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Effect of nickel ions on electron paramagnetic resonance, DC conductivity and thermal behavior in vanadyl doped $\text{NiO} \cdot \text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ glasses

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Abstract

Electron paramagnetic resonance (EPR), DC conductivity and differential scanning calorimetry (DSC) of the $x\text{NiO} \cdot (0.3 - x)\text{Li}_2\text{O} \cdot 0.7\text{B}_2\text{O}_3$ ($0.0 \leq x \leq 0.15$) containing 1.0 and 2.0 mol% of V_2O_5 have been studied. Spin Hamiltonian parameters, dipolar hyperfine coupling parameter, P , and Fermi contact interaction parameter, K , have been calculated. It is found that the size of the $3d_{xy}$ orbit of unpaired electron in the vanadium ion is increased with NiO contents in the sample. The DC conductivity decreases with increase in the $\text{NiO}:\text{Li}_2\text{O}$ ratio. Characteristic glass transition temperature, T_g , is found to increase with increase in NiO content. Theoretical optical basicity of the samples is also calculated. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Electron paramagnetic resonance; DC conductivity; Differential scanning calorimetry; $\text{NiO}:\text{Li}_2\text{O}$ ratio

1. Introduction

Glasses containing transition metal oxide can be expected to possess interesting and unusual properties arising from the fact that transition metal ion can exist in more than one valence state in glasses [1–6]. Khan and Al-Rfooh [7] found that nickel produces different base color when introduced into different base glass, and the color produced depends on the equilibrium between Ni ion in the sixfold and fourfold coordinates. Juza and Schultz [8] attributed the color change in the different glasses to a change in the equilibrium between NiO_4 and NiO_6 with changing glass composition. In the present work, we have carried out the measurement of EPR, DC conductivity and differential scanning calorimetry (DSC) in order to study

1. The effect of Ni ion on the features of EPR spectra of the VO^{2+} doped in $x\text{NiO} \cdot (0.3 - x)\text{Li}_2\text{O} \cdot 0.7\text{B}_2\text{O}_3$ ($0.0 \leq x \leq 0.15$) glasses.
2. The effect of variation of NiO on the electrical conductivity of the vanadyl doped lithium borate glasses.
3. The effect of heat treatment (DSC) on the course of glass transition.

2. Experimental details

2.1. Glass preparation

NiCO_3 (as a source of NiO) in glasses $x\text{NiO} \cdot (0.3 - x) \cdot \text{Li}_2\text{O} \cdot 0.7\text{B}_2\text{O}_3$ ($0.0 \leq x \leq 0.15$) containing 1.0 and 2.0 mol% of V_2O_5 were prepared from Analar grade reagents melted in porcelain crucibles at about 1000°C in an electric muffle furnace for 1 h. The melt was shaken occasionally for proper mixing and was finally poured onto a clean carbon plate and pressed with another. A part of each sample was annealed at 200°C for 2 h.

2.2. Electron paramagnetic resonance (EPR) measurements

The first derivative EPR spectra of annealed and unannealed samples were recorded at RT (27°C) in the X-band frequency ($\nu \approx 9.4\text{ GHz}$) on an EPR spectrometer (Varian-E-109). A magnetic field modulation of 100 kHz with peak to peak amplitude of 0.1 mT was applied. Polycrystalline diphenyl picryl hydrazyl (DPPH) was used as a standard g marker ($g = 2.0036 \pm 0.0002$).

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2.3. DC conductivity measurements

For electrical conductivity measurements, silver paste electrodes were used on uniformly thick glass (thickness ≥ 1 mm) slices. Electrical measurements were made by standard technique in the temperature range 27–250°C first by increasing and then by decreasing the temperature. Measurements of DC conductivity were carried out using the device described by Khasa et al. [4] which could employ one sample at a time. A constant voltage of 10 V is applied across the sample and circulating current was measured by using a Keithley 617 programmable electrometer/source.

2.4. DSC measurements

Glass characteristic temperatures were measured on a Perkin-Elmer differential scanning calorimetry (DSC-4). Sample handling as well as thermal measurements were done under a flowing nitrogen atmosphere. All measurements were made on approximately 10–30 mg samples using graphite pan for both glass and reference samples.

Sample thickness was always greater than 3 mm. A heating rate of $10^\circ\text{C min}^{-1}$ was used and samples were scanned over a wide range of temperature typically from 300 to 550°C. Only one T_g was observed for each sample. The T_g 's were taken on the second order transitions observed as a step change in baseline i.e. at the point lying at the middle of the curve between the two tangents. The maximum estimated experimental error in T_g is $\pm 2^\circ\text{C}$.

3. Results

3.1. EPR

Fig. 1 shows the EPR spectra of VO^{2+} in unannealed samples at room temperature. The spectra have structures which are characteristics of a hyperfine interaction arising from an unpaired electron with ^{51}V nucleus whose spin is $\frac{7}{2}$. NiO is an antiferromagnetic compound with spin 1 and magnetic moment 4.6 and therefore no hyperfine line (hfs) is observed in the EPR spectra. Malik et al. [9] also could

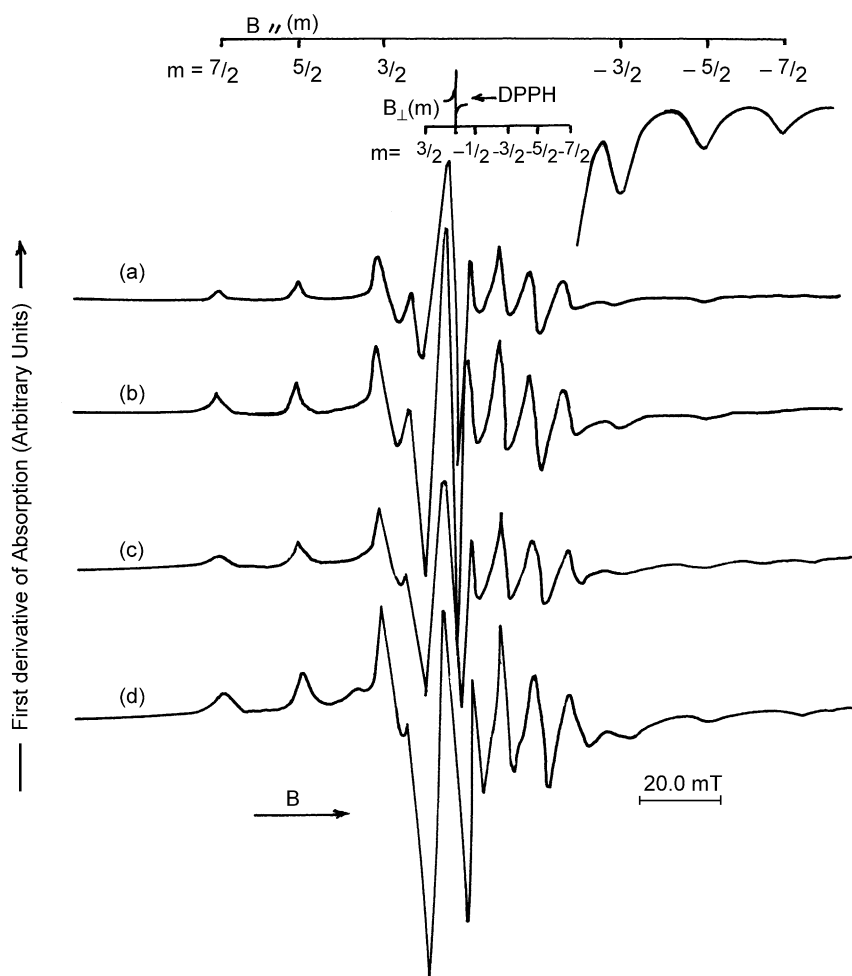


Fig. 1. The EPR spectra of VO^{2+} ion in unannealed $x\text{NiO} \cdot (0.3 - x)\text{Li}_2\text{O} \cdot 0.70\text{B}_2\text{O}_3$ samples in the X-band ($\nu \approx 9.4\text{ GHz}$) at 27°C . (a) Glass L7, (b) glass L8, (c) glass L11, and (d) glass L13.

Table 1

Spin Hamiltonian parameters, A_{th} and glass transition temperature (T_g) of VO^{2+} in $x\text{NiO} \cdot (0.3 - x)\text{Li}_2\text{O} \cdot 0.7\text{B}_2\text{O}_3$ glasses at room temperature^a

Glass No.	x	V_2O_5 (mol%)	g_{\parallel} (± 0.001)	g_{\perp} (± 0.001)	$ A_{\parallel} \times 10^{-4} \text{ cm}^{-1}$ (± 1.0)	$ A_{\perp} \times 10^{-4} \text{ cm}^{-1}$ (± 1.0)	T_g ($^{\circ}\text{C}$)	A_{th}
LN1	0.00	1.0	1.9409	1.9725	169.0	58.5	485	0.4940
LN2	0.02	1.0	1.9410	1.9731	169.0	58.5	489	0.4897
LN3	0.04	1.0	1.9409	1.9731	169.0	58.5	493	0.4854
LN4	0.05	1.0	1.9410	1.9731	169.0	58.5	496	0.4831
LN5	0.06	1.0	1.9390	1.9740	170.6	59.0	496	0.4809
LN6	0.08	1.0	1.9382	1.9743	170.5	60.4	499	0.4767
LN7	0.00	2.0	1.9405	1.9729	169.4	58.5	479	0.4940
LN8	0.02	2.0	1.9407	1.9736	169.4	58.5	485	0.4897
LN9	0.05	2.0	1.9405	1.9744	170.3	59.9	488	0.4831
LN10	0.08	2.0	1.9401	1.9744	170.3	59.9	492	0.4767
LN11	0.10	2.0	1.9400	1.9752	170.3	60.4	494	0.4724
LN12	0.12	2.0	1.9392	1.9764	171.1	60.9	497	0.4681
LN13	0.15	2.0	1.9384	1.9762	171.4	62.3	490	0.4616
LNA1	0.00	1.0	1.9410	1.9728	169.0	58.5	–	0.4940
LNA2	0.02	1.0	1.9410	1.9731	169.0	58.5	–	0.4897
LNA3	0.04	1.0	1.9411	1.9731	169.0	58.5	–	0.4854
LNA4	0.05	1.0	1.9410	1.9734	169.0	58.5	–	0.4831
LNA5	0.06	1.0	1.9396	1.9734	171.2	59.0	–	0.4809
LNA6	0.08	1.0	1.9380	1.9734	171.5	59.9	–	0.4767
LNA7	0.00	2.0	1.9405	1.9733	169.9	58.5	–	0.4940
LNA8	0.02	2.0	1.9405	1.9733	169.9	58.5	–	0.4897
LNA9	0.05	2.0	1.9405	1.9733	170.9	58.9	–	0.4831
LNA10	0.08	2.0	1.9403	1.9733	170.9	58.9	–	0.4767
LNA11	0.10	2.0	1.9401	1.9734	170.7	59.4	–	0.4724
LNA12	0.12	2.0	1.9394	1.9736	171.1	59.9	–	0.4681
LNA13	0.15	2.0	1.9387	1.9736	172.0	59.9	–	0.4616

^a A_{\parallel} and A_{\perp} are negative.

not observe hfs in the oxide glasses. The EPR spectra of VO^{2+} were analyzed by using axial spin Hamiltonian [1] for different samples having the same compositions discussed in earlier papers [4,10]. Spin Hamiltonian parameters (SHPs) are given in Table 1. The uncertainty in the value of g is ± 0.001 and in the value of A is $\pm 1.0 \times 10^{-4} \text{ cm}^{-1}$ to satisfy the calculated values of line position with the corresponding experimental value.

Using the expressions developed by Kivelson and Lee [11] the values of the dipolar hyperfine coupling parameter $P = 2\gamma\beta\beta_N\langle r^{-3} \rangle$ and the Fermi contact interaction term, K , are calculated [4,10], where γ , β , β_N and $\langle r^{-3} \rangle$ are the gyromagnetic ratio (1.468 for ^{51}V), Bohr magneton, nuclear magneton and average of reciprocal of cube of radius of d_{xy} orbital, respectively. Molecular orbital theory shows [12] that the parallel (A_{\parallel}) and perpendicular (A_{\perp}) components can be expressed as

$$A_{\parallel} = -PK + A'_{\parallel} \quad (1)$$

$$A_{\perp} = -PK + A'_{\perp} \quad (2)$$

where $A'_{\parallel} = -P(\frac{4}{7} - \Delta g_{\parallel} - \frac{3}{7}\Delta g_{\perp})$, $A'_{\perp} = P(\frac{2}{7} + \frac{11}{14}\Delta g_{\perp})$ with $\Delta g_{\parallel} = g_{\parallel} - g_e$, $\Delta g_{\perp} = g_{\perp} - g_e$ and $g_e = 2.0023$ is the g factor of free electrons [12]. Both A_{\parallel} and A_{\perp} are found to be negative by the method proposed by Muncaster and Parke [13]. The term $-PK$ in Eqs. (1) and (2) is due to the s character of the magnetic spin of the vanadium.

This s character results from the partial unpairing or polarization of the s electrons as a result of an interaction with the unpaired d electrons [14]. The estimate of polarization was made by Heine [14] and the contribution to the hyperfine coupling due to $-PK$ is included. For transition ions K is found to be positive [15]. The calculated values of A_{\parallel} , A'_{\perp} , P , K and $\Delta g_{\parallel}/\Delta g_{\perp}$ are given in Table 2 which manifests that the value of $\Delta g_{\parallel}/\Delta g_{\perp}$ which measures the tetragonality of the vanadium site increases with increase in NiO.

The SHP of VO^{2+} for annealed samples are also given in Tables 1 and 2. At low concentration (≤ 5.0 mol%) of NiO, the EPR spectra of annealed samples are virtually identical with the EPR spectra of the corresponding unannealed samples. Tables 1 and 2 also show that for 0.0–5.0 mol% of NiO there is practically no change in the SHP of the VO^{2+} in unannealed and annealed $\text{NiO} \cdot \text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ glasses. At higher mol% of NiO, there is detectable change in the spin Hamiltonian parameters i.e. g_{\perp} , A_{\perp} , A_{\parallel} , K and $\Delta g_{\parallel}/\Delta g_{\perp}$ increase and g_{\parallel} , P and A'_{\parallel} decrease.

The theoretical optical basicity A_{th} was also calculated using the relation [16]

$$A_{\text{th}} = \frac{\sum Z_i r_i}{2} \gamma_i^2 \quad (3)$$

where Z_i is the oxidation number of cation i , r_i the ratio of cation i with respect to the total number of oxides and γ_i

Table 2

 P , K , $|A'_{\parallel}|$, $|A'_{\perp}|$, $\Delta g_{\parallel}/\Delta g_{\perp}$ of VO^{2+} in $x\text{NiO} \cdot (0.3 - x)\text{Li}_2\text{O} \cdot 0.7\text{B}_2\text{O}_3$ glasses at room temperature

Glass No.	P (10^{-4} cm^{-1})	K	$ A'_{\parallel} $ (10^{-4} cm^{-1})	$ A'_{\perp} $ (10^{-4} cm^{-1})	$\Delta g_{\parallel}/\Delta g_{\perp}$
LN1	121.7	0.742	78.6	31.9	2.0592
LN2	121.7	0.743	78.5	32.0	2.1003
LN3	121.7	0.743	78.5	32.0	2.1003
LN4	121.7	0.743	78.5	32.0	2.1004
LN5	120.6	0.744	79.3	32.3	2.2300
LN6	120.9	0.763	78.3	31.8	2.2883
LN7	122.1	0.742	78.8	32.1	2.1024
LN8	122.1	0.742	78.8	32.1	2.1501
LN9	122.1	0.745	79.1	32.3	2.2164
LN10	122.5	0.745	78.9	32.3	2.2365
LN11	120.7	0.765	77.9	31.9	2.3076
LN12	120.9	0.769	78.1	32.1	2.4159
LN13	119.3	0.787	77.1	31.6	2.4478
LNA1	121.7	0.743	78.5	32.0	2.0796
LNA2	121.7	0.743	78.5	32.0	2.1003
LNA3	121.7	0.743	78.5	32.0	2.1004
LNA4	121.7	0.743	78.5	32.0	2.1215
LNA5	122.3	0.744	79.1	32.2	2.1703
LNA6	122.5	0.752	79.4	32.9	2.2286
LNA7	122.8	0.741	79.3	32.3	2.1361
LNA8	122.8	0.740	79.3	32.3	2.1412
LNA9	123.3	0.741	79.6	32.4	2.1304
LNA10	122.5	0.741	79.6	32.4	2.1390
LNA11	122.9	0.746	79.4	32.3	2.1608
LNA12	122.8	0.750	79.4	32.3	2.1922
LNA13	123.1	0.749	79.7	32.4	2.2117

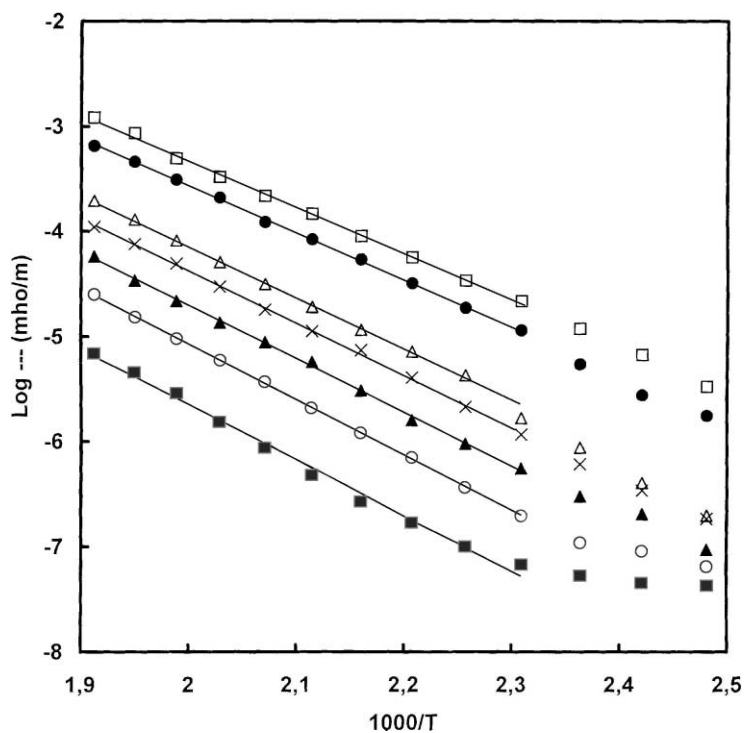


Fig. 2. Variation of $\log \sigma$ as a function of $1000/T$ for glass L7 (\square), glass L8 (\bullet), glass L9 (\triangle), glass L10 (\times), glass L11 (π), glass L12 (\circ) and glass L13 (\blacksquare). For all glasses the linear region of the curve with least square fitting is shown.

Table 3

DC conductivity σ , and activation energy W of the $x\text{NiO} \cdot (0.3 - x)\text{Li}_2\text{O} \cdot 0.7\text{B}_2\text{O}_3$ glasses

Glass No.	x	V_2O_5 (mol%)	σ at 513 K ($\Omega^{-1}\text{m}^{-1}$)	σ at 423 K ($\Omega^{-1}\text{m}^{-1}$)	W (eV)
LN1	0.00	1.0	4.00×10^{-4}	5.27×10^{-6}	0.90
LN2	0.02	1.0	2.48×10^{-4}	2.74×10^{-6}	0.93
LN3	0.04	1.0	2.17×10^{-4}	1.88×10^{-6}	0.95
LN4	0.05	1.0	1.63×10^{-4}	1.51×10^{-6}	0.96
LN5	0.06	1.0	9.59×10^{-5}	7.54×10^{-7}	0.98
LN6	0.08	1.0	5.75×10^{-5}	5.01×10^{-7}	1.00
LN7	0.00	2.0	8.07×10^{-4}	1.18×10^{-5}	0.88
LN8	0.02	2.0	4.58×10^{-4}	5.44×10^{-6}	0.88
LN9	0.05	2.0	1.29×10^{-4}	8.79×10^{-7}	0.96
LN10	0.08	2.0	7.53×10^{-5}	6.11×10^{-7}	1.00
LN11	0.10	2.0	3.39×10^{-5}	2.99×10^{-7}	1.01
LN12	0.12	2.0	1.54×10^{-5}	1.10×10^{-7}	1.05
LN13	0.15	2.0	4.58×10^{-6}	5.27×10^{-8}	1.05

the basicity moderating parameter for cation i given by

$$\gamma_i = 1.36(x_i - 0.26) \quad (4)$$

where x_i is the Pauling electronegativity [17]. The value of A_{th} for different compositions are included in Table 1.

3.2. DC conductivity

The results of conductivity measurements as a function of temperature over the range 27–250°C for different compositions containing 2.0 mol% of V_2O_5 are shown in Fig. 2. It is clear that conductivity of $\text{NiO} \cdot \text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ glasses decreases with NiO concentration. For the temperature higher than 130°C, the data fitting and the value of activation energy W are determined by using the expressions as discussed in our earlier paper [4] and is given in Table 3. From the table, it is found that conductivity increases when 1.0 mol% of V_2O_5 is replaced by 2.0 mol% of V_2O_5 in the same glass composition i.e. activation energy decreases when we add 2.0 mol% of V_2O_5 instead of 1 mol%.

3.3. DSC

Typical DSC curves of $x\text{NiO} \cdot (0.3 - x) \cdot \text{Li}_2\text{O} \cdot 0.7\text{B}_2\text{O}_3$ unannealed glass samples containing 1.0 and 2.0 mol% V_2O_5 recorded at heating rate $10^\circ\text{C min}^{-1}$ are shown in Fig. 3(a) and (b), respectively. The characteristic glass transition temperature is presented in Table 1. The T_g decreases when V_2O_5 is varied from 1.0 to 2.0 mol%. The compositional dependence of T_g on $0 \leq x \leq 0.12$ in these glasses is observed to increase with x .

4. Discussion

4.1. EPR

Hecht and Johnston [1] studied extensively the EPR and optical spectra of V^{4+} ion in soda boric oxide glasses and

found that vanadyl exists in the sample with one of the two possible symmetries i.e. threefold symmetry or fourfold symmetry. An octahedral site symmetry with tetragonal compression would give $g_{\parallel} < g_{\perp} < g_e$ and $A_{\parallel} > A_{\perp}$ [1]. The value of SHP obtained in the present study satisfies this relation. Thus it is concluded that V^{4+} ion in nickel borate glasses exist as VO^{2+} ions in octahedral coordination with a tetragonal compression and belongs to C_{4v} symmetry.

Tables 1 and 2 indicate that in $\text{NiO} \cdot \text{Li}_2\text{O} \cdot \text{B}_2\text{O}_3$ glasses SHP do not vary for $\text{NiO} \leq 5.0$ mol%, whereas for higher (≥ 8.0 mol%) of NiO the value of g_{\perp} , A_{\perp} , A_{\parallel} , K and $\Delta g_{\parallel}/\Delta g_{\perp}$ increase and g_{\parallel} , P and A'_{\parallel} decrease with NiO content.

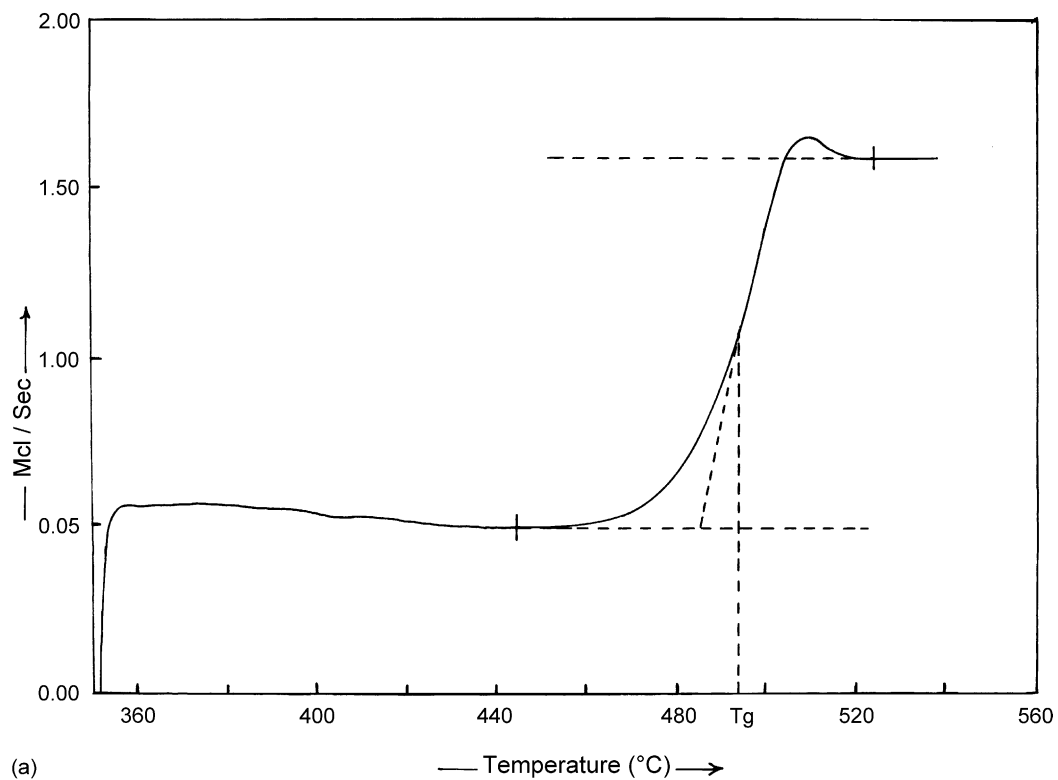
The increase in the value of K with increase in $\text{NiO}:\text{Li}_2\text{O}$ ratio suggests an increase in the tetragonal nature of the V^{4+}O_6 complex due to strongly bonded atom at the V^{4+} ion in the site opposite to the vanadyl oxygen [2]. The increase in $\Delta g_{\parallel}/\Delta g_{\perp}$ with increasing NiO content of the unannealed glass also supports the observation that tetragonal distortion around vanadyl ion is increased with the concentration of the NiO. The decrease in the value of P with NiO indicates that the $3d_{xy}$ orbit of unpaired electron in vanadium expands and so its interaction with the nucleus decreases. Decrease in the value of $|A'_{\parallel}|$ to the hyperfine splitting also support the argument that due to expansion of the $3d_{xy}$ orbital, there is a decreased interaction between the magnetic electron with the vanadium nucleus.

g_{\parallel} and g_{\perp} are related to bonding parameters by the following equations [12]:

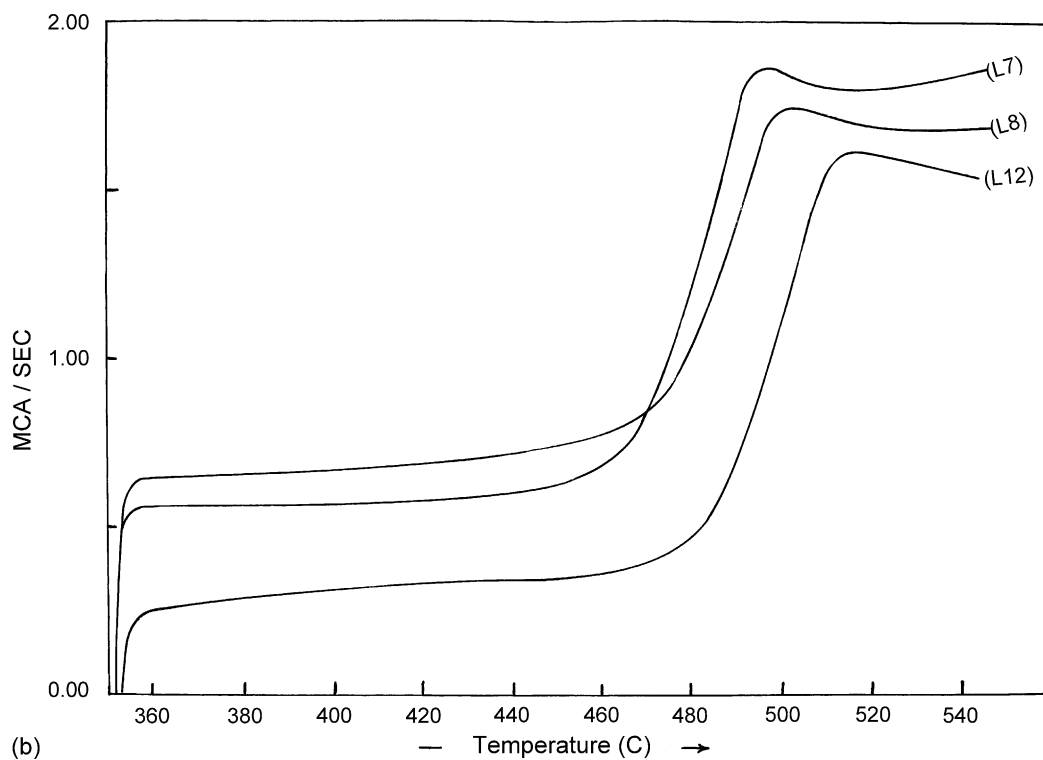
$$(1 - \alpha^2) = 1 - \left[1 - \frac{g_{\parallel}}{g_e} \right] \frac{E_2}{4\lambda\beta^2} \quad (5)$$

$$(1 - \gamma^2) = 1 - \left[1 - \frac{g_{\perp}}{g_e} \right] \frac{E_1}{\lambda\beta^2} \quad (6)$$

where E_1 and E_2 are the energy of transitions $\Delta E(b_2 \rightarrow e_{\pi}^*)$ and $\Delta E(b_2 \rightarrow b_1^*)$, respectively. β^2 is the measure of the in-plane π bonding with the equilateral ligands and is assumed to be equal to 1 for many glasses containing VO^{2+}



(a)



(b)

Fig. 3. (a) Typical DSC trace with heating rate of $10^{\circ}\text{C min}^{-1}$ showing the glass transition temperature (T_g) for glass L3. (b) Typical DSC traces with heating rate of $10^{\circ}\text{C min}^{-1}$ showing the glass transition temperature for glass L7, glass L8 and glass L12.

ion [13]. λ is the spin orbit coupling constant and $(1 - \alpha^2)$ gives an indication of the effect of σ bonding between vanadium atom and equatorial ligands, while $(1 - \gamma^2)$ indicates the effect of π bonding with the vanadyl oxygen. Assuming E_1 and E_2 to be the constant for our samples, a decrease in g_{\parallel} gives a decrease in $(1 - \alpha^2)$ and increase in g_{\perp} gives an increase in $(1 - \gamma^2)$ which indicate a decrease in the σ bonding and increase in π bonding with increase in NiO:Li₂O ratio i.e. the covalency of the vanadium oxygen bonds decreases, thus the $3d_{xy}$ expands which is consistent with the variation in the A'_{\parallel} , A'_{\perp} and P .

As shown in Table 1, the theoretical value of optical basicity, A_{th} decreases from L1 to L13 glass samples with an increase in the NiO:Li₂O ratio. In a first approximation, A_{th} gives a measure of the ability of the oxygen to donate a negative charge to the probe ion [18]. In other words, it reflects the Lewis basicity of oxide glasses. As the ability of the equatorial ligands to donate the electron (i.e. the Lewis basicity) decreases with increase in concentration of NiO, it reduces [18] the σ bondings between V^{4+} and the equatorial ligands. This reduction, in turn, increases the positive charge of V^{4+} and increases π bonding between V^{4+} and the vanadyl (oxygen). As a result, bond length of V^{4+} and the vanadyl (oxygen) decreases and the tetragonal distortion of $V^{4+}O_6$ complex increases. This is in agreement with the experimental findings.

4.2. DC conductivity

The dependence of temperature on DC conductivity of the studied glasses is shown in Fig. 2 for ternary borate glasses containing 2.0 mol% of V_2O_5 . The DC conductivity increases and activation energy decreases when concentration of V_2O_5 varies from 1.0 to 2.0 mol%. From Fig. 2, following observations can be made

1. DC conductivity decreases when Li₂O is replaced by NiO.
2. The change in conductivity with temperature is larger at high temperature than that at low temperature.

Similar results are observed by others [7,19–22], in different oxide glasses. Decrease in conductivity with increase in NiO:Li₂O ratio indicates that the mobility of alkali ions responsible for conduction are blocked by Ni ions. Hence addition of NiO in the samples shows “blocking effect” on the overall mobility of lithium ions. Similar argument was considered by Khan and co-workers [7,22] for decrease in conductivity of sodium borate glass when nickel is added to it.

4.3. DSC

The correlation between T_g and glass structure has been studied extensively. In general, it is found that T_g of oxide glasses increases with the bond strength, cross-link density and closeness packing of the glass [23,24]. There is a tendency for the value of T_g to decrease with increasing

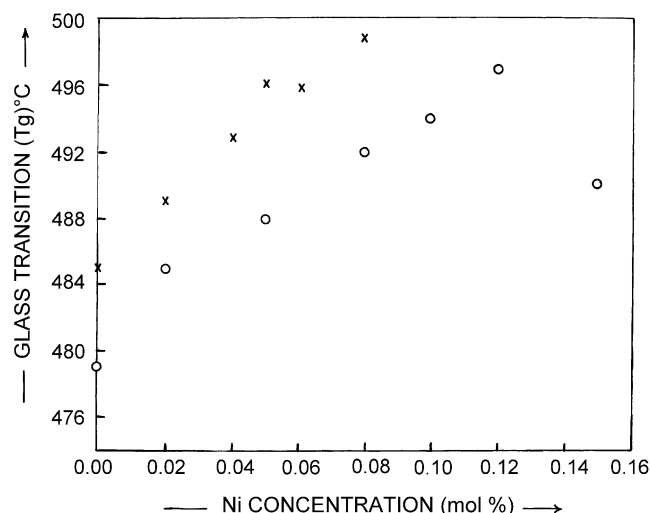


Fig. 4. Variation of T_g of $xNiO \cdot (0.3 - x)Li_2O \cdot B_2O_3$ glasses containing 1.0 mol% (x) and 2.0 mol% (o) of V_2O_5 determined by DSC.

single bond strength in alkali alkaline earth metaphosphate glasses [25]. This shows that single bond strength is one of the factors which controls the glass transition temperature in lithium borate glasses. In 1991, Koritala et al. [26] studied the glass transition temperature in lithium alkali borate glasses and found that T_g is in increasing order for the Li-Cs, Li-Rb, Li-K and Li-Na borate glass at low alkali contents. These differences were explained in terms of structural changes occurring in the glasses. In the present system, we consider the relationship between T_g and valence state of glass former and glass modifier. In oxide glasses, the divalent cations act as network modifier and they influence the glass transition temperature directly because the changing of the bond strength takes place during solid to liquid state transition. The variation of glass transition temperature with the ratio of NiO:Li₂O is shown in Fig. 4. From the figure, it is observed that T_g of the glass system increases with the increase in the concentration of NiO except at 15 mol% of NiO. The addition of NiO may strengthen the bonding of the glass network. This is due to the fact that lithium ions are monovalent and nickel ions are divalent. Hence with increasing concentration of NiO, the nickel ions are strongly bonded and the glass transition temperature of the system increases. At 15.0 mol% of NiO, the T_g decreases, it may be due to the change in the structure of the glass network. The above discussion suggests that the bond strength of the glass network increases which is indicated by the increased value of activation energy and glass transition temperature.

5. Conclusions

From the present study, we conclude that the change in concentration of V_2O_5 from 1.0 to 2.0 mol% results in virtually no change in the microscopic structure around the vanadium ion and $3d_{xy}$ orbit of unpaired electron in the

vanadium ion is expanded with increase in the ratio of NiO:Li₂O. Theoretical optical basicity of the NiO·Li₂O·B₂O₃ samples decrease when NiO is substituted for Li₂O suggesting that tetragonal distortion of V⁴⁺O₆ complex increases, which is in agreement with the experimental findings. DC conductivity increases when V₂O₅ is varied from 1.0 to 2.0 mol% and with increase in temperature. Ni ions show a “blocking effect” on the overall mobility of the ions and as a result conductivity of the samples decreases with increase in NiO:Li₂O ratio. The glass transition temperature T_g of NiO·Li₂O·B₂O₃ samples decreases when concentration of V₂O₅ varies from 1.0 to 2.0 mol%, which is supported by the decrease in the activation energy. The increase in T_g with NiO:Li₂O ratio indicates that the network is modified by the concentration of NiO in the glass system.

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