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The X-Ray Fluorescence Spectroscopy of Inorganic Solids. VII. The Fe $K\beta_{1,3}$ Energy Shifts in Oxide Glasses

Michiko Yoshioka, Takashi Maekawa,* and Toshio Yokokawa
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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The Fe $K\beta_{1,3}$ energy shifts in the binary sodium borate, silicate, and phosphate glasses containing small amounts of the iron ion were examined. The Fe $K\beta_{1,3}$ energy decreases with an increase in the sodium oxide content in the borate and silicate glasses. The data are in accordance with those of previous studies that the coordination number of the Fe(III) ion is four in the borate and silicate glasses and six in the phosphate glasses. The structure of the coordination sphere around the Fe(III) ion in the borate glasses was also discussed.

Many studies have been reported about the chemical state of the transition metal ions in oxide glasses and melts. Especially, the optical and magnetic studies have provided much information about the valency state and the coordination number of these ions in the various host glasses.[1] Recently the coordination number of the Fe(III) ion in the binary glasses was estimated by means of Mössbauer spectroscopy; thus, it can be said the coordination number of the Fe(III) ion is six in Na_2O-P_2O_5 glasses and nearly four in Na_2O-SiO_2 and K_2O-B_2O_3 glasses.[2–4] The X-ray energy of the constituents of the oxide glasses varies slightly depending on their chemical surroundings (coordination number, bond polarity, and so on), as the previous studies of Al, Si, K have revealed.[5–7] In the present work, a two-crystal spectrometer was used for the measurement of the X-ray energy of the iron ion in the binary sodium borate, silicate, and phosphate glasses. The results were discussed in terms of the effective positive charge and the coordination number of the Fe(III) ion in these glasses.

Experimental

Apparatus. The iron fluorescence spectra were obtained by means of a two-crystal spectrometer as has been described in a previous paper.[8] The analyzing crystals were Ge ($2d$=0.6533 nm). The chromium X-ray tube (50 kV, 30 mA) was used for the primary excitation. The energy shifts were obtained by the "standard spectra method" developed in our laboratory.[9] The reference material was α-Fe_2O_3. The measurements were repeated at least ten times, and the limit of error was estimated, assuming the t-distribution, with a 95% certainty.

Samples. The glassy samples were prepared by melting weighed quantities of SiO_2, $NaH_2PO_4\cdot 2H_2O$, H_3BO_3, and Na_2CO_3 of a guaranteed reagent grade in a platinum crucible for 10—12 h at around 1000 °C (at around 1200 °C for silicates). The iron ion was added in the form of Fe_2O_3 or sometimes $Fe(COO)_2$. No appreciable difference was observed between the chosen starting materials.

Valency Change by X-ray Irradiation. High-energy irradiation generates the various defect centers in the glasses. When the transition metal ions are present in the glasses, they may react with defect centers to change their valency state. Bishay and Makar reported that a part of the Fe(II) ions change to Fe(III) ions when γ-ray irradiation in $CaO\cdot P_2O_5$ glass.[10] However, no differences were observed in the energy shifts of the same sample with different durations of the irradiation time. This means that the degree of the valency change is negligibly small under the present experimental conditions.

Results and Discussion

The $K\beta_{1,3}$ energy shifts in the binary glasses are summarized in Table 1 and are plotted in Fig. 1. The energy shifts depend on the composition and on the

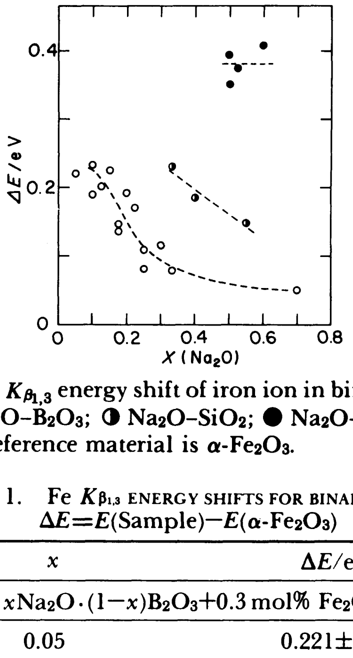

Fig. 1. $K\beta_{1,3}$ energy shift of iron ion in binary glasses.
○ Na_2O-B_2O_3; ◑ Na_2O-SiO_2; ● Na_2O-P_2O_5.
The reference material is α-Fe_2O_3.

Table 1. Fe $K\beta_{1,3}$ energy shifts for binary glasses
$\Delta E = E(\text{Sample}) - E(\alpha\text{-}Fe_2O_3)$

x	ΔE/eV
$x Na_2O\cdot(1-x)B_2O_3 + 0.3$ mol% Fe_2O_3	
0.05	0.221±0.027
0.10	0.189±0.057 0.232±0.026
0.125	0.201±0.073
0.15	0.225±0.015
0.175	0.135±0.043 0.146±0.068
0.20	0.193±0.025
0.225	0.170±0.038
0.25	0.080±0.024 0.108±0.073
0.30	0.115±0.054
0.333	0.078±0.035
0.70	0.049±0.058
$x Na_2O\cdot(1-x)SiO_2 + 1.0$ mol% Fe_2O_3	
0.333	0.230±0.033
0.40	0.184±0.019
0.55	0.148±0.020
$x Na_2O\cdot(1-x)P_2O_5 + 1.0$ mol% Fe_2O_3	
0.50	0.351±0.043 0.395±0.040
0.525	0.375±0.031
0.60	0.409±0.040

kind of glass in which the iron ion was doped. In each system, the characteristic behavior is as follows.

i) Fe ion in sodium borate glasses: The Fe $K\beta_{1,3}$ energy gets smaller with an increase in the sodium oxide content, and the energy drops abruptly at the particular mole fraction of the sodium oxide.

ii) Fe ion in sodium silicate glasses: The Fe $K\beta_{1,3}$ energy also decreases with an increase in the sodium oxide content. However, there seems to be no such sharp change in the shift with the composition as is seen in the sodium borate glasses.

iii) Fe ion in sodium phosphate glasses: The energy shifts are more positive than those in the above two systems. The composition dependence of the energy shifts could not be detected because of the narrow composition range covered in this work.

In the preliminary experiments, the X-ray energy shifts of Fe $K\beta_{1,3}$ in various crystalline iron compounds were measured. The results were in quantitative agreement with that of the previous author$^{11)}$ and so will not be presented here. However, the data suggest that the energy depends primarily on the effective positive charge on the Fe atom rather than on its formal charge, and that it changes with the coordination number. Thus, CN^-, S^{2-}, O^{2-}, and SO_4^{2-} as the counter anion in compounds gives rise to a negative shift of Fe $K\beta_{1,3}$ in that descending order nearly irrespective of the formal charge of the Fe atom. When O^{2-} is the common counter ion (*i.e.*, Fe_2O_3, FeO, FeO(OH), Fe_3O_4), the structure of the coordination polyhedron affects the shift. On the other hand, iron is substantially in the trivalent state in the glasses examined in the present study.$^{12)}$ Therefore, the data of the energy shift will be discussed from the viewpoint of the effects of the bulk basicity of host glasses and of the coordination number upon the iron(III) ion.

In our laboratory, the basicities of oxide melts have been measured in terms of the thermodynamic activity of Na_2O in Na_2O–P_2O_5, –B_2O_3, –SiO_2, and other binary systems. P_2O_5 was found to be a quite acidic oxide. The Na_2O activity in borate melts changes drastically (by an order of 10^4) at around 20 mol% Na_2O.$^{13)}$ These observations are in good agreement with the present results. Thus, the Fe(III) ion is the most positively charged in phosphate glasses, and becomes firmly coordinated with oxygen atoms with an increase in the basicity.

Kurkjian and Sigety concluded that the Fe(III) ion is tetrahedrally coordinated in silicate and octahedrally coordinated in phosphate glasses.$^{2)}$ Park and Chen, from their EXAFS measurements, showed that the Fe(III) ion coordinates six oxygens in sodium disilicate glass.$^{14)}$ Morinaga *et al.* also found the same Fe(III) ion in the acidic range of the system.$^{3)}$ Nishida and Takashima showed that the Fe(III) ion coordinated with four oxygen atoms is predominant in potassium borate glasses.$^{4)}$ These results, taken together, enable us to conclude that the Fe(III) ion coordinates six oxygen atoms in such an acidic range as in phosphate glass and four oxygens in a less acidic range. The boundary seems to be somewhere around a $K\beta_{1,3}$ energy of 0.25 eV referred to that of α-Fe_2O_3. Koster and Rieck's work$^{15)}$ on the Fe $K\beta_{1,3}$ energy shift in crystalline compounds in relation to the coordination number are in qualititative agreement with the present results for the glassy materials, although the absolute values differ between the two systems.

B_2O_3 is more acidic than SiO_2 as long as the Na_2O activity is compared at the same composition on a molar basis. Considering the number of atoms of B and Si in one mole of the oxide, however, the order of their acidity becomes nearly the same. This partly accounts for the sequential difference between the basicity, (silicate>borate>phosphate), and the Fe $K\beta_{1,3}$ shifts (borate>silicate>phosphate).

It is worthwhile to consider further the energy shift as a function of the composition in the borate glasses. In the low concentration range of the alkali metal oxide, the borate network consists mainly of a tetrahedral unit, accompanied by the alkali ions as charge compensators, in addition to the trigonal unit without the non-bridging oxygen ions. The further addition of the alkali oxide produces in the network a non-bridging oxygen ($-BO^-$). In the latter composition range, the Fe(III) ion can coordinate with the $-BO^-$ end group and make a coordination sphere with four bridging oxygens and one sodium ion ($[FeO_4]Na$). In the former range, however, some discussion is needed. The Fe(III) ion in this range is forced to accommodate itself to poor O^{2-} or O^- circumstances. Thus, the Fe(III) ions dissolve in the borate network without joining the sodium ions. Lacy proposed a tricluster model about the structure of the aluminium ions, a model in which the aluminium ion coordinates the bridging oxygen in the acidic glasses.$^{16)}$ From the similarity in the atomic dimensions between the Al(III) and Fe(III) ions, one possible explanation of the structure of the coordination sphere around the Fe(III) ion can be made by means of the above picture. On the other hand, Kawazoe *et al.* introduced a π-electron concept to aid in understanding the borate anomaly.$^{17)}$ In the low alkali content glasses, the p_π electrons of the oxygens delocalize among the network composed of the trigonal unit (for example, the boroxol ring). The appearance of a tetrahedral unit in the network (tetraborate, diborate, and so on) reduces the degree of resonance and causes an abrupt change in the basicity. Thus, either a tricluster type or an interstitial dissolution among boroxol groups may explain the existence of the Fe(III) ion in the network of the low alkali content glasses. The abrupt change in the $K\beta_{1,3}$ energy at 20 mol% Na_2O may correspond to the structural change in the coordination sphere around the Fe(III) ion in conjunction with the large structural change in the glass matrices.

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