Spectroscopic studies on Lithium Iodide Borate glasses with small concentration of silver iodide doped with transition metal ion vanadium

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Abstract: The study on conductivity of super ionic glasses like LiI–AgI mixed with transition metal ions has been subject extensive investigation in the recent years due to their potential applications in solid state batteries. When these glasses are doped with multivalent transition metal ions like vanadium, mixed electronic and ionic, pure electronic or pure ionic conduction is expected depending upon the composition of the glass constituents.

Key words: Iodide Borate glasses, metal ion vanadium, vanadyl cations

Introduction

The study on conductivity of super ionic glasses like LiI–AgI mixed with transition metal ions has been subject extensive investigation in the recent years due to their potential applications in solid state batteries. When these glasses are doped with multivalent transition metal ions like vanadium, mixed electronic and ionic, pure electronic or pure ionic conduction is expected depending upon the composition of the glass constituents. Electronic conduction in this type of materials is predicted due to polaron hopping between different valent states of transition metal ions, whereas the ionic conduction is expected due to the diffusion of Li and Ag ions. Among various transition metal ions, the vanadium ions are considered as effective and useful dopant ions owing to the fact that they exist in different valence states with different co ordinations simultaneously in the glass network. Further, V_2O_5 containing glasses are being extensively used in memory and switching devices. Presence of vanadium ions in the multivalent states (viz., V^{4+} and V^{5+}) facilitate to accelerate the rate of hopping of electron between ions which ultimately lead to the enhancement of conductivity. The process of hopping of the electrons between V^{4+} and V^{5+} ions in the presence of larger concentrations of mobile cations like lithium and silver ions is highly interesting and useful to investigate, in view of technological importance of this material. The main objective of this paper is to explore the changes in conduction mechanism that take place with the varied oxidation states of vanadium ions in the glass network and the role of silver and lithium ions in this process by a systematic study on d.c conductivity and dielectric properties (viz., dielectric constant, loss and a.c conductivity over a wide range of frequency and temperature)

of LiI–AgI–B_2O_3 glasses mixed with varied concentrations of V_2O_5 from 0 to 1.0 mol %. Auxiliary experimental data viz., optical absorption and ESR that help to have some pre–assessment over the valence states of vanadium ions and their environment in the glasswork have also been reported.

1. Experimental

For the present study, a particular compositions (39–x) LiI–1.0 AgI–60 B_2O_3: x V_2O_5 with x ranging from 0 to 1.0 mol% is chosen. The detailed compositions are as follows:

V_0: 39 LiI–1.0 AgI–60 B_2O_3

V_2: 38.8 LiI–1.0 AgI–60 B_2O_3: 0.2 V_2O_5

V_4: 38.6 LiI–1.0 AgI–60 B_2O_3: 0.4 V_2O_5

V_6: 38.4 LiI–1.0 AgI–60 B_2O_3: 0.6 V_2O_5

V_8: 38.2 LiI–1.0 AgI–60 B_2O_3: 0.8 V_2O_5

V_{10}: 38.0 LiI–1.0 AgI–60 B_2O_3: 1.0 V_2O_5

Analytical grade reagents of H_3BO_3, LiI, AgI and V_2O_5 powders in appropriate amounts (all in mol%) were thoroughly mixed in an agate mortar and melted in a platinum crucible at 900 ± 10 °C in a PID temperature controlled furnace for about 1 h. The resultant bubble free melt was then poured in a brass mould and subsequently annealed at 250 °C. The amorphous nature of the samples was verified by X–ray diffraction technique (using Xpert's PRO panalytical X–ray diffractometer with CuK_α radiation).

Infrared transmission spectra were recorded on a JASCO–FT/IR–5300 spectrophotometer with a resolution of 0.1 cm^{-1} in the spectral range 400–2000 cm^{-1} using potassium bromide pellets (300 mg) containing pulverized sample (1.5 mg). These pellets were pressed in a vacuum die at ~ 680 MPa. The optical absorption spectra of the glasses were recorded at room temperature in the spectral wavelength range covering 400–1200 nm with a spectral resolution of 0.1 nm using JASCO Model V–670 UV–vis–NIR spectrophotometer. The electron spin resonance (ESR) spectra of the fine powders of the samples were recorded at liquid nitrogen temperature on JEOL JES–TES100 X–band EPR spectrometer.

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Spectroscopic properties

Optical absorption spectra

The absorption edge observed at 380 nm for the glass doped with 0.2 mol % of V_2O_5 is found to be shifted to slightly higher wavelength side with increase in the concentration of V_2O_5 upto 0.8 mol %. The spectrum of glass V_2 exhibited two absorption bands at 651 and 1070 nm. With the gradual increase in the concentration o of V_2O_5 upto 0.8 mol % in the glass matrix, the intensity of these bands is observed to increase with the shift of meta-centers towards slightly higher wavelength.

The vanadyl cations similar to lithium and silver ions are expected to depolymerize the glass network by creating more bonding defects and non-bridging oxygens (NBOs). Normally in the modifier oxides the oxygens break the local symmetry by rupturing the weak bonds whereas the cations occupy interstitial positions. Hence the higher the concentration of modifiers the higher is the concentration of defect centers. With the increase in concentration of vanadyl cations in the glass network , a large number of donor centers are thus created, and subsequently, the excited states of localized electrons originally trapped on V^{4+} sites begin to overlap with the empty 3d states on the neighboring V^{5+} sites, and as a

result, the impurity or polaron band becomes more extended into the main band gap. This new polaronic development might have shifted the absorption edge to the lower energy.

ESR Spectra

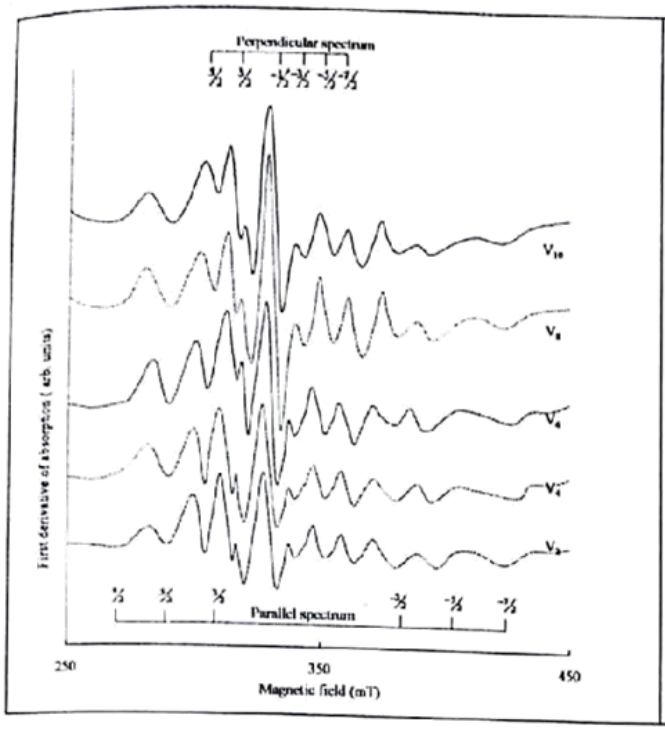
The ESR spectra are observed to be complex made up of resolved hyperfine components arising from unpaired $3d^1$ electron of V isotope. As the concentration of the dopant V_2O_5 is increased, an increasing degree of resolution and the intensity of the signal has been observed. The variation of ESR line intensity and the resolution with the concentration of V_2O_5 is obviously due to the variation in the concentration of V^{4++} ions and also due to the structural and microstructural modifications, which produce fluctuations of the degree of distortion or even of the coordination geometry of V^{4+} sites. The observed increase in the intensity of ESR signal with the concentration of V_2O_5 indicates the growing presence of V^{4+} ions and may also be due to the exchange coupling between V^{3+} ions and V^{4+} ions.

When the concentration of V_2O_5 is increased beyond 0.8 mol%, suppression in the hyperfine Data on ESR spectra of LiI–AgI–B_2O_3: V_2O_5 glasses structure has been observed. Such suppression may be due to the various interactions of electronic spins with their surroundings. In electronically conducting vanadate glasses such interaction occurs via so called super exchange of an electron, i.e., hopping of a mobile electron along a V^{4+}-o -V^{5+} bond. Thus, both optical absorption and ESR studies clearly suggest that there is an increasing fraction of vanadyl cations in the glass network with the increase in the concentration of V_2O_5 upto 0.8 mol%.%.

Data on ESR spectra of LiI – Ag I- V_2O_5 glasses

Glass	$g_{\parallel}$	$g_{\perp}$	$\Delta g_{\parallel}$	$\Delta g_{\perp}$	$\Delta g_{\perp}/\Delta g_{\perp\perp}$
V_2	1.914	1.946	0.090	0.056	0.622
V_4	1.915	1.947	0.089	0.053	0.596
V_6	1.919	1.949	0.086	0.051	0.593
V_8	1.923	1.952	0.085	0.049	0.576
V_{10}	1.910	1.943	0.088	0.052	0.591

Summary of data on optical absorption spectra of LiI-AgI-B_2O_3:V_2O_5
An illustration of transfer of electron from V4+ site to the neighboring new V5+ site.



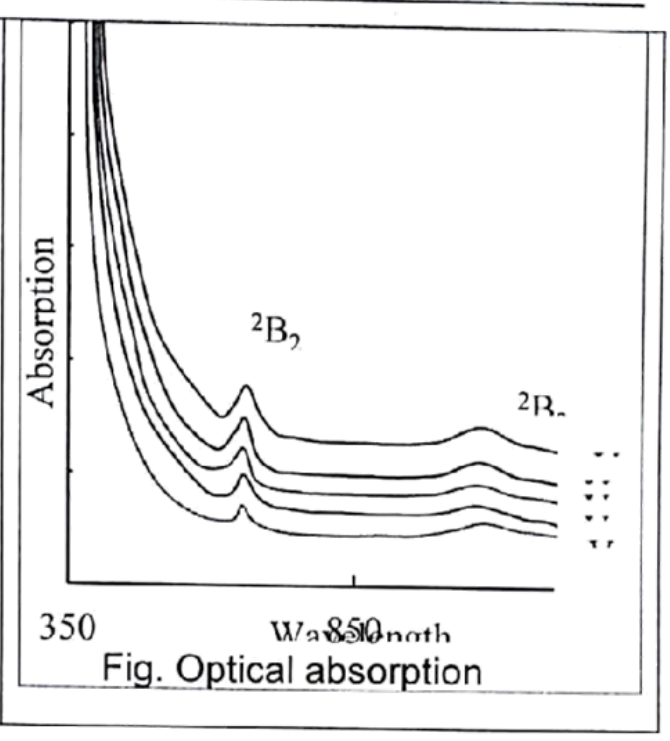
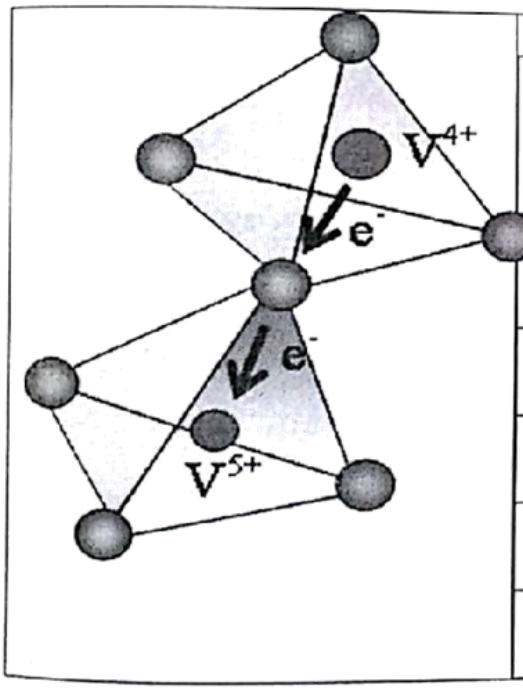


Fig. Optical absorption



Glass	Cut-off wave length (nm)	Band position (nm) $^2B_2 \rightarrow {}^2B_1$	Band position (nm) $^2B_2 \rightarrow {}^2E_1$	Optical bandgap (ev)
V_2	407	652.7	1077.7	3.05
V_4	397.7	655	1066.9	3.075
V_6	380	660	1072.9	3.1
V_8	394.4	658	1131	3.15
V_{10}	401.3	654.9	1063.9	3.25

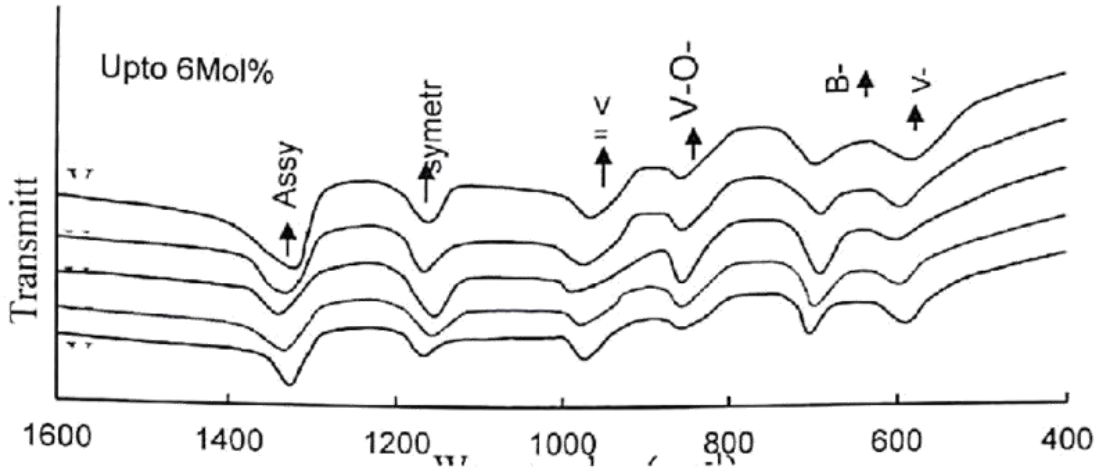


Fig. IR spectra of LiI-AgI-B_2O_3: V_2O_5 glasses

Conclusions:

- LiI–AgI–B2O3 glasses mixed with different concentrations of V_2O_5 (ranging from 0 to 1.0 mol %) were prepared.
- IR, Optical absorption, ESR of these glasses as a function of concentration of V_2O_5 have been investigated.
- Optical absorption and ESR studies have indicated that vanadium ions exist in V^{4+} state in addition to V^{5+}state.
- Thus, both optical absorption and ESR studies clearly suggest that there is an increasing fraction of vanadyl cations in the glass network with the increase in the concentration of V_2O_5 upto 0.8 mol %.

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