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PARAMAGNETIC PROPERTİES OF THE DİVALENT NİCKEL IONS IN SOME ALKALİ RORATE GLASSES

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ABSTRACT

Paramagnetic properties of some alkali borate *glasses containing* nickel oxide vere studied to throw some light on thc cquiHbrîunı betveen thc octahedral and the tetrahedral States of the divalent nickel ions.

The experimental resuits obtained indicated that ali the glasses studied are paramegnetic and NiO_2 / NiO< equilibrium depends on several factors such as the polarizability of the oxygen ligands surrounding the nickel ions, mobility of thc alkali ions, field strength and thc ability *of* some divalent, trivalent and tetravalent metal oxides as network forming units.

INTRODUCTION

The magnetic susceptibility measurements of coloured glasses have been found to be of particular interest to follow the different forms in which the elements *of* the transitionmetals group can exist in glass[1]. According to the earlier works in this subject, it was found that the magnetic properties of different compounds are influenced vith the change in their Chemical combination and this was conıpletely explained in the work of Pascal[2]. From the other hand, Sehvood[1] had summarized the earlier works on the tıansition elements compounds in his monograph. Conseguently, other studies have been published concerning the magnetic properties of some glasses containing different transition metal elements[1]. Briet and Juza[1] studied the magnetic properties of nickel ions in glass of tertiary system, boric oxide-alkali oxide-nickel oxide. Juza and et al[1] measured the magnetic properties of nickel ions in different types of glasses and attributed the colour changes to the change in the coordination number of nickel. The magnetic measurements of nickel ions in glasses of different compositions have been explained on the basis of the ligand field theory[1].

In the present work, the effect of different factors such as the glass composition and the nickel ion concentration in some selected alkali borate glasses were studied.

Experimental details and calculations

All the glass batches, after pulverization, were melted in Pt-2 % Rh crucibles in an electrically heated furnace at a temperature of 1100- 1250 °C, depending on the glass composition, for 4 hr. The molten glass samples were then poured as rods of ten cm long and of one cm^2 cross- sectional area. The glasses, after setting, were annealed to give strain free samples as could be detected by the polarized light. Grinding and polishing were carried out with minimum amount of water. The magnetic measurements for all the glass samples were determined following the Gouy method[1] using an electromagnet of approximately 14700 Gauss field strength. The volume susceptibility for each glass sample was determined using the equation:

$K_1 = K_2 + 2\ \underline{A}\ mg / aH^2$ . .. where,

K_1 is the volume susceptibility of the glass sample;

K_2 is the volume susceptibility of the air (approsimately Zero);

$\triangle m$ is the weight difference due to the magnetic pull;

g is the gravity acceleration;

a is the cross sectional area of the glass sample; and

H is the magnetic field strength.

The value of the mass susceptibility of each glass sample was then calculated using the equation:

$0 = K_1 / p$ ... where,

0 is the mass susceptibility of the glass sample; and

‘0 is the glass density.

Similar measurements were also carried out on the base glass (free from nickel) for each glass composition, and the difference gives the mass susceptibility values for the nickel ion.

RESULTS

The experimental results obtained for the glasses studied can be summarized in the following:

1. Fig. (1) represents the experimental results obtained for the binary lithium-borate, sodium-borate and potassium-borate glasses. Each glass sample contains a constant amount of nickel oxide (0.25 g NiO *i* 100 g glass). It can be seen from the above figure that the values of the paramagnetic susceptibility increased as the alkali oxide was gra- dually increased in these glasses. in the glasses containing low and moderate proportions of the alkali oxide content, the values of the paramag- netism for lithium borate glasses ar e higher than those for sodium bora- te glasses and the latter values are higher than those for potassium borate glasses; while in the glasses containing high proportions of the alkali oxide content, the values of the paramagnetism are in the following or- der: potassium borate sodium borate)> lithium borate

2. The values of the paramagnetic susceptibility for the sodium borate glasses of the same base composition B_2O_2 80 % -Na_2O 20 % containing different proportions of nickel oxide are linearly increased with the gradual increase of the nickel oxide content, Fig. (2).

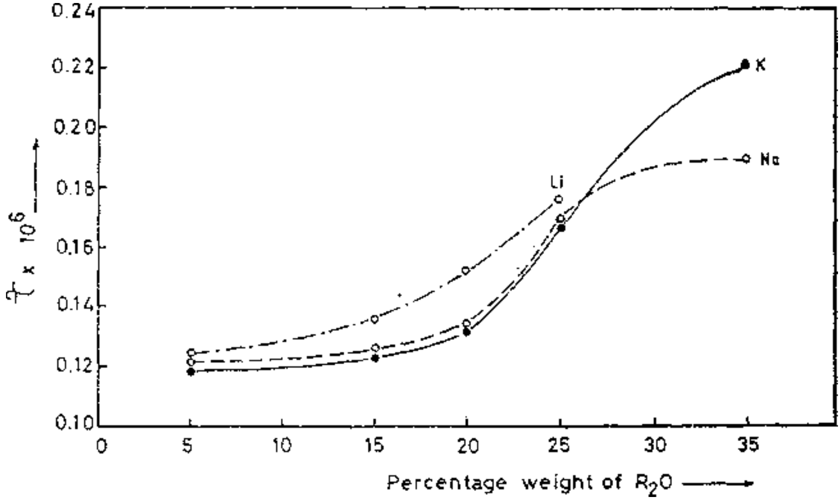

Fig. 1. The relation betweeen the mass susceptibility and the alkali oxide content in alkali borate glasses containing 0.25 gm. NiO/100 gm. glass.

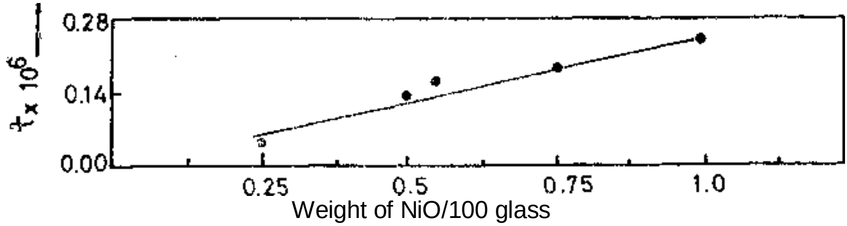

Fig. 2. The relation between the mass susceptibility and the concentration of nickel oxide in the glass of the composition B_2O_3 80 % —• Na_2O 20 %.

3. The replacement of soda in the glass of the basc composition B_2O_3 80 %-Na_2O 20 % containing 0.25 g NiO /100 g glass by one of the divalent metal oxides, magnesia, cadmium oxide, zinc oxide, lime, strontium oxide or barium oxide increases the values of the paramagne- tic susceptibility of these glasses as shown in Fig. (3). Also it can be seen that the values of the paramagnetism follow the order:

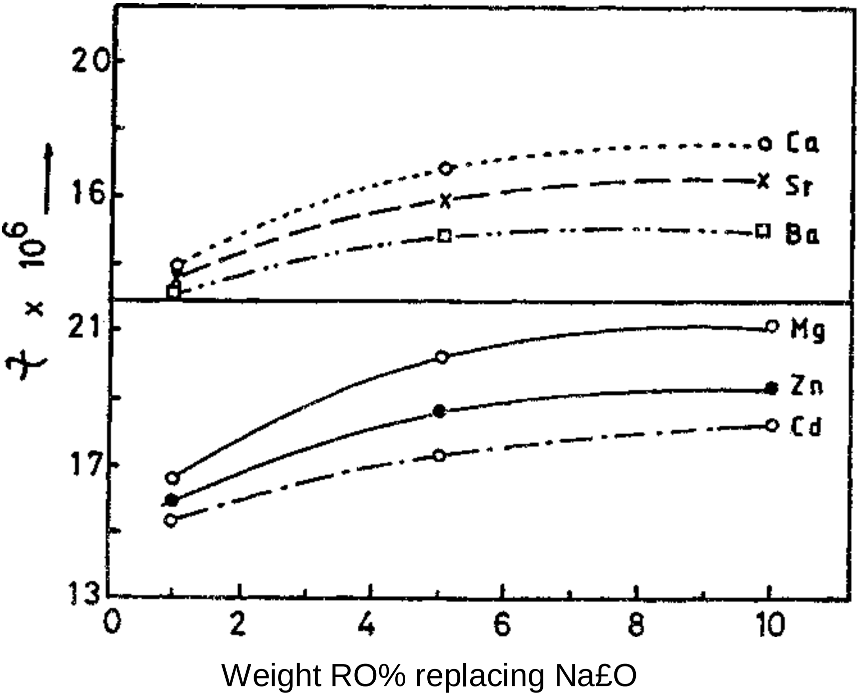

Fig. 3. The relation between the values of the mass susceptibility and the parts of soda replaced by one of the divalent metal oxides in the glass of the composition B_2O_3 80 % -Na_2O 20% containing 0.25 gm. NiO /100 gm. glass.

i. MgO > ZnO > CdO for the glasscs containing magnesia, cadmium oxide or zinc oxide.

ii. CaO > SrO > BaO for the glasscs containing lime, strontium oxidc or barium oxide.

4. The replacement of boric oxide by alumina, titania or zirconia increases the values of the paramagnetic susceptibility as tabulated in table(l).

Table 1. Compositions and values of mass susceptibility for sodium borate glasses of the base composition B_2O_3 80 % Na_2O 20 % containing 0.25 g NiO/lOO g glass, with parts of boric oxide replaced by alumina, titania or zirconia.

Glass No.	Glass composition wt %			Values of— X 10'''
	B,O_3	Na,O	R_2O_3 or RO_2	
1	80	20		0.1339
			Aİ,O_3	0.1692
3	79	20	- I % T'»	0.2222
	75	20	= 5% B 4 >	
4	79	20	TİO$_2$ == 1% B,O_3	0.1428
5	79.9	20	ZrO_2 = d.1% B,O_3	0.1375

DISCUSSION

It is well known that the paramagnetism introduced into a glass by the incorporation of the transition metal ions arises from the unpaired electrons of the unfilled 3d-subshell of these metals. The d-shell contains five orbitals, each of which may be occupied by one or two electrons. On considering the outer electronic configuration of nickel, it is appeared that nickel has paramagnetic properties in either the atomic or the ionic form. It will be also paramagnetic when it exists either in the octahedral or in the tetrahedral field[1]. Accordingly, the experimental results obtained for our glass samples can be discussed as follows:

1. The values of the paramagnetic susceptibility for the glasses containing soda, lithia or potash show a prograssive increase as the alkali oxide is increased, Fig. (1). According to Moore et al[1], the change exihibited in the value of the paramagnetism takes place at about the same content of the metal alkali oxide as the colour of the glasses change which can be related to the change in the coordination number of nickel ion from octahedral to tetrahedral State. Hence, it can be concluded that the equilibrium between octahedral and tetrahedral coordinations of the nickel ion shifts towards the formation of more tetrahedral and less octahedral forms as the alkali oxide content increases. The relative effect of soda, lithia and potash can be explained when we relaise that the lithium ion can fill the spaces in the alkali borate glasses without distorting the structure itself, and hence facilitating the formation of the nickel ion in the octahedral coordinationl[1]; also the oxygen ion in proximity to a sodium or a potassium ion must be more polarized than an oxygen in proximity to a lithium ion, hence in the glasses containing sodium or potassium ions the presence of the relatively easily polarizable oxygen ions shift the equilibrium between the octahedral and the tetrahedral coordinated nickel ion to the formation of more tetrahedral and less octahedral States with the

gradual increase of thc alkali oxide content, soda or potash. This is in complete agreement vith the work of Berkes et al[11] on some alkali borate glasses containing nickel from which they conc- luded that therc is a contanuous increase in the proportion of the tetra- hedıal coordinated nickel ion as the atomic number of the alkali is rai- sed.

2. The increase of the values of thc paramagnctic susccptibility as the nickel oxide content was gradually increases in the sam e base glass of the composition B_2O_2 80 %-Na_2O 20 %, can be attıibuted to the pa- ramıgnetic character of thc divalent nickel ion itself due to its two un- paircd electıons.

3. . In the samc base glass of thc composition B_2O_3 80 %-Na_2O 20 % containing 0.25 g NiO / 100 g glass, when magnesia, cadmium oxide or zinc oxide was introduced replacing soda, Fig. (3), a considerable proportion of these different divalent oxides will form MgO^. CdO4 or ZnO4 groups, while the rest ions remain enelosed in the glass structure inters- lices. The oxygen ions which are deformcd by one of the divalent cations arc found to be less polarizable ıhan those which are defoımed by the sodium ions and this can be due to the relatively small size and the high field strength of the group II-A metal ions. Thus, on replacing more soda by one of these divalent metal oxides, in thc base glass of the composition B_2O_3 80 %-Na_2O 20 % which contains high proportions of nickel ions mainly in the octahedral State, the amount of MgO4, CdO4 or ZnO4 are reduced and some of these divalent metal ions act as bridges between the network forming units. Consequently, the proportion of the nickel ion in thc octahedral coordination tend to increase. The relative effect of these oxides may be due to the highcr tendeney of magnesia form MgO_4 groups than zinc oxidc or cadmium oxidc'°.

4. In the same sodium bora te base glass, if soda is gradually repla- ced by lime, strontium oxide or barium oxide, Fig. (3), these ions will act partly as bridges between thc glass forming groups and partly enc- losed in the interstices of the glass structure. Since the oxygen ions aro- und the divalent cations are strongly held and less polarized than with sodium ions, thus the propoıtion of the nickel ions in the octahedral coordination will tend to increase with the gradual increase of one of the divalent metal oxides replacing soda. The relative of these oxides may be dne to their relative sizes and their ionic potentials[11].

5. When alumina is introdueed into the same base glass replacing boric oxide, Table (1), it will exist as AIO4 groups separated from cach othcr by BO_3 triangles. However, each tetrahedron would require an alkali ion in its immediate vicinity. Hence, the number of singly bonded oxygen ions would be large giving a considerable flixibility in the glass structure. Thus, it can be expected that the proportion of the nickel ion in the octahedral form would be also increased as more boric oxide was replaced by alumina.

6. The resulting effect of adding titania or zirconia replacing boric oxide in the same base glass, Table (1), depends partly on the strength of the linkages of the oxygen

at the corners of the adjoining units. Ho- wever, in these glasses the polarizability of the oxygen ligands will dec- rease. Then, the nickel ions would be expected to be found in the octahedral coordination.

Ali the above conclusions are in complete agreement with the cx- perimental results obtained.

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