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Author(s)	Sakka Sumio
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Application of X-Ray Emission Spectroscopy to the Study of Glass Structure

Sumio SAKKA*

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The problem of coordination of aluminum in various glasses has been discussed on the basis of the literatures and the present author's recent works. In addition, possibilities of applying x-ray emission spectroscopy to the other problems of glass structure have been presented.

I. INTRODUCTION

In the previous review paper¹⁾ entitled "X-Ray K-Emission Spectroscopy and its Application to Oxides and Silicates", it was pointed out that x-ray emission spectroscopy might be a powerful technique for obtaining short-range structural and chemical informations on inorganic glasses because the lack of long range order does not affect the chemical shift of emission x-rays and many of practically important glasses contain silicon and aluminum as major constituents that are suitably subjected to this technique but not to the other techniques²⁾ such as ESR, NMR, optical spectroscopy and Mössbauer measurements. In the same paper some subjects on glasses to be studied by this technique were suggested. Since then a number of experiments have been conducted in our laboratory using a fluorescence x-ray instrument and some pertinent papers have been published by the other research groups. These works were reviewed critically and the future scope of the x-ray emission spectroscopy as applied to glasses was described in the present paper.

It will be convenient to have a rough idea of chemical compositions of inorganic glasses³⁾ currently being used practically or studied from the scientific and technical interest. They are:

1. Simple oxides such as SiO_2 , B_2O_3 , P_2O_5 and GeO_2 .
2. Multicomponent oxides such as silicates, borates, phosphates, germanates, aluminates, tellurites and tungstates.
3. Simple chalcogenides such as As-S, As-Se, As-Te and Ge-S glasses.
4. Multicomponent chalcogenides such as As-Si-Se, As-Si-Ge-Te and $\text{Li}_2\text{S-CdS-GeS}_2$ glasses.
5. Oxychalcogenides such as $\text{As}_2\text{S}_3\text{-Sb}_2\text{O}_3$ and $\text{As}_2\text{S}_3\text{-CuO}$.
6. Nitrates, sulfates and chlorides such as $\text{KNO}_3\text{-Ca}(\text{NO}_3)_2$, KHSO_4 and ZnCl_2 glasses.
7. Metallic alloys such as Au-Si-Ge glasses.

* 作花濟夫: Laboratory of Ceramic Chemistry, Institute for Chemical Research, Kyoto University, Uji, Kyoto.

II. COMMENTS ON THE EXPERIMENTAL PROCEDURE

There are two ways of generating x-ray emissions: the x-ray irradiation using an x-ray fluorescence spectrometer and the electron bombardment using an electron microprobe x-ray spectrometer. Although the latter is characterized by a high efficiency in producing x-rays, the former would give more reliable data for glasses which often undergo the irradiation damage caused by electron bombardment.⁴⁻⁶⁾ Therefore, a commercially available x-ray fluorescence spectrometer has been used by the present author as well as most of the others. It should be noted, however, that many efforts have been made by Gohshi⁷⁾ to raise the precision in the determination of x-ray emission peaks by the use of a high precision double-crystal spectrometer.

Usual way of dealing with the emission data of glass is to determine the position (angle 2θ) of an x-ray peak for a particular element in a glass sample and a reference material and compare the difference in the peak position

$$42\theta = 2\theta (\text{reference}) - 2\theta (\text{glass})$$

with 42θ obtained for the element in the crystals whose structure is well examined by the x-ray diffraction analysis. Then, experimentally, the determination of 42θ is important. The most obvious factor affecting the measured values of the peak position 2θ is the temperature of the analysing crystal. With commercial x-ray instruments, this problem appears to be solved by keeping the room temperature constant during a series of measurements, warming up the instrument for 4 to 5 hours⁸⁾ and frequently repeating the determination of the 2θ value of the reference material.

Continuous scanning with a rate of $1/4^\circ (2\theta)/\text{min.}$, for example, could be employed for the $\text{AlK}\alpha_{1,2}$, $\text{SiK}\alpha_{1,2}$ and $\text{ClK}\alpha_{1,3}$ lines from alkali- and alkaline earth-silicate, borate, phosphate and germanate glasses when they contained as much as 10% Al_2O_3 , 10% SiO_2 and 1% Cl, respectively. The noise/signal ratio was much higher for the other lines of $\text{K}\alpha$ and the lines of $\text{K}\beta$ because of lower efficiency in excitation. For such lines it would be necessary to employ the time-consuming step scanning procedure in order to obtain reliable line profiles.

One of the important precautions to be taken in the continuous scanning with a commercially available fluorescence spectrometer is to use the same specimen size (diameter of the disc to be exposed to activating x-rays) for the samples to be examined and the reference material. The use of different size was found to cause a quite serious difference in the position of the peak. This kind of precaution may be taken for granted in itself. In the case of the x-ray fluorescence spectroscopy, however, the use of the same sample size means that we have to vary the power of the primary x-ray generator, because the intensity differences of emission x-ray between samples are too great to be adjusted for recording by regulating the rate meter and scaler ranges alone.

Let us suppose that the 2θ for the $\text{AlK}\alpha_{1,2}$ line from $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ glasses containing 20 mole% Al_2O_3 is compared with that from Al metal. Since the metal is 100% in Al concentration and contains no other element which absorbs the x-ray, the intensity of the fluorescence x-ray is much higher than for the glass if the size of the specimens are the same. It may happen that one uses a smaller size specimen for

the Al metal and a larger size for the glass, in order to avoid frequently switching the voltage and current of the x-ray generator. The present author checked the effect of specimen size on the observed position of $\text{AlK}\alpha_{1,2}$ using the specimens having the irradiation surface diameters of 38 mm and 15 mm under the condition of measurements: scanning rate of goniometer $1/4^\circ/\text{min}$, chart speed 20 mm/min, fine solar slit (dispersion angle 0.115) used, analysing crystal EDDT, x-ray tube Cr (50 kV, 40 mA). A commercially available Rigakudenki x-ray fluorescence spectrometer was used. With all the specimens tested (Al metal, $\alpha\text{-Al}_2\text{O}_3$, $\text{Al}(\text{PO}_3)_3$ crystal and some glasses) the peak position for 38 mm diameter was found at the 2θ value 0.030° higher than that for 15 mm diameter, when the peak position was identified as the center at half-height and 0.006° higher when the peak position was identified as the center at 95% height of the peak. This clearly indicates that the specimens of the same size must be used for a series of measurements. The displacement caused by the specimen size would be attributed to an insufficient collimation of emitted x-rays by the solar slit. Incidentally, no such displacement of the peak position was observed with the variation of voltage and current of the x-ray generator. The shift $\Delta 2\theta$ for $\alpha\text{-Al}_2\text{O}_3$ relative to Al metal obtained by Day and Rindone⁹⁾ was about 0.030° smaller than the values published by other workers, and the reason might have been their use of a smaller specimen for Al metal as a reference.

III. COORDINATION OF ALUMINUM IN GLASSES

1. Aluminum in glasses

Aluminum is an important constituent in glasses not only because it is present in practical glasses more or less, but because its addition often improves the glass properties very much. For instance, Al_2O_3 endows conventional silicate glasses with improved chemical durability¹⁰⁾ and resistance to devitrification in a small concentration, reduces the tendency to liquid immiscibility of alkaline earth silicates and borates, enlarging glass-forming region¹¹⁾ and plays an essential role in a large concentration in preparation of low-expansion transparent glass-ceramics¹²⁾ of the $\text{Li}_2\text{O-Al}_2\text{O}_3\text{-SiO}_2$ system and ferroelectric glass-ceramics as constituents of precipitating crystals and/or a promotor of the favorable phase separation.

Thus far, numerous studies have been made of the properties of glasses containing Al_2O_3 . Many authors attributed anomalies on the property-composition curves such as minimum, maximum and abrupt change in the slope to the formation of sixfold-coordinated Al^{3+} ions, that is, AlO_6 groups, as shown in Table 1. Aluminum has been known to exist both as AlO_4 tetrahedra and AlO_6 octahedra in aluminosilicate minerals depending upon their compositions and polymorphs.

A more or less direct evidence for the presence of the AlO_6 groups in glasses was not demonstrated, however, until Day and Rindone⁹⁾ applied fluorescence x-ray spectroscopy to this problem. Infrared spectroscopy²⁹⁾ is known to contribute to the confirmation of the presence of AlO_4 groups in glasses but to be applicable for AlO_6 groups with considerable difficulty. NMR spectrum of ^{27}Al cannot distinguish AlO_6 groups from AlO_4 groups, according to Bishop and Bray.³⁰⁾

Table 1. Properties of Glasses Explained on the Basis of Presence or Non-Presence of 6-Coordinated Aluminum Ions.

Investigator	Glass system	Property	Remark	Reference
Isard	Na ₂ O-Al ₂ O ₃ -SiO ₂	Activation energy for electrical conduction	AlO ₄ -AlO ₆	14 (1959)
Galant	Na ₂ O-Al ₂ O ₃ -SiO ₂ and K ₂ O-Al ₂ O ₃ -SiO ₂	Refractive index	AlO ₄ -AlO ₆	15 (1960)
Kind and Makhlina	SiO ₂ + addition	Crystallization	AlO ₆	16 (1960)
Day and Rindone	Na ₂ O-Al ₂ O ₃ -SiO ₂	Refractive index, density, molar refractivity, IR spectra	AlO ₄ -AlO ₆	17 (1962)
Day and Rindone	Na ₂ O-Al ₂ O ₃ -SiO ₂	Internal friction	AlO ₄ -AlO ₆	18 (1962)
Lacy	Na ₂ O-Al ₂ O ₃ -SiO ₂	(Geometrical consideration)	AlO ₄ -only (Tricluster)	19 (1963)
Graham and Rindone	Na ₂ O-Al ₂ O ₃ -SiO ₂	EMF	AlO ₄ -AlO ₆	20 (1964)
Bonetti, Locardi and Tornati	Na ₂ O-Li ₂ O-Al ₂ O ₃ -SiO ₂	Refractive index and chemical durability	AlO ₄ -AlO ₆	21 (1965)
Riebling	Na ₂ O-Al ₂ O ₃ -SiO ₂ (melt)	Viscosity, density	AlO ₄ -AlO ₆	22 (1966)
Everest and Napier	Na ₂ O-Al ₂ O ₃ -SiO ₂	Liquidus	AlO ₄ -AlO ₆	23 (1966)
Heckman, Ringlien and Williams	Na ₂ O-Al ₂ O ₃ -SiO ₂	Na ⁺ Diffusion	AlO ₄ -only	24 (1967)
Riebling and Duke	BeO-Al ₂ O ₃ -SiO ₂ (melt)	Electrical conduction and viscosity	AlO ₄ -AlO ₆	25 (1967)
Terai, Kuroda and Ueno	Na ₂ O-Al ₂ O ₃ -SiO ₂	Na ⁺ diffusion, Knoop hardness, softening and transition temperatures	AlO ₄ -only (Tricluster)	26 (1969)
Taylor and Rindone	Na ₂ O-Al ₂ O ₃ -SiO ₂	Low-temperature viscosity	AlO ₄ -AlO ₆	27 (1970)
Naruse, Abe and Takami	CaO-Al ₂ O ₃ -B ₂ O ₃ and BaO-Al ₂ O ₃ -B ₂ O ₃	Transition temperature	AlO ₄ -only (Tricluster)	28 (1971)

2. Coordination of Al in Na₂O-Al₂O₃-SiO₂ glasses based on x-ray emission spectroscopy

In 1962, Day and Rindone⁹⁾ measured the peak position 2θ for the AlK α emission from Al metal and from Na₂O-Al₂O₃-SiO₂ glasses, and the difference $\Delta 2\theta$ was determined. The displacement of the peak was compared with those for α -Al₂O₃ and AlPO₄, Al ions being 6-coordinated in the former and 4-coordinated in the latter. It was concluded that glasses with an Al/Na ratio equal to or less than 1 contain only Al ions in 4-coordination, while glasses with the Al/Na ratio over 1 contain the Al ions in excess of the Na ions in 6-coordination. As the authors themselves pointed out, however, the experimental value of displacement for the AlK α from α -Al₂O₃ appeared a little too small ($2\theta=0.06$) compared with the values obtained by other workers ($\Delta 2\theta=0.08-0.10$), but no explanation was given to the reason for the discrepancy.

Later, Na₂O-Al₂O₃-SiO₂ glasses emerged as practically important ones, because such glasses were found suitable for strengthening by ion exchange,³¹⁾ and recently, Terai, Kuroda and Ueno,²⁶⁾ Tagai, Iwai and Mori³²⁾ and Sakka and Yamamoto³³⁾ reexamined the chemical shift of the AlK $\alpha_{1,2}$ emission from Na₂O-Al₂O₃-SiO₂ glasses. Their results are summarized in Fig. 1, together with the data of Day and Rindone.⁹⁾

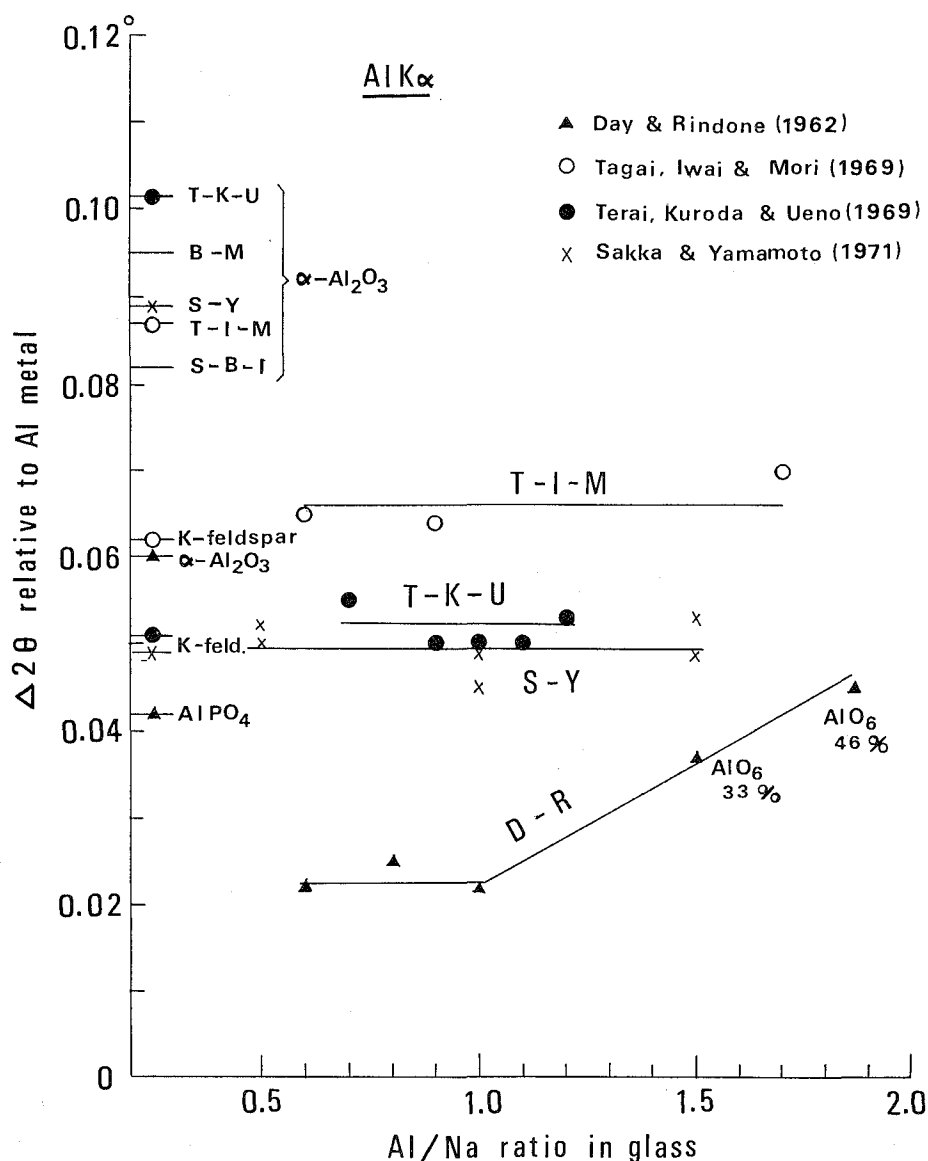


Fig. 1. Chemical shifts of AlK $\alpha_{1,2}$ for Na₂O-Al₂O₃-SiO₂ glasses with varying Al/Na atomic ratio.

It is seen that except for the values obtained by Day and Rindone, the values of the chemical shift do not change with the Al/Na ratio even when the ratio exceeds 1, and correspond approximately to those for potassium feldspar containing only 4-coordinated Al³⁺ ions. In other words, all the recent data show that essentially all Al³⁺ ions remain 4-coordinated throughout the Al/Na ratio range examined in contrast with the conclusion of Day and Rindone. Small differences between the chemical shift data of the respective research groups would be attributed to the difference in experimental conditions and the way of reading the angles of the peak on the spectra; Terai

*et al.*²⁶⁾ and Sakka *et al.*³³⁾ read the center at 90 and 95% height, and Tagai *et al.*³²⁾ the center at half height. Considering that the values of the chemical shifts obtained by Day and Rindone are too small for α -Al₂O₃ and glasses as seen in Fig. 1, it will be reasonable to adopt the data of the other workers and conclude that essentially no 6-coordinated Al³⁺ ions are found in Na₂O-Al₂O₃-SiO₂ glasses within the composition range studied.

Besides the x-ray fluorescence spectroscopy, the study of the x-ray radial distribution of soda aluminosilicate glasses³⁴⁾ indicated that Al³⁺ ions appeared to have fourfold coordination for an Al₂O₃/Na₂O ratio of 1.63 as well as for that of 0.87; in both the low alumina and high alumina glasses the Al-O distance obtained was 1.73 Å, a value near to that for fourfold-coordinated aluminum (1.77–1.80 ± 0.06 Å) and much shorter than that for sixfold-coordinated aluminum (1.85–1.98 ± 0.03 Å). From a geometrical consideration, Lacy¹⁹⁾ proposed that no Al ion is in a coordination state higher than 4 when the ratio Al/Na exceeds 1 and suggested that the Al is 4-coordinated in "triclusters" consisting of three tetrahedral groups sharing a common oxygen.

In a recent paper of Taylor and Rindone,²⁷⁾ Rindone modified his view on the concentration of 6-coordinated Al³⁺ ions in Na₂O-Al₂O₃-SiO₂ glasses on the basis of their low-temperature viscosity measurements. The modified model suggested that in the glasses with the ratio Al/Na over 1 only one third of the Al ions in excess of Na goes into 4-coordination, in contrast with the formerly proposed model in which every Al in excess of Na went into octahedral coordination. It would not be easy to confirm or deny the adequacy of this model experimentally by the x-ray fluorescence method because the concentration of 6-coordinated Al ions calculated on the basis of this model is too small to be detected reliably by the method.

The limit of increasing the ratio Al/Na in the Na₂O-Al₂O₃-SiO₂ system constitutes the Al₂O₃-SiO₂ binary system. The well-known refractory minerals sillimanite (Al₂O₃·SiO₂) and mullite (3Al₂O₃·2SiO₂) have half of the Al ions in 4-coordination and the other half in 6-coordination, and the chemical shift of AlK $\alpha_{1,2}$ from these minerals are situated between the region for 4-coordinated Al and that of 6-coordinated Al, as shown in Table 2. It would be interesting to measure the chemical shift in Al₂O₃-SiO₂ glasses and compare the coordination of Al in such glasses with the crystals although melting of corresponding glasses needs very high temperatures as high as 1800–2000°C.

Table 2. Chemical Shift of AlK $\alpha_{1,2}$ for Mullite and Sillimanite.

Sample	$\Delta 2\theta$ relative to Al metal (EDDT)
Mullite 3Al ₂ O ₃ ·2SiO ₂ (Electrocast)	0.065
Sillimanite Al ₂ O ₃ ·SiO ₂ (South Africa)	0.077
K-Feldspar K ₂ O·Al ₂ O ₃ ·6SiO ₂	0.049
α -Al ₂ O ₃	0.089

3. Coordination of Al in phosphate glasses

In general, phosphate glasses are believed to be poor in chemical durability compared with silicate glasses, and for that reason are often excluded from practical application. However, glasses of metaphosphate compositions containing aluminum oxide (added as aluminum metaphosphate) are highly resistant to acids and may be applied for practical use. Those resistant to hydrofluoric acid³⁵⁾ are aluminum containing metaphosphate glasses. The author of the present paper prepared a family of photochromic glasses³⁶⁾ with TiCl crystallites as activator and potassium barium aluminum metaphosphate as matrix glass, which showed almost no weight loss after immersing in 10% hydrochloric acid solution for 10 days. Although the presence of aluminum seemed important in phosphate glasses, no attempt has yet been published to examine the coordination of Al in phosphate glasses.

There are two crystalline compounds in the $\text{Al}_2\text{O}_3\text{-P}_2\text{O}_5$ system: aluminum metaphosphate $\text{Al}(\text{PO}_3)_3$ having Al^{3+} ions in 6-fold coordination³⁷⁾ and aluminum orthophosphate AlPO_4 having Al^{3+} ions in 4-fold coordination.³⁸⁾ It is not possible to compare pure aluminum phosphate glasses with the crystals of the same composition because the AlPO_4 composition does not form glass, although the $\text{Al}(\text{PO}_3)_3$ composition

Table 3. Phosphate glasses used in the measurements of $\text{AlK}\alpha_{1,2}$
(Composition: % in mole)

	NAP-1	KAP-2	KAP-3	KAP-4	CAP-1	CAP-2	CAP-3	CAP-4
$\text{Al}(\text{PO}_3)_3$	60	80	60	40	34.6	50	67.4	84
NaPO_3	40	—	—	—	—	—	—	—
KPO_3	—	20	40	60	—	—	—	—
$\text{Ca}(\text{PO}_3)_2$	—	—	—	—	65.4	50	32.6	16
P/O ratio	0.25	0.25	0.25	0.25	0.25	0.25	0.25	0.25
	AP-1	AP-2	AP-3	NAP-20	NAP-21	NSAP-1	NSAP-2	NSAP-4
$\text{Al}(\text{PO}_3)_3$	77.5	53.7	57.8	—	—	—	—	—
AlPO_4	22.5	46.3	42.2	60.5	66.7	54.0	42.8	24.9
Na_2O	—	—	—	39.5	33.3	30.4	28.1	24.5
SiO_2	—	—	—	—	—	15.6	29.0	50.6
P/O ratio	0.323	0.309	0.300	0.215	0.222	0.219	0.216	0.200
	T-1	T-3	T-4					
P_2O_5	7.6	13.6	9.7					
Al_2O_3	15.8	18.6	18.0					
MgO	23.2	26.0	25.1					
CaO	7.1	6.8	6.6					
B_2O_3	37.8	35.4	40.6					
SiO_2	8.7	—	—					
P/O ratio	0.131	0.174	0.113					

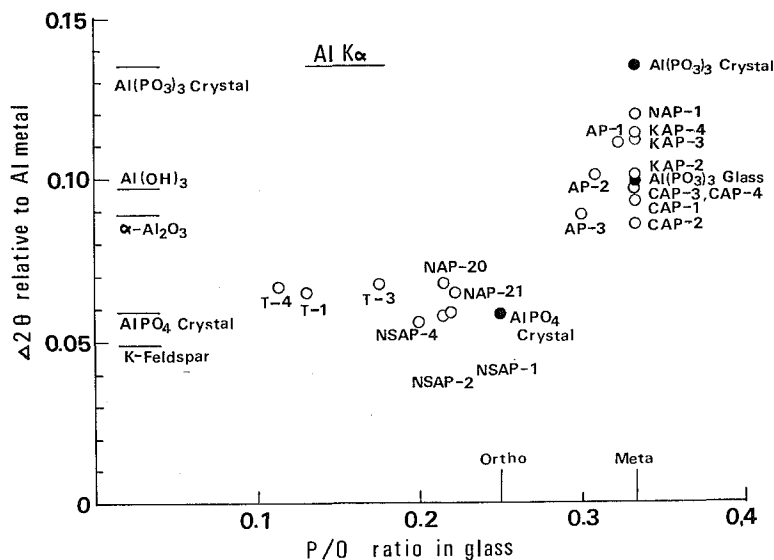


Fig. 2. Chemical shifts of $AlK\alpha_{1,2}$ for phosphate glasses.

can be obtained in the glassy form. Therefore, a wide variety of glasses with varying P/O ratio were melted from the batches containing various constituents besides Al_2O_3 and P_2O_5 , and subjected to measurements of the chemical shift of the $AlK\alpha_{1,2}$ lines,³⁹⁾ assuming that the P/O ratio would be used for representing the compositional characteristics of metaphosphate and orthophosphate. The P/O ratio near to 0.33 was assumed to correspond to the metaphosphate and the ratio near 0.25 to the orthophosphate. The compositions of glasses used in the measurement are shown in Table 3 and the observed values of the chemical shift are shown in Fig. 2. As seen from the figure, glasses with the P/O ratio equal or near to 0.33 (metaphosphate) appeared to contain most of the Al^{3+} ions in 6-fold coordination ($\Delta 2\theta$ values are similar to that of $\alpha-Al_2O_3$) and those with the P/O ratio near or less than 0.25 (orthophosphate) contained most of the Al^{3+} ions in 4-fold coordination ($\Delta 2\theta$ values are similar to that of potassium feldspar). This implies that in the aluminum phosphate systems the coordination number of the Al^{3+} ions in glasses corresponds to those in crystals of the corresponding composition. It should be noted here, however, that this may not be the case necessarily for many other glass-forming systems, and an evidence must be given for each system before any such conclusion is drawn.

Kurkjian and Sigety⁴⁰⁾ showed that Fe^{3+} ions are 6-coordinated in metaphosphate crystals (*e.g.* $Fe(PO_3)_3$) and glasses (*e.g.* $Fe(PO_3)_3$ and $NaPO_3 + 5\% Fe_2O_3$), while they are 4-coordinated in orthophosphate crystal (*e.g.* $FePO_4$). These results correspond to our results on Al^{3+} ions and this is understood from the similarity of Al^{3+} and Fe^{3+} ion species in valence (+3 for both) and ionic radius (0.50 for Al^{3+} and 0.60 for Fe^{3+} , according to Pauling).

Dietzel and Poegel,^{41,42)} in the discussion of the comparison between $AlPO_4$ and SiO_2 which are isomorphous with each other, speculated that the coordination number of Al might be 6 in the molten $AlPO_4$ from the fact that the melting point of $AlPO_4$ is much

higher than that of SiO_2 in contrast with all other transition temperatures which are lower for AlPO_4 . Our results mentioned above indicate, however, that the coordination number of Al might be 4 in the molten state. The coordination number of an atom in the molten state would be equal to that in the glassy state, because the glassy state may be regarded as being formed from the molten state without any drastic change of the structure.

4. Coordination of Al in borate and other glasses

Cabal glasses, that is, borate glasses of the $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ system have been known as excellent electrical insulators because they are non-alkali glasses and, in addition, relatively low melting. In the structural explanation of the change of electrical, thermal, optical and mechanical properties^{28,43)} of these glasses as a function of glass composition, the investigators somehow assumed the coordination number of the Al^{3+} ions, but no direct measurement was attempted except that Bishop and Bray³⁰⁾ tried to apply the NMR method to this problem.

In a preliminary experiment⁴⁴⁾ in which limited number of glasses with varying compositions were subjected to the fluorescence x-ray measurements, it was found that the chemical shift of the $\text{AlK}\alpha_{1,2}$ peak increased, that is, the average coordination number increased from 4 toward 6 with increasing B_2O_3 content, as shown in Fig. 3. Some measurements were started also for glasses in the systems $\text{Na}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3$, $\text{K}_2\text{O-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ and $\text{SrO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$, expecting to be able to find a general rule as to the relation between the coordination of Al^{3+} ions and the composition in borate glasses.

It should be noted that an accurate estimation of the $\text{AlK}\alpha_{1,2}$ emission peak for barium-containing glasses such as $\text{BaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses, which may be as useful as Cabal glasses practically, is very difficult to achieve with a commercially available x-ray fluorescence spectrometer for chemical analysis. The resolution of such an instrument is not sufficient for separating the $\text{AlK}\alpha_{1,2}$ peak from $\text{BaL}\alpha_1$ peak into a well defined peak, which is compulsory to detect such a small shift of the peak position as

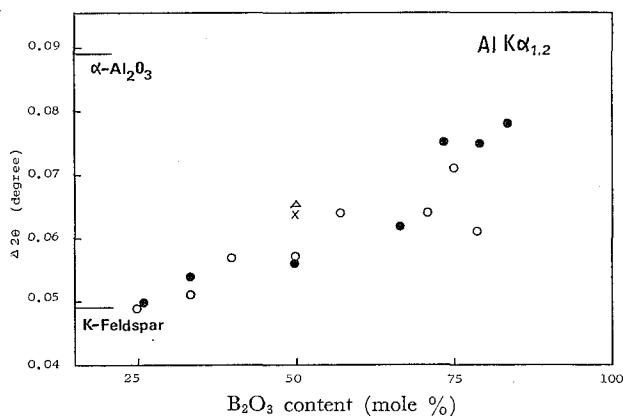


Fig. 3. Chemical shifts of $\text{AlK}\alpha_{1,2}$ for $\text{CaO-Al}_2\text{O}_3\text{-B}_2\text{O}_3$ glasses.

$\text{Al}_2\text{O}_3/\text{CaO}$ ratio in glass:

○ 0.5, ● 1.0, × 0.25, △ 1.5

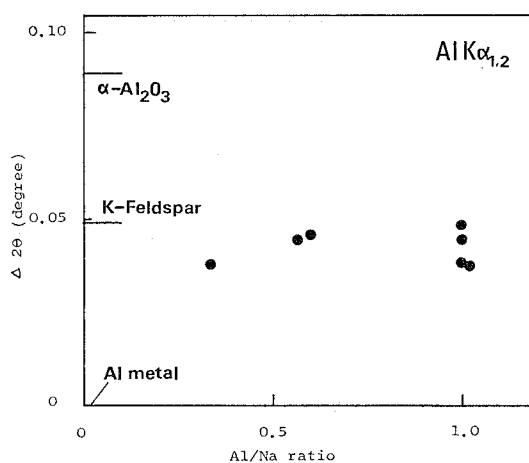


Fig. 4. Chemical shifts of $\text{AlK}\alpha_{1,2}$ for $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{GeO}_2$ glasses.

the chemical shift of the x-ray emission lines. With the EDDT analysing crystal, the angle 2θ of the $\text{AlK}\alpha_{1,2}$ peak (the first order) is found at about 142.5° and that of the $\text{BaL}\alpha_1$ peak (the third order) at about 142.0° .

Measurements on a number of germanate glasses of the system $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{GeO}_2$, shown in Fig. 4, and aluminates glasses of the $\text{K}_2\text{O}-\text{Nb}_2\text{O}_5-\text{Ta}_2\text{O}_5-\text{Al}_2\text{O}_3$ system⁴⁵⁾ appeared to indicate that the Al^{3+} ions were 4-coordinated, although more extensive measurements are necessary to draw a definite conclusion.

Very roughly speaking, all the above results on Al^{3+} ion coordination seems to indicate that the more acidic composition of glass is favorable for the formation of 6-coordinated Al^{3+} ions. The detailed discussion will be done elsewhere.

IV. HIGH PRESSURE EFFECT ON Al^{3+} SITES IN GLASS

The most characteristic effect of application of high pressure to glass is semi-permanent densification;⁴⁵⁾ glasses compressed at room temperature, for instance, show higher densities than before compression and the densification remains so long as the glasses are kept at room temperature. In order to find what kind of change in local structure has occurred in such densified glasses and in glasses under compression, optical absorption and NMR measurements were applied to the study of coordination of transition metal ions, such as Co, Ni and Fe,^{47,48)} and boron.⁴⁹⁾ Co^{2+} and Ni^{2+} , which are network modifiers, changed their coordination number from 4 to 6, while no change was found for boron atoms. Accordingly, whether Al changes its coordination number upon application of high pressure or not was of great interest, since Al is an intermediate cation from the viewpoint of classification of glass constituents. It should be recalled that, in general, high pressure favors the higher coordination number, if the change is induced.

The peak positions of the $\text{AlK}\alpha_{1,2}$ lines from a sodium aluminosilicate glass of the composition Na_2O 16, Al_2O_3 24, SiO_2 60 mole % were measured³⁹⁾ before and after application of 50 kbar at room temperature and 500°C by an opposed anvil type ap-

paratus. The 42θ values obtained were 0.049, 0.048 and 0.053 for the samples before compression, after compression of 50 kbar at 25°C and after compression of 50 kbar at 500°C. It can be said from the result that no substantial change in coordination number occurs within this experiment. It would be useful to know that the refractive index increased by application of pressure from 1.5114 to 1.5270 (50 kbar, 25°C) and 1.5383 (50 kbar, 500°C).

As mentioned before, $\text{Na}_2\text{O}-\text{Al}_2\text{O}_3-\text{SiO}_2$ glasses are suitable for strengthening by ion exchange. After ion exchange, the surface layer of the glass is in compressive stress and, in other words, the surface layer is under a high pressure. Yokota and Gohshi,⁵⁰ with a double crystal x-ray fluorescence spectrometer, measured the peak of the $\text{AlK}\alpha_{1,2}$ from the glass of the composition Na_2O 20, Al_2O_3 20, SiO_2 60 mole% before and after strengthening by the ion exchange between Na^+ and K^+ . They did not detect the displacement of the peak position within the precision of the measurement, indicating that a substantial coordination change of the Al^{3+} ions did not occur.

So far no other experiment of this type has been published and more extensive works are awaited.

V. PHASE SEPARATION AND CRYSTALLIZATION OF GLASS

As mentioned before, alumina is often an important constituent for glass-ceramics or crystallized glass and, in addition, presence of Al ions in glass often affects the process of crystallization, changing the microstructure and, accordingly, the properties of resultant glass-ceramics. Ferroelectric glass-ceramics which are activated by the ferroelectric crystallites such as BaTiO_3 , PbTiO_3 and NaNbO_3 present in glassy matrix are examples of such glass-ceramics. It is known⁵¹ that a glass containing no alumina and having the composition PbO 40, TiO_2 25, SiO_2 35% in mole crystallizes at 630°C directly to a glass-ceramic containing pyrochlore-type non-ferroelectric crystals, whereas the addition of 10% Al_2O_3 leading to the glass composition PbO 40, TiO_2 25, Al_2O_3 10, SiO_2 25% in mole causes the glass to separate into two glassy phases at 620°C in the first step and to crystallize into ferroelectric lead titanates of perovskite type at 640°C in the second step.⁵¹ The structural change concerning the Al^{3+} ions in glass which occurred in the process of phase separation and crystallization was studied by measuring the chemical shift of the $\text{AlK}\alpha_{1,2}$ and it was found that no change of coordination number took place.⁵¹ This type of study would be particularly useful for finding the structural change during glass-glass phase separation where x-ray diffraction method is not available because of glassy nature of the separated phases.

Shuvaev, Blokhin and Izrailevich⁵² compared the shift of the $\text{AlK}\alpha_{1,2}$ from a $\text{BaO}-\text{Al}_2\text{O}_3-\text{TiO}_2-\text{SiO}_2$ glass with that from its crystallized product (glass-ceramic) and drew the conclusion that the coordination number of Al is 4 in the glass-ceramic, while it is less than 4 in the parent glass. The coordination number of less than 4 for Al is not conceivable, however. It is true that the use of x-ray emission spectroscopy for this type of study may be interesting, but more careful interpretation of the results is required, considering that the coordination number is not the only factor that affects the shift of the x-ray peaks. In addition, the results of x-ray diffraction analysis should be referred to so far as any crystalline species are involved as in the case of glass-ceramics.

VI. CHEMICAL BONDING INVOLVING Si, Al AND Mg IN GLASSES

The ions Si^{4+} , Al^{3+} and Mg^{2+} ions are believed not to change their valence in oxides and silicates and so the main factor affecting the chemical shift of the fluorescence x-ray is, presumably, the change in their coordination number, as discussed in the preceding sections. A more detailed examination of the values of the chemical shift indicates, however, that other factors also affect the shift. As shown in Fig. 2, for instance, the value of displacement of the $\text{AlK}\alpha_{1,2}$ for the $\text{Al}(\text{PO}_3)_3$ glass is slightly different from its crystalline counterpart and also from metaphosphate glasses of different composition, although the values are all within the range assigned to the 6-coordinated Al^{3+} ions.

This fact may be used for obtaining more detailed informations on the chemical state of Al and other atoms in glass. Such an idea was realized for silicate minerals (crystals).^{53,54} White and Gibbs⁵³ examined the $\text{SiK}\beta$ emission from many silicate minerals with the silicon atom in tetrahedral coordination and plotted $\Delta 2\theta$ for $\text{SiK}\beta$, relative to the peak position for quartz (SiO_2), against the known Si-O bond length. The plotted points fell along a straight line within the experimental error of the measurement, indicating that the shift $\Delta 2\theta$ for $\text{K}\beta$ can be used for predicting the mean Si-O bond length. It is quite obvious that this method is immediately applicable to silicate glasses.

The bond length is, however, only one of the manifestations of the chemical bonding. Dodd and Glen⁵⁵⁻⁵⁷ applied the concepts of molecular orbital theory to the interpretation of $\text{SiK}\beta$ and $\text{AlK}\beta$ x-ray spectra of oxide and silicate crystals. The main $\text{K}\beta$ -band observed in spectra of magnesium, aluminum and silicon oxides is designated as an M-K electronic transition, which involves an outer electronic shell (M-shell) than the main $\text{K}\alpha$ -band designated as an L-K transition. With the assumption that the main $\text{K}\beta$ -band may be ascribed to a $3p$ - $1s$ electronic transition and on the basis of a tentative MO energy level diagram, they explained its splitting, which is more or less clearly seen in SiO_2 , Al_2O_3 and other silicate minerals. The intense peak of the two splitted, but unresolved peaks was assigned to a $3p(\sigma^b)$ - $1s$ transition for tetrahedrally coordinated Al and Si and octahedrally coordinated Al. The higher-energy weaker peak was assigned to a $3d(\pi^b)$ - $1s$ transition for tetrahedrally coordinated Al and Si and to $3p(\pi^b)$ - $1s$ transition for octahedrally coordinated Al (α - Al_2O_3).

Bearing in mind that the relative Si-O and Al-O bond energies should be a function of degree of orbital overlap and this, in turn, should be a function of both bond length and bond angle,⁵⁵ Dodd and Glen compared the bond energies of Si-O bonds, accordingly, relative destabilization energies, for various silicate crystals. It was assumed that the $1s$ orbital level is constant and all binding orbitals would be shifted to the same extent as the $3p(\sigma^b)$ orbitals, relative to the orbital energy levels in quartz SiO_2 , a reference material. The results are quoted in Table 4. It is seen that Si-O bonds in the framework silicate beryl are as stable as those in quartz, that the isolated SiO_4 tetrahedral orthosilicates, the framework silicates, and the chain silicates all are destabilized to about the same degree, and that the Si_2O_7 double-tetrahedra, pyrosilicate structures have the weakest Si-O bonds of the silicates studied.

Using the same procedure, Dodd and Glen⁵⁸ estimated the $3p$ - σ bonding orbital

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 Table 4. Decrease in Stability of Si-O Bonds in Silicates Relative to Si-O Bonds in Quartz (Dodd and Glen⁵⁵).

Sample	SiK β -band main peak position (ev)	Displacement of peak relative to SiO ₂ (ev)	Approx. Destabilization energy of Si-O bond (kcal/mole)
Reference			
SiO ₂	1831.3	—	—
Framework silicates			
Cordierite Mg ₂ Al ₄ Si ₅ O ₁₈	1832.2	+0.9	21
Anorthite CaAl ₂ Si ₂ O ₈	1832.4	+1.1	25
Beryl Be ₃ Al ₂ Si ₆ O ₁₈	1831.3	0	0
Chain silicates			
α -spodume LiAlSi ₂ O ₆	1831.8	+0.5	12
Enstatite MgSiO ₃	1832.5	+1.2	28
Si ₂ O ₇ silicates			
Thortveitite	1832.8	+1.5	35
Gehlenite Ca ₂ Al ₂ SiO ₇	1832.8	+1.5	35
Orthosilicates			
Zircon ZrSiO ₄	1832.0	+0.7	16
Olivine > 80% Mg ₂ SiO ₄	1832.2	+0.9	21
Monticellite MgCaSiO ₄	1832.3	+1.0	23
Pyrope garnet Mg ₃ Al ₂ Si ₃ O ₁₂	1832.5	+1.2	28

destabilization energies of an average Si-O bond in Li₂O-Al₂O₃-SiO₂ glasses with varying SiO₂ content. SiK β emission spectra of the glasses measured (the measurements were done with an electron microprobe spectrometer) and the destabilization energies are quoted in Fig. 5 and Table 5, respectively. It can be seen from Fig. 5 that the lower the silica content of a glass, the greater the displacement of SiK β peak to a shorter wavelength relative to pure silica. Especially, the displacement for Li₂O-Al₂O₃-2SiO₂ glass is considerable. In other words, the Si-O bond becomes weak

 Table 5. Decrease in Si-O Bond Strength in Glasses and Silicates Relative to Bond Strength in Pure Silica Glass and Quartz (Dodd and Glen⁵⁸).

Sample	Position of main K β peak (ev)	Displacement of peak relative to SiO ₂ (ev)	Approx. Destabilization energy of Si-O bond (kcal/mole)
SiO ₂ glass and quartz	1831.1 ₅	—	—
Li ₂ O·Al ₂ O ₃ ·8SiO ₂ glass	1831.3 ₀	+0.1 ₅	4
Li ₂ O·Al ₂ O ₃ ·4SiO ₂ glass	1831.8 ₁	+0.6 ₆	15
Li ₂ O·Al ₂ O ₃ ·2.5SiO ₂ glass	1831.9 ₆	+0.8 ₁	19
Li ₂ O·Al ₂ O ₃ ·2SiO ₂ glass	1832.6 ₂	+1.4 ₇	34
Cordierite MgO·Al ₂ O ₃ ·5SiO ₂	1831.5 ₈	+0.4 ₃	10
β -eucryptite single crystal (Li ₂ O·Al ₂ O ₃ ·2SiO ₂ β -quartz phase)	1831.8 ₅	+0.7 ₀	16

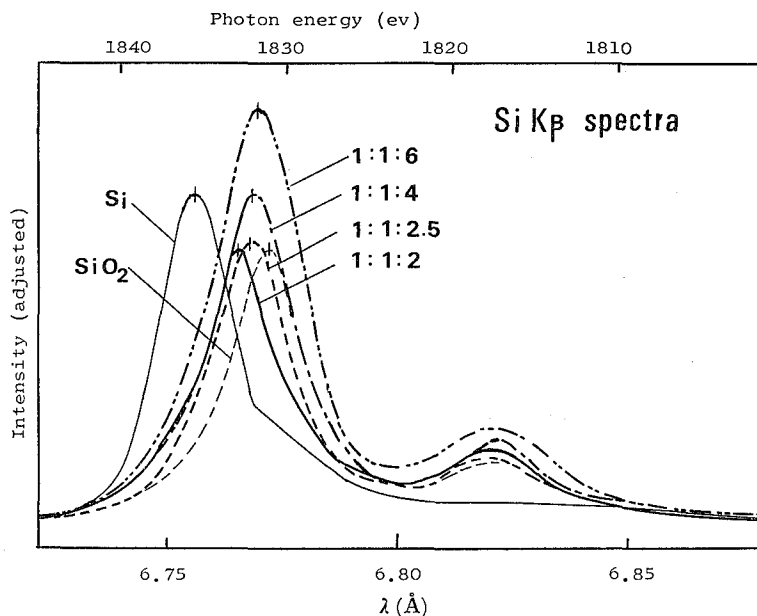


Fig. 5. SiK β emission spectra of Li₂O-Al₂O₃-SiO₂ glasses (Dodd and Glen⁵⁸⁾).

—	1 : 1 : 2	Li ₂ O·Al ₂ O ₃ ·2SiO ₂ glass
----	1 : 1 : 2.5	Li ₂ O·Al ₂ O ₃ ·2.5SiO ₂ glass
- - - -	1 : 1 : 4	Li ₂ O·Al ₂ O ₃ ·4SiO ₂ glass
-----	1 : 1 : 6	Li ₂ O·Al ₂ O ₃ ·6SiO ₂ glass
.....	SiO ₂	Fused SiO ₂ and quartz
—	Si	Si metal

as the silicon content of a glass decreases, as shown in Table 5. Dodd and Glen pointed out that the strength of the Si-O bonds in the Li₂O-Al₂O₃-2SiO₂ glass is approximately 79% of the strength of the Si-O bond in fused silica and quartz crystal, if the energy of a single Si-O bond is taken as 168 kcal/mole.⁵⁹ The relative strengths of Al-O bonds was also discussed on the basis of the AlK β bands. It can be said that so far no information comparable to the above one could be obtained by other methods, although the precision of the measurement and the validity of the assumption for this study has to be reexamined.

It seems pertinent to point out that the effective charge of atoms Na, Mg, Al, Si, P, S and Cl can be estimated from the displacement of the x-ray K $\alpha_{1,2}$ emission peak.^{60,61} The effective charge should be another way of expressing the bond character or bond strength.

VII. SULFUR AND CHLORINE IN GLASS

It has been known that a small amount of sulfur can be dissolved in silicate and borate glasses by replacing oxygen or in the form of molecular sulfur or sulfate ions. The measurement of the SK $\alpha_{1,2}$ band will serve for analysing the state of the dissolved

sulfur, since $SK\alpha_{1,2}$ wavelength is different with the oxidation state of sulfur.

A wide variety of sulfide and oxysulfide glasses have been known. Infrared spectra are informative^{63,64)} for investigating the structure of such glasses to some extent, but the $SK\beta$ emission band spectra may give further information, in view of the fact that the peak wavelength of the $SK\beta$ bands for sulfide crystals is affected by the coordination of S atom.⁶⁵⁾

Here, the author of the present paper would like to take the problem of coordination number of germanium in glasses as a subject related to the x-ray emission of S atom. There are two forms of GeO_2 crystal; the tetragonal form in which the Ge atoms have sixfold coordination with oxygen and the hexagonal one in which the Ge atoms have fourfold coordination. The coordination number of the Ge atom in GeO_2 glass has been determined as 4 from the infrared spectra.⁶⁶⁾ On the other hand, it was reported that the addition of Na_2O to GeO_2 glass causes some of the Ge atom to have 6-coordination.⁶⁷⁾ This problem has not been solved yet,⁶⁸⁾ however, and remains to be examined more thoroughly. The similar problem can be applied to sulfide glasses such as those in the $Li_2S-CdS-GeS_2$ system⁶⁹⁾ and the Ge-S system. It is known that the Ge atom is 4-coordinated in GeS_2 crystal and 6-coordinated in GeS crystal. Kawamoto and Tsuchihashi⁷⁰⁾ proposed, on the basis of their observation of glass-forming regions in the Ge-S system, that in the region GeS_2 to GeS_3 the glasses have a three-dimensional polymeric structure with polymeric S chains cross-linked with Ge (Ge is likely to be 4-coordinated) and in the region $GeS_{1.31}$ to $GeS_{1.51}$ the glasses consist of the network Ge^{4+} ions (GeS_2 , 4-coordinated Ge) and the modifier Ge^{2+} ions (GeS , 6-coordinated Ge). The x-ray emission spectra of S might be helpful to elucidate this matter and prove the presence of 6-coordinated Ge. The x-ray emission spectra of Ge within the scope of this paper is not likely to give useful informations, since Ge is a rather heavy element, and so the spectra of oxygen may be the only means to be applied to the germanate (oxide) glasses, although not the fluorescence instrument but the electron microprobe instrument has to be used for obtaining the emission spectra.

The state of chlorine atoms incorporated into silicate and borate glasses is of interest from the practical as well as scientific aspects. Chlorine atoms are known to change the color caused by transition metal ions such as Co, Ni and Fe in colored glasses^{71,72)} and to precipitate as $AgCl$ ⁷³⁾ or $TiCl_3$ ⁶⁶⁾ crystals in photochromic glasses. So far, uv and visible absorption and ESR spectra have been the only means to afford informations on the state of Cl. For example, replacement of ligand oxygens by chlorine caused the displacement of the absorption peak of Co^{2+} ions in glass. According to the experience of the present author, no difference could be detected in the peak wavelength of the $ClK\alpha_{1,2}$ x-ray emission band between the ionic chlorides such as $LiCl$, $NaCl$, KCl and NH_4Cl and the rather covalent chlorides such as $AgCl$, $PbCl_2$, $CoCl_2$ and $NiCl_2$. Similarly, no difference in the $ClK\alpha_{1,2}$ peak was found between a silicate glass containing Cl ions or $AgCl$ crystals and a borate glass containing Cl ions with Co^{2+} ions. These results would only show that chlorine atoms in the glasses do not form chlorite or chlorate, but exist as chlorides. The fact that the $K\alpha_{1,2}$ band does not give much information is not disappointing, however, since there may be many other emission bands such as $K\beta$ lines that may work for more close examination of the state of atoms in the glass structure.

VIII. TRANSITION METAL IONS Ti, V, Cr, Mn AND Fe IN GLASS

A variety of experimental methods are available for determining the state of transition metal ions in glasses. Chemical analysis, optical spectroscopy and ESR and magnetic susceptibility measurement can be used for the determination of the oxidation state⁷⁴⁾ and optical spectroscopy and ESR for the determination of the coordination number and the electronic state. Mössbauer spectroscopy is particularly useful for determining the valence and coordination number of iron ions.⁴²⁾ However, these methods cannot be applied to all cases necessarily. Chemical analysis can distinguish the two oxidation states of an element but not three oxidation states. Optical spectroscopy cannot be applied to glasses containing much amount of a transition element because of a too high optical density. Only some of the oxidation states of an element give ESR spectra.

Then, the x-ray emission spectroscopy might be effective in providing informations as major or supplementary means. It appears that the application of the method to semiconducting oxide glasses⁷⁵⁾ such as V_2O_5 - P_2O_5 and Fe_2O_3 - P_2O_5 glasses is of particular interest. The glasses of this type contain several tens percent of transition metal oxide and exhibit the semiconduction due to, presumably, hopping of electrons between the higher valent state and the lower valent state of the transition metal ion. It is conceivable that more or less direct structural information on the transition metal ions in such glasses, so far very poor, is necessary in order to elucidate the mechanism of conduction.

To proceed with this work, however, much experimental data obtained on the known crystalline compounds are essential. Koster's group showed that the $K\beta$ lines from oxidic compounds of iron⁷⁶⁾ and other transition metals^{77,78)} give some structural informations. The position of the line $K\beta_5$ gives the valence of iron with an accuracy of about 15%, and the $FeK\beta_1$ peak position contains information about the valence and coordination of iron, as cited in Table 6.⁷⁶⁾ Other related data have been published in the works.^{79,80)}

It should be noted that for the measurements of the emission spectra much care has to be taken and a long time is needed because of small displacement of the peaks and, for some peaks, weak intensity. Koster recorded the spectra by step scanning with intervals $0.02^\circ 2\theta$. The counting time was kept as 10 min for points in the

Table 6. Shifts of $FeK\beta_1$ Line from Iron in Oxidic Compounds (Spinel) with Respect to α - Fe_2O_3 (Koster and Rieck⁷⁶⁾).

State of iron	Degrees 2θ (LiF 2nd order)	(ev)
Octahedral Fe^{3+}	-0.005	-0.2
Octahedral Fe^{2+}	+0.006	+0.2
Tetrahedral Fe^{3+}	+0.009	+0.3
Tetrahedral Fe^{2+}	+0.020	+0.7
Accuracy	0.001-0.002	0.05

FeK β_5 region and 1 min in the FeK $\beta_{1,3}$ region, using a chromium x-ray tube operated at 50 kV and 40 mA, which resulted in about 10 hr for recording the spectrum.

IX. X-RAY EMISSION FROM OXYGEN IN GLASS

Most of the practically important glasses are oxides in a wider sense, and it is reasonable to expect that the measurements of oxygen x-ray peaks might give valuable informations. For this purpose, however, an electron microprobe instrument has to be employed, because only electron bombardment can excite the secondary x-rays with an intensity sufficient for the measurement.

Brückner, Poch and Vollath measured OK α lines of Na₂O-SiO₂ glasses,^{8,11} expecting to differentiate bridging oxygens from non-bridging oxygens. The concept of bridging oxygens (oxygen which is connected to two network former cations as in the scheme -Si-O-Si-) and non-bridging oxygens (oxygen which is connected to one network former cation and one network modifier cation as in -Si-O-Na⁺, forming a breaking site of the glass network) is valuable in the field of glass science and technology, because the presence and number of non-bridging oxygens often control various properties of glass. Brückner *et al.* concluded, however, that OK $\alpha_{1,2}$ lines do not work for this purpose, although they found a certain rule that controls the variation of the line profile with the composition of glass.

X. CONCLUSION

In view of the fact that the x-ray diffraction structural analysis is not powerful for amorphous substances and that many glasses consist of the elements to which the x-ray emission spectroscopy can be easily and effectively applied, this method has a great possibility of increasing our knowledge on the short range structure of a wide variety of glasses. Compilation of sufficient experimental data on the crystalline compounds with well-defined structures, improvement in precision and accuracy of the measurements of the peak displacement and line profile of emission x-rays, and generation of simple theories on the chemical effects would be the basis for the future progress in the application of this method to glass.

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