X-ray photoelectron spectroscopy and Fourier transform–infrared studies of transition metal phosphate glasses

E. E. KHAWAJA, S. M. A. DURRANI, F. F. AL-ADEL, M. A. SALIM*,
M. SAKHAWAT HUSSAIN ‡
*Energy Research Laboratory, Research Institute, *Department of Physics, and ‡Department of Chemistry, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia*

X-ray photoelectron spectroscopy and Fourier transform–infrared studies were carried out on phosphate glasses containing oxides of iron, cobalt, nickel, copper and zinc. The results suggest that the glasses containing iron and zinc may have structures in which both the phosphorus and the iron (or zinc) atoms are tetrahedrally coordinated by oxygen into three-dimensional structures which resemble the polymorphic forms of silica, whereas the glasses containing cobalt, nickel and copper may consist of polymeric chains of PO_4 tetrahedra bonded to adjacent tetrahedra via bridging oxygens. These polyphosphate chains are linked together by the interaction between the metal cation and the oxygens of the network former. In addition, the core level 2p shake-up satellites of the 3d-transition metal ions in these glasses were studied. The results support a suggestion that the satellites in the glass are most likely due to the electron transfer from ligand to metal 3d orbitals.

1. Introduction

Oxide glasses containing transition metal ions were reported to have semiconducting properties as early as 1954 [1]. Since then a great deal of work has been carried out on semiconducting glasses [2–5]. The general condition for this semiconducting behaviour is that the transition metal ion should exist in more than one oxidation state, so that conduction can take place by the transfer of electrons from low to high valence states. According to this condition, the dependence of the electrical conductivity on the ratio of the ion concentration in the low valence state to the total concentration of transition metal ions, C, should be such that the maximum conductivity is at $C \sim 0.5$. In fact, among all the glasses which have been so far investigated, maximum conductivity at $C \sim 0.5$ only occurs in iron phosphate glasses [2–5]. Various explanations have been proposed for this deviation from $C = 0.5$ [2–5]. However, it is realized that the effects of phase variation have not been adequately treated [3–5].

We have earlier applied X-ray photoelectron spectroscopy (XPS) to obtain an understanding of the role played by transition metals in changing the electrical conductivity [6, 7]. Phase separation was noted in some oxide glasses [6, 7]. In the present work, phosphate glasses containing 3d-transition metal ions (such as iron, cobalt, nickel, copper and zinc), with compositions similar to those used by Sayer and Mansingh [2], were studied using XPS and Fourier transform–infrared spectroscopy (FT–IR).

The present work deals with a study of 2p shake-up satellites of 3d-transition metal ions in these glasses.

Inner-shell X-ray photoelectron spectra (e.g. 2p of Co^{2+}, Ni^{2+}, and Cu^{2+} compounds) show intense satellites at 5–10 eV higher binding energy (i.e. lower kinetic energy) than at the main peak. This is the result of the ejected electron created in the photoejection process undergoing some energy loss. The appearance of the satellite has been the subject of many experimental and theoretical studies [8–12]. Their explanation still remains incomplete. One of the suggested processes is the transfer of the valence-like electron to an excited higher orbital of final state. The excitation of one 3d electron to 4s or 4p (roughly localized on the central atom) was initially put forward to explain the observed satellites [8]. Several other authors now consider the interatomic electron transfer from ligand to metal 3d orbits to be the most probable cause of satellites in crystalline compounds [9–12]. Little attention has been paid to the satellite structure in glasses containing transition metal ions. The present results suggest that the satellites in the glasses are most likely due to the electron transfer from ligand to metal 3d orbits.

2. Experimental procedure

The glasses were prepared by melting dry mixtures of $0.67\,P_2O_5$–$0.33\,Fe_2O_3$, $0.75\,P_2O_5$–$0.25\,Co_3O_4$, $0.50\,P_2O_5$–$0.50\,NiO$, $0.50\,P_2O_5$–$0.50\,CuO$, and $0.50\,P_2O_5$–$0.50\,ZnO$ in alumina crucibles. All the chemicals used were of reagent grade. The above compositions were such that the atomic ratio of phosphorus to metal in the glass was $2:1$. The P_2O_5 was

heated to 150 °C for 2 h prior to weighing the components for the batch. The crucible and contents were placed in a furnace maintained at 300 °C for 1 h prior to melting the mixture, to minimize volatilization. The crucible was then transferred to a melting furnace maintained at temperatures ranging from 1200–1400 °C depending on the glass [2]. The melt was left for about 4 h under atmospheric conditions in the furnace. During this time the melt was occasionally stirred with an alumina rod. The homogenized melt was then cast on to a stainless steel plate mould (pre-heated to 300 °C). The samples were disc-shaped with diameters of 1.5 cm and thicknesses of about 3 mm. The zinc–phosphate sample had a dull look, while all the other samples had the usual shiny appearance of glass. The samples were ground and polished with diamond paste down to a minimum grit size of 0.1 μm.

The XPS measurements were carried out in a V. G. Scientific ESCALAB MKII spectrometer equipped with dual aluminium–magnesium anodes. Details of the system are given elsewhere [13]. The energy scale of the spectrometer was calibrated using Cu $2p_{3/2}$ = 932.67 eV, Cu $3p_{3/2}$ = 74.9 eV, and Au $4f_{7/2}$ = 83.98 eV. The charging of non-conducting glass samples was avoided by flooding the sample with a separate source of low-energy electrons [7]. The energy and intensity of these external electrons were adjusted to obtain the best resolution as judged by the narrowing of the full width at half maximum (FWHM) of photoelectron peaks. It was found that at the optimum settings of the neutralizing gun (electron kinetic energy between 5 and 10 eV, electron emission current at the sample between 1 and 5 nA), the position of the adventitious C 1s line was within ± 0.5 eV of 284.6 eV. This peak arises due to hydrocarbon contamination, and its binding energy is generally accepted as remaining constant irrespective of the chemical state of the sample. For the sake of consistency, all energies are reported with reference to the C 1s transition at 284.6 eV.

For XPS measurements, the standard oxide powder samples were embedded in substrates of indium foil supported by metallic backing. The samples were loaded through a fast-entry airlock into a preparation chamber and finally into the analysis vessel. The base pressure in the analysis chamber during these measurements was less than 5×10^{-11} mbar.

Several kinds of deposition process have been proposed for the formation of thin films of multicomponent oxides [14]. Dijkkamp et al. [14] have reported that the laser-beam deposition of a high-temperature superconducting film resulted in the composition of films close to that of the bulk material. Following Dijkkamp et al. [14], thin glass films needed for infrared measurements were prepared by laser evaporation on KBr substrates. Similar methods have been detailed elsewhere [15], therefore only a brief description is given here. The glass disc was mounted in a vacuum chamber with a base pressure of the order of 10^{-6} torr (1 torr = 133.322 Pa) and irradiated through a KBr window with a pulsed CO_2 laser. A ZnSe lens was used to obtain an energy density of

about 60 J cm^{-2} on the target. Thin films were prepared from untreated (unpolished) glass samples. After the films were deposited, they were removed from the coating chamber and exposed to the ambient atmosphere, prior to XPS measurements. It was found that the XPS and infrared spectra of the films were somewhat different from those for the corresponding glasses. This difference in composition of the films compared to the targets from which they were prepared may be because of different evaporation rates for different components in the multicomponent glasses. Also, their structure may be different from those of the bulk, because they were condensed very quickly from the vapour. Present measurements suggest that the films were not truly representative of the glass from which they were prepared.

Infrared spectra were recorded with an Nicholet FT–IR spectrophotometer model 5DXD, in the range 360–1600 cm^{-1}. Glass sample pellets were prepared for infrared investigation by mixing approximately 10–15 mg glass powder with about 150 mg spectroscopic grade KBr powder and compressing the resulting mixture in an evacuable die under 20 000 lb (∼ 9072 kg) pressure. The KBr powder was dried at 110 °C and allowed to cool in a vacuum desiccator to avoid adsorption of moisture. The infrared spectra of thin films of all the glasses were also recorded.

3. Results
3.1. XPS: core levels O 1s and P 2p
In Fig. 1 spectra for the core level O 1s for the glasses are compared with that of the P_2O_5 powder. The O 1s
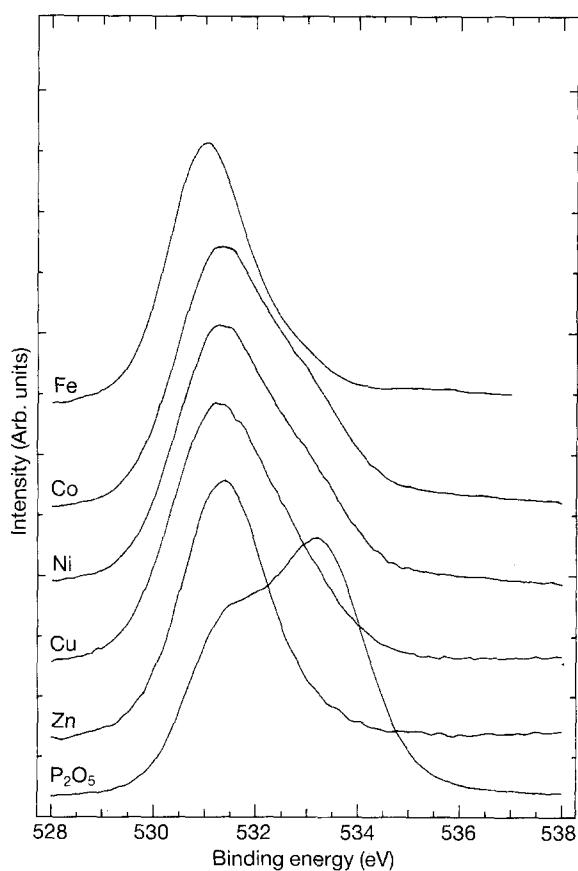

Figure 1 Core level spectra of the O 1s for glasses and the P_2O_5 powder.

TABLE I Peak positions and their FWHM for the core levels P 2p and O 1s of glasses and films in (eV). The P 2p for the P_2O_5 was at 134.7 eV with FWHM of 2.1 eV.

Metal	P 2p				O 1s			
	Position		FWHM[a]		Position		FWHM[a]	
	Glass	Film	Glass	Film	Glass	Film	Glass	Film
Zn	133.5	134.1	2.1	2.2	531.3	531.8	2.1	2.4
Cu	133.9	134.4	2.3	2.3	531.3	531.8	2.6	3.1
Ni	133.9	134.5	2.4	2.4	531.3	531.8	2.7	2.9
Co	133.9	134.4	2.4	2.4	531.3	531.8	2.8	3.1
Fe	133.3	134.2	2.1	2.3	531.0	531.7	2.0	2.9

[a] The O 1s spectra for some glasses and films were composed of broad and asymmetrical peaks (Figs 1 and 3). While assigning the above values, all the spectra were treated as being composed of single peaks.

spectrum for the P_2O_5 consists of two overlapping peaks. It is well known that the orthorhombic P_2O_5, being based on an assembly of discrete molecules, consists of PO_4 tetrahedra shared by three neighbouring tetrahedra; the fourth oxygen atom is considered to be double bonded to the phosphorus atom [16]. Therefore, in Fig. 1 the lower binding energy peak may be associated with non-bridging oxygen (P–O, bonding), and the high-energy peak with the bridging oxygen (P–O–P). The ratio of the area of the P–O and the P–O–P peaks, if our peak assignment is correct, should be 1 : 1.5, respectively. For every phosphorus atom there should be one non-bridging oxygen atom and 1.5 bridging oxygen atoms. As judged from Fig. 1, the ratio of the two peaks seems to be not too far from the expected value. The above assignment of the peaks can be justified from the well-known research results on sodium silicate glasses in which the bridging oxygen atoms are covalently bonded to two silicon atoms, while the non-bridging oxygen atoms are covalently bonded to one silicon atom and ionically bonded to one sodium ion. It is known [17] that the charge density on the non-bridging oxygen atom is about − 0.96 and the same on the bridging atom is − 0.65. This charge difference is reflected in a shift of the non-bridging atom peak (O 1s) towards a lower binding energy with respect to the bridging oxygen atom peak (O 1s) of about 2.3 eV [17]. In the present case, the corresponding shift in the P_2O_5 is about 1.8 eV (Fig. 1).

In Fig. 2 the XPS spectra of the core level P 2p for the glasses are compared with that of the P_2O_5 powder. The results of Figs 1 and 2 are summarized in Table I. In Fig. 1 the O 1s spectra for the iron and zinc glasses show narrow peaks when compared with those for the cobalt, nickel and copper glasses. Perhaps the O 1s peaks from all glasses are composed of more than one peak which may correspond to a different bonding mode of oxygen atoms in these glasses. However, in assigning the values given in Table I to all the cases, the spectra were treated as being composed of single peaks. In accordance with the width of the P 2p and the O 1s peaks (Table I), the glasses may be placed into two relatively well-defined types. Iron and zinc form one, say Type A, with full width a half maximum (FWHM) of both P 2p and O 1s peaks of about 2.1 eV, while the second, Type B

(cobalt, nickel and copper), has an increased FWHM for the P 2p to about 2.4 eV and for the O 1s to about 2.7 eV.

The O 1s peaks (Fig. 1) are broader in the Type B glass than those of the Type A glass. A point worth noting is the asymmetry on the high-energy side of the peaks for Type B. This suggests the presence of an additional high-energy component in the O 1s spectra for Type B. The build-up of the high-energy oxygen peak is clearer in the O 1s spectra for the laser-evaporated glass films (Fig. 3). The composition and the structure of a film, as already discussed, may not be the same as the bulk glass from which the film was prepared. Therefore, the film may not be regarded as being truly representative of the glass.
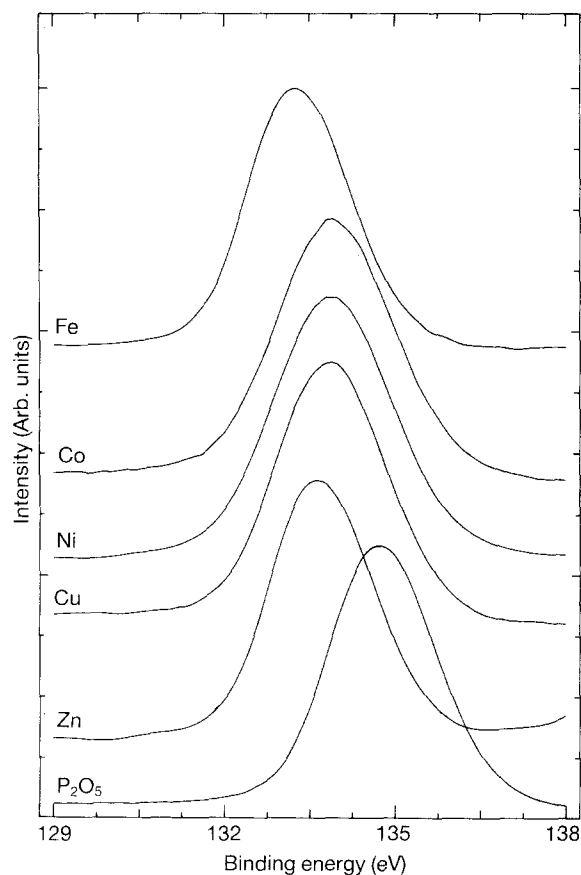

Figure 2 Core level spectra of the P 2p for glasses and the P_2O_5 powder.
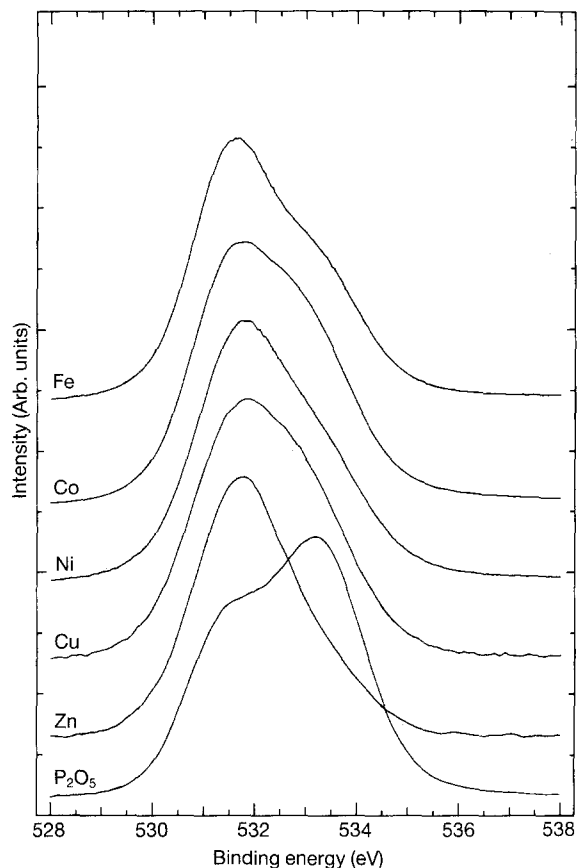
227

Figure 3 Core level spectra of the O 1s for the laser-evaporated glass films and the P_2O_5 powder.
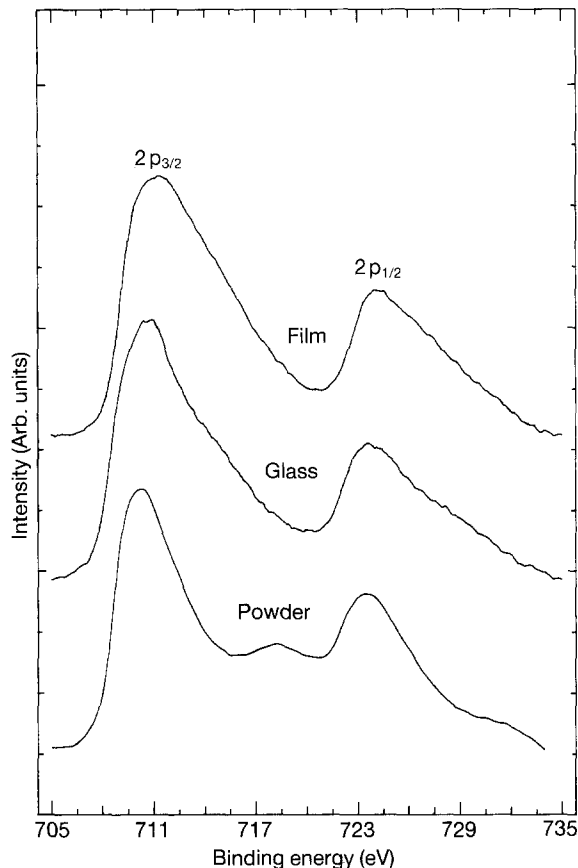

Figure 4 Core level spectra of the Fe 2p for the Fe_2O_3 powder, iron phosphate glass and a laser-evaporated glass film.

3.2. XPS: Shifts of metal 2p core levels

Various oxidation states of the first row transition metals in glasses are well established [4, 16, 18, 19], and for quick reference, these are listed in Table II. The oxidation states of the standard oxides are also given in Table II. For the glasses, besides the states that are given in Table II, other oxidation states for some of the metals may be possible, but their concentrations are known to be relatively small [4, 16, 18, 19], For example, less than 10^{-5}% of the cobalt would be expected in the trivalent form [18]. The present XPS results, as will be discussed, seem to agree with those given in Table II.

Core level spectra of the Fe 2p for the Fe_2O_3 powder, iron glass, and a laser-evaporated glass film are shown in Fig. 4. Similar spectra are shown for cobalt in Fig. 5, nickel in Fig. 6, copper in Fig. 7, and zinc in Fig. 8. The results are summarized in Table III. The results for the metal oxides are in good agreement with

TABLE II The most common valence states of metal ions in glasses [4, 16, 18, 19]

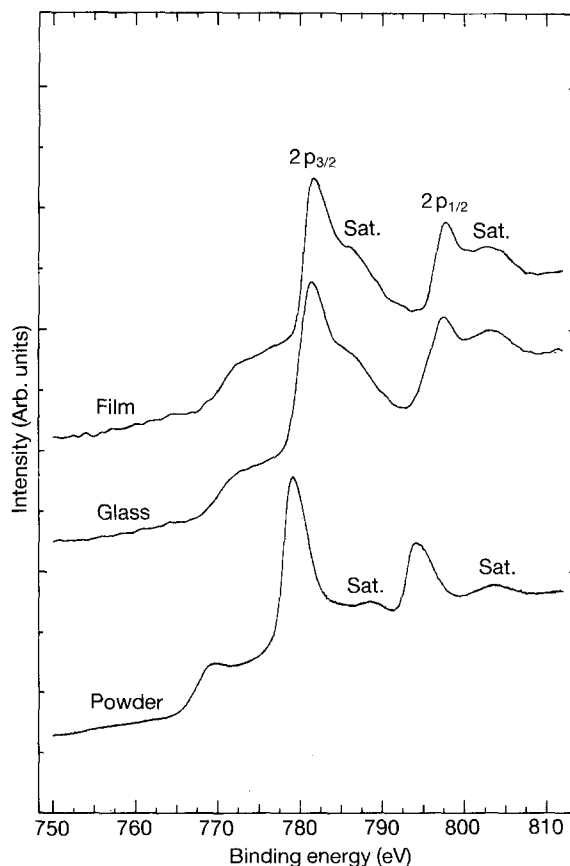| Metal	Metal oxide	Ionic states	
		Metal oxide	glass
Fe	Fe_2O_3	Fe^{3+}	Fe^{2+}, Fe^{3+}
Co	Co_3O_4	Co^{2+}, Co^{3+}	Co^{2+}
Ni	NiO	Ni^{2+}	Ni^{2+}
Cu	CuO	Cu^{2+}	Cu^+, Cu^{2+}
Zn	ZnO	Zn^{2+}	Zn^{2+}

Figure 5 Core level spectra of the Co 2p for the Co_3O_4 powder, cobalt phosphate glass and laser-evaporated glass film.

228

TABLE III Satellite structure in the photoelectron spectrum of the 2p shell of transition metal oxides

Metal	Specimen	$2p_{3/2}$		$2p_{1/2}$		
		BE[a] (eV)	ΔE_{sat}[b](eV)	BE[a] (eV)	ΔE_{sat}[b](eV)	ΔE_p^c (eV)
Zn	ZnO	1021.5	–	1040.6	–	23.1
	Glass	1022.4	–	1045.4	–	23.0
	Film	1022.7	–	1045.7	–	23.0
Cu	CuO	932.9	9.1	952.8	8.8	19.9
	Glass	932.5	–	952.4	–	19.9
		935.0	9.0	955.0	7.8	20.0
	Film	932.7	–	952.6	–	19.9
		935.5	8.9	955.6	7.7	20.1
Ni	NiO	854.0	6.0	871.7	6.3	17.6
	Glass	856.5	5.5	874.3	5.9	17.7
	Film	856.8	5.5	874.6	6.0	17.8
Co	Co_3O_4	779.2	9.3	794.3	9.5	15.1
	Glass	781.6	5.3	797.4	5.8	15.8
	Film	782.0	5.1	797.9	5.5	15.9
Fe	Fe_2O_3	710.3	7.8	723.5	d	13.2
	Glass	710.8	d	723.5	d	12.9
	Film	711.3	d	724.0	d	12.7

[a]Binding energy of the main peak.
[b]Energy separtion between the main peak and the satellite.
[c]Energy between $2p_{1/2}$ and $2p_{3/2}$
[d]Obscure.

those reported in the literature (for example [20, 21]). However, for the glass, we did not find such results. In going from a standard metal oxide to glass, the binding energies of the core levels $2p_{3/2}$ and $2p_{1/2}$ shift to higher energies (Table III) in all metals other than the peak marked (A) in Fig. 7 for the copper. It is well known [22] that the presence of non-equivalent atoms of the same element in a solid give rise to core level peaks with measurably different binding energies. Non-equivalence of atoms can be a result of (a) the difference in formal oxidation state, (b) the difference in molecular environment, etc. The binding energy
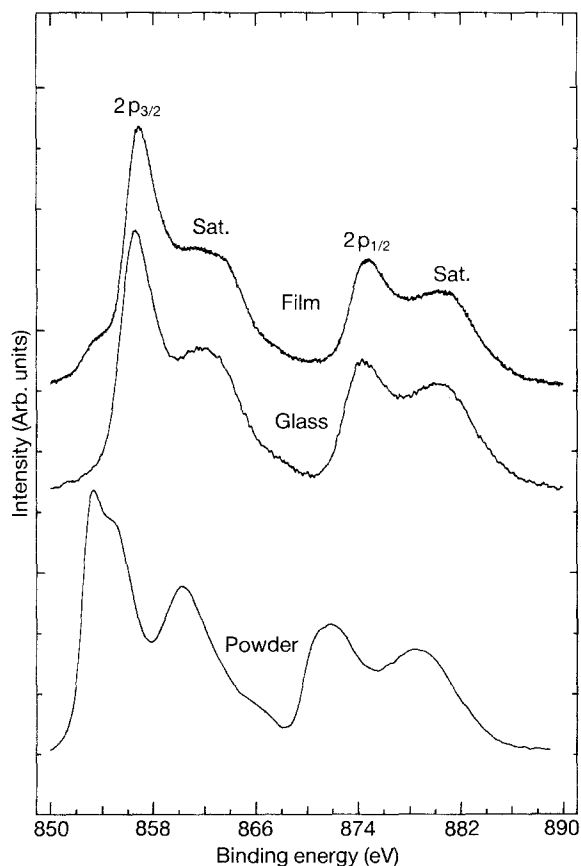

Figure 6 Core level spectra of the Ni 2p for the NiO powder, nickel phosphate glass and a laser-evaporated glass film.
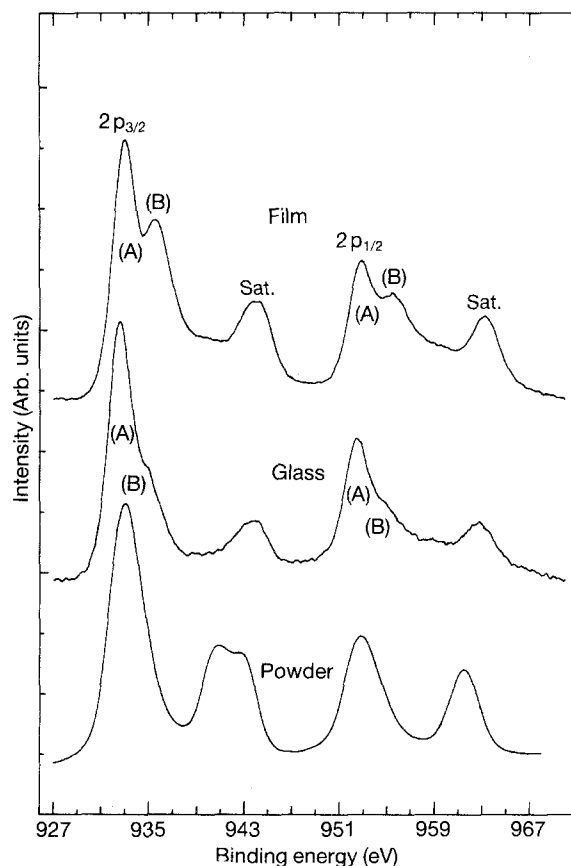

Figure 7 Core level spectra of the Cu 2p for the CuO powder, copper phosphate glass and a laser-evaporated glass film.
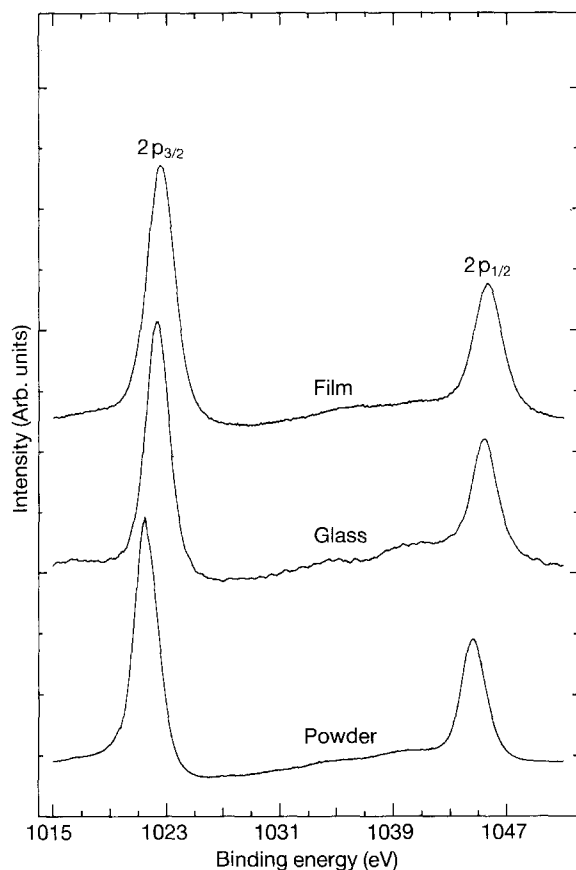
Figure 8 Core level spectra of the Zn 2p for the ZnO powder, zinc phosphate glass and a laser-evaporated glass film.

increases with an increase in the oxidation state of a metal atom. In the situation where the formal oxidation state is the same, the general rule is that the core level binding energy of the metal atom increases as the electronegativity (electron withdrawing power) of attached atoms or groups increases [22]. It is clear from Table II that the oxidation states of the transition metals either remain unchanged or are reduced to lower valence states, while going from metal oxide to glass. According to this, the energy of the metal 2p level should either remain unchanged or decrease upon going from oxide to glass, contrary to the observed increase in energy. Therefore, process (a) alone cannot account for the observed shifts. Perhaps formation of metal phosphates (process b) could be the dominant process responsible for the high-energy shift of the metal 2p levels. For example, the $Cu\,2p_{3/2}$ in CuO is reported to be at 933 eV, in $CuSO_4$ at 935.5 eV and in CuF_2 at 937 eV [21]. It may be mentioned that the group electronegativity of the $(PO_4)^{3-}$ ion is close to that of the $(SO_4)^{2-}$ ion [23]. Therefore, following on from the above, the $Cu\,2p_{3/2}$ in copper phosphate is expected to have an energy close to that of the $CuSO_4$. Indeed this is the case, as is discussed below.

Surface contamination, such as the formation of carbonates and hydroxide over the glass surfaces could also lead to a shift of the metal 2 p level to a higher energy with respect to that of the standard oxide. However, the absence of the higher energy components of the C 1s rule out any significant amount of carbonate present over the surfaces of the samples. McIntyre and Cook [24] have carried out an

XPS study on the oxides and hydroxides of divalent cobalt, nickel and copper. In going from an oxide to hydroxide they observed shifts to higher energies for the metal 2p levels: cobalt (1.0 eV), nickel (1.6 eV) and copper (0.6 eV). In the present work, the shifts in the 2p levels for the divalent ions, in going from an oxide to glass, are much larger (Table III): cobalt (2.4 eV), nickel (2.5 eV) and copper (2.1 eV). Therefore, the observed shifts in glass may not be due to the formation of hydroxide. Furthermore, the absence of component peaks due to the hydroxides in the 2p spectra rules out any significant amount of hydroxide that may have been present on the sample surfaces.

The Cu' 2p spectrum (Fig. 7) for the CuO exhibits the spin-orbit components $Cu\,2p_{3/2}$ and $Cu\,2p_{1/2}$ at binding energies of about 933 and 953 eV, respectively, with satellites at about 9 eV higher binding energy (Table III). In glass as well as in film, the 2p peaks show doublet structure (peaks marked A and B in Fig. 7). The separation between peaks A and B is about 2.5 eV. A doublet structure similar to this has been observed in the Cu 2p spectrum of the high-temperature superconductor $YBa_2Cu_3O_{6.85}$ [25], where the authors have assigned peak A to Cu^{2+} and peak B to Cu^{3+}. However, we believe that peak A is associated with Cu^+ and B with Cu^{2+} for the reasons discussed below. Monovalent and divalent are the only two oxidation states in which copper exists in various glasses (Table II). Furthermore, it is well known that copper compounds containing Cu^{2+} are associated with strong satellites (e.g the CuO spectrum in Fig. 7), while compounds with Cu^+ have no satellites [9–12]. A decrease in the intensity of the satellite peak is observed upon going from the CuO to glass (Fig. 7), which following the above, suggests that some of the Cu^{2+} are reduced to Cu^+ in the glass. Moreover, the satellite structure in Fig. 7 clearly follows the trend of peak B. Thus it may be concluded that peaks A and B are associated with Cu^+ and Cu^{2+}, respectively. The shift of peak B to high energy relative to the same peak for CuO is most likely due to the formation of copper phosphate, as observed in other glasses. Phosphate may also be formed by Cu^+ but in the case of monovalent copper the shifts due to a change of molecular environment are known to be small (less than 0.7 eV) compared to as high as 4 eV in divalent copper [20, 21]. The change in the $2p_{1/2}$–$2p_{3/2}$ separation of metal ions with different spin-states has been used diagnostically [26]. High- and low-spin complexes are possible for transition metal ions containing between 4 and 7 inner d-electrons (Fe^{2+}, Fe^{3+}, and Co^{2+} in the present case) while others (Ni^{2+}, Cu^+, Cu^{2+}, and Zn^{2+}) generally form one type of complex. Ni^{2+} in NiO and various glasses is known to exist in high-spin states [16], although in some other complexes which have square planar geometry, Ni^{2+} can be diamagnetic. The present results (Table III) agree with this, because the separation does not change significantly from sample to sample in the case of nickel, copper and zinc, while separation changes are large for cobalt and iron.

It was stated above that the binding energy of a metal core level increases (i) with an increase in its

230

oxidation state, and/or (ii) as the electronegativity of attached atoms groups increases (both of which lead to an increase in the effective positive charge on the metal ion). Hence, it may be said that an increase in the effective positive charge on a metal ion would result in an increase in the binding energy of its core level. Now, the shift of the metal core level 2p (Table-III) upon going from the metal oxide to the glass, is less than 1 eV for Type A glass, while it is greater than 2 eV for Type B glass (except for Cu^+, which is known to have small shifts in the 2p level upon a change of molecular environment). The larger shifts in Type B, compared to those in Type A, suggest that the metal ions in Type B have larger effective positive charge than those in Type A. This may be due to a difference in bonding of the metal ion between the two.

3.3 XPS: metal 2p satellites

The Fe (2p) spectrum of Fe_2O_3 powder (Fig. 4) shows a weak satellite at about 718 eV. However, the 2p peaks become asymmetrical in the case of both glass and film, with long tails on the higher energy sides. The spectra for glass and film are similar to that of the Fe_3O_4 observed by Kuivila et. al. [27]. It has been pointed out by Kuivila et. al. that the Fe (2p) spectrum of Fe_3O_4 is characterized by an apparent lack of satellite structure, which is actually the result of super-positioning of the Fe^{2+} and Fe^{3+} satellites. Therefore, it is possible that, in glass and film, iron exists as Fe^{2+} and Fe^{3+} and their broad satellites (known to be at 715 eV for Fe^{2+} and 719.8 eV for Fe^{3+}) [27] overlap, resulting in long tails on the high-energy side of the peaks (Fig. 4).

The Co (2p) spectrum of the Co_3O_4 powder (Fig. 5) shows weak satellites at 9.4 eV above the main peaks. This spectrum is similar to those reported for Co_3O_4 by Tyulier and Angelor [28] and McIntyre et al. [29]. In the glass and in the film, intense satellite lines which are closer to the main peaks are observed (Fig. 5 and Table III). Intense satellite lines have been observed for Co 2p in the case of high-spin $Co^{2+}(s = 3/2)$ compounds and complexes but not for diamagnetic Co^{3+} ($s = 0$) compounds and complexes [26, 30]. Furthermore, in high spin Co^{2+}, for example $CoCl_2$, the intensity of the shake-up peaks is far larger than those in a low spin Co^{2+} ($s = 1/2$) complex such as $Co(CN)_2$ [30]. The change in $2p_{1/2}-2p_{3/2}$ separation for cobalt ions with different spin states has been used diagnostically [26]; for example, this separation was found to be 15.0 eV for diamagnetic Co^{3+}, 15.4. eV for low-spin Co^{2+} and 16.0 eV for high-spin Co^{2+} complexes [26]. In the light of the above, we suggest that in the Co_3O_4 spectrum (Fig. 5) the weak satellites are associated with Co^{2+}, while diamagnetic Co^{3+} has no contribution. The observed increase in the intensity of the satellites on going from the Co_3O_4 to glass (or film) and also the increase in the Co $2p_{1/2}$–Co $2p_{3/2}$ separation (Table III) may be linked to the formation of high-spin Co^{2+} complexes in the glass. This is in line with the well-established result that the oxidation state of cobalt in glasses is generally Co^{2+} (Table II).

The Ni (2p) spectra of the NiO, glass, and film in Fig. 6 all show strong satellites with little variation in

intensity. Similar spectra were observed for some other nickel-containing glasses [6]. However, on going from the NiO to glass (or film) the satellites do show some shift towards the main peaks (Table III). This is most likely due to the formation of metal phosphate complexes in glass as well as in film. Nickel in glass is known to exist mainly as Ni^{2+}.

The Cu (2p) spectra of the CuO, glass, and film in Fig. 7 all show some satellite structure. The satellites are strongest in CuO because all the copper ions are in a divalent state. Compounds or complexes containing Cu^{2+} ions are known to exhibit strong satellites while those containing monovalent copper ions show no satellite structure. As already discussed in Section 3.2, in glass as well as in film, copper exists as Cu^{2+} and Cu^+. It is obvious from Fig. 7 that the intensity of satellites increases with an increase of peak B which is associated with Cu^{2+}.

The Zn (2p) spectra of ZnO, glass and film in Fig. 8, all show the absence of satellite structure.

3.4. FT–IR absorption

The FT–IR spectra of KBr pellets of glasses containing iron, cobalt, nickel, copper and zinc are shown in Fig. 9 and the corresponding peak positions are listed in Table IV along with those for the P_2O_5 from [31]. The P_2O_5 bands can be approximately identified as follows using the results of previous workers [31]:

$(PO_4)^{3-}$ group 500 cm^{-1}
P–O–P ring frequency at 780 cm^{-1}
P–O$^-$ stretching bond from 900–1035 cm^{-1}
P=O double stretching bond at 1260 cm^{-1}

As pointed out by Arzeian and Hogarth [31], there are two main differences when P_2O_5 infrared absorption is compared with the absorption spectra of glass.

1. Firstly, the $(PO_4)^{3-}$ band at 500 cm^{-1} is replaced by a much broader band (cobalt and copper glasses, Fig. 9) or by a number of bands (iron, nickel and zinc glasses, Fig. 9). These seem to be due to metal ions in the glass because the pure metal oxides have absorption bands in this region (for example, see Fig. 8 in [2]).

2. Secondly, the broadening and shift of the P–O$^-$ and P=O bands are noted in the glass spectra because of the presence of metal ions in the glass which altered these stretching frequencies. Other workers have also observed a shift in band position when a transition metal oxide is added to P_2O_5 glass, with a broadening of the band. This suggests the existence of a partial bond such as P–O–metal which may result in infrared absorption in the region 900–1100 cm^{-1}.

Earlier, on the basis of the XPS results (Section 3.1), two types of relatively well-defined glasses were identified: zinc and iron glasses forming Type A, and cobalt, nickel and copper forming Type B. The infrared spectra of these glasses (Fig. 9) suggest a similar trend. The P–O–P absorption band at about 760 cm^{-1} appeared as a very weak shoulder in the iron and zinc glasses (Type A) suggesting negligible P–O–P linkage in these glasses, while strong P–O–P bands were observed in the cobalt, nickel and copper glasses (Type B). Also,

TABLE IV Characteristic infrared absorption peaks for the P_2O_5 and phosphate glasses containing iron, cobalt, nickel, copper, and zinc ions (see also Fig. 9)

Specimen	Absorption peaks (cm^{-1})				Reference
	P=O	P–O$^-$	P–O$^-$	P–O–P	
P_2O_5	1260	1035	900	780[a]	[33]
Fe-glass	–	1084	940	779[b]	present work
Co-glass	1270	1072	917	753[a]	present work
Ni-glass	1205	1045	970	741[a]	present work
Cu-glass	1185	–	932	762[a]	present work
Zn-glass	–	1108	965	777[b]	present work

[a]Strong absorption band.
[b]Extremely weak shoulder.

the absorption band associated with P=O is present for Type B glass but not for Type A glass (Table IV). Similar infrared spectra have been observed for phosphate glasses containing iron, cobalt, nickel and copper by Sayer and Mansingh [2]. In fact, they also suggested the formation of two well-defined types in such glasses, again based on the 760 cm^{-1} bands. These results are in agreement with the XPS results,

Figure 9 Infrared spectra for glasses, from powdered glass samples in KBr pellets.

especially with the O 1s spectra in Fig 1. The development of the high-energy peak in the O 1s spectra (associated with the oxygen in P–O–P) follow a similar trend to the 760 cm^{-1} absorption band in the infrared spectra.

4. Discussion

The O 1s peaks for the glasses may be composed of more than one component peak, which may correspond to different bonding of the oxygen, such as P=O, P–O–P, and P–O–M (M refers to 3d-transition metal). The energy separation between the O 1s components associated with P=O and P–O–P is about 1.8 eV (Fig. 1) for the P_2O_5. The O 1s component associated with P–O–M will probably be located in between the locations of the P=O and P–O–P components. In fact, Goldman's study [32] of sodium–iron silicate glasses has concluded that the O 1s components associated with Si–O–Fe^{2+} and Si–O–Fe^{3+} are nearly coincident with the non-bridging (Si–O–Na) peak. Therefore, it may be possible that in the present case, the O 1s components of the P–O–M and P=O are close to each other. A careful examination of the O 1s spectra (Fig. 1) indicates some differences in the spectra of the two types. A build-up of high-energy component (in the vicinity of the P–O–P in P_2O_5) is observed in the spectra for Type B glasses (cobalt, nickel and copper), while this is absent in Type A glasses (iron and zinc). Thus the possible bondings of the oxygen, as suggested by the XPS study, are Type A glass P = O and P–O–M, and Type B glass P=O, P–O–M and P–O–P. Because the binding energies of the core level O 1s for the oxygen in the P–O and P–O–M are close to each other, the XPS fails to make a clear distinction between the two modes of bondings. On the other hand, FT–IR can easily distinguish between these two bonding modes because the absorption peaks corresponding to the two modes are well separated (Table IV). The absence of characteristic P=O absorption for Type A glass (Table IV), suggests that the oxygen bonding in this type is mainly P–O–M, whereas for Type B glass, infrared absorption peaks corresponding to all the three bonding modes of the oxygen are observed (Table IV), suggesting the presence of all three oxygen bonding modes in this type of glass.

Although identification of the structure of the two types of glasses is difficult, based on the present results,
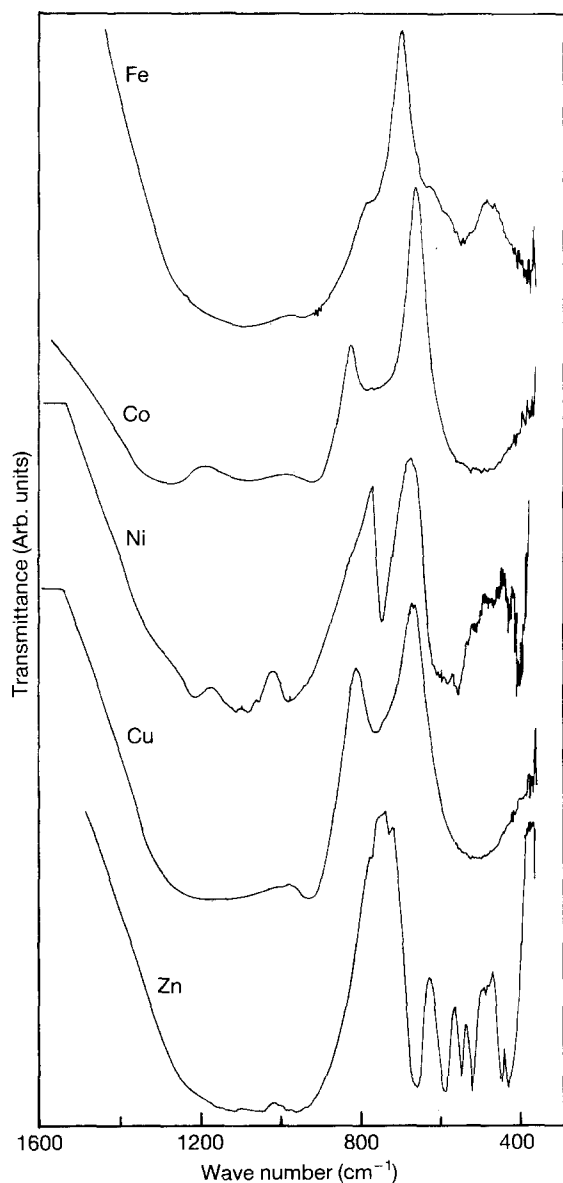
some structural difference between the two types are speculated. The binding energy of the core level P 2p for the P_2O_5 was found to be 134.7 eV with FWHM of 2.1 eV (Table I). All the phosphorus atoms in the P_2O_5 are expected to have nearly the same environment. Upon formation of glass with metal oxides, the P 2p peaks do show some shifts in energy (Table I) but their widths remain unchanged in Type A glass (zinc and iron), whereas the widths increase in Type B glass (cobalt, nickel and copper). The FWHM of various peaks, as reported by Mizokawa et al. [33] are, for P_2O_5 O 1s (3.45 eV) and P 2p (2.35 eV), and for $GaPO_4$; O 1s (2.1 eV) and P 2p (2.05 eV). In Fig. 1, if the O 1s spectrum for the P_2O_5 is treated as a single peak, then its FWHM is close to the value that is reported by Mizokawa et al. [33] for the $GaPO_4$. Furthermore, it is known that $GaPO_4$ (and also $FePO_4$) constitutes a unique class of orthophosphates in which both the phosphorus and another kind of atom (gallium or iron) are tetrahedrally coordinated by oxygen. Alternative tetrahedra are linked to form continuous three-dimensional structures which geometrically resemble the known polymorphic forms of silica [34]. In this type of structure the only possible bonding of oxygen is P–O–M. Now, for Type A glass it was suggested earlier that the oxygen was predominantly bonded as P–O–M and the FWHM of the O 1s and P 2p for the glass are nearly equal to those of $GaPO_4$. Therefore, it appears that Type A glasses have a structure similar to the orthophosphates. However, the long-range periodicity of the crystalline lattices would not be present in the case of the glasses.

It follows from the above that for Type A glass the majority of the cations (zinc or iron) may be found in a distribution of network forming (tetrahedral) sites. Ferric ion is expected to act as a network former, whereas ferrous iron in modifier sites is based upon charge balance considerations and Mössbauer data [32]. In the present work, the Fe 2p spectrum for the glass closely resembles that of the Fe_3O_4 (Section 3.3), therefore it is possible that a major portion of iron in the glass is in the Fe^{3+} state. Zinc in different compounds and complexes is known to have a Zn^{2+} ($3d^{10}$) state and its preference [16] to form tetrahedral species arises from: (a) the absence of any d-electron-driven preference for octahedral coordination, and (b) high polarizability and its tendency to form covalent bonds.

Nelson and Exarhos [35], in a study of binary metaphosphate glass with the stoichiometry $M(PO_3)_x$ where x equals the oxidation state of metal cation, have found that binary phosphates have the same basic structure regardless of the particular metal M (alkali, alkaline earth, transition metals, etc.). The glass consists of polymeric chains of PO_4 tetrahedra bonded to adjacent tetrahedra via bridging oxygens [35]. These polyphosphate chains are linked together by the interaction between the metal cation and the nonbridging oxygens of the network former [34, 35]. However, Type A glass forms a different structure, though Type B may have a structure of polyphosphate chains. This is supported by the following points:

(i) oxygen bonding: in polyphosphates, the modes of bonding [35] are P–O, P–O–M and P–O–P. In Type A the predominant bonding observed is P–O–M, while in Type B all three bondings have been observed;

(ii) metal bonding: in polyphosphates, metal cations exhibit ionic interactions with the polyphosphate anionic chains [35]. It was suggested earlier in Section 3.2, that the metal cations in Type B glass may have a larger effective positive charge than the cations in Type A glass. A large value of the effective positive charge on a metal cation is expected in an ionic mode of bonding. The results concerning the satellites may be summarized as follows: (i) satellites are absent when 3d orbitals are completely filled (for example Cu^+ and Zn^{2+}), and (ii) for a given metal ion, satellite separations and intensities differ for different ligands (Table III and Figs 4–8). In general, the present results are not much different from those obtained for compounds containing transition metals [9]. The two points noted above, and the well-known fact that satellites are absent in the metallic state suggest that the presence of satellites is most likely due to the electron transfer from ligand-to-metal 3d orbitals.

5. Conclusion

Binary phosphate glasses containing oxides of iron, cobalt, nickel, copper and zinc have been studied. XPS in combination with infrared spectroscopy can lead to a better understanding of the structural properties of a glass. Possible bondings of different atoms in the glass have been suggested. Based on this, some structures for the glass have been proposed. Glasses containing iron and zinc may have a structure similar to those of the orthophosphates in which both phosphorus and the iron (or zinc) atoms are tetrahedrally coordinated by oxygens: three-dimensional structures which resemble the polymorphic forms of silica. However, the long-range periodicity of the crystalline lattices would not be present for the glasses, whereas the glasses containing cobalt, nickel and copper may consist of polymeric chains of PO_4 tetrahedra bonded to adjacent tetrahedra via bridging oxygens. These polyphosphate chains are linked together by the interaction between the metal cation and the oxygens of the network former. These structural differences may have some effect on the electrical conductivity of the glasses.

The core level 2p shake-up satellites of the 3d-transition metal ions in phosphate glasses have been also studied. The present study suggests that the presence of satellites in the glass are most likely due to the ligand-to-metal 3d orbital electron transfer.

References

1. E. P. DENTON, H. RAWSON and J. E. STANWORTH, *Nature* **173** (1954) 1030.
2. M. SAYER and A. MANSIGH, *Phys. Rev.* **B6** (1972) 4629.
3. D. L. KINSER and L. K. WILSON, in "Recent Advances in Science and Technology of Materials", Vol. 1, edited by A. Bishay (Plenum Press, New York, 1973), p. 77.
4. L. MURAWSKI, C. H. CHUNG and J. D. MACKENZIE, *J. Non-Cryst. Solids* **32** (1979) 91.
5. C. H. CHUNG and J. D. MACKENZIE, *ibid.* **42** (1980) 357.
6. E. E. KHAWAJA, M. A. SALIM, M. A. KHAN, F. F. AL-ADEL, G. D. KHATTAK and Z. HUSSAIN, *ibid.* **110** (1989) 33.
7. Z. HUSSAIN, M. A. SALIM, M. A. KHAN and E. E. KHAWAJA *ibid* **110** (1989) 44.
8. A. ROSENCWAIG, G. K. WERTHEIM and H. J. GUGGENHEIM, *Phys. Rev. Lett.* **27** (1971) 479.
9. G. A. VERNON, G. STUCKY and T. A. CARLSON, *Inorg. Chem.* **15** (1976) 278.
10. K. S. KIM, *J. Electron Spectrosc. Rel. Phenom.* **3** (1974) 217.
11. SVEN LARSSON and M. BRAGA, *Chem. Phys. Lett.* **48** (1977) 596.
12. G. VAN DER LAAN, C. WESTRA, C. HAAS and G. A. SAWATZKY, *Phys. Rev.* **B23** (1981) 4369.
13. E. E. KHAWAJA, Z. HUSSAIN, M. S. JAZZAR and O. B. DABBOUSI, *J. Non-Cryst. Solids* **93** (1987) 45.
14. D. DIJKKAMP, T. VENKATESAN, X. D. WU, S. A. SHAHEEN, N. JISRAWI, Y. H. MIN-LEE, W. L. McLEAN and M. CROFT, *Appl. Phys. Lett.* **51** (1987) 619.
15. E. E. KHAWAJA, M. A. KHAN, F. F. AL-ADEL and Z. HUSSAIN, *J. Appl. Phys.* **68** (1990) 1205.
16. J. WONG AND C. A. ANGELL, "Glass Structure by Spectroscopy" (Marcel Dekker, New York, 1976).
17. B. M. J. SMETS and D. M. KROL, *Phys. Chem. Glasses* **25** (1984) 113.
18. C. R. BAMFORD, "Colour Generation and Control in Glass" (Elsevier Scientific, Amsterdam, 1977).
19. T. BATES, in "Modern Aspects of the Vitreous State", edited by J. D. Mackenzie (Butterworths, London, 1962) p. 195.
20. G. E. MULLENBERG (ed.), "Handbook of X-ray Photoelectron Spectroscopy" (Perkin–Elmer Corporation, Eden Prairie, MN, 1979).
21. C. D. WAGNER, in "Practical Surface Analysis by Auger and X-ray Photoelectron Spectroscopy", edited by D. Briggs and M. P. Seah (Wiley, Chichester, 1988) p. 477.
22. D. BRIGGS and J. C. RIVIERE, *ibid.*, p. 119.
23. J. E. HUHEEY, *J. Phys. Chem.* **70** (1966) 2086.
24. N. S. McINTYRE and M. G. COOK, *Anal. Chem.* **47** (1975) 2208.
25. A. BALZAROTTI, M. DeCRESCENZI, N. MOTTA, F. PATELLA and A. SGARLATA, *Phys. Rev.* **B38** (1988) 6461.
26. D. BRIGGS and V. A. GIBSON, *Chem. Phys. Lett.* **25** (1974) 493.
27. C. S. KUIVILA, J. B. BUTT and P. C. STAIR, *Appl. Surf. Sci.* **32** (1988) 99.
28. G. TYULIER and S. ANGELOR, *ibid.* **32** (1988) 381.
29. N. S. McINTYRE, D. D. JOHNSTON, L. L. COATESWORTH, R. D. DAVIDSON and J. R. BROWN, *Surf. Inter. Anal.* **15** (1990) 265.
30. D. C. FROST, C. A. McDOWELL and I. S. WOOLSEY, *Mol. Phys.* **27** (1974) 1473.
31. J. M. ARZEIAN and C. A. HOGARTH, *J. Mater. Sci.* **26** (1991) 5353.
32. D. S. GOLDMAN, *Phys. Chem. Glasses* **27** (1986) 128.
33. Y. MIZOKAWA, O. KOMODA, H. IWASAKI, D. H. SHEN and S. NAKAMURA, *J. Electron Spectrosc. Rel. Phenom.* **31** (1983) 335.
34. D. E. C. CORBRIDGE, "The Structural Chemistry of Phosphorus" (Elsevier Scientific, Amsterdam, 1974), p. 81.
35. B. N. NELSON and G. J. EXARHOS, *J. Chem. Phys.* **71** (1979) 2739.