JOURNAL OF MATERIALS SCIENCE 31 (1996) 1445–1448

ESR and optical absorption spectra of Ni(II) ions in lithium fluoroborate glasses

B. SREEDHAR, C. H. SUMALATHA, K. KOJIMA
Department of Chemistry, Faculty of Science and Engineering, Ritsumeikan University, Noji, Kusatsu, Shiga 525-77, Japan

The results of the investigation of the structure of Ni(II) ions in x LiF–$(100 - x)$ B_2O_3 glasses with $5 \leqslant x \leqslant 30$ mol% using ESR and optical absorption techniques are reported. Electron spin resonance spectra of Ni(II) ions doped glasses exhibit a symmetric line shape centred at $g = 2.36 \pm 0.01$ at room temperature. Remarkable changes have been observed in the intensity and line shape with changes in concentration of LiF and when the spectra were recorded in the temperature range 123–453 K. The optical absorption spectra were recorded at room temperature. The observed bands have been interpreted in terms of ligand field theory. From the spectral analysis, the crystal field parameter, Dq, and the Racah interelectronic repulsion parameters, B and C, have been evaluated. By correlating the ESR and optical absorption data, the covalency parameter has been evaluated.

1. Introduction

In recent years, glasses doped with transition metal ions have attracted considerable attention because of their potential applications in the development of new tunable solid-state lasers, solar-energy converters and fibre optic communication devices. Extended investigations in fluoride glass-forming systems have led to the discovery of various fluoride glass progenitors which define several families, fluoroberyllates, fluorozirconates, fluoroaluminates, fluoroindates, etc., while in recent years fluoroborate glasses (FBG) have also become of considerable interest because of their fast ionic conductivity [1].

Electron spin resonance (ESR) and optical absorption techniques have been extensively used to obtain a detailed information about some of the structural and dynamic phenomena of the material and to identify the site symmetry around the paramagnetic ions, not only in crystals but also in glasses. To our knowledge, the study of Ni(II) ions in lithium fluoroborate glasses has not yet been reported. Thus we prepared lithium fluoroborate glasses doped with Ni(II) ions and studied the ESR and optical absorption spectra.

2. Experimental procedure

Approximate molar quantities of Analar grade LiF and H_3BO_3 were weighed to yield a 10 g glass batch and mixed homogeneously. Each batch was first sintered at 623 K and then melted in an electric furnace at 1173 K for 4 h. The melt was then quenched at 573 K in air between two brass plates. The glasses so formed were annealed at 573 K for 15 min before their properties were measured.

ESR spectra were recorded at room temperature on an ESR spectrometer (Jeol-FE3X) operating at 9.214 GHz and using 100 kHz field modulation. The magnetic field was scanned in between 0 and 5000 G. The temperature dependence of the ESR spectra was studied from 123–423 K using an NM–VT variable temperature controller with a precision of ± 1 K.

Optical absorption spectra were recorded at room temperature on a Shimadzu 340 recording spectrophotometer between 300 and 2500 nm. The optical measurements could be measured with an accuracy of ± 5 cm^{-1}.

3. Results and analysis

3.1. ESR studies

No ESR signal was detected in the spectra of undoped glass samples. When Ni(II) ions are introduced into lithium fluoroborate glasses, the spectra of all investigated samples exhibit resonance lines. Fig. 1 shows the ESR spectra of 1 mol% Ni(II) ions in lithium fluoroborate glasses at room temperature. The ESR spectra exhibit a symmetrical line shape centred at $g = 2.36 \pm 0.01$. The effective g values obtained in the present work and those reported by various authors, are given in Table I.

ESR spectra were recorded at different temperatures to measure the temperature dependence of the intensity and line shape of the resonance line. At higher temperatures the resonance signal is more symmetrical, which broadens asymmetrically as the temperature is reduced, until at the lowest temperature there is appreciable absorption in the low-field regions. ESR spectra at different temperatures are shown in Fig. 2. The inverse temperature dependence

0022–2461 © *1996 Chapman & Hall*

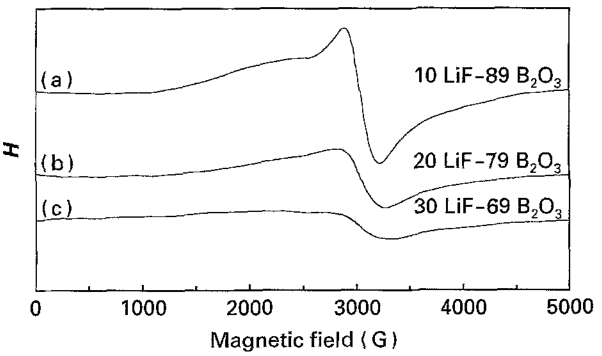

Figure 1 ESR spectra of Ni(II) ions doped in (a) 10 LiF–89 B_2O_3, (b) 20 LiF–79 B_2O_3, and (c) 30 LiF–69 B_2O_3 glasses at room temperature.

TABLE I *g* factors reported for various Ni(II) ion-doped glasses

	Sample	*g*	Reference
1	Na_2O–B_2O_3 glass	2.223	[2]
2	Fluoroberyllate glass	2.33	[3]
3	BaO–B_2O_3 glass	2.286	[4]
	SrO–B_2O_3 glass	2.263	
	CaO–B_2O_3 glass	2.243	
4	Fluorophosphate glass	4.19; 2.179	[5]
5	ZrF_4-based glass	2.38	[6]
6	LiF–B_2O_3 glass	2.36 ± 0.01	Present work

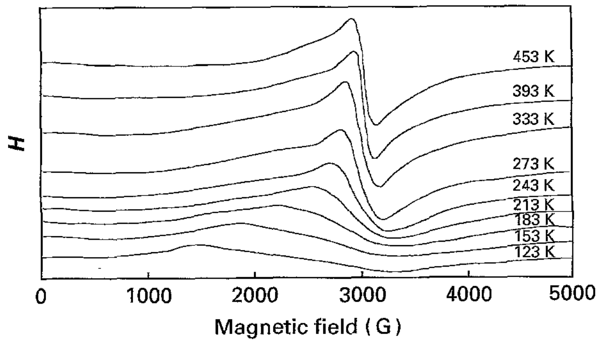

Figure 2 ESR spectra of 1 mol % Ni(II) ions doped in lithium fluoroborate glasses at different temperatures.

of the intensity for 1 mol % Ni(II) ions-doped lithium fluoroborate glass is shown in Fig. 3.

3.2. Optical absorption studies

Nickel occurs in glass as Ni(II) ions in octahedral, square-planar and tetrahedral symmetries depending upon the composition of the glass [7]. The optical absorption spectra recorded at room temperature for 1 mol % Ni(II) ions-doped lithium fluoroborate glass is shown in Fig. 4. The nature and position of the band maxima observed, are consistent with an octahedral environment.

At room temperature, three main bands are observed centred at 6800, 11 900 and 22 730 cm^{-1}, corresponding to Ni(II) in six-fold coordination. These three intense bands are assigned to the spin-allowed triplet–triplet transitions, $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$, respectively. The remaining weak bands in the spectra are identified with the spin-forbidden triplet–singlet transitions. The assignments of the transitions for all the observed bands are given in Table II.

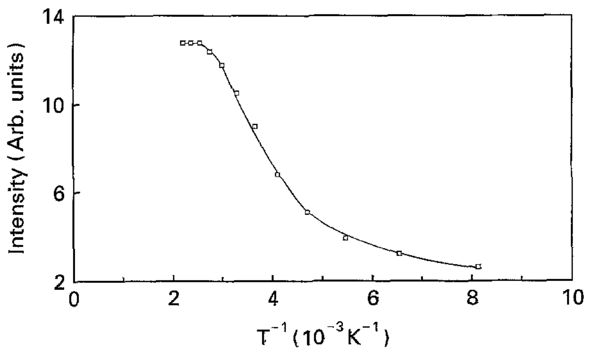

Figure 3 Inverse temperature dependence of the resonance line at $g = 2.36$ for 1 mol % Ni(II) ions in lithium fluoroborate glass.

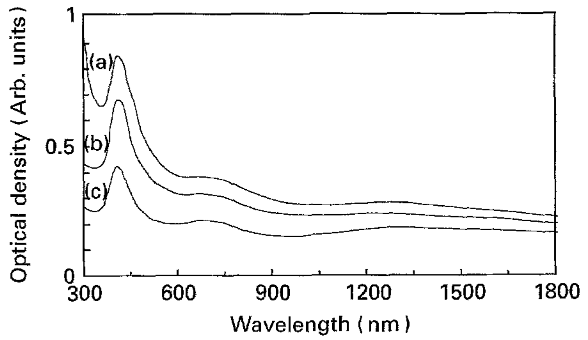

Figure 4 Optical absorption spectra of 1 mol % Ni(II) ions doped in (a) 10 LiF–89 B_2O_3, (b) 20 LiF–79 B_2O_3, and (c) 30 LiF–69 B_2O_3 glasses at room temperature.

TABLE II The observed and calculated energies for the bands of nickel(II) ions in lithium fluoroborate glasses. $Dq = 680\ cm^{-1}$, $B = 925\ cm^{-1}$ and $C = 3790\ cm^{-1}$

Transition $^3A_{2g}(F) \rightarrow$	Observed energy (cm^{-1})	Calculated energy (cm^{-1})
$^3T_{2g}(F)$	6 800	6 800
$^3T_{1g}(F)$	11 900	11 535
$^1E_g(D)$	14 285	14 285
$^1A_{2g}(D)$	20 000	20 600
$^3A_{1g}(P)$	22 730	22 725

4. Discussion

The ESR spectra of Ni(II) ions are analysed using a spin-Hamiltonian as follows [8]

$$\mathscr{H} = g\beta HS + D[S_z^2 - S(S+1)/3] + E(S_x^2 - S_y^2) \quad (1)$$

where β is the Bohrmagnetron, *H* is the external magnetic field, *S* is the effective spin operator, and *D* and *E* are the axial and rhombic components, respectively, of the zero-field splitting.

The ESR spectrum of Ni^{2+} ions in lithium fluoroborate glass at room temperature exhibits a single symmetric absorption. This spectrum can be understood in the following way. The degenerated free-ion 3F ground state of Ni^{2+} splits as a consequence of crystal field. In an octahedral environment, the orbital

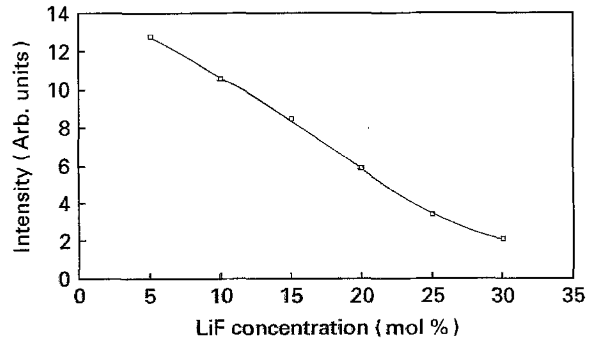

Figure 5 Dependence of the intensity of the resonance line at $g = 2.36$ on the LiF concentration.

singlet $^3A_{2g}$ has the lowest energy level. Using the spin-Hamiltonian

$$\mathscr{H} = g\beta HS \qquad (2)$$

with $S = 1$ and an isotropic g factor, an isotropic line is obtained which corresponds to the $|0\rangle - |\pm 1\rangle$ magnetic dipole transitions. Owing to the moderately high spin-orbit coupling, the isotropic g factor of octahedrally coordinated Ni(II) departs from the free electron value, g_e. In the frame work of ligand field theory, it is given by [9]

$$g = g_e - 8\lambda/\Delta \qquad (3)$$

where λ is the effective spin-orbit coupling constant and Δ is the energy difference between the ground state $^3A_{2g}$ and the first excited state $^3T_{2g}(3F)$. Optical absorption measurements give a Δ value of 6800 cm^{-1}. The observed g value (2.36 ± 0.01) can be obtained using a λ value of 304 cm^{-1} which is 92% of the free ion value. A comparison with the free ion value, $\lambda = 335\ cm^{-1}$, suggests a certain amount of covalency.

As the LiF concentration is increased in the host glass, the intensity of the resonance lines decreased and there was a large broadening in the ESR line shape. Fig. 5 shows the dependence of the intensity on the LiF concentration. This decrease in the signal intensity with an increase in LiF concentration may be attributed to the development of distorted structures, which lead to the formation of tetragonal and tetrahedral structures. Paul and Douglas [7] have observed that in Ni(II) ions-doped alkali borate glasses the formation of tetra-coordinated Ni(II) begins at about 19 ± 1 mol% alkali ion concentration. Yuhu Wang *et al.* [1] from the vibrational spectral observations suggest that the addition of LiF to the glass converts the boroxyl units to the borate rings with BO_4 units in $LiF–Li_2O–B_2O_3$ glass. From the infrared spectra they conclude that the addition of fluorine to the binary glass help in the formation of B–F bonds due to the high electronegativity and small ionic radius of F^- ions. Thus, in the present work, increasing LiF concentration helps in forming the BO_4 groups and B–F non-bridging bonds, and the nickel ions change from the octahedral to the tetrahedral state, resulting in a decrease in the ESR signal intensity.

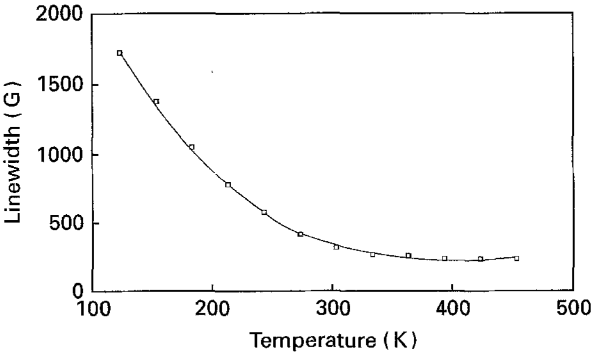

Figure 6 Temperature dependence of the linewidth of the resonance line at $g = 2.36$ for 1 mol% Ni(II) ion-doped lithium fluoroborate glass.

ESR spectra are also recorded in the temperature range 123–453 K to study the temperature dependence of the intensity and line width, ΔH, of the resonance line at $g = 2.36$. Fig. 6 shows the temperature dependence of ΔH for 1 mol% Ni^{2+} ions in lithium fluoroborate glass. It can be seen from Fig. 3 that the intensity of the resonance lines at $g = 2.36$ decreases gradually as the temperature is decreased, similar to that reported by Hecht [2] in borate glasses, which was attributed to the freezing in of distortions which give rise to large zero-field splittings. The line width increases with a decrease in temperature. The narrowing observed at higher temperatures is attributed to an averaging by the thermal motions of the lattice of the distortions from octahedral. Abdrashidova [10] observed a broad non-structured spectrum in BeF_2 glass at room temperature which disappeared at low temperature. Gan Fuxi *et al.* [5] observed a similar behaviour for a phosphate glass. In the present case, the resonance signal at low temperatures behaves similarly to those reported by Hecht [2] and Gan Fuxi *et al.* [5]. At higher temperatures, it is observed that both I and ΔH are almost constant after 393 K and the line shape is more symmetrical, which implies that the ion is located in a well-defined cubic field.

The Ni(II) ion belongs to d^8 configuration. By diagonalizing the energy matrices for the d^8 Ni^{2+} configuration [11], the crystal field parameter, Dq, and the Racah interelectronic repulsion parameters, B and C, have been evaluated. The observed and calculated energies along with their assignments are given in Table II. The Dq and B values obtained in the present work are as expected for Ni(II) ions in an octahedral symmetry.

The interelectronic repulsion parameter, B, for Ni(II) ion is 1080 cm^{-1} [12]. In the present work, the value of B obtained for Ni(II) is 925 cm^{-1}, which suggests that the bonding between the transition metal and the ligands is significantly ionic.

By correlating the ESR and optical absorption spectral data, Owen's ionic parameter, α^2 can be evaluated by

$$g = 2.0023 - \alpha^2 8\,\lambda/\Delta \qquad (4)$$

where g is the observed g factor, λ is the effective spin-orbit coupling constant and Δ is the energy difference between the ground state ${}^3A_{2g}$ and the first excited state ${}^3T_{2g}{}^3(F)$. It has a value which lies between 0.5 and 1.0, the limits of pure covalent and pure ionic bonding. The calculated value of $\alpha^2 = 0.90$, indicates that the bonding between the Ni^{2+} ions and the ligands is significantly ionic.

5. Conclusions

From the ESR and optical absorption studies of nickel ions in lithium fluoroborate glasses we conclude that

1. there are Ni(II) ions in lithium fluoroborate glasses in octahedral coordination;
2. with increase in the lithium ion concentration in the host glass, the number of Ni(II) ions in octahedral coordination decreases;
3. the decrease in the signal intensity with decrease in temperature is due to freezing in of distortions which give rise to large zero-field splittings.

Acknowledgement

B. S. thanks the INOUE Foundation for Science, Japan for the award of post-doctoral fellowship.

References

1. YUHU WANG, AKIYOSHI OSAKA, YOSHINANI MIURA and KATSUAKI TAKAHASHI, *J. Non-Cryst. Solids* **95**, **96** (1987) 571.
2. H. G. HECHT, *J. Chem. Phys.* **47** (1967) 1840.
3. D. M. YUDIN, G. A. TSURIKOVA and G. T. PETROVSKII, *Sov. Phys. Dokl.* **12** (1967) 337.
4. K. TAKAHASHI and Y. GOTA, *Yogyo-Kyokai-shi* **78** (1970) 370.
5. GAN FUXI, DENG HE and LIU HUIMING, *J. Non-Cryst. Solids* **52** (1982) 143.
6. E. A. HARRIS, *Phys. Chem. Glasses* **28** (1987) 196.
7. A. PAUL and R. W. DOUGLAS, *ibid.* **8** (1967) 233.
8. A. ABRAGAM and B. BLEANEY, "Electron Paramagnetic Resonance of Transition Metal Ions" (Oxford University Press, London, 1970).
9. J. E. WERTZ and J. R. BOLTON. "ESR: Elementary Thoery and Practical Applications" (McGraw-Hill, New York, 1972).
10. E. I. ABDRASHITOVA and G. T. PETROVSKI, *Dokad. Nauk. SSSR* **175** (1967) 1305.
11. Y. TANABE and S. SUGANO, *J. Phys. Soc. Jpn* **9** (1954) 253.
12. B. N. FIGGIS, "Introduction to Ligand Fields" (Wiley Eastern, New Delhi, 1976).

Received 4 January
and accepted 8 September 1995