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Optical Spectra of Transition Metals in Na_2O-P_2O_5 Glasses

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The optical spectra and the magnetic susceptibilities were obtained in sodium phosphate glasses containing transition metal ions. It was shown that the content of the transition metal ions of higher valency states increases with an increase in that of Na_2O whenever an oxidation equilibrium occurs between two or more valency states. By combining the visible spectra analyzed from the viewpoint of the ligand field theory with the results of the magnetic susceptibility measurement, it was shown that most transition metals coordinate six oxygen atoms in the phosphates.

The studies of the coloration of the transition metal ions in fused salts have, so far, greatly progressed with regard to the halide and nitrate systems especially. Bates applied the ligand-field theory to the analysis of the spectra of the colored glass.[1) In a sodium silicate and a sodium borate, the variation of the visible spectra with the sodium concentration was observed by Bamford.[2) Recently, the concept of the formation of non-bridging oxygen ions in a borate was used in explaining the fact that the intensity of absorption rapidly changed at a definite alkali concentration.[3) In contrast with the borates and the silicates, however, those have been few experimental measurements of the phosphates. The ligand-field absorption of the manganous ion in $3K_2O\cdot 7P_2O_5$ and $3Na_2O\cdot 7P_2O_5$ glass was obtained by Bingham and Parke.[4) Recently, the optical spectra and the magnetic susceptibility of cobalt(II) ion in Na_2O-P_2O_5 glass at various sodium oxide concentrations were measured.[5)

In this experiment the variation in the intensity and position of the visible absorption spectra were examined in sodium phosphate glasses with various compositions of Na_2O in order to investigate the structure of the phosphate network as well as their relation to the transition metal ions. The magnetic susceptibilities of this glass were also measured, since those quantities provide important information on the valency states of transition metal ions as well as their coordination numbers.

Experimental

Materials. The sample glass was prepared by melting $NaPO_3$, P_2O_5, and H_3PO_4 of a guaranteed reagent grade. The transition metals which were added as oxides were V_2O_5, Cr_2O_3, MnO_2, Co_2O_3, Fe_2O_3, NiO, and CuO. These were added, in amounts up to about 0.5 wt per cent, to the sodium phosphate, melted in a platinum crucible, and kept in the liquid state for 10 hr in order to get uniform mixtures.

Measurement of Optical Absorption Spectra. The melt in a crucible was cast into a mould of brass. The thickness of the sample plate was 0.5 cm. To avoid the moisture and the scattering caused by the rough surface, the sample was immersed in a benzene-chlorobenzene solution in an absorption cell.

Measurement of Magnetic Susceptibility. Use was made of a Gouy balance. The strength of the magnetic field was 15000 gauss. The net susceptibility due to the transition metal ions was obtained after the correction for the blank from the solvent glass was applied.

Determination of the Composition of the Glass Solvent. The sample was dissolved in an aqueous solution of nitric acid, and all the phosphates were converted to orthophosphate. From the quantity of NaOH required to neutralize the solution from the first to the second neutralization point, the quantity of P_2O_5 was determined. The Na_2O content was determined by the difference from the total weight.

Water Content in Glass. In the phosphate glass it is important to consider the presence of water. It is quite difficult to remove the water completely by the ordinary procedure. A considerable amount of water will still be present, especially when the sodium oxide concentration is low. This water was, however, ignored because water dissolves in glass not as H_2O molecules by as a network modifier, like sodium oxide. Although the presence of water alters the so-called basicity of the glasses, this doesn't have as much effect on transition metal ions as free H_2O molecules.

Results

Visible Absorption Spectra. *1) Vanadium.* The glasses containing vanadium were yellow when

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1) T. Bates, "Modern Aspect of the Vitreous State," Vol. 2, Butterworths, London (1962), Chap. 5.

2) C. R. Bamford, *Phys. and Chem. of Glasses,* **3(6)**, 189 (1962).

3) A. Paul and R. Douglas, *ibid.,* **9(1)**, 21 (1968).

4) K. Bigham and S. Parke, *ibid.,* **6(6)**, 224 (1965).

5) M. Kuto *et al.,* Preprints for the 21st Annual Meeting of the Chemical Society of Japan (Osaka, 1968).

the Na_2O content was high, but they turned green as the Na_2O content decreased. The extinction curves of the glasses are given in Fig. 1. The small absorption around 700 mμ increased in intensity as the Na_2O content decreased. Vanadium is able to have three valency states, V(III), V(IV), and V(V), in the glasses. V(V) has a $3d^0$ electronic configuration, so it has no absorption bands caused by the crystal field of oxygen ligands. V(IV) ($3d^1$) has a single spin-allowed band which occurs in the infrared region,[6] so it could not be detected in this experiment either. Therefore, it is considered that the small absorption is due to the V(III) ion in the glass and that the proportion of the V(III) decreases as the Na_2O content increases. The proportion of the higher valency state usually increases with the Na_2O content in glasses containing transition metals,[7] as may also be seen below.

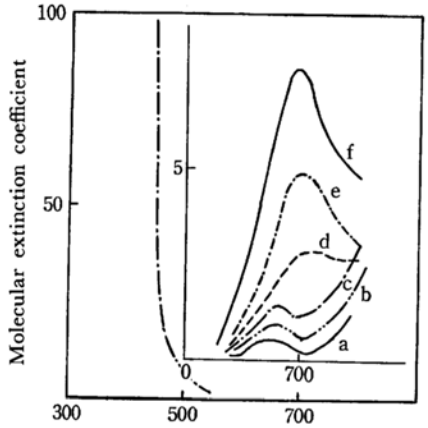

Fig. 1. The optical absorption of vanadium in sodium phosphate glasses with various sodium oxide concentration.

a 53.6 mol% Na_2O, b 52.5, c 50.3, d 27.7, e 17.4, f 0

2) Chromium. The glass containing chromium was green, and the color did not change with the composition. The extinction curves of the glasses are shown in Fig. 2. This glass has three prominent peaks, around 450, 635 and 600 mμ; they are considered to be three spin-allowed transitions in an octahedral crystal field of Cr(III). The assignment of these bands will be discussed later.

3) Manganese. The glasses changed from pale brown to pale purple with an increase in the Na_2O content. The extinction curves are shown in Fig. 3; they consist of a single band at 500 mμ. This band increases in intensity with an increase in the Na_2O content. Manganese is present in glasses as divalent or trivalent ions. The absorption at 500 mμ is considered to be the spin-allowed transition of Mn(III), whose content increases with an increase in the Na_2O content. Mn(II) has a $3d^5$ electronic configuration and has no spin-allowed crystal-field bands.

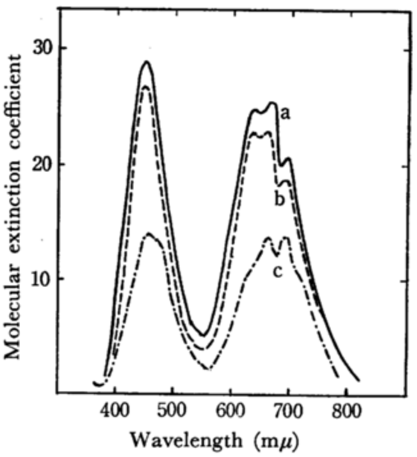

Fig. 2. The optical absorption of chromium in sodium phosphate glasses with various sodium oxide concentrations.

a 55.4 mol% Na_2O, b 50.8, c 0

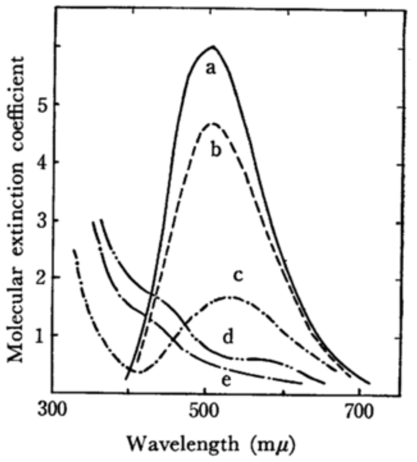

Fig. 3. The optical absorpion of manganese in sodium phosphate glasses with various sodium oxide concentrations.

a 56.1 mol% Na_2O, b 51.4, c 44.6, d 22.1, e 0

4) Iron. The glasses were yellowish brown. The extinction curves are shown in Fig. 4. Iron is present in glasses as divalent or trivalent ions. Fe(II) ($3d^6$) has a single spin-allowed absorption band in the infrared region, but the band could not be detected in this experiment. Fe(III)($3d^5$) has an *iso*-electronic configuration with Mn(II) and has no spin-allowed crystal-field band. The weak absorption is due to the spin-forbidden crystal-field

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[6] W. Johnstone, *J. Am. Ceramic Soc.*, **48(12)**, 608 (1965).

[7] R. W. Douglas, P. Nath and A. Paul, *Phys. and Chem. of Glasses*, **6(6)**, 216 (1965).

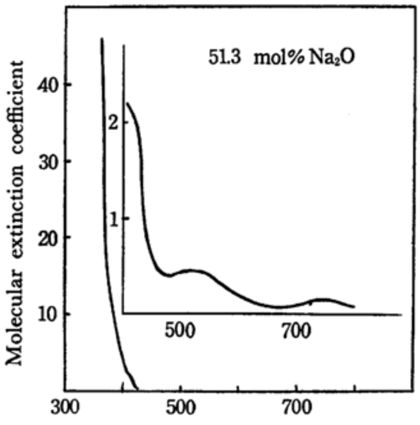

Fig. 4. The optical absorption of iron in sodium phosphate glass.

band. Chemical analysis showed that most of the iron ions are present as trivalent (about 95%) in the sodium metaphosphate glass.

5) Cobalt. The glasses change from pink to blue with an increase in the Na_2O content. The extinction curves are shown in Fig. 5. Cobalt is divalent in the glass. When the Na_2O content is low, Co(II) is surrounded by six oxygen atoms, but as the Na_2O content increases the proportion of the tetrahedrally-coordinated cobalt ion increases. The variation in color is consistent with this change. The change from octahedral to tetrahedral coordination occurs in other glasses.[3]

6) Nickel. The glasses were yellow but became greenish with an increase in the Na_2O content. The extinction curves are shown in Fig. 6. The nickel in the glasses is in the form of the divalent ion, which has a $3d^8$ electronic configuration. In the octahedral field, the nickel(II) ion has three spin-allowed bands.

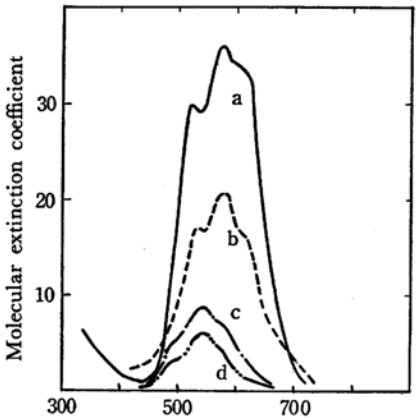

Fig. 5. The optical absorption of cobalt in sodium phosphate glasses with various sodium oxide concentrations.

a 57.4 mol% Na_2O, b 50.6, c 44.0, d 0

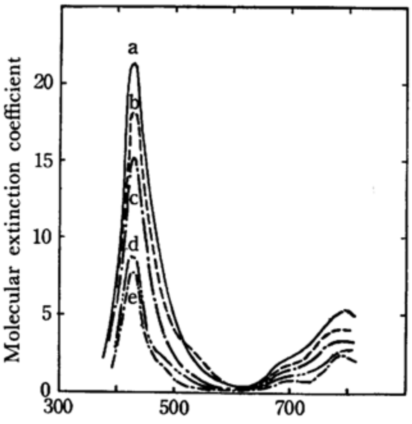

Fig. 6. The optical absorption of nickel in sodium phosphate glasses with various sodium oxide concentrations.

a 59.0 mol% Na_2O, b 55.5, c 51.4, d 36.6, e 0

The absorptions around 425 and 780 mμ correspond to these bands, and the other band appears in the infrared region. It was shown in the sodium borate glasses that the tetrahedrally-coordinated nickel ion is present in the higher-alkali-content glasses.[8] In the phosphate glasses this is shown by the variation in the intensity of the absorption, which will be discussed later.

7) Copper. All the sodium glasses containing copper were pale blue. The extinction curves of the glasses are shown in Fig. 7. The main absorp-

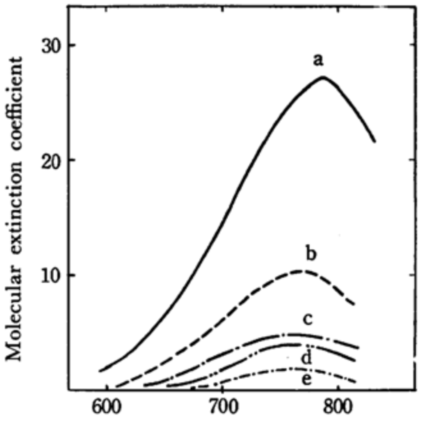

Fig. 7. The optical absorption of copper in sodium phosphate glasses with various sodium oxide concentrations.

a 50.9 mol% Na_2O, b 45.6, c 41.8, d 34.1, e 0

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[8] J. Berkes and W. White, *Phys. and Chem. of Glasses,* **7(6)**, 191 (1966).

TABLE 1. ASSIGNMENT OF THE ABSORPTION BAND OF TRANSITION METALS IN SODIUM PHOSPHATE GLASSES

Ion	Band assignment	$-6H_2O$ (mμ)	Na-Glass (mμ)
V +3	$^3T_1 \rightarrow {}^3T_2$	562	665
Cr +3	$^4A_2 \rightarrow {}^4T_1$	410	450
	$^2T_1$		634
	$^4T_2$		658
	^2E	671	690
Mn +3	$^5E \rightarrow {}^5T_2$	476	500
Fe +3	$^6A_1 \rightarrow {}^4E, {}^4A_1$	406	410
	$^4T_2$	540	520
	$^4T_1$	793	740
Co +2	$^4T_1 \rightarrow {}^4T_1$	465 515	490 530
	$^4A_2 \rightarrow {}^4T_1$ (Tetrahedral)	600	620
Ni +2	$^3A_2 \rightarrow {}^3T_1$	395	425
	^1E	649	700
	$^3T_1$	741	782
Cu +2	$^2E \rightarrow {}^2T_2$	796	760

tion band appeared at 760 mμ, its intensity increasing with the Na_2O content. The copper in the glasses is in the divalent state with a $3d^9$ electronic configuration. This absorption band is due to the transition in an octahedral field. The apparent ligand field strength is 13000 cm^{-1}.

Discussion

The observed bands are summarized in Table 1. The corresponding values in octahedrally-coordinated aquo-complex are also included. A comparison of the two sets of data shows that the bands may be identified as transitions in the octahedral-ligand field. In Co and Ni, however, the tetrahedral-ligand field must be taken into consideration.

In general the field strength of the phosphate glass is smaller than tnat of the corresponding aquo-complex by about 10%. This fact is also seen in other glasses.[1)] In copper, on the other hand, the splitting of *d* levels due to the ligand field is greater than that of the copper(II) aquo-complex. This result may be explained by considering that there occurs a large tetragonal distortion.[1)]

Figure 8 shows the relation between the intensity of the absorption and the Na_2O content in nickel(II), copper(II), and chromium(III) glasses. The increase in intensity is probably caused by the following two effects:

(1) the increase in the portion of ions which occupy the sites under the octahedral and/or tetrahedral crystal field and cause the optical absorption. This increase is closely related to the structure of the glasses, and

(2) the increase in the number of the ions in the relevant valency state, which is related to redox equilibrium of the transition metal ions.

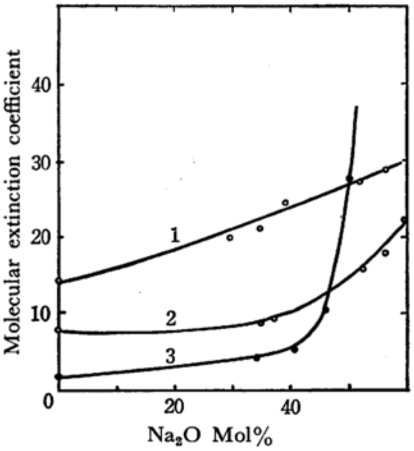

Fig. 8. The variation of the intensity with sodium oxide concentration.

1 Cr ~450 mμ, 2 Ni ~420 mμ, 3 Cu ~760 mμ

In chromium, the intensity increases moderately with the Na_2O content. This suggests that the proportion of Cr(III) increases with an increase in the Na_2O content, although no divalent chromium ions were detected. In copper, on the other hand, the intensity changes abruptly at an Na_2O content of 40 mol%. This shows that, in addition to a possible increase in the proportion of Cu(II), the structure of the glasses changes at this composition; that is, the glass network disintegrates into discrete ions so that the probability of occupying the octahedral site increases at this composition.

In nickel, an abrupt change in intensity occurs at the composition of 40 mol% Na_2O. As in the borate glasses, it is considered that the proportion of tetrahedral Ni(II) coordination increases from this point.

Magnetic Susceptibilities. From the magnetic susceptibilities, the effective magnetic moments of

TABLE 2. EFFECTIVE MAGNETIC MOMENT OF TRANSITION METAL IONS IN SODIUM METAPHOSPHATE GLASSES

		$-6H_2O$ μ_{eff} (B.M.)	Sodium metaphosphate	
			μ_{eff} (B.M.)	Ion
V	+4	1.70	1.10	V^{3+}, V^{4+}, V^{5+}
	+3	2.61		
	+2	3.80		
Cr	+3	3.80	3.77	Cr^{2+}, Cr^{3+}
	+2	4.80		
Mn	+3	4.80	5.62	Mn^{2+}, Mn^{3+}
	+2	5.83		
Co	+2	4.90	4.70	Co^{2+}
Ni	+2	3.12	3.21	Ni^{2+}
Cu	+2	1.83	2.02	Cu^{2+}

transition metal ions in sodium metaphosphate glasses were derived from the relation:

$$\mu_{\mathrm{eff}} = 2.84\sqrt{\chi_{\mathrm{M}}\cdot T}$$

where χ_{M} is the molar susceptibility, and T, the absolute temperature. These results are summarized in Table 2. The corresponding values in octahedral aquo-complex are included. In general, the effective magnetic moment of the transition metal ions in a crystal field can be represented by the following relation:

$$\mu_{\mathrm{eff}} = \mu_0\left(1 - \alpha\frac{\lambda}{\Delta}\right)$$

where Δ is the strength of the crystal field, λ is a parameter of spin-orbit interaction, μ_0 is a spin-only magnetic moment, and α is a positive constant. λ is positive when there are fewer than five 3d electrons and is negative when there are more.

Therefore, if it is assumed that the transition metal ions in the glasses coordinate six oxygen atoms and that λ does not differ much between the glasses and aquo-complexes, the μ_{eff}'s of V, Cr, and Mn become smaller, and those of Co, Ni, and Cu become larger than those of the corresponding aquo-complex. Table 2 shows that this relation holds except in the case of Co. It is known that the magnetic moment in the tetrahedral field is smaller than that in the octahedral field.[9] Therefore, in cobalt this result can be explained by the existence of the tetrahedrally-coordinated cobalt ions, which is consistent with spectra results.

As to vanadium, the values suggest that the V(IV) and V(V) are predominant, as has also been implied from the spectral measurements. The μ_{eff} of Mn shows that there are a considerable number of Mn(II) ions which can not be detected spectroscopically. It may be concluded from the table that nickel and copper are predominant in the divalent state in the phosphate glasses.

In conclusion, the coordination of oxygen atoms on the transition metal ion is closely related to the structure of the glass. Thus, when the Na_2O content is low, most of the transition metal oxides act as network modifiers and the coordination number is 6, while some of them (Ni, Co) act as network formers at a high Na_2O content when the coordination number becomes 4. This is also reflected in the fact that, at a high basicity, transition metal ions of high valency state form stable coordination complexes.

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9) R. L. Carlin, "Transition Metal Chemistry," Vol. 1, Marcel Dekker, New York (1965), Chap. 1.