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Structural and Optical properties of Ni doped borate glassy system

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ABSTRACT
The optical absorption spectra of nickel (II) ions in borate glass system have been studied at room temperature. The investigated system is of composition [(100 - x)(50 B2O3 - 30Na2O – 20ZnO)x NiO]. The spectra several an absorption edge is observed in short wavelength range (200-1100nm) beside five absorption bands in the range between (200-1100nm) the bands are due to d-d transitions in nickel ions. The absorption bands have been interpreted in terms of ligand field theory. The crystal field strength (Dq) has been evaluated.

INTRODUCTION

The analysis of the absorption spectra indicates that the nickel exhibits divalent state Ni^{+2}. Transition metal (T.M.) doped glasses find enhanced interest due to their peculiar properties. Their addition gives colour to glasses and improves their optical and magnetic behavior. T.M. ions are characterized by their incomplete 3d shell, which mean the presence of unpaired electrons.

Generally, T.M. ions are acted upon by a ligand field, which cause splitting of T.M. energy terms. The splitting depends on both the symmetry and strength of the ligand field. Ni in glasses exhibits usually divalent state and is surrounded by oxygen ion. .The most probable symmetry is either octahedron or tetrahedron. Hence optical absorption depends on the ligand field symmetry (Kutub, A.A., *et al*., 1986; Tanabe, Y. and S. Sugano, 1964; Medvedev, E.F. and A. Sh. Komarevskaya, 2007; Syamprasad, D., *et al*., 2008; Srinivasa Rao, N., *et al*., 2012; Safyanarayana, T., *et al*., 2009; Krishna Kumari, G., *et al*., 2012).

At the same time the glass has an absorption edge which extends over wide wave length range. This is due to the amorphous nature of glasses, where indirect transition is the dominant absorption mechanism In non-crystalline systems the absence of translation symmetry means that the wave vector (momentum) is not good quantum number .i.e. it is not measureable defined or conserved. In the present article Ni doped glass system was prepared by conventional melt quenching method and characterized by optical techniques.

Experimental:

The glass system under investigation has the general formula:

$[(100-x)(50B_2O_3\text{-}30Na_2O–20ZnO)xNiO]$withX=0,0.1,0.3,0.5,0.7,1mol.%.It is prepared by conventional melt- quenching technique which have been prepared using reagent grade materials. The starting materials used were: ZnO, Na_2CO_3, all with 99.9%purityand NiO of 99.9% purity .Corresponding weights of each composition were well mixed and grinded then preheated at 300 ^{0}C for one hour to set red of undesired gases in porcelain crucible. Then the temperature is raised to 850 ^{0}C for half an hour. The molt were stirred several times during preparation to ensure complete homogeneity, the melts were quenched after quenching the samples were annealed at 350 ^{0}C for 3hours in electric furnace, then the furnace was left to cool to room temperature. The

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samples show high transparency with slight brown colour. The annealing technique is required to remove the internal stress that remained in the glass during the quenching.

RESULTS AND DISCUSSION

The density (ρ) of the investigated system [(50 - x) B_2O_3 - 30Na_2O – 20ZnO –x NiO],x = 0.1 was measured and the molar volume (Mv) was calculated (table 1). The addition of NiO by 0.1 gives rise to sharp increase in density. Additive of NiO by 0.2 leads to sharp decrease in density, for higher x the density attains almost constant values as shown in Fig (1).

On the other hand molar value increases sharply at x = 0.1, then it exhibits linear increase up to x = 1 as shown in fig. (2). The sharp increase in the density at x = 0.1 is the most likely due to the deference in atomic weight of B and Ni atoms. The behavior of ρ and M_v for high values of x ≥0.3 can be accounted for by assuming structural charges. Such structural charges can be studied by estimating the ratio N_4= BO_4/ BO_3 + BO_4.The estimation of the latter needs study of IR absorption spectra

Table 1: The dependence of density and molar volume on NiO concentrate(X)

NiO(%)	Density(g/cm^3)	Molar volume(cm^3)
0	1.592	69.6658
0.1	1.642224	78.48294
0.3	1.75282	79.83742
0.5	1.879387	81.1919
0.7	2.025656	82.54638
1	2.293389	84.5781

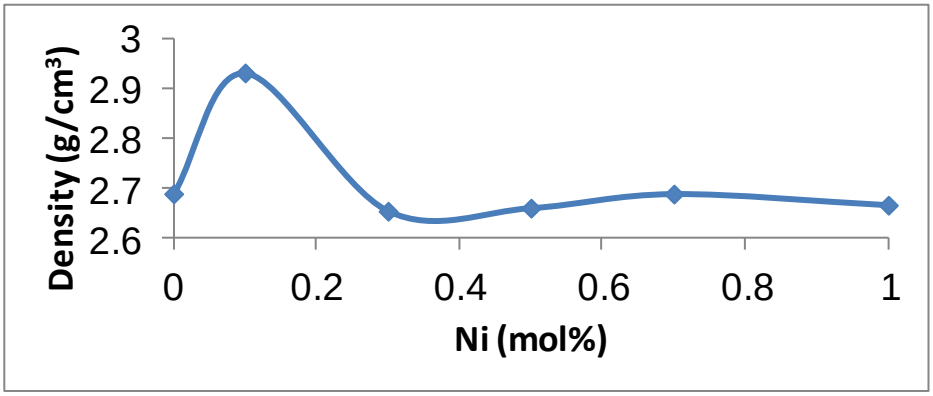

Fig. 1: variation of density with Ni concentrate

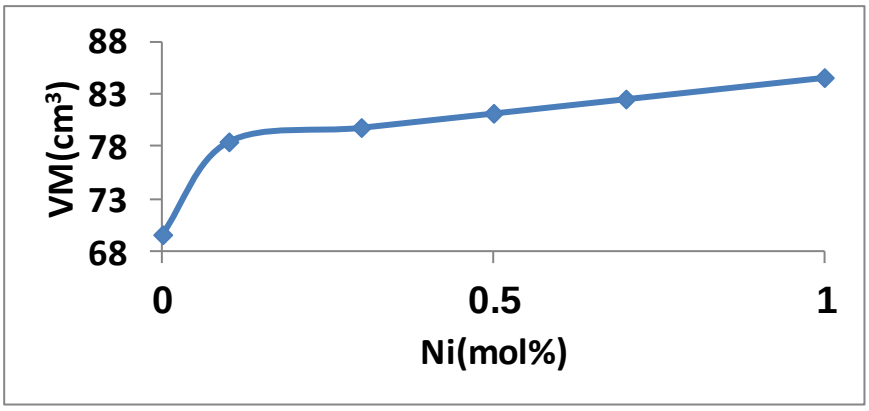

Fig. 2: variation of molar value with Ni concentrate

FTIR absorption spectra:

The infrared absorption spectra of glass system doped with NiO are shown in Fig.(3). The band positions along with their assignments are given in Table (2).

The vibrational modes of the borate network are seen to be mainly active in the three infrared spectral regions, which are similar to those reported by several workers (Karthikeyan, B., S. Mohan, 2003; Doweidar, H., Y. Saddeek, 2010). The first group of bands, which occur at 1200-1600 cm−1, are due to the asymmetric

stretching vibration of the B-O band of trigonal BO3 units. The second group lies between 800 and 1200 cm−1 and is usually assigned as B–O bond stretching of the tetrahedral BO4 units. The third group is usually observed around 680 cm-1 and is due to the bending vibrations of B-O-B in [BO3] trigonal (Sindhu, S., *et al*., 2006; Kumari, G., *et al*., 2012). Three broad bands are observed around 713, 909 and 1380cm-1 for all investigated samples. The spectra show little changes in the center of the bands around 713, 909and 1380 cm-1 and their width become broader as the NiO content increased. The strongest absorption bands of the borate glass located in the range of 1216 to 1553 cm-1 are usually attributed to B-O symmetric stretching of [BO3] units. The absorption bands that lie in the range from 909 to 1025 cm-1 are assigned to B-O stretching of [BO4]. To get quantitative information about the structural groups in glass, the spectra have been deconvoluted. This was made by using the Spectra Manager program assuming Gaussian type function that allowed us a better identification of the absorption bands which appear in these spectra in order to perform their assignment. Fig. 4, illustrated the results of the deconvolution for NiO mol% doped glass system. The obtained broad bands are a result of the overlapping of some individual bands. Each individual band has its characteristic parameters such as its center, which is related to some type of vibrations of a specific structural group, and its relative area, which is proportional to the concentration of this structural group. These characteristic parameters can be used to calculate the fraction N4 of BO4 units in the borate matrix for each composition. N4 can be defined as the ratio of the total of BO4 units to the of (BO3+BO4) units (Tanabe, S., 2006). From Fig. (5), it is clear that N4 decreases up to 0.3 of NiO content, and then it increases with increasing of NiO content. This means that, the intensity of BO3 units is observed to increase, where the band due to BO4 units is decreased as nickel oxide decreases up to 0.3 mol%. In compliance with the structural changes inferred from IR studies, the observed decrease in the band gap induced by the doping of NiO concentrations, can be accounted for the changes in BO4 and BO3 structural units.

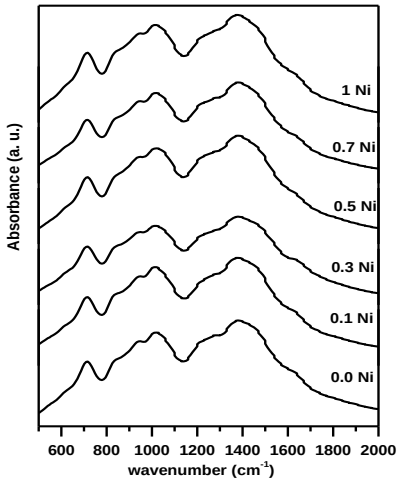

Fig. 3: The absorption FTIR spectra of glass system at different concentration

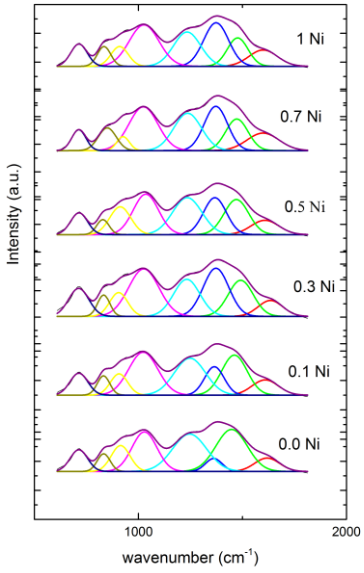

Fig. 4: The absorption FTIR spectra after decmvoluted

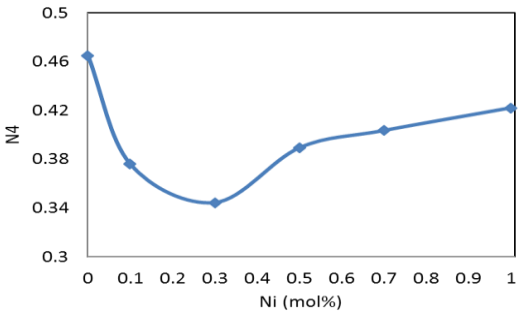

Fig. 5: The dependence of N_4 on Ni**O** concentrate(X)

Table 2: Assignment of absorption bands in the infrared spectra of the glassy system

Ni mol%/peak position						Assignment
0	0.1	0.3	0.5	0.7	1	
713	716	713	714	714	713	B-O-B bending vibrations
835	831	833	834	836	835	Vibrations of NBOs in BO4 units
909	905	905	906	909	903	B-O bond stretching in BO4
1031	1026	1025	1030	1026	1025	Vibrations of BO4 units
1216	1246	1232	1231	1230	1235	B-O smy stretch in BO3 units from pyro and orthoborate groups
1380	1356	1373	1361	1356	1352	
1484	1423	1492	1460	1443	1444	BO sym stretch in BO3 units from various types of borate groups
1553	1534	1635	1568	1554	1547	

Optical absorption spectra:

Optical absorption spectra of the prepared samples are shown in Fig(6). The investigated wave length range was (200-1500nm). All samples follow one common pattern where an UV edge along with five absorption bands in the visible range are observed. The position of former depends on composition and the latter is related to d-d transitions Ni ions.

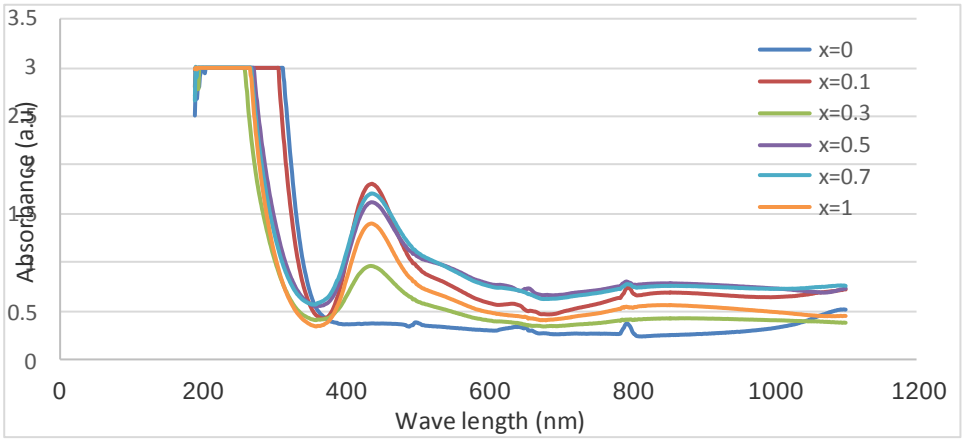

Fig. 6: The absorption spectra of the prepared samples

In glasses the most probable optical transition mechanism is the indirect this is due to the lake of translation symmetry. In such case Hamiltonian does not commute with translation operator and then the wave vector K is not measurable or defined i.e.it is not good quantum number.

Generally the optical absorption at edge obey the relation (Davis, E.A., N.F. Mott, 1970) $(\alpha h\upsilon)^n=A(\hbar w - E_g)$ where : α=absorption coefficient, A = constant and E_g = the band gab and n is the exponent depends on the absorption mechanism.

In case of indirect optical transition linear relation is observed between $(\alpha\ \hbar w)^{1/2}$and $\hbar w$. Such relation is shown in Fig. (7) Where E_g the band gap is the intersection with energy axis. The estimated values of the band gap are shown in Fig. (8) and are listed in table (3).

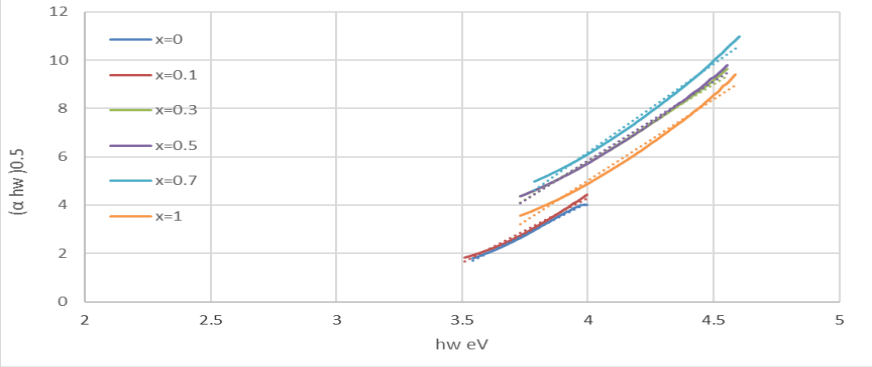

Fig. 7: The linear relation of indirect optical transition between $(\alpha\ \hbar w)^{1/2}$and $\hbar w$.

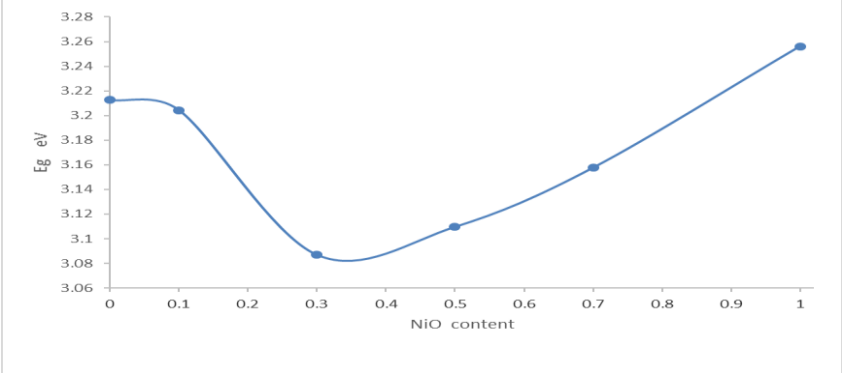

Fig. 8: The dependence of E_g on Ni**O** concentrate(X)

Table 3: The dependence of Eg on NiO concentrate(x)

X(mol%)	E_g (ev)
0	3.212
0.1	3.204
0.3	3.087
0.5	3.109
0.7	3.157
1	3.256

It is clear that the dependence of E_g on NiO concentrate is not linear. It decrease by increasing Ni up to x = 0.3and 0.5. At x = 1 starts to increase. This is most likely due to the change of average bond energy of the system. This may be due to change of BO_3 and BO_4 concentrations, which was studied by (FTIR) absorption spectra.

Ni absorption spectra:

In most cases nickel divalent ion Ni^{+2}in glass is acted upon by octahedral, square planar or tetrahedral symmetries. The symmetry and color depends on the glass composition. The prepared glasses exhibit brownish –green colour which suggests that we have divalent ions Ni^{+2}acted upon by octahedral field.

The absorption spectra of the prepared samples are shown in Fig. (6). All samples follow are common pattern where five absorption bands are observed at about 9090, 12345, 14925, 18520and 25000cm^{-1}.

Among them bands located at 9090, 14925and25000cm^{-1}show high intensity. This allows to assume the they are related to spin allowed triplet-triplet transitions(1), from the ground state $^3A_{2g}(F)$, $^3T_{2g}(F)$, $^3T_{1g}(F)$and $^3T_{1g}(P)$ respectively.

On the other hand the other two transitions are most likely due to spin-forbidden triplet-si $\upsilon_1$nglet transitions: $^3A_g(F)$- $E_g(D)$

$^3A_g(F) \longrightarrow {}^1T_{2g}(P)$observed at 12345 and 18520 respectably.

The value of D_q and Ruckah constant B were estimated according to the equations (Hammad, H.A., *et al*., 1992; Lakshmana Rao, J., *et al*., 1990; Suzuki, T., *et al*., 2005)

$\upsilon_1 = 10D_q$ and, $B = (\upsilon_{1+} \upsilon_2 - \upsilon_3)/15$ the values are listed in table(3).

$B = 391 cm^{-1}$

Table 3: the dependence of Dq on NiO concentrate

NiO(%)	Dq (cm^{-1})
0.1	441.95
0.3	435.05
0.5	436.95
0.7	440.05
1	439.2

The value of D_q don't show linear dependence on the NiO concentration.

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