interactive least-squares fitting method (Nelder/Mead Simplex) provided in the toolbox was used for this purpose. We terminated the fitting program at 100 steps and the RMS deviation obtained was about 0.035 except for VBR glass, which did not yield any better value than 0.0616 even after 200 steps. Spin-Hamiltonian parameters thus obtained are tabulated in Table 2 along with other parameters of significance.

3. RESULTS AND DISCUSSIONS

3.1. Basic Characterization of Glass Samples. Figure 1a shows the XRD pattern of three glass samples with rubidium content $0, 15$, and 30 mol %, respectively (please refer to Table 1 for batch code and content). The absence of any sharp peaks is an indication of amorphous nature of the samples. Broad humps in the XRD correspond to nearest neighbors.

Figure 1b shows the variation of glass transition temperature T_g with Rb content. We observe that T_g decreases as Li^+ is gradually replaced by Rb^+ . The addition of barium fluoride and the alkali metal fluoride modifies the network by opening it up, resulting in more nonbridging oxygen. An increase in the number of nonbridging oxygen makes the glass "softer"; hence, T_g decreases.

Figure 2 shows the variation of molar volume with Rb content. Molar volume is calculated as $V_m = M/\rho$, where M is the total molar mass of a particular glass composition and ρ is the density of that particular glass. The density of the glass (accurate to ± 0.01 g/cm³) was measured using Archimedes' principle using xylene as immersion liquid (density of xylene = 0.86 g/cm³). Error in molar volume shown as an error bar in Figure 2 was determined by using the usual error propagation formula

$$\Delta z = \sqrt{\left(\frac{\partial z}{\partial x}\right)^2 (\Delta x)^2 + \left(\frac{\partial z}{\partial y}\right)^2 (\Delta y)^2}$$

where Δz , Δx , and Δy are the errors involved in respective variables of a calculated variable $z = z(x, y)$, where x and y are the two measured variables. The extent of error thus calculated is represented as length of the error bar. The value of molar volume increases gradually as Rb content in the glass increases. As the network opens up because of the addition of alkali metal fluoride, more voids are created. Because Rb^+ is a larger ion than Li^+ , introduction of Rb^+ creates more open space (void) in the structure, which increases the molar volume and decreases the density.

3.2. EPR of Glass Samples. Figure 3 shows experimental and simulated EPR spectrum of one of the glass compositions viz., VBL. It represents a typical vanadyl ion (VO^{2+}) spectrum. With $S = 1/2$ and $I = 7/2$, VO^{2+} should show a single

Table 2. EPR Spin-Hamiltonian Parameters along with Rb Mole Fraction

composition	Rb/[Li + Rb] mole fraction	$A_{ }$ (10^{-4} cm ⁻¹)	A_{\perp} (10^{-4} cm ⁻¹)	$g_{ }$	g_{\perp}	$\Delta g_{ }/\Delta g_{\perp}$ ^a
VBL	0	161.531	54.2761	1.9307	1.9757	2.6894
VBLR1	0.17	162.17	54.7424	1.9307	1.9760	2.7216
VBLR2	0.33	163.045	55.5273	1.9308	1.9762	2.7397
VBLR3	0.5	164.432	56.0769	1.9309	1.9761	2.7204
VBLR4	0.67	165.578	56.7296	1.9310	1.9760	2.7058
VBLR5	0.83	167.250	57.6490	1.9313	1.9758	2.6760
VBR	1	168.855	58.7071	1.9316	1.9752	2.6042

^aSee text for calculation of these parameters.

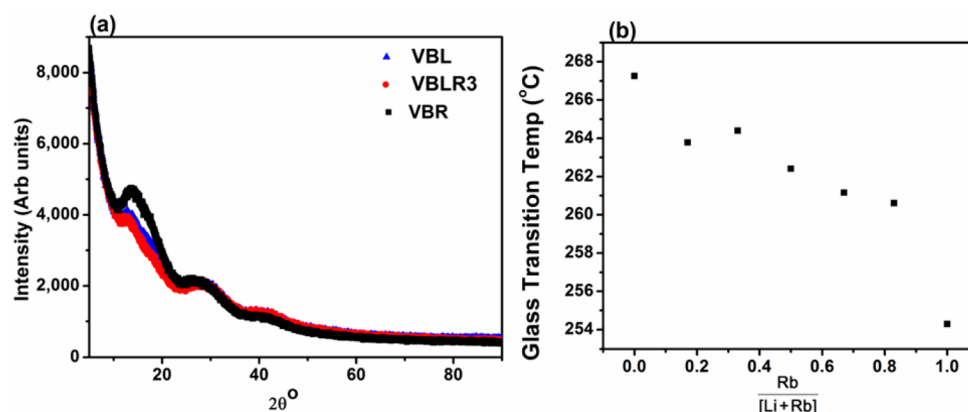


Figure 1. (a) XRD pattern of three representative glasses. (b) Variation of glass transition temperature T_g vs Rb content.

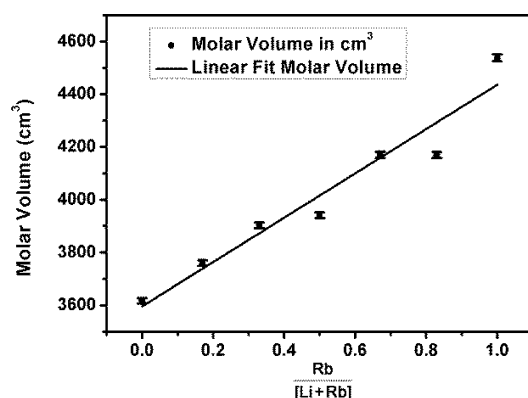


Figure 2. Variation of molar volume vs Rb content.

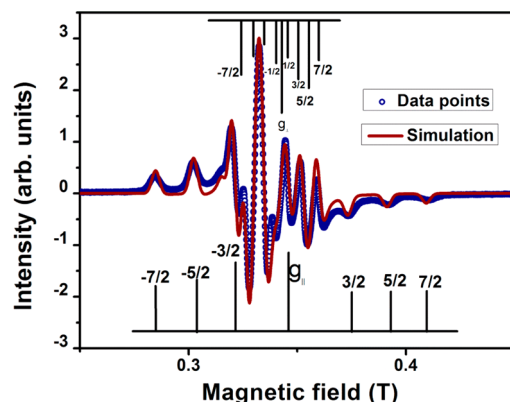


Figure 3. Representative plot of experimental and simulated EPR spectrum of VBL glass. Positions of parallel and perpendicular spin peaks and the position of $g_{||}$ and g_{\perp} are shown by drawing vertical bars. (Positions of parallel $-1/2$ and $+1/2$ spins are not shown to retain the clarity of the figure.)

absorption line split into eight hyperfine components ($2I + 1$). But some of these components overlap because of g anisotropy and broad absorption. Thus in the observed spectra some of these lines are not well resolved.

In the case of glasses, like powder samples, the magnetic species are arranged in random. Hence the spin-Hamiltonian used to evaluate powder spectra can be used with good effect for glasses. Spin-Hamiltonian in axial symmetry can be written as¹⁹

$$H = g_{||}\beta B_z S_z + g_{\perp}\beta(B_x S_x + B_y S_y) + A_{||}S_z I_z + A_{\perp}(S_x I_x + S_y I_y) \quad (1)$$

where $g_{||}$ and g_{\perp} are the parallel and perpendicular components of the principal component of the g tensor. $A_{||}$ and A_{\perp} are the parallel and perpendicular components of hyperfine coupling tensor A . B_x , B_y , and B_z are the components of the magnetic field along x , y , and z coordinates, S_x , S_y , and S_z and I_x , I_y , and I_z are the components of electronic and nuclear spins respectively. β is the Bohr magneton. The first two terms represent the Zeeman energy, and the last two terms, the contribution from the hyperfine interaction to the total Hamiltonian H .

The intensity and shape of the spectrum obtained will be an average of the total magnetic species oriented in different directions. For complicated spectra like the one we have, it is always instructive to simulate the desired spectra and fit to the experimental one to extract the spin-Hamiltonian parameters. EasySpin provides several functions to compute the EPR spectra. The function “pepper” is particularly useful for simulation of continuous wave, powder spectra in the “rigid limit” regime.

It is now an established fact that the vanadyl ion in various glasses^{20,21} or in complexes²² exists in tetragonally distorted octahedral symmetry. For this to happen, the conditions $g_{||} < g_{\perp} < g_e$ and $A_{||} > A_{\perp}$ should be satisfied.^{23,24} Here g_e is free electron g parameter with value 2.0023. A perusal of spin-Hamiltonian parameter values in Table 2 would reveal that the above-mentioned condition is satisfied by these samples. This shows that VO^{2+} in these systems exhibit the same kind of symmetry as mentioned above.

The ratio $\Delta g_{||}/\Delta g_{\perp}$, where $\Delta g_{||} = (g_e - g_{||})$ and $\Delta g_{\perp} = (g_e - g_{\perp})$, is sensitive to the tetragonal distortion of the octahedral crystal field.¹⁸ A higher value of this ratio corresponds to larger tetragonal distortion. The non monotonous variation of $\Delta g_{||}/\Delta g_{\perp}$ with increasing Rb mole fraction as shown in Figure 4, indicates that addition of rubidium modifies the neighboring environment of the vanadyl ions. The error in the ratio is estimated using the method mentioned earlier. The variation in $\Delta g_{||}/\Delta g_{\perp}$ can be thought of as a combined effect of variation of V=O bond length (Figure 7) and variation in the distance of four oxygen ligands in the basal plane.²⁵ It is interesting to see that the EPR signal is from group of V^{4+} ions, whose number decreases with the addition of rubidium (Figure 5).

In Figure 5, variation of concentration of vanadium ($[V]_{total}$) and the relative number of V^{4+} spins obtained from double

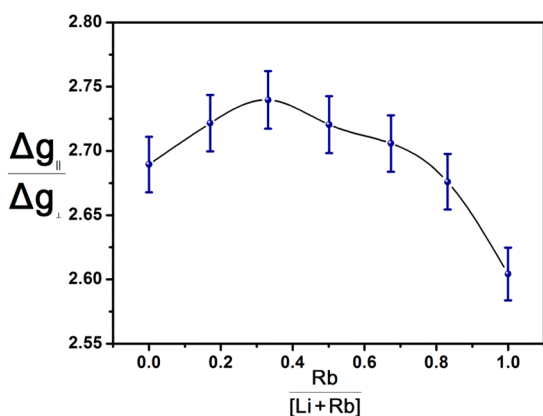


Figure 4. Variation of g parameter vs Rb content. The line drawn to connect the data points is a guide to eye.

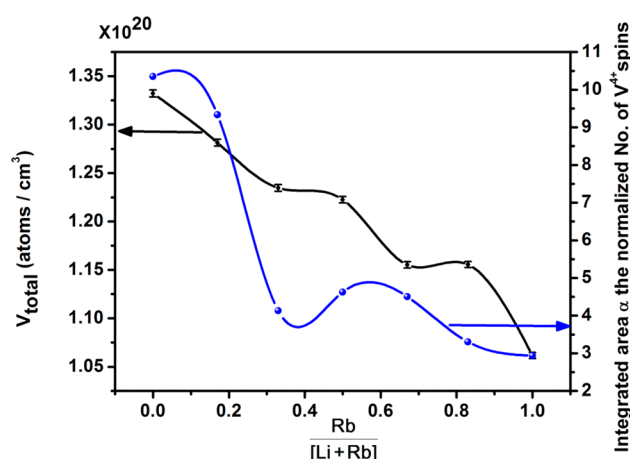


Figure 5. Variation of concentration of V and the integrated area of the EPR spectra (proportional to number of V^{4+} spins) normalized to the weight of the samples. Lines drawn are guides to the eye.

integrated intensity (scaled to equal weights of the samples) of the EPR signals with Rb content is plotted. $[V]_{\text{total}}$ was calculated from the molar volume of the glass composition.¹² Because V^{4+} ions are EPR active, the concentration of V^{4+} ions was estimated by taking the double integral of the first derivative EPR spectra. From the plot of $[V]_{\text{total}}$ vs Rb content we observe that $[V]_{\text{total}}$ decreases almost monotonically as Rb increases, where we observe a minimum in concentration of V^{4+} ions at about 33% of Rb.

We measured the magnetic property of these glass samples by SQUID magnetometer. Measurements were carried out at room temperature with 5 kOe variations and up to 50 kOe. Samples were diamagnetic in nature, as shown in Figure 6. This observation confirms that the EPR signal is from a small number of paramagnetic species (V^{4+}) over a large background of diamagnetism. The variation of V^{4+} in Figure 5 reflects the change in the number of these paramagnetic species with variation in alkali metal content.

Siegel was the first to take up the study of VO^{2+} in glasses.²⁶ He and others^{20–22} considered V_2O_5 as a six-coordinated structure with four oxygen atoms in plane with the vanadium atom and two oxygen connected to vanadium in the polar positions, one on top of the plane and the other below the plane making up an octahedral structure. One of the axial V—O bond (viz., $V=O$) has a different bond length than the

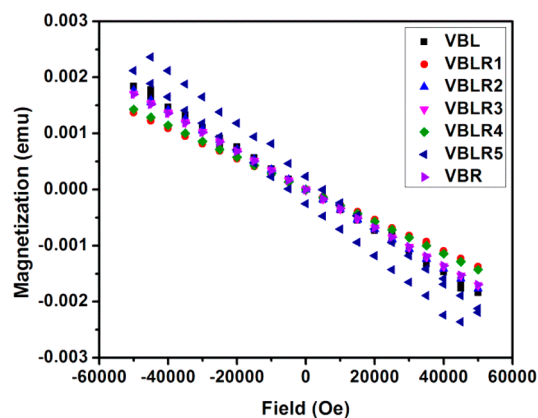


Figure 6. Variation of magnetization with magnetic field for the VB series glasses.

planar bonds due to its strong covalent nature. This leads to a tetragonal distortion²⁶ of the octahedron, as shown in Figure 7.

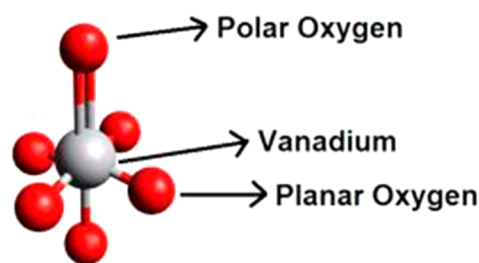


Figure 7. Sketch of V_2O_5 molecule showing polar and planar oxygen.

In the present study of VB series glasses, it is assumed that the variation in surrounding environment of V_2O_5 is due to the variation in alkali metal halides because the barium fluoride content is kept constant. Li^+ constitutes the first coordination in the VBL glass. The system settles to a particular crystal field orientation (Figure 8a). When the Li^+ ions are gradually replaced by the Rb^+ , the latter ions, initially, have a preferential choice to occupy the polar positions (Figure 8b).

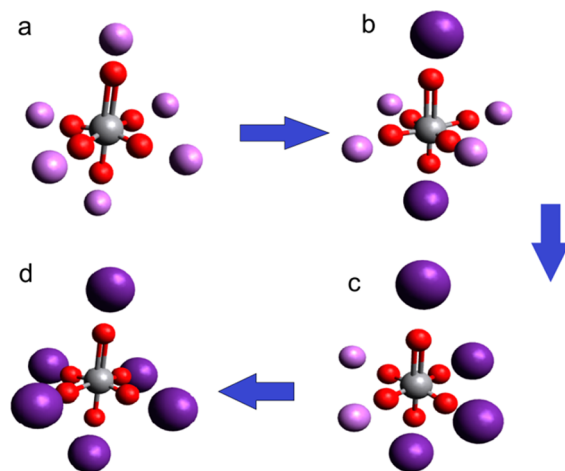


Figure 8. Sketch showing the variation of alkali metal environment around V_2O_5 as Li is replaced by Rb. Small spheres around V_2O_5 represent Li whereas large spheres represent Rb.

This substitution of axial (polar) Li^+ with Rb^+ will continue up to 33% of the Rb content in VB series glass. We see an increase in tetragonality of octahedral symmetry of the vanadyl ion (Figure 4) because of this substitution. Continued substitution of Rb^+ then replaces the two Li^+ (Figure 8c) at the planar position thereby reducing the tetragonality from the value attained at 33% of Rb, which continues up to 67% of the Rb content. From this point onward, an increase in Rb^+ will replace the other two Li^+ from the planar positions, making a complete Rb coordination sphere surrounding the vanadyl complex (Figure 8d). The $\Delta g_{\parallel}/\Delta g_{\perp}$ value is the least for the VBR glasses, suggesting that the crystal field is most symmetric (has least tetragonal distortion) in this case. Similar results were obtained by Swenson et al.,²⁷ from neutron diffraction experiments in mixed alkali metal phosphate glasses where they conclude that first Rb—Rb coordination sphere is both large and more well-defined than in the case of Li and Na. A recent Raman spectroscopic study of these VB series glasses communicated elsewhere also confirms this observation.²⁸ This communication also brings out the fact that the polar $\text{V}=\text{O}$ bond length and $\text{V}-\text{O}$ bond length in the basal plane varies, as lithium is replaced by rubidium, which supplements the observed variation in $\Delta g_{\parallel}/\Delta g_{\perp}$.

The variation in oxidation states of vanadium can also be explained with this model. The V^{4+} ion has a $3d^1$ electron and is EPR active. When Li^+ are substituted by Rb^+ at the polar positions, this electron is pulled toward polar oxygen because Rb^+ is more electropositive than Li^+ . The effect is that vanadium will be more V^{5+} , which is not EPR active; hence, we observe a decrease in EPR signal. This will continue up to 33% Rb in glass at which all the polar Li^+ are replaced by Rb^+ and we see minima in the concentration of V^{4+} (Figure 5). The EPR signal intensity drops because of the small concentration of V^{4+} . On the other hand, when Rb^+ replaces Li^+ at planar sites, the $3d$ electron finds an averaged potential around V that keeps the electron in the planar position and hence a slight increase in V^{4+} concentration is seen. When Rb makes a complete coordination sphere around vanadium, the concentration of V^{5+} is largest.

4. CONCLUSIONS

In summary, MAE in oxyfluorovanadate glasses has been investigated using EPR as the probe. The spectra were simulated and fitted to the experimental data to get the best fit, using EasySpin and the spin-Hamiltonian parameters like g_{\parallel} , g_{\perp} , A_{\parallel} , and A_{\perp} are obtained.

It is observed that the ratio $\Delta g_{\parallel}/\Delta g_{\perp}$, which is a measure of tetragonality of octahedral crystal symmetry of V_2O_5 , varies nonmonotonically with rubidium content. A model based on this observation is proposed. The essential idea of this model is that Rb atoms that are substituted for Li atoms initially prefer terminal positions over planar positions. Continued substitution then replaces planar Li atoms. It is seen that this model of “preferential substitution” explains the observation very well. Another observation is that the EPR signal intensity, which is due to concentration of V^{4+} ions, also shows nonmonotonous behavior with Rb content. This is also explained using preferential substitution, taking into consideration the oxidation states of the vanadium ions. The value of $\Delta g_{\parallel}/\Delta g_{\perp}$ is a minimum for all rubidium environments around V_2O_5 , which infers that Rb coordination is more symmetric than all Li or Li—Rb coordination.

■ ASSOCIATED CONTENT

Supporting Information

File containing the MATLAB script for simulation using EasySpin v4.5. This material is available free of charge via the Internet at <http://pubs.acs.org>

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Notes

The authors declare no competing financial interest.

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