Supporting material

Short-range structural insight into lithium substituted barium vanadate glasses using Raman and EPR spectroscopy as probes

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S1. Experimental Studies:
Figure S1 DSC curves for 60V$_2$O$_5$-(40-x) BaO-xLi$_2$O glasses (at 5°C/min.) where $T_g$ is glass transition temperature, $T_x$ is onset of crystallisation and $T_c$ is crystallization temperature.

Molar Volume calculation

The molar volume was calculated using the relation

$$V_m = \frac{M}{\rho} \quad (S1)$$

where $M$ is the molecular weight of the glass sample calculated using formula $M = \sum_i x_i m_i$.

Here $x_i$ and $m_i$ are the mole fraction and molecular weight of the $i^{th}$ component respectively.

The error in molar volume was determined as

$$dV_m = V_m \frac{d\rho}{\rho} \quad (S2)$$

where $d\rho$ is the error in density.

Average cross-link density calculation

So, the thermal parameters can be related to the structural properties using the relation

$$\bar{n}_c = \frac{\sum_i x_i (n_c)_i (N_C)_i}{\sum_i x_i (N_C)_i} \quad (S3)$$

where $x_i$ is the mole fraction of each component oxide, $n_c$ is the cross-link density per cation, $N_C$ is the number of cations per glass formula unit and $i$ denotes the component oxide. The cross-link density per cation ($n_c$) is calculated as $n_c = n_f - 2$, where $n_f$ is coordination number for each component oxide ($n_f$ is given as: Li$_2$O is 4, V$_2$O$_5$ is 6 as it is octahedral structure and BaO is 6$^{3,4}$).
S2. Results and Discussion:

Calculation of Packing density and short separation distance between identical ions from density data:

The packing density is given as

\[ V_t = \frac{\rho}{M} \sum x_i V_f \]  

(S4)

where \( \rho \) and \( M \) are glass density and its molecular weight respectively, \( x_i \) is mole fraction and \( V_f \) is the packing factor which is given as

\[ V_f = \frac{4\pi N}{3} (a r_A^3 + b r_B^3) \]

for a glass composition \( A_a B_b \) where \( A \) is a cation, \( B \) is anion and \( a \) and \( b \) are valencies of cation and anion respectively, \( N \) is Avagadro’s number and \( r_A \) and \( r_B \) are ionic radii of cation and anion. The packing factor calculated using this equation for Li2O is 9.13 cm³, V2O5 is 35.5 cm³ and BaO is 13.10 cm³.

The concentration of ions A and B is calculated as:

\[ n(A) = \frac{a x N}{100 V_m} \]

and

\[ n(B) = \frac{b x N}{100 V_m} \]

and the short separation distance \( r \) between identical ions is determined as:

\[ r = \left( \frac{1}{n} \right)^{1/3} \]

and the values are given in Table S1.

Table S1: Packing density, the concentration of Ba, Li and O ions and the short distance between Li-Li, V-V and O-O.

| Sample name | Packing Density (V_t) | n(Li) | r_{Li-Li} | n(V) | r_{V-V} | n(O) | r_{O-O} |
|-------------|-----------------------|-------|-----------|------|---------|------|---------|
| VBL10       | 0.578                 | 0.397 | 2.662     | 3.994| 3.994   | 0.292|
| VBL15       | 0.583                 | 0.395 | 4.060     | 3.383| 4.060   | 0.291|
| VBL20       | 0.578                 | 0.394 | 5.459     | 2.729| 4.094   | 0.290|
| VBL25       | 0.585                 | 0.392 | 6.899     | 2.070| 4.140   | 0.289|
Fitted Raman spectra of other glass samples:
Figure S2 Fitted Raman spectra of VBL10, VBL15 and VBL25.

EPR spectra of other glass samples:

![EPR spectrum of VBL10]
**Figure S3** EPR spectra of VBL10, VBL15, VBL20.

**Calculation of values of $g_{||}$ and $g_{\perp}$ from EPR spectra of VBL25 glass given in paper:**

Equations (5) and (6) from the paper can be written respectively as

\[ f_1 = y_1 - x_1 m_{||} - y_3 \]  
\[ f_2 = y_2 - x_2 m_{\perp} - y_4 \]  

**S5**

\[ f_2 = y_2 - x_2 m_{\perp} - y_4 \]  

**S6**
Here, $m$ is the nuclear magnetic quantum number which is denoted by $m_\parallel$ in equation (S5) and $m_\perp$ in equation (S6),

\[ f_1 \equiv H_\parallel(m), y_3 \equiv H_\parallel(0), x_1 \equiv A_\parallel \text{ and } y_3 \equiv \frac{A_\parallel^2}{2H_\parallel(0)} \left( \frac{63}{4} - m_\parallel^2 \right) \]

And \[ f_2 \equiv H_\perp(m), y_2 \equiv H_\perp(0), x_2 \equiv A_\perp \text{ and } y_4 \equiv \frac{(A_\perp^2 + A_\parallel^2)}{4H_\perp(0)} \left( \frac{63}{4} - m_\perp^2 \right) \]

So, \[ y_3 \equiv \frac{x_2^2}{2y_1} \left( \frac{63}{4} - m_\parallel^2 \right) \text{ and } y_4 \equiv \frac{(x_1^2 + x_2^2)}{4y_2} \left( \frac{63}{4} - m_\perp^2 \right). \]

Ignoring the second order terms i.e. $y_3$ and $y_4$, we can write these equation as linear equations similar to equations (7) and (8) in the paper:

\[ f_1 = y_1 - x_1 m_\parallel \]  \hspace{1cm} (S7)
\[ f_2 = y_2 - x_2 m_\perp \]  \hspace{1cm} (S8)

After finding values of $y_1$ and $x_1$ from linear fit in figure S4 (a) as intercept and slope respectively and values of $y_2$ and $x_2$ from linear fit in figure S4 (b), the values of second order terms in equations (S5) and (S6) i.e. $y_3$ and $y_4$ were calculated and substituted in equations (S5) and (S6) which after rearrangement give:

\[ f_3 = y'_1 - x'_1 m_\parallel \]  \hspace{1cm} (S9)
\[ f_4 = y'_2 - x'_2 m_\perp \]  \hspace{1cm} (S10)

Here $f_3 = f_1 + y_3$ and $f_4 = f_2 + y_4$

So, we again find the final (accurate) values of $y_1$ and $x_1$ as $y'_1$ and $x'_1$ from linear fit in figure S4 (c) and final values of $y_2$ and $x_2$ as $y'_2$ and $x'_2$ from linear fit in figure S4 (d).

From the paper, $H_\parallel(0) = \frac{hv}{g_\parallel \beta}$ and $H_\perp(0) = \frac{hv}{g_\perp \beta}$.

So, \[ g_\parallel = \frac{hv}{y'_1 \beta} \]  \hspace{1cm} (S11)
\[ g_\perp = \frac{hv}{y'_2 \beta} \]  \hspace{1cm} (S12)
The values of \(y_1^\prime\) and \(y_2^\prime\) are the intercept values in figure S4 (c) and figure S4 (d) respectively, \(\nu\) is the experimental resonance frequency (9439.535 MHz for VBL25) and \(\beta\) is Bohr magneton, \(\beta = \frac{e\hbar}{4\pi m_e}\), where \(\hbar\) is Planck’s constant and \(m_e\) is the mass of electron. Substituting all the values in right hand side of equations (S11) and (S12), we find the values of \(g_{||} = 1.9171\) and \(g_{\perp} = 1.9735\) with the error limit. Similar calculation was done for all glass samples. The value of \(x_1^\prime\) gives the final value of \(A_{||}\) in units of Tesla. The magnitude of slope in figure S4 (c) is 0.01838. So, \(A_{||} = 183.8\) G. The magnitude of slope in figure S4 (d) is 0.00639. So, \(A_{\perp} = 63.9\) G. \(A_{||}\) and \(A_{\perp}\) can be converted to required units using appropriate formulas.

*All the calculations are done according to the method given in references (18) and (30) in the paper.
Figure S4 (a) Linear fit to equation (S7), (b) Linear fit to equation (S8), (c) Linear fit to equation (S9), (d) Linear fit to equation (S10).

References:

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