International Archive of Applied Sciences and Technology
Int. Arch. App. Sci. Technol; Vol 5 [1]March 2014: 65-69

[ISO 9001: 2008 Certified Organization]
www.soeagra.co/iaast.html

IAAST
ONLINE ISSN 2277- 1565
PRINT ISSN 0976 - 4828

CODEN: IAASCA ORIGINAL ARTICLE

Optical Absorption Study of Different Concentration of Nd^{3+} ion in Zinc Lithium Bismuth Borate Glass

Vishal Parihar[1], Beena Bhatia[1] and Sanjay Singh[2]
[1]Ceramic Laboratory, Department of Physics, Jai Narain Vyas University Jodhpur 342001(Raj.) India
[2]Department of Physics, Chintamani College of Arts And Science Gondpipri (GU)442702(MS.) India
E-mail address - vishalsekhala@yahoo.co.in,sanjay2010.in@rediffmail.com

ABSTRACT
A new family of three optical glasses of (60-x) B_2O_3-10Bi_2O_3-20Li_2O-10ZnO-xNd_2O_3 with x =1, 1.5 and 2 were prepared by melt quenching technique. The amorphous nature of the prepared glass samples was confirmed by X-ray diffraction. The absorption spectra of three Nd^{3+} doped zinc lithium bismuth borate (ZLiBiB) glasses have been recorded at room temperature. Nine bands in the region 450-900 nm have been observed. Slater-Condon parameters F_k (k=2, 4 and 6), Lande's parameter ξ_{4f} and Racah parameters E^k (k=2, 4 and 6) have been computed. Using these parameters energies and intensities of these bands has been calculated. To study the nature of bonding in doped glasses nephelauxetic ratio (β') and bonding parameter ($b^{1/2}$) have also been computed. The intensities of the f-f transitions in the absorption spectra have been analyzed by the application of the Judd-Ofelt theory. J-O parameters (Ω_λ) have been computed. The spectroscopic quality factor related with the rigidity of the glass system is aso discussed.
***Keywords**: Nd^{3+}: ZLiBiB glasses, Energy interaction parameters, optical properties, Judd-Ofelt analysis*

Received 01/01/2014 Revised 19/01/2014 Accepted 01/02/2014

INTRODUCTION

Glasses containing heavy metal oxides (HMO) are of great interest due to their wide range of applications in the area of glass ceramics. Borate glasses containing unconventional Bi_2O_3 as network modifiers possess high density, high refractive index, high optical basicity, extended far IR transmission and high non-linear optical susceptibility [1-4]. It has been made clear that B_2O_3 could be used as a good network former (NWF) and other chemicals such as Bi_2O_3, Li_2O and ZnO could be found as network modifiers (NWM) when these are added to the B_2O_3 content. Bismuth oxide cannot be considered as a glass network former due to low field strength (0.53) of Bi^{3+} ion. However, in combination with B_2O_3 glass former it is possible to obtain glasses in a relatively large compositional ranges. A survey of literature shows that there are many reports available on ternary bismuth borate glasses [5-8].

In rare earth doped borate glasses the central rare earth ion is surrounded by BO_3 polymeric structure (boroxol ring) and BO_4 units. When Bi_2O_3 is added to the glass, a progressive conversion of BO_3 units to BO_4 units takes place [9, 10]. With the increase of BO_4 units surrounding the central rare earth ion, the glass becomes more covalent, enhances the line strengths, effective fluorescence line widths decreases and the refractive index of the material increases. Covalency of the rare earth doped bismuth borate glass can be further increased [11- 13] by co-doping the glass with Li_2O and ZnO.

In the present work, the absorption spectra of Nd^{3+}doped ZLiBiB glasses have been investigated. From the spectral data various energy interaction parameters like Slater-Condon parameters F_k (k=2, 4 and 6), Lande parameter ξ_{4f} and Racah parameters E^k (k=2, 4 and 6) have been computed. Nephelauxetic Ratio (β') and Bonding Parameters ($b^{1/2}$) have also been computed from these parameters to study the nature of bonding in doped glasses. The intensity of the transition for the RE^{3+} -ions has been calculated in term of Judd-Ofelt theory [14, 15]. This theory is known for a set of three intensity parameter Ω_λ (λ = 2, 4 and 6) which are useful to the environment of trivalent rare earth ions. To understand the laser efficiency of these materials, the value of spectroscopy quality factor (Ω_4/ Ω_6) has been evaluated.

EXPERIMENTAL

Nd^{3+}- zinc lithium bismuth borate glasses were synthesized by the conventional melt quenching method [16]. The starting chemicals used were reagent grade of H_3BO_3, Bi_2O_3, Li_2CO_3 and ZnO, Nd_2O_3 with more than 99.99% purity. The chemical compositions of the prepared glasses are as follows: (60-x) B_2O_3-10Bi_2O_3-

$20Li_2O$-$10ZnO$-xNd_2O_3 where x =1, 1.5 and 2 mol%. The raw materials were thoroughly mixed and ground in an agate pestle mortar in 15 g batches. The mixture was then melted in alumina crucibles in silicon carbide based an electrical furnace for 2h at 1050^0 C. The molten glass was then poured in a muffle furnace on to a steel mould and annealed at temperature of 350^0 C for 1 h to remove thermal strains and stresses. Every time fine powder of cerium oxide was used for polishing the samples. Optically transparent and bubble-free glasses were selected for optical studies.

1, 1.5 and 2 mol% of Nd^{3+}: ZLiBiB glasses are labeled as ZLiBiB (1), ZLiBiB (1.5) and ZLiBiB (2) respectively. By Applying Archimede's principle, the glass densities were measured with Xylene as an immersion liquid on a single-pan electrical balance to the nearest 0.0001 g. The error in density measurement is estimated to be ±0.004 g cm^{-3}. The refractive indices of these glasses have been measured at λ = 589.3 nm on an Abbe refractometer with an accuracy of ±0.001. The sample being glassy, it requires an adhesive coating on its surface, preferably 1-monobromonaphthalene as the contact layer between the sample and prism of the refractometer by using a sodium vapor lamp.

X-ray diffractogram of glass samples were studied with PANalytical X'pert Pro MPD diffractometer of CuKα radiation (1.5406 Å) system. The absorption spectra of these glasses were recorded between wavelength ranges 450-900 nm with a Perkin-Elmer Lambda 750 UV/VIS/NIR Spectrophotometer at room temperature.

Table 1. Physical properties of Nd^{3+} doped ZLiBiB glasses

Physical properties	ZLiBiB (1)	ZLiBiB (1.5)	ZLiBiB (2)
Refractive Index n_d, at 589.3 nm	1.662	1.661	1.659
Density, d (g/cm)	3.8602	3.8608	3.8610
Thickness, t (cm)	0.304	0.309	0.308
Average molecular weight $\overline{M}$ (g)	105.15	106.49	107.82
Rare earth ions concentration N ($\times 10^{21}$ ions/cms)	2.211	3.275	4.314
Dielectric Constant (ε)	2.762	2.759	2.752
Optical Dielectric Constant (pdt/dp)	1.762	1.759	1.752
Molar Volume V_m (gm/cm^3)	27.240	27.582	27.925
Mean atomic volume (gm/cm^3/atom)	0.0633	0.0641	0.0649
Reflection losses (R)	6.184	6.170	6.142
Molar refractivity (R_m)	10.080	10.194	10.297
Polaron radius (r_p)(A^0)	3.093	2.714	2.475
Interionic distance (r_i)(A^0)	7.676	6.734	6.143
Electronic polarizability α_e (10^{-23} ions cm^{-3})	3.996	2.695	2.041
Field strength F($10^{16}\times cm^{-2}$)	0.3178	0.4195	0.5028

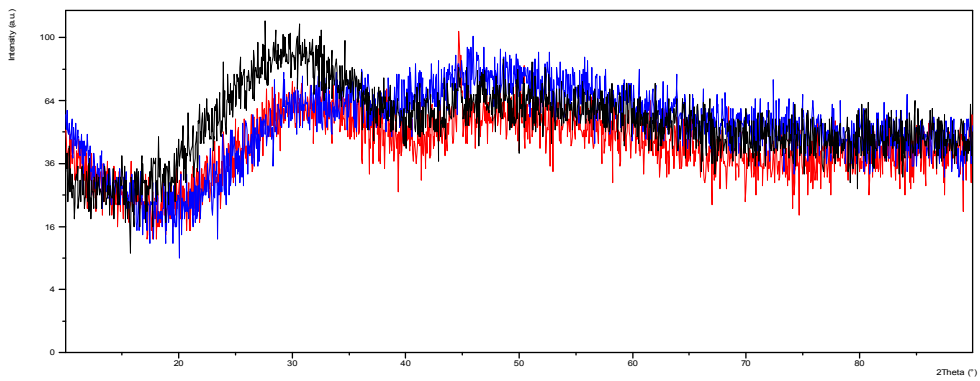

Fig.1. XRD Pattern of Nd^{3+} : ZLiBiB glasses

Result and discussion

The XRD patterns of all the glasses are shown in Fig.1, which confirmed its amorphous nature. The various physical properties of all the glass samples are presented in Table 1. An increase in the average molecular weight ($\overline{M}$) influences significantly both the refractive index and density. However the electronic polarizability (α_e), polaron radius (r_p), interionic distance (r_i) slightly decreased with the increase of rare

earth ions. The absorption spectra of Nd^{3+} doped ZLiBiB glass specimens have been presented in Fig. 2 in terms of relative absorption $\log(I_0/I)$ versus wavelength (nm), where I and I_0 are intensities of the radiation transmitted through doped specimens and undoped specimens of equal thickness. Nine absorption bands have been observed from the ground state $^4I_{9/2}$ to excited states $^4F_{3/2}$, $^4F_{5/2}$, $^4F_{7/2}$, $^4F_{9/2}$, $^2H_{11/2}$, $^4G_{5/2}$, $^4G_{7/2}$, $^4G_{9/2}$, and $^2G_{9/2}$ for Nd^{3+} doped ZLiBiB glasses.

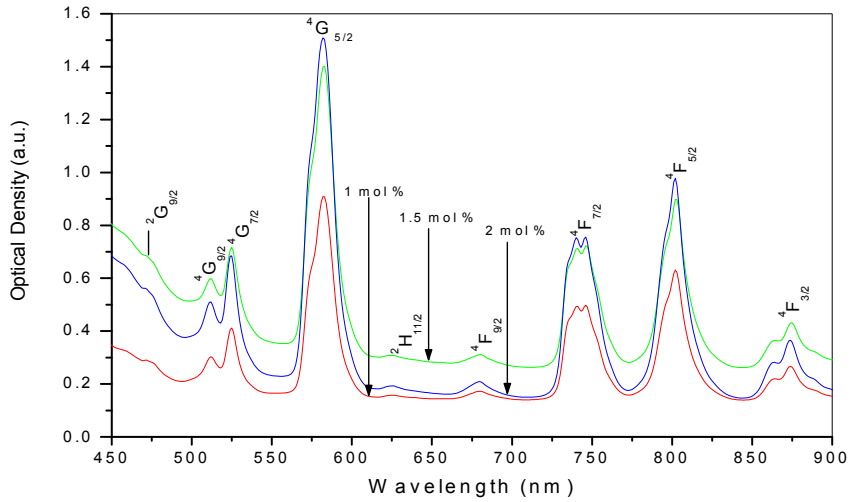

Fig.2. Vis-NIR absorption spectra of Nd^{3+}:ZLiBiB glasses

The absorption spectra of lanthanide ions lie in the visible and near infrared regions and correspond to transitions from the ground state to various excited states of $4f^N$ configuration. The various energy interaction parameters viz. Slater-Condon parameters F_k (k=2, 4 and 6), Lande parameter ξ_{4f} and Racah parameters E^k (k=2, 4 and 6) have been computed using partial regression method and formulae described elsewhere [17]. The computed values of these parameters for Nd^{3+} doped ZLiBiB glass specimens along with those for the free ion for comparison have been presented in Table 3.

Table 2- Experimental energy (E_{exp}) and calculated energy (E_{cal}) with their difference (ΔE) for various absorption bands of Nd^{3+} doped ZLiBiB glass specimens of different doping concentrations

Absorption levels	ZLiBiB (1)			ZLiBiB (1.5)			ZLiBiB (2)		
	E_m (cm^{-1})	E_c (cm^{-1})	ΔE (cm^{-1})	E_m (cm^{-1})	E_c (cm^{-1})	ΔE (cm^{-1})	E_m (cm^{-1})	E_c (cm^{-1})	ΔE (cm^{-1})
$^4F_{3/2}$	11442	11402	40	11435	11394	41	11448	11410	38
$^4F_{5/2}$	12469	12469	0	12461	12464	-3	12469	12476	-7
$^4F_{7/2}$	13405	13308	97	13396	13302	94	13405	13313	92
$^4F_{9/2}$	14706	14772	-66	14706	14770	-64	14717	14778	-61
$^2H_{11/2}$	15974	15974	0	15974	15975	-1	15987	15987	0
$^4G_{5/2}$	17167	17176	-9	17167	17167	0	17197	17191	6
$^4G_{7/2}$	19048	19155	-107	19048	19158	-110	19066	19176	-110
$^4G_{9/2}$	19531	19558	-27	19531	19561	-30	19550	19575	-25
$^2G_{9/2}$	21209	21158	51	21222	21169	53	21231	21180	51
rms deviation (σ)		±58.090			±58.205			±56.844	

The values of F_2 parameters exhibit a reduction of 1.22% in glass ZLiBiB (1), 1.703% in glass ZLiBiB (1.5) and 1.455% in glass ZLiBiB (2) from the corresponding free ion value. $F_4/F_2 \sim (0.154\text{-}0.152)$ and $F_6/F_2 \sim (0.0157\text{-}0.0156)$ are nearly same as reported in other glasses [18]. The values of E^1, E^2 and E^3 parameters have been given in Table 3. The ratio of $E^1/E^3 \sim (10.16\text{-}10.13)$ and $E^2/E^3 \sim (0.0484\text{-}0.0478)$ are found to remain almost constant over the entire range of Nd^{3+} doping concentrations and are in good agreement with the corresponding hydrogenic ratios.

The values of nephelauxetic ratio β' and bonding parameter $b^{1/2}$ for Nd^{3+} ion in ZLiBiB glasses indicate covalent nature of bonding between the rare earth ion and the surrounding glass matrix. Small values of r.m.s. deviation 'σ' between experimental energy (E_{exp}) and calculated energy (E_{cal}) of absorption levels in

neodymium ion doped LBB glass specimens justify the suitability of the use of Taylor series expansion method [19, 20].

Table 3- Calculated values of Slater-Condon, Lande's, Racah, Nephelauxetic ratio and bonding parameters of Nd^{3+} doped ZLiBiB glass specimens of different doping concentrations

Parameters	Free ion	ZLiBiB (1)	ZLiBiB (1.5)	ZLiBiB (2)
F_2 (cm^{-1})	331.16	327.12	325.52	326.34
F_4 (cm^{-1})	50.71	49.95	50.25	50.29
F_6 (cm^{-1})	5.154	5.147	5.087	5.109
ξ_{4f} (cm^{-1})	884.0	893.46	893.90	892.08
E^1 (cm^{-1})	5024.0	4971.33	4953.20	4965.75
E^2 (cm^{-1})	23.90	23.701	23.37	23.468
E^3 (cm^{-1})	497.0	488.96	488.73	489.52
F_4/F_2	0.1531	0.1527	0.1543	0.1541
F_6/F_2	0.0155	0.015735	0.015627	0.015656
E^1/E^3	10.1086	10.1671	10.1347	10.1441
E^2/E^3	0.0481	0.048471	0.047829	0.047941
β'	-	0.9878	0.9829	0.9854
$b^{1/2}$	-	0.0781	0.0922	0.0852

From the observed absorption spectra, the intensities of the observed bands have been calculated in terms of oscillator strengths, f_{exp}, and line strengths, s_m, spectral region wise and have been collected in Table 3. The Judd-Ofelt [14, 15] intensity parameters Ω_λ (λ = 2, 4 and 6) for all the glasses have been computed using line strengths and matrix element values by partial regression method [21] and have been presented in Table 5. The intensities of all the nine observed bands have been included in this calculation. Computation of Ω_λ parameters is very important since they have been further used in the calculation of different radiative properties. The calculated line strengths agree well with the experimental values. For Nd^{3+} doped ZLiBiB glasses, Ω_λ values vary as $\Omega_2>\Omega_6>\Omega_4$. The Ω_2 parameter is affected by the covalency, the Ω_6 parameter is related to the rigidity of the glass hosts, and Ω_4 parameter is determined by Ω_2 and Ω_6 parameters [22, 23]. In Nd^{3+} doped glasses the contribution to Ω_2 parameters are mainly due to the hypersensitive transition $^4I_{9/2}\rightarrow{}^4G_{5/2}$. The bonding environment surrounding the rare earth ion has been discussed on the basis of the value of Ω_λ parameters. The success of Judd-Ofelt theory has been shown by low value of goodness of fit between the measured (S_m) and calculated (S_c) line strengths.

Table 4- Experimental oscillator strength (f_{exp}), measured (S_m) and calculated (S_c) absorption line strength for Nd^{3+} doped ZLiBiB glass specimens of different doping concentrations

Absorption Levels	ZLiBiB (1)			ZLiBiB (1.5)			ZLiBiB (2)		
	f_{exp} (10^{-6})	S_m (10^{-20}) cm^2	S_c (10^{-20}) cm^2	f_{exp} (10^{-6})	S_m (10^{-20}) cm^2	S_c (10^{-20}) cm^2	f_{exp} (10^{-6})	S_m (10^{-20}) cm^2	S_c (10^{-20}) cm^2
$^4F_{3/2}$	2.224	1.182	1.047	2.153	1.146	0.997	2.015	1.073	0.947
$^4F_{5/2}$	7.206	3.514	3.698	6.424	3.137	3.354	6.283	3.071	3.293
$^4F_{7/2}$	8.423	3.820	3.813	7.336	3.332	3.393	7.278	3.309	3.378
$^4F_{9/2}$	0.584	0.241	0.267	0.546	0.226	0.239	0.481	0.199	0.237
$^2H_{11/2}$	0.155	0.059	0.067	0.124	0.047	0.060	0.095	0.036	0.060
$^4G_{5/2}$	23.180	8.210	8.279	21.589	7.652	7.768	20.384	7.224	7.348
$^4G_{7/2}$	3.004	0.959	1.141	2.204	0.704	1.073	2.083	0.666	1.022
$^4G_{9/2}$	1.018	0.317	0.546	0.623	0.194	0.505	0.612	0.191	0.488
$^2G_{9/2}$	0.873	0.386	-0.136	0.473	0.136	0.365	0.392	0.113	0.348
Goodness of fit		0.02694			0.06193			0.05965	

The spectroscopic quality factor (Ω_4/Ω_6) related with the rigidity of the glass system has been found to lie between 0.58 and 0.64 in the present glasses. This shows that these glasses are fairly rigid as compared to CdBiB [24] and zinc fluoride borophosphate [25] glasses.

Table 5- Judd-Ofelt intensity parameters, Ω_λ for Nd^{3+} doped ZLiBiB glass specimens of different doping concentration and compare with other similar glasses.

Glass Specimen	Ω_2(pm^2)	Ω_4(pm^2)	Ω_6(pm^2)	Ω_4/ Ω_6	Ref.
ZLiBiB (1)	5.923	3.239	5.551	0.583	p
ZLiBiB (1.5)	5.508	3.170	4.919	0.644	P
ZLiBiB (2)	5.212	2.952	4.911	0.601	p
CdBiB	4.893	2.976	5.789	0.514	24
ZFBP	1.46	0.38	0.75	0.50	25

CONCLUSIONS

In summary, it is concluded that we have successfully developed transparent, moisture resistant and more stable (60-x) B_2O_3-10Bi_2O_3-20Li_2O-10ZnO-xNd_2O_3 glasses where x =1, 1.5 and 2 mol% for their optical characterization. The calculated energies of the transitions using least square fit method are exactly coinciding with the experimentally obtained energies of the transitions, reflecting the good accuracy of the experimentation. The hypersensitive transition $^4I_{9/2}\rightarrow{}^4G_{5/2}$ exhibits high intensity as a function of Judd-Ofelt intensity (Ω_2) parameter in the case of 1 mol% Nd^{3+} glass system. The spectroscopic quality factor related with the rigidity of the glass system has been found to lie between 0.58 and 0.64 in the present glasses, which is fairly large as compared to other glasses. The large values of spectroscopic quality factor (Ω_4/Ω_6) make them suitable for optical devices.

ACKNOWLEDGEMENT

The authors are thankful to Prof. S.S.L. Surana (Retired), Jai Narain Vyas University, Jodhpur (Raj.) for his valuable suggestions. This work has been presented in the form of thesis for the degree of Ph.D. to the J.N.V. University, Jodhpur.

References

1. V. Dimitrov, Y.Dimitriev, A.Montenero, J.Non-Cryst. Solids, 180 (1994) 51.
2. J.C. Lapp, W.H. Dumbaugh, M.L. Powley, Riv. Staz. Sper. Vetro. 1(1989) 91.
3. D.W. Hall, M.A. Newhause, N.F. Borrelli, W.H. Dumbaugh, L.A. Weidman, Phys. Lett. 54 (1989) 1293.
4. V.R. Chowdari, Zhou Rong, Solid State Ionics 90 (1996) 151.
5. H. Sun, L. Wen, S. Xu, S. Dai, L. Hu, and Z. Jiang, Novel Lithium–Barium–Lead–Bismuth Glasses, Mater. Lett. 59, (2005) 959-962.
6. S. Lee, S. Hwang, M. Cha, H. Shin, and H. Kim, Role of Copper Ion in Preventing Silver Nanoparticles Forming in Bi_2O_3–B_2O_3–ZnO Glass., J. Phys. Chem. Solids, 69, (2008) 1498-1500.
7. D. Saritha, Y. Markandeya, M. Salagram, M. Vithal, A. K. Singh, and G. Bhikshamaiah, (2008). Effect of Bi2O3 on Physical, Optical and Structural Studies of ZnO–Bi2O3–B2O3 Glasses. J. Non-Cryst. Solids, 354, 5573-5579.
8. H. H. Qiu, T. Ito, and H. Sakata, DC Conductivity of Fe2O3–Bi2O3–B2O3 Glasses. Mater. Chem. Phys., 58, (1999) 243-248.
9. Y.C. Ratnakaram, A. Vijaya Kumar, D. Thirupathi, Naidu and N.O. Gopal, Materials Lett, 58, (2004) 3908.
10. Q. Nie, X. Li, S. Dai, T. Xu, Z. Jim and X. Zhang, Spectro. Chem. Acta Part A, 70, (2008) 537.
11. B.P. Dwivedi, M.H. Rahman, Y. Kumar and B.N. Khanna, J. Phys. Chem. Solids, 54, (1993) 621.
12. Y.C. Ratnakaram, A. Vijaya Kumar and R.P.S. Chakradhar, J. Lumin., 118, (2006) 227.
13. Y.K. Sharma, S.P. Tandon and S.S.L. Surana, Mater. Sci. Eng., B77, (2000) 167.
14. B.R. Judd, Phys. Rev., 127, (1962) 750.
15. G.S. Ofelt, J. Chem. Phys., 37, (1962) 511.
16. Quenching Media, "Metal Handbook", Pt IV., American Society for Metals, Metals Park, Ohio, 1981, p.615.
17. C.H. Goublen, "Method of Statistical Analysis", Asia Publishing House, Bombay, Ch. 8, (1964) 134.
18. S.S. Surana, Y.K. Sharma and S.P Tandon, Mater. Sci. Eng., Vol. B 83, (2004) 204.
19. E.Y. Wong, J. Chem. Phys., Vol. 35, (1961) 544.
20. E.Y. Wong, J. Chem. Phys., Vol. 38, (1963) 976.
21. W.T. Carnall, P. R. Fields, and K. Rajnak, J. Chem. Phys. (USA), 49, (1968) 4412, 4424, 4443, 4447, 4450
22. H.E.Y. Lin, B. Pun and X.R. Liu, J. Non-Cryst. Solids, 283, (2001) 27.
23. R. Rolli, K. Gatterer and M. Wachtler, Spectrochim. Acta Part A, 57, (2001) 2009.
24. C. Nageswara Raju, C. Adinarayana Reddy, S. Sailaja, H. Jin Seo and B., Sudhakar Reddy, (2012). J. Matter. Sci., Vol. 47, 772.
25. Y.K. Sharma, R.P. Dubedi, V. Joshi, K.B. Karnataka and S.S.L. Surana, (2005). Indian J. Eng. Mater. Sci., Vol 12,65.

Ciation of this article

Vishal Parihar, Beena Bhatia and Sanjay Singh . Optical Absorption Study of Different Concentration of Nd^{3+} ion in Zinc Lithium Bismuth Borate Glass. Int. Arch. App. Sci. Technol; Vol 5 [1]March 2014: 65-69

