The X-Ray Fluorescence Spectroscopy of Inorganic Solids. VI. The P *Kα* Energy of Phosphate Glasses and Crystals

Takashi MAEKAWA,* Masakazu FURUKAWA, and Toshio YOKOKAWA
Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

(Received June 29, 1983)

Synopsis. The P *Kα* emission spectra of several phoshorus compounds and phosphate glasses were examined. The P *Kα* energies decrease with an increase in the basicities of the matrices. The results also suggest that in order to interprete the chemical shift one must take into account the effects due to changes in the short range structure around the phosphorus atom in the PO_4 tetrahedron.

The present note reports an extension of our earlier studies concerning the X-ray fluorescence spectroscopy of inorganic glasses. Phosphorus is one of the most important constituents of oxide glasses and slags. However, in contrast with silicates, there have been few spectroscopic studies of the chemical state of phosphorus in phosphates. As to the X-ray spectroscopy, Fichter reported the *Kα* energies of phosphorus in various compound.[1] Although he found a relation between the effective charges on phosphorus and the P *Kα* energies, no chemical shifts of the P *Kα* energy among phosphates were observed. In this work, the P *Kα* energy shifts are obtained for several phosphate glasses and crystals. The results are discussed in connection with the effective positive charges on phosphorus and the basicity of the glasses.

Experimental

Apparatus. The P *Kα* from crystals and glasses were measured by means of a high resolution 2-crystal spectrometer (Toshiba AFV 701). The analyzing crystals were ADP. A Cr X-ray tube was used for the primary excitation. Pulses from a gas-flow proportional counter were stored in a multichannel analyzer. The other details including the procedure for determining the chemical shifts were described in previous papers.[2–4]

Samples. The glassy samples were prepared by melting desired quantities of commercial $NaH_2PO_4 \cdot 2H_2O$, P_2O_5, H_3BO_3, and Na_2CO_3 in a platinum crucible and then pouring them onto a stainless steel plate. The sodium ion concentration in glasses with a high P_2O_5 content was determined by the ion-selective electrode method. SiP_2O_7 and BPO_4 were synthesized by direct reactions of phosphoric acid with silica or boric acid. The other anhydrous phosphates were obtained by the dehydration of commercial reagents in an electric furnace. All the crystalline samples were examined by means of an X-ray diffraction method.

Results and Discussion

In Table 1 are compiled the results of the P *Kα* energy shifts of phosphates (crystals and glasses) referred to that of $NaPO_3$ glass. In contrast to the results of the previous author,[1] it could be detected that the P *Kα* energy depends on the kind and the content of the metal ion, even among phosphates. This behavior may become clearer when looking at the relation between the energy shifts of the glassy samples and their composition. In Fig. 1 the composition dependence of the P *Kα* energy of Na_2O–P_2O_5 and Na_2O–P_2O_5–B_2O_3 glasses is shown. In the binary glasses, the P *Kα* energy decreases with an increase in the Na_2O contents, which is consistent with the previous results for Si *Kα*.[3] The addition of B_2O_3 to $NaPO_3$ glass results in smaller shifts than in binary glasses.

It has been shown that the *Kα* energies of the third period elements increase with an increase in the partial positive charges on the corresponding elements.[5] Therefore, the P *Kα* energy reflects the degree of polarity of the phosphorus–oxygen bond in the PO_4 tetrahedron. Around an one-to-one mole ratio of Na_2O to P_2O_5, *i.e.*, $NaPO_3$, phosphate changes its form with an increase in the Na_2O contant as follows:

$$PO_{2.5} \longrightarrow PO_3^- \longrightarrow PO_{3.5}^{2-} .$$

Because of the rather strong acidic character of P_2O_5,

TABLE 1. PHOSPHORUS *Kα* CHEMICAL SHIFTS OF PHOSPHATES
$\Delta E = E(\text{Sample}) - E(\text{NaPO}_3)$

Sample			ΔE/eV	
Crystals				
1	SiP_2O_7		0.079±0.007[a]	[10][b]
2	$AlPO_4$		0.079±0.005	[10]
3	$Mg_2P_2O_7$		0.054±0.007	[10]
4	BPO_4		0.048±0.007	[10]
5	$FePO_4$		0.040±0.007	[10]
6	$Zn_3(PO_4)_2$		0.016±0.004	[7]
7	$Mg_3(PO_4)_2$		0.010±0.005	[9]
8	Li_3PO_4		0.007±0.005	[10]
9	KH_2PO_4		−0.007±0.009	[11]
10	$Ca_3(PO_4)_2$		−0.008±0.009	[10]
11	Na_3PO_4		−0.009±0.005	[9]
12	K_3PO_4		−0.010±0.004	[13]
13	K_2HPO_4		−0.022±0.004	[7]
14	$Na_4P_2O_7$		−0.027±0.005	[7]
Glasses				
Na_2O(mol%)	P_2O_5	B_2O_3		
20.0	80.0	—	0.027±0.004	[7]
40.0	60.0	—	0.016±0.007	[10]
50.0	50.0	—	0.0 (reference)	
55.0	45.0	—	−0.005±0.004	[9]
60.0	40.0	—	−0.002±0.004	[9]
8.3	8.3	83.3	0.034±0.006	[11]
20.0	20.0	60.0	0.022±0.005	[8]
25.0	25.0	50.0	0.011±0.004	[12]
33.3	33.3	33.3	0.009±0.004	[10]
45.5	45.5	9.1	0.004±0.006	[10]

a) Error limit; t-distribution 95% certainty. b) Number of measurements.

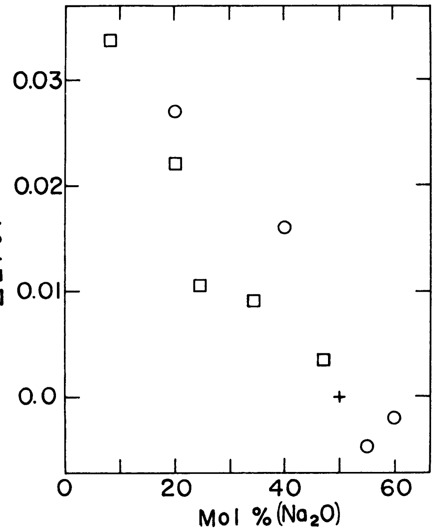

Fig. 1. Composition dependence of P $K\alpha$ energy shifts of Na_2O–P_2O_5 (○) and Na_2O–P_2O_5–B_2O_3 (□) glasses. The reference material is $NaPO_3$ (+).

this sequential transformation is sensitive to the composition, especially at the equivalent points. This transformation naturally leads to the changes in the effective charge on the phosphorus atom. The effect of the B_2O_3 addition, therefore, is understandable, though B_2O_3 is a weak acid compared with P_2O_5.⁶⁾ Figure 2 shows the dependence of the P $K\alpha$ energy shifts on the theoretical optical basicity, as defined by Duffy and Ingram.⁷⁾ The P $K\alpha$ energy increases with a decrease in the optical basicities. However, the P $K\alpha$ energy shifts are larger in the Si and Al phosphates than in alkali phosphates, even with the same optical basicity.

The addition of alkali or alkaline earth metal oxides to a pure P_2O_5 causes the breakage of a P–O–P bond, giving rise to a non-bridging oxygen ion, accompanied by adjacent metal ions as charge compensators. In this case, the isostructural picture with the corresponding silicate can be expected. If more electronegative elements, such as silicon or aluminium, are located, they will form a linkage such as -P-O-Si-O- at the expence of the P=O double bond. The electrons which have been localized on a PO_4 tetrahedron as a double bond with oxygen then diffuse to adjacent polyhedra (SiO_6 in the above case). In other words, the effective positive charge on phosphorus should increase much more than would be expected from the average electronegativity or theoretical optical basicity. The $K\alpha$ energy increases in proportion to the increased positive charges on the phosphorus atom. A further quantitative discussion will be made after measuring the P $K\alpha$ spectra, which give direct information about the chemical bond in phosphates.

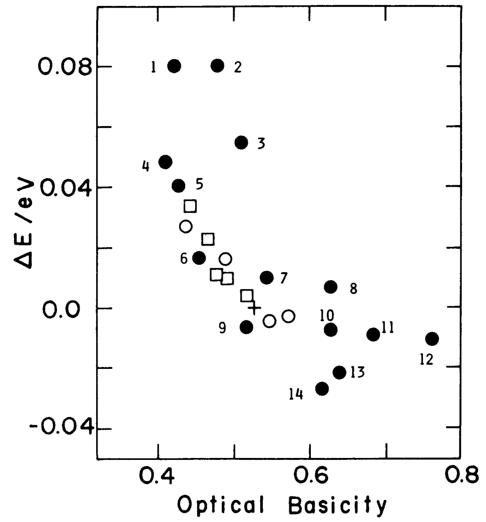

Fig. 2. The relation between P $K\alpha$ energy shifts and theoretical optical basicities of Na_2O–P_2O_5 (○), Na_2O–P_2O_5–B_2O_3 (□) and phosphates (●). The reference material is $NaPO_3$ (+). Numbers indicated in the figure correspond to the compounds in Table 1.

The present work was partially supported by a Grant-in-Aid for Foundamental Scientific Research from the Japan Society of Promotion Science. (T. Maekawa).

References

1) M. Fichter, *Spectrochim. Acta, Part B*, **30**, 417 (1975).

2) T. Maekawa, N. Kikuchi, N. Fukuda, and T. Yokokawa, *Bull. Chem. Soc. Jpn.*, **51**, 777 (1978).

3) T. Maekawa, N. Kikuchi, S. Sumita, and T. Yokokawa, *Bull. Chem. Soc. Jpn.*, **51**, 780 (1978).

4) N. Kikuchi, T. Maekawa, and T. Yokokawa, *Bull. Chem. Soc. Jpn.*, **52**, 1260 (1979).

5) G. Leonhardt and A. Meisel, *J. Chem. Phys.*, **52**, 6189 (1970).

6) T. Yokokawa and S. Kohsaka, *J. Chem. Eng. Data*, **24**, 167 (1979).

7) J. A. Duffy and M. D. Ingram, *J. Non-Cryst. Solids*, **21**, 373 (1976).