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Application of Metal Oxide in Litho-Vanadium Glasses Containing Non-Magnetic Metal Ions: Physical and Optical Properties Analysis

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Abstract

Sodium-modified litho-vanadium glasses containing non-magnetic Aluminium ions of composition $50Li_2CO_3$ *- (30-X)* Na_2CO_3*-* $20V_2O_5$ *-x*Al_2O_3 *(*$30 \leq x \geq 5$*) (LNVA) glasses were prepared by melt quenching technique. The density of the glass samples was measured and found to increase with the Aluminium content of the glass matrix. The measured values of refractive index and polaron radius of the glass network show opposite behaviour with an increase of Aluminium content. Through band gap energy and refractive index, Oxide ion polarizability and electronic polarizability were determined by using the Lorentz-Lorenz equation. The value of Oxide ion polarizability and electronic polarizability is found to be decreased with decreasing band gap energy and increasing refractive index. The value of optical basicity was measured using electronic polarizability and is found to be decreased with decreasing inter-nuclear distance. The band gap energy values of the glass network were found to decrease from 3.241 to 2.134 eV. The metallisation criterion of the glass material was calculated and found to decrease with Aluminium content.*

Keywords: *Basicity, Lithium, Metal Oxide, Refractive Index*

1.0 Introduction

Glasses have many more applications in the field of technology and industrial domine. The Lithium and Sodium, the mixed Alkali outcome is one of the upright problems in the glass discipline[1-4]. The physical properties of the Oxide glasses show non-linear behaviour in the presence of Alkali content. The content of one Alkali ion is steadily substituted by another Alkali ion with the condition of total Alkali content in the glass matrix remaining constant, this is known as the mixed Alkali effect. Not much study has been done on the mixed Alkali effect with Vanadium glasses. However, the literature survey shows some studies on the effect of mixed Alkali ions, which are purely based on dynamic study. On the other hand, the optical and spectroscopic studies reveal valuable information on the mixed Alkali effect[5,6].

The V_2O_5, transition metal Oxide (semiconductor) glasses have much attenuation towards material science and solid-state chemistry with much affection to their application as switching devices[7-10].

Oxide glasses containing V_2O_5 behave as semiconductors and take part in the exchange of electrons among vanadium (V) and vanadium (IV) cores.

$$V^{5+} - O - V^{4+} \text{ or } V^{4+} - O - V^{5+}$$

Vanadate glasses are recognized as n-type semiconductors with a low V^{4+}/V^{5+} ratio. It is also identified that V^{5+} in low ratio arrives at the amorphous structure as an impurity but V^{5+} in high ratio in the structure behaves

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as glass former[11]. Oxide glasses containing transition metal ions show outstanding spectroscopic properties. The alumina crucibles are extensively used in glass preparation and the Aluminium Oxide inset in the glass matrix improves the stability and reduce the non-linear optical properties[12].

In the present study, we discussed some of the physical and optical properties of the Sodium-modified Litho-vanadium glasses containing Aluminium Oxide for their stability and to know the metallic nature of the glass network.

2.0 Experimental

Litho-vanadium Sodium glasses containing non-magnetic metal ions were prepared using pure Sigma-Aldrich chemicals of Lithium Carbonate (Li_2CO_3), Sodium Carbonate (Na_2CO_3), Vanadium Oxide (V_2O_5) and Aluminium Oxide (Al_2O_3) in composition $50Li_2CO_3$ - (30-X) Na_2CO_3- $20V_2O_5$ -xAl_2O_3. The 12g mixture of each sample was taken in a porcelain crucible and kept in an electrical furnace at 500^0C for about 2 hours and gradually increased up to 900^0C to get a homogeneous liquid. This molten liquid was quenched between two brass plates to get the glass sample. The glass sample was then kept for annealing at 200^0C for about 4 hours to remove the thermal strain developed at the time of quenching.

After the annealing process, the glass samples were polished and cut into the desired shape to study their metallic nature and some of the physical and optical properties

3.0 Results and Discussion

3.1 Density and Molar Volume Measurement

The density of the investigated samples was determined using the principle of Archimedes at normal room temperature. The sample weight was measured in air first and then measured in acetone liquid. Using the above weights, the density of the samples was calculated by the relation

$$\rho = \frac{W_{air}}{W_{air} - W_{acetone}} X\, 0.791\ g/c\,c \tag{1}$$

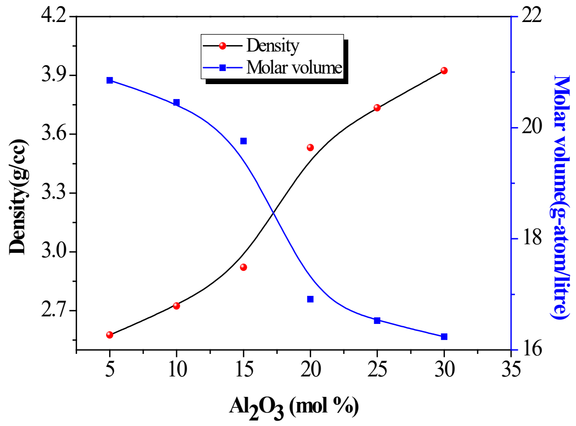

Figure 1. Variation of density and molar volume with Al_2O_3 content.

The molar volume of the glass samples was measured based on the density and molecular weight of the sample. The density and molar volume of the glass sample were measured three times for the sample glass sample for its consistency. The value of density is found to be increased and the molar decreases due to the increase in compactness of the glass samples with the addition of non-magnetic metal ions.

3.2 Molar Refractive Index

Using the values of refractive index (n) and molar volume (Vm), the molar refractive index (Rm) can be calculated by Lorentz-Lorenz formula[13].

$$R_m = \left(\frac{n^2 - 1}{n^2 + 1}\right) V_m \tag{2}$$

3.3 Refractive Index

The refractive index of Sodium-modified Litho-vanadate glasses was estimated from the band gap energy values using the equation:

$$\frac{n^2 - 1}{n^2 + 1} = 1 - \sqrt{\frac{E_g}{20}} \tag{3}$$

The refractive index increases with Al^{3+} ions content in the glass matrix. The decrease in the polaron radius of Al^{3+} ions may be the reason for the increase of the

Table 1. The code, composition, band gap energy, density, molar volume and oxygen packing density

Code	Composition in mol%				Eg	ρ	Vm	OPD
	Li_2O	Na_2O	V_2O_5	Al_2O_3	(Ev)	(g/cm³)	(cm³/mol)	(g-atom/cc)
LNVA0	50	25	20	5	3.241	2.5763	24.3281	57.5474
LNVA1	50	20	20	10	2.978	2.7241	25.3922	63.5545
LNVA2	50	15	20	15	2.794	2.9213	20.3598	70.8558
LNVA3	50	10	20	20	2.657	3.5314	22.8038	88.6996
LNVA4	50	5	20	25	2.413	3.7346	25.2171	96.816
LNVA5	50	0	20	30	2.134	3.9241	25.2171	104.695

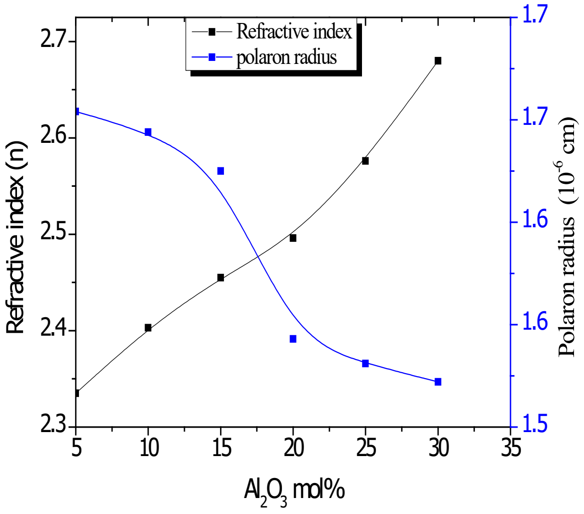

Figure 2. Variation of refractive index and polaron radius with Al_2O_3 content.

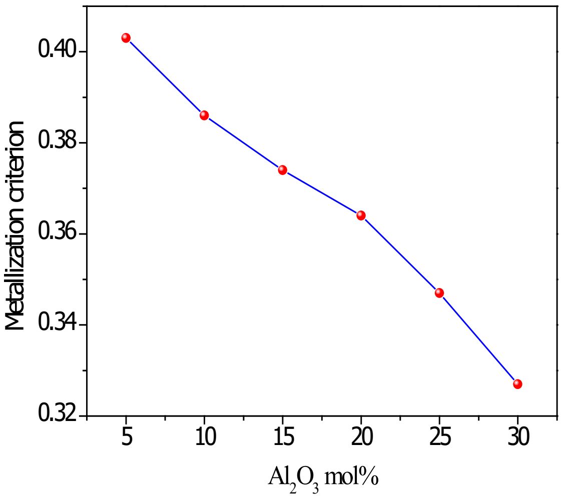

Figure 3. Variation of metallization criterion with Al_2O_3 content.

refractive index. Figure 2 shows the variation of refractive index and polaron radius with Al_2O_3 content[14].

3.4 Reflection Loss

The reflection loss of the glass surface increases with the increase of the refractive index. The values of reflection loss can be estimated using the equation:

$$R_L = \frac{(n-1)^2}{(n+1)^2} \tag{4}$$

3.5 Transmission Coefficient

The Transmission Coefficient (T) of the glass can be estimated using the refractive index values by the equation[15]:

$$T = \frac{2n}{n^2+1} \tag{5}$$

3.6 Polaron Radius

The polaron radius of LNPA glasses decreases with the increase of Al^{3+} ions concentration. The polaron is said to be a small polaron if the polaron radius is equal to the order of the lattice constant. The polaron is said to be large polaron if the polaron radius is greater than the order of lattice constant. Normally, the polaron radius and polarizability of the glass samples show the opposite behaviour[16]. The LNVA glasses show the same decreasing trend between polaron radius and Oxide polarizability suggesting that present glasses are more basic. The polaron radius of the glass matrix was calculated using the equation:

$$R_p = \frac{1}{2}\left(\frac{\pi}{6N}\right)^{\frac{1}{3}} \tag{6}$$

3.7 Oxygen Packing Density

Oxygen packing density refers to the compactness of the glass network and it can be calculated using the relation[17]:

$$OPD = X\left(\frac{\rho}{m_w}\right) \tag{7}$$

Where X is the number of oxygen atoms in a glass, is the density of the glass and is the molar weight of the glass sample. The values of OPD for different concentrations of Aluminium in the glass network are listed in Table 1. It can be seen from the Figure that OPD increases with Aluminium content which depicts the rigidness of the glass increases. As Na^+ is replaced by Al^{3+}, its occupation in the interstitial position leads to a decrease in the volume occupied by the atoms.

3.8 Electronic Polarizability

The electronic polarizability of the glass matrix depends on the molar refraction and is given by the equation:

$$\propto_m = R_m\left(\frac{3}{4\pi N}\right) \tag{8}$$

Where R_m is the molar refraction and N is Avogadro's number.

The electronic polarizability is built up in the glass which depends on how the electrons respond to an electric field represented by the Lorentz-Lorentz equation[18].

3.9 Optical Basicity

Optical basicity means the acid-base Oxide glass properties. The polarization effect produces the transferring of electron density to the surrounding cations by the Oxygen atoms. Determination of an optical basicity using electronic polarizability by the Duffy relation[19] and the values are presented in Table 2.

Table 2. Physical and optical properties of glass samples

Physical and Optical Properties	LNVA-0	LNVA-1	LNVA-2	LNVA-3	LNVA-4	LNVA-5
Li^{2+} concentration (x 10^{16} ion/cm3)	1.444	1.472	1.524	1.78	1.822	1.854
Polaron radius (rp)(x 10^{-6}cm)	1.654	1.644	1.625	1.543	1.531	1.522
Inter nuclear distance (ri) (x 10^{-3}cm)	4.106	4.08	4.033	3.829	3.8	3.777
Field Strength(F)(x10^{16} cm-2)	1.095	1.109	1.135	1.26	1.279	1.294
Refractive Index (n)	2.335	2.403	2.455	2.496	2.576	2.680
Reflection loss (%)	0.16	0.169	0.177	0.183	0.194	0.208
Dielectric constant(ε)	5.452	5.774	6.026	6.231	6.636	7.184
Optical dielectric constant(dpt/dp)	4.452	4.774	5.026	5.23	5.636	6.184
Molar Refraction (R_M) (cm-3)	12.4588	12.562	12.373	10.747	10.786	10.933
Electronic polarizability(αm)(A')3	4.941	4.982	4.907	4.262	4.277	4.336
Glass Oxide polarizability (αm2-)(A')3	3.199	2.991	2.729	2.121	2.003	1.923
Optical basicity (∧)	0.821	0.811	0.802	0.791	0.782	0.772
Transmission coefficient	0.723	0.709	0.698	0.69	0.674	0.655
Metallization criterion	0.403	0.386	0.374	0.364	0.347	0.327

$$\Lambda = 1.61\left(1 - \frac{1}{\alpha_m}\right) \tag{9}$$

Where α_m is electronic polarizability

The optical basicity values are found to decrease with the increase of Aluminium content which indicates the stability of the glass network[20].

3.10 Dielectric Constant

The dielectric constant of the glass depends on the band gap energy of the glass. The dielectric constant can be calculated using the equation[21].

$$\varepsilon = n^2 \tag{10}$$

3.11 Metallization Criterion of the Glass Sample

Dimitrov and Komatsu explained the metallization criterion of the glass samples, metallic and non-metallic nature of the glass could be verified under two regimes: 1) If the ratio of molar refraction (Rm) to molar volume (Vm) is greater than 1 depict the metallic nature of the glass 2) If the ration of molar refraction (Rm) to molar volume (Vm) is less than 1 depicts the non-metallic nature of the glass[22]. Subtracting the ratio of Rm/Mv gives the metallization criterion.

$$M = 1 - \frac{R_m}{V_m} \tag{11}$$

Using the Lorenz-Lorenz equation, the metallization criterion based on band gap energy and refractive index can be determined by the equation

$$M = 1 - \frac{(n^2 - 1)}{(n^2 + 2)} = \sqrt{\frac{E_g}{20}} \tag{12}$$

The metallic state of the glass occurs when Equation (12) is equal to zero. Owing to the resemblance of the two quantities inclined to be zero, Duffy projected that there is a relationship between molar refraction and the energy gap of the glass sample[23]. Dimitrov and Sakka estimated the metallization criterion for Oxide glass samples and found that glass sample with high refractive index and low band gap energy has low metallization criterion compared to the low refractive index and high band gap energy[24]. The glass sample which has a high metallization criterion close to 1 said to be insulators. The values obtained for the metallization criterion are presented in Table 2. It can be seen from Figure 3 that the metallization criterion of the glass decreases with Al_2O_3 content. This is due to the increasing refractive index and decreasing band gap energy. Figure 4 shows the variation of band gap energy with Al_2O_3 content.

4.0 Conclusion

The Sodium-modified Litho-vanadium glasses tend to have a metallic behaviour with Aluminium content. The metallization criterion of the current samples decreases with increasing Aluminium content in the network. This kind of nature is produced due to decreasing band gap energy and increasing refractive index values for the LNVA glasses. The decreased value of the metallization criterion in the glass sample depicts that the glass is metalizing. Many other physical and optical properties have been calculated and show that the glass material has high reflection loss and low transmission coefficient. The optical basicity of the network indicates a linear decrease with a decreasing number of Oxide ion polarizability. The optical basicity values indicate the glass sample is more basic.

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6.0 References

1. Paramesh SO, Hanumantharaju N, Gowda VVC, Venkateshulu A. Influence of Boron ions on physical and optical properties of Gd3+ ions doped Lithium borate glasses. Sambodhi. 2021; 44:2249-6661.
2. Isard JO. The mixed Alkali effect in glass. J Non-Cryst Solids. 1969; 1:235-261.https://doi.org/10.1016/0022-3093(69)90003-9
3. Maass P, Bunde A, Ingram MD. Ion transport anomalies in glasses. Phys Rev Lett. 1992; 68:3064. https://doi.org/10.1103/PhysRevLett.68.3064 PMid:10045598
4. Greaves GN, Ngai KL. Reconciling ionic-transport properties with atomic structure in Oxide glasses.

Phys Rev B. 1995; 52:6358. https://doi.org/10.1103/PhysRevB.52.6358 PMid:9981865

5. Ratnakaram YC, Sreekanth Chakradhar RP, Ramesh KP, Rao JL, Ramakrishna J. The effect of host glass on optical absorption and fluorescence of Nd^{3+} in $xNa_2O-(30-x)K_2O-70B_2O_3$ glasses. J Phys Condens Matter. 2003; 15:6715.
6. Chakradhar RPS, Ramesh KP, Rao JL, Rama-Krishna J. Mixed alkali effect in borate glasses- EPR and optical absorption studies in $xNa_2O-(30-x)K_2O-70B_2O_3$ glasses doped with Mn^{2+}. J Phys Chem Solids. 2003; 64:641. https://doi.org/10.1016/S0022-3697(02)00365-7
7. El-Damrawi G, Moustafa YM, Meikhail MS. Phase separation and NMR studies on Sodium Boro-silicate glasses containing V_2O_5. Mans Sci Bull C (Nat Sci). 1993; 20:83-97.
8. Singh K, Ratnam JS. Electrical conductivity of the Li_2O-B_2O_3 system with V_2O_5. Solid State Ionics. 1988; 31:221-6. https://doi.org/10.1016/0167-2738(88)90272-X
9. Khattak GD, Salim MA, Wenger LE, Gilani AH. X-ray Photoelectron Spectroscopy (XPS) and magnetic susceptibility studies of copper– vanadium phosphate glasses. J Non-Cryst Solids. 2000; 262:66-79. https://doi.org/10.1016/S0022-3093(99)00700-0
10. Rao RB, Veeraiah N. Study on some physical properties of $Li_2O-MO-B_2O_3$: V_2O_5 Glasses. Physica B. 2000; 348:256-71.
11. Dawy M, Salama AH. Electrical and optical properties of some Sodium borate glasses. Mater Chem Phys. 2001; 71:137-47.
12. Dimitrov V, Sakka S. Linear and nonlinear optical properties of simple Oxides. II. J Appl Phys. 1996; 79:1741-5. https://doi.org/10.1063/1.360963
13. Bhatia B, Meena SL, Parihar V, Poonia M. Optical basicity and polarizability of Nd^{3+} doped bismuth borate glasses. New J Glas Ceram. 2015; 44-52.
14. Eevon C, Halimah MK, Zakaria A, Azurahanim CAC, Azlan MN, Faznny MF. Linear and nonlinear optical properties of Gd^{3+} doped zinc borotellurite glasses for all-optical switching applications. Results Phys. 2016; 6:761-6. https://doi.org/10.1016/j.rinp.2016.10.010
15. Ismail RA. Characteristics of bismuth triOxide film prepared by rapid thermal oxidation. J Surf Sci Nanotech. 2006; 4:563-5. https://doi.org/10.1380/ejssnt.2006.563
16. Guo H, Wang Y, Gong Y, Yin H, Mo Z, Tang Y, Chi L. Optical band gap and photoluminescence in heavily Tb^{3+} doped GeO_2 -B_2O_3 -SiO_2 -Ga_2O_3 magneto-optical glasses. 2016; 686:635-40. https://doi.org/10.1016/j.jallcom.2016.06.074
17. Pavani PG, Sadhana K, Chandra Mouli V. Optical, physical and structural studies of boro-zinc tellurite glasses. Phys B Condens Matter. 2011; 406(6–7):1242–7. https://doi.org/10.1016/j.physb.2011.01.006
18. Dimitrov V, Komatsu T. An interpretation of optical properties of oxides and oxide glasses in terms of the electronic ion polarizability and average single bond strength. J Univ Chem Technol Metall. 2010; 45:219-50.
19. Duffy JA. Electronic polarisability and related properties of the Oxide ion. Phys Chem Glasses. 1989; 30:1-4.
20. Hammad AH, Abdelghany A. Optical and structural investigations of zinc phosphate glasses containing vanadium ions. J Non-Crystal Solids. 2016; 433:14-9. https://doi.org/10.1016/j.jnoncrysol.2015.11.016
21. Meena SL, Bhatia B. Polarizability and optical basicity of Er^{3+} ions doped zinc Lithium bismuth borate glasses. J Pure Appl Ind Phys. 2016; 6(10):175-83.
22. Dimitrov V, Komatsu T. Classification of oxide glasses: A polarizability approach Journal of solid state chemistry. 2005; 178 (2005):831-46. https://doi.org/10.1016/j.jssc.2004.12.013
23. Duffy JA, Ingram MD. An interpretation of glass chemistry in terms of the optical basicity concept. J non-cryst Solids. 1976; 21:373-410. https://doi.org/10.1016/0022-3093(76)90027-2
24. Dimitrov V, Sakka S. Electronic oxide polarizability and optical basicity of simple Oxides. J Appl Phys. 1996; 79:1736-40. https://doi.org/10.1063/1.360962