
LIGAND FIELD SPECTRA IN METAPHOSPHATE GLASSES^{1, 2}

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ABSTRACT

The ligand field absorption spectra in the ultraviolet, visible, and near-infrared regions of metaphosphate glasses containing the first-row (3d) transition elements, Ti, V, Cr, Mn, Fe, Co, Ni, and Cu, were compared with spectra for the same elements in aqueous orthophosphate solution. In general, the positions of the glass ligand field absorption bands correspond to those of the solution, indicating that the transition element species in glass is coordinated in a similar manner to that of the same element ion complexed in the aqueous solution. Furthermore, when an effort is made to keep the surroundings of the transition metal species similar in glass and in aqueous solution, as in the present work, the ligand field spectra do not differ greatly. Variations from these similarities are discussed.

Ligand field spectra have been studied extensively since the work of Werner (1893). However, it was not until Bethe (1929) developed the crystal field theory that the nature of the precise process which leads to radiant energy absorption was defined for these spectra. The theory was applied successfully to solutions by Ilse and Hartman (1951) and then to glasses by Bates and Douglas (1959).

Since 1960, ligand field spectra in glass have been discussed in a number of papers in *Physics and Chemistry of Glasses*, and Bates (1962) has furnished an

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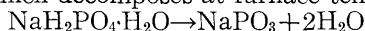
extensive ligand field analysis of his own work plus that of previous workers. Mention should also be made of the book by Weyl (1959), which provides a summary of experimental spectral data up to that time, although a ligand field treatment is not given. Jørgenson (1962) provided a summary of data on ligand field spectra of solutions.

It should be noted that both metaphosphate glasses and concentrated orthophosphoric acid solutions have an essentially random structure beyond nearest-neighbor bonding distances (Zachariassen, 1932; Cotton and Wilkinson, 1966).

EXPERIMENTAL

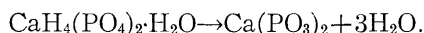
Melts were made of sodium metaphosphate base glass (NaPO_3) and of calcium metaphosphate base glass ($\text{Ca}(\text{PO}_3)_2$) containing small amounts of the first-row (3d) transition series elements: Ti, V, Cr, Mn, Fe, Co, Ni, and Cu. (Sc(III) has no 3d electrons available for promotion, while Zn(II) has no 3d orbitals available for occupancy in the splitting caused by the ligand field perturbation, and therefore neither of these ions has ligand field spectra absorption bands.)

Batch materials for these melts were Fisher Certified Reagent chemicals or the equivalent. For the sodium metaphosphate glasses, the base material was sodium dihydrogen phosphate, which decomposes at furnace temperatures as follows:



The iron content of this base material was listed at 0.002% and the heavy-metal content at 0.001%.

For the calcium metaphosphate glasses, calcium tetrahydrogen phosphate was the base material:



This starting material had even lower contents of iron (0.001 to 0.000%) and heavy metal (0.001 to 0.000%) than the sodium dihydrogen phosphate. Small amounts, on the order of 0.5%, of the 3d transition elements were added as the oxide, nitrate, or sulfate.

After mixing, the batches were transferred to Coors glazed porcelain crucibles of the type used in gravimetric analysis, and melted in a Blue M global furnace equipped with an inconel muffle. An atmosphere of commercial cylinder oxygen was used for oxidizing condition melts and an atmosphere of commercial cylinder argon for reducing condition melts. Small amounts of dextrose, about 0.1%, were added to the reducing condition melts. Melt time was an hour (at 1150°C for the sodium metaphosphate glasses and at 1315°C for the calcium metaphosphate glasses) and during this time the melts were stirred occasionally with a platinum rod.

After melting, the glasses were poured into a mold made by piling up small steel blocks and were heated by a Bunsen burner. The spacing of the blocks was set to produce glass samples of 1 cm by 1 cm by 5 cm, a size which fits into the cell holder of a Beckman DK-2 spectrometer. After the glass had become sufficiently rigid in the mold, it was transferred to a beaker full of glass wool to cool more slowly, thus preventing cracking of the glass from cooling too fast. The sodium metaphosphate glasses were stored in desiccators to avoid the formation of a surface film from atmospheric moisture. The calcium metaphosphate glass is more resistant to attack by atmosphere moisture, not needing to be stored in desiccators.

Absorption spectra were measured in the visible and near-infrared ranges on these glasses containing transition element additions, without any further preparation by annealing or polishing. A blank prepared in the same way, but without additions, was used in the reference side of the DK-2 spectrometer.

Furnace and mold temperatures were higher for the calcium metaphosphate glasses and these glasses were strained in the cooling procedure. However, a comparison of the spectra of the glasses before and after annealing showed that these were the same.

Ligand field spectra of the same transition elements were also determined in orthophosphate solution in concentrations comparable to those in the metaphosphate glasses. This was done by dissolving soluble salts of the elements in 86.5% phosphoric acid (Baker Analyzed, listed iron content = 0.001%, listed metal content = 0.0003%). Absorption spectra were measured with the Beckman DK-2 spectrometer on these solutions in matched silica cells for both the ultra-violet and visible ranges, using the phosphoric acid as the reference solution.

A comparison of the spectra of the sodium metaphosphate and calcium metaphosphate glasses containing the transition series elements showed that these were similar, in general, and that, furthermore, the melts made under reducing and oxidizing conditions did not differ in most cases. The discussion below is applicable to the calcium metaphosphate glasses melted under reducing conditions, because these had the most complete spectra, and, if there are exceptions due to base glass or to melting conditions, these are noted at the appropriate place.

DISCUSSION

Titanium

Ti(IV) in glass or solution is colorless (no 3d electrons). Ti(III) is of historical interest, because it was the first ion for which radiation absorption energy was calculated (by Ilse and Hartmann, 1951).

In calcium metaphosphate glass melted under oxidizing conditions, Ti(III) has a weak absorption maximum at 20,200 cm^{-1} , corresponding to the Δ value given for $\text{Ti}(\text{H}_2\text{O})_6^{3+}$ by Jørgenson (1962), who also assigned a lower energy band at 17,700 cm^{-1} to a transition between states arising from Jahn-Teller distortion. Following this, the assignment of the ligand field energy Δ (=10Dq) for Ti(III) in octahedral coordination in metaphosphate glass is 20,200 cm^{-1} .

Sodium metaphosphate glass containing titanium melted under oxidizing conditions is colorless, probably because of lesser thermal reduction of Ti(IV) to Ti(III) at the lower temperature required for the sodium metaphosphate melt. Both the calcium metaphosphate and sodium metaphosphate glasses melted under reducing conditions have broad absorption bands centered at about 18,000 cm^{-1} , stronger than those for the calcium metaphosphate glass melted under oxidizing conditions. This broadening of the band is possibly due to the effect of the Jahn-Teller splitting at the higher Ti(III) concentration found under reducing conditions. This single broad band at 18,000 cm^{-1} is also shown in solutions of Ti(III) in 86.5% H_3PO_4 .

The anomaly of the assignment of a single absorption band at 18,500 cm^{-1} by Smith and Cohen (1963) for titanium in a sodium silicate glass melted under reducing conditions, while Bamford (1962b) found a maximum absorption at 20,800 cm^{-1} for a similar glass, can possibly be explained by reference to the above data on metaphosphate glasses. Variation in experimental conditions, such as furnace temperature and extent of reduction, results in a variation in Ti(III) content, with the more highly reduced glasses exhibiting broad absorption maxima near 18,000 cm^{-1} . These published data, however, do not permit an exact analysis of the difference in spectra.

Vanadium

V(III) in metaphosphate glass has absorption maxima at 14,500 and 22,200 cm^{-1} . The assignment of the lower energy band to the octahedral ${}^3\text{F}_1$ to ${}^3\text{F}_2$ transition (corresponding to 0.8 Δ) results in $\Delta = 18,000 \text{ cm}^{-1}$. The higher energy band then is assigned to the ${}^3\text{F}_1$ to ${}^3\text{F}_1(\text{P})$ transition. The band for the ${}^3\text{F}_1$ to ${}^3\text{A}_2$ transition is apparently too weak to be observed, as it corresponds to a forbidden two-electron jump. Kumar (1964) ascribed bands in an aluminum borophosphate glass at 14,000 and 21,500 cm^{-1} to the V(III) energy level transitions shown above. In 86.5% H_3PO_4 solution, the ${}^3\text{F}_1$ to ${}^3\text{F}_2$ absorption band appears at 14,400 cm^{-1} ,

but the higher energy transition is obscured by a strong, wide absorption band in the ultraviolet, apparently due to V(IV).

In silicate glasses, other absorption bands appear, which have been variously ascribed to V(IV) and V(V) by Kumar and Sen (1960) and by Kakabadse and Vassiliou (1965). This emphasizes the practical advantages of phosphate glasses, in that the oxidation states are limited and pure colors result.

Chromium

Cr(III) in metaphosphate glass has absorption maxima at 14,600, 15,200, 15,800 and 22,100 cm^{-1} , the same as those obtained for Cr(III) in 86.5% H_3PO_4 solution. The assignment of these to the corresponding octahedral transitions: ${}^4\text{A}_2$ to ${}^2\text{E}$, ${}^4\text{A}_2$ to ${}^4\text{F}_2$, ${}^4\text{A}_2$ to ${}^2\text{F}_1$ and ${}^4\text{A}_2$ to ${}^4\text{F}_1$ gives $\Delta = 15,200 \text{ cm}^{-1}$. Bates and Douglas (1959) assigned $\Delta = 15,300 \text{ cm}^{-1}$ to octahedrally ligated Cr(III) in a soda-lime-silica glass.

Manganese

Manganese has two absorption maxima in the visible spectrum, at 19,300 cm^{-1} and at 24,600 cm^{-1} . These are found both in the metaphosphate glass and in 86.5% H_3PO_4 solution.

The 19,300 cm^{-1} maximum corresponds to that found by Purdy and Hume (1955) for Mn(III) in octahedral coordination in concentrated H_3PO_4 solution. An assignment of an apparent $\Delta = 19,300 \text{ cm}^{-1}$ for the ${}^5\text{E}$ to ${}^5\text{F}_2$ transition is somewhat higher than that for other trivalent ions (cf. Ti(III), V(III), Cr(III), Fe(III)) indicating that there is a Jahn-Teller distortion of octahedral symmetry for Mn(III) in both the metaphosphate glasses and the orthophosphate solution. This corresponds to the report of McClure (1957) that the apparent Δ value for Mn(III) in octahedral hydrates is several thousand wave numbers higher than that for V(III), Cr(III), and Fe(III). This increase is attributed to Jahn-Teller distortion of the octahedral symmetry. The red color contributed by Mn(III) was found useful, in the early days of the glass industry, in the "decolorization" of commercial glasses (Dingledy, 1965), although it is present in these glasses in small amounts relative to the Mn(II).

The 24,600 cm^{-1} maximum is that found by Bingham and Parke (1965) for Mn(II) in sodium borate glass and in various phosphate glasses, and is also that listed by Jørgenson (1962) for a number of octahedrally coordinated ligand structures of Mn(II) in solution. If this absorption is assigned to the $4\text{A}_1, 4\text{E}(\text{G})$ (doublet) transition for Mn(II) in octahedral coordination, $\Delta = 7000 \text{ cm}^{-1}$. It is possible that part of all of the Mn(II) is in tetrahedral coordination, the corresponding tetrahedral Δ being approximately $4/9 \Delta$ octahedral = 3100 cm^{-1} . Mn(II) in the metaphosphate glasses exhibits an orange fluorescence under ultraviolet radiation.

Iron

Relatively large amounts of iron can be dissolved in a metaphosphate glass without a great deal of visible coloration. Bamford (1962a) ascribes this to the existence of iron in phosphate glass largely as Fe(II), which absorbs uniformly in the visible region.

The metaphosphate glasses melted under either oxidizing or reducing conditions exhibit a broad strong absorption band from 8000 to 13,000 cm^{-1} , centered approximately at 10,000 cm^{-1} , and corresponding to the ${}^5\text{F}_2 \rightarrow {}^5\text{E}$ transition for octahedrally coordinated Fe(II) having $\Delta = 10,000 \text{ cm}^{-1}$. The same band appears in solutions of Fe(II) in 86.5% H_3PO_4 ; it appears that, as Bamford (1962a) suggested, even in the glasses melted under oxidizing conditions, there is sufficient Fe(II) to effectively dominate the spectral absorption.

A well defined absorption maximum at 24,700 cm^{-1} is exhibited by Fe(III) in 86.5% H_3PO_4 , with weaker bands at 22,500, 19,500, 13,800, and 10,500 cm^{-1} .

These correspond to the transitions from 6A_1 to the doublet 4A , $4E(G)$, to the doublet 2A_2 , ${}^3F_1(I)$, and to ${}^4F_2(G)$, ${}^6A_1(G)$, and $4F(G)$ for Fe(III) in octahedral coordination with Racah's B parameter = 740 and $\Delta = 15,500$.

Cobalt

Co(II) exhibits absorption maxima in metaphosphate glass in bands centered at 17,400 and 6600 cm^{-1} in the visible spectrum and in the near infrared. These are the same as found by Bamford (1962b) for Co(II) in sodium borate glass. Assignment of these triplet bands to the 4A_2 to ${}^4F_1(P)$ and 4A_2 to 4F_1 transitions for tetrahedrally coordinated Co(II) leads to $\Delta = 3900 \text{ cm}^{-1}$ corresponding to the 4A_2 to 4F_2 transition, and $B = 850$. This latter transition was not experimentally observed, because it was too far in the infrared for measurement by available instrumentation. The splitting of the absorption bands has been attributed to large-spin orbit parameters (departure from Russell-Saunders coupling) by McClure (1957). In 86.5% H_3PO_4 , Co(II) shows maxima at 18,000 cm^{-1} and 7200 cm^{-1} , giving the $\Delta = 3850$ and $B = 850$ by the above assignments, corresponding to the values obtained by Dunn (1960) for tetrahedrally coordinated Co(II).

Nickel

The position of the absorption spectrum maxima varies more for nickel than for any of the other first-row transition elements:

$\text{Ca}(\text{PO}_3)_2$	7600 cm^{-1}	13,200 cm^{-1}	14,700 cm^{-1}	23,200 cm^{-1}
NaPO_3	7600	13,700	14,700	23,900
H_3PO_4 (86.5%)	8200	14,100	15,200	25,000

Assignment of these frequencies to the transitions from 3A_2 , to 3F_2 , 3F_1 , 3A_2 to 1E , and 3A_2 to ${}^3F_1(P)$ for Ni(II) in octahedral coordination leads to $\Delta = 7600 \text{ cm}^{-1}$ for $\text{Ca}(\text{PO}_3)_2$ and NaPO_3 , and $\Delta = 8200 \text{ cm}^{-1}$ for 86.5% H_3PO_4 solution (corresponding to the position of the first band). Bates (1962) assigned $\Delta = 7,500 \text{ cm}^{-1}$ for nickel in a potassium borate glass. The Racah B parameters are 880 for $\text{Ca}(\text{PO}_3)_2$ glass, 910 for NaPO_3 glass, and 940 for 86.5% H_3PO_4 solution.

Bamford (1962b) noted a similar shift to lower wave numbers with higher Na_2O in sodium silicate and sodium borate glasses containing Ni(II) and attributed this to lower ligand field strengths, due to an increase in d-p orbital mixing at higher Na_2O content. Applying this explanation to the above data gives the expected result of the greatest d-p mixing for calcium metaphosphate, less for the sodium metaphosphate, and the least for the 86.5% H_3PO_4 solution.

A shift to higher wave number was observed by Schmitz-Dumont (1965) in octahedrally coordinated Ni(II) in crystalline structures when a smaller lattice dimension was introduced as, for example, by replacing Zr with Ti in a garnet. Application to the above spectral absorbance data for Ni(II), in phosphate glasses and in solution, gives the expected result: the 86.5% H_3PO_4 solution has the tightest structure (smallest octahedral-hole dimensions), the sodium metaphosphate glass is intermediate, and the calcium metaphosphate glass has the most expanded structure.

Copper

Cu(II) in metaphosphate glass has a strong absorption maximum at 11,800 cm^{-1} and a small shoulder absorption band at 14,400 cm^{-1} , this being ascribed to splitting of the 2F_2 upper electronic state by Jahn-Teller distortion. For Cu(II) in octahedral coordination, $\Delta = 11,800 \text{ cm}^{-1}$. Cu(II) in 86.5% H_3PO_4 has the corresponding absorption maximum at 12,200 cm^{-1} . Cu(I) in the glasses melted under reducing conditions displays a blue fluorescence under ultraviolet irradiation.

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