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CHEMICAL SHIFTS OF SiKa AND AlKa IN OXIDE GLASSES

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Abstract. - Chemical shifts of SiKa and AlKa in oxide glasses have been measured to find out the structure of SiO2-complex anion and the oxygen co-ordination number of Al3+ by using High Resolution X-ray Fluorescence Spectrometer (double crystal type). Optical basicity of these glasses proposed by Duffy and Ingram has been measured to discuss the chemical shifts of SiKa and AlKa. The relation between SiKa chemical shifts and the type of SiO2-complex anions was derived by comparing with those standard samples. The distribution of SiO2-complex anions was also determined by calculation with computer analysis. The results indicate that the chemical shift of SiKa has a linear relationship with the optical basicity of corresponding glasses. The structure and distribution of SiO2-complex anions are discussed in terms of basicity of glasses. The chemical shift of AlKa has also a relationship with the optical basicity, which will lead to the discussion about the change of oxygen co-ordination number of Al3+ in oxide glasses in terms of the basicity of glass.

1. Introduction. - It is well known fact that Si4+ ion is in the tetrahedrally coordinated state and forms a silicate anion. The polymerization degree and structure of silicate anion are controlled by the content or the kind of net-work modifier ions, that is, the basicity of the system.

On the other hand, Al2O3 in glasses is amphoteric oxide and Al3+ ion can be in the both tetrahedral and octahedral site. Recently much research has been done on the chemical state analysis trying to find out the coordination number or the form of complex anions of Si or Al in glasses.

It is reported that the energy of the Kα characteristic X-ray of Si or Al is not always constant, but changes with the state of Si or Al atom according to the difference in the valency, the ligand or the coordination number.(1) (2) (3). However, the change of energy appeared as a chemical shift of Kα is very small and often difficult to detect.

The conventional fluorescent X-ray analyser has single crystal for analyzing technique. In this study the analyser with double crystals was used to increase the resolution power for chemical shift. The purpose of this study is to discuss the state of Si or Al atom contained in silicate or phosphate with the change of the basicity by measuring the chemical shift of Si or AlKa. In this work the optical basicity pro-
posed by Duffy et al. (4) was adopted as a scale of the basicity (5). The optical basicity is considered to be able to express the basicity in unit scale of oxide glass and can be derived from the ability to provide a pair of electrons to Pb$^{2+}$ (probe ion), which can be obtained by measuring the change of wave number of s-p spectrum of Pb atom in UV region (nephelauxetic effect).

2. Experimental.
2-1. Chemical shift.- All samples were prepared from special grade carbonate and oxide reagents. Mixed samples were melted in Pt crucible and quenched to be glass. The glass was then ground to powder and pressed to disk of 40mm in diameter. Fluorescent X-ray analyser with double crystals (made by Rigaku Co.) was used for measuring the Si or AlKα, which conditions are listed in Table 1. The peak position of spectrum was determined by approximating about 40 intensity values larger than 80% of maximum to second order equation. To eliminate the error the Si or AlKα in quartz or α-Al₂O₃ was measured respectively before and after the sample.

2-2. Optical basicity.- Duffy et al. (4) proposed to measure the optical basicity utilizing the sharp absorption in UV region of Ti$^{3+}$, Pb$^{2+}$ or Bi$^{3+}$ as probe ion in glasses. The results obtained by the authors using Pb$^{2+}$ as probe ion will be published in more detail (5). The optical basicity ($\Lambda$) is calculated from equ. (1) normalizing the change of wave number in UV spectra.

$$\Lambda = \frac{v_{\text{free ion}} - v_{\text{glass}}}{v_{\text{free ion}} - v_0^{2-}} \quad \cdots \cdots (1)$$

where $\Lambda$ is the optical basicity (0 to 1), and $v_{\text{free ion}}$ is the peak wave number in s-p spectra of free Pb$^{2+}$ ion, to which a pair of electrons is not donated by a ligand (i.e. O$^{2-}$). $v_{\text{free ion}}$ may be calculated by extrapolation of linear relationship between measured spectroscopic shifts and orbital expansion parameters for various ligand environments. In this study, $v_{\text{free ion}}$ is 60700 cm$^{-1}$. $v_0^{2-}$ is the peak wave number of the s-p spectra of Pb$^{2+}$ ion which exists in free O$^{2-}$. For Pb$^{2+}$ a value for $v_0^{2-}$ of 29700 cm$^{-1}$ is taken from comparison with data in CaO. For Pb$^{2+}$ probe ion $\Lambda$ can be calculated by equ. (2).

$$\Lambda = \frac{60700 - v_{\text{glass}}}{31000} \quad \cdots \cdots (2)$$

$v_{\text{glass}}$ is the peak wave number in s-p spectra of Pb$^{2+}$ ion, which exists in the present quenched glass.

For measuring the optical basicity, PbO reagent as probe was added about 0.004g to 10g sample (1×4×10$^{-4}$wt% Pb). Mixed samples were melted in Pt crucible and quenched to be glass. Glasses were annealed enough to prevent the breakage during the cutting of the sample into a piece for polishing. Pieces were about 0.2mm in thickness. $v_{\text{glass}}$ was measured by UV spectrometer (made by Hitachi Co.).

3. Results and discussion.- Fig.1 shows the chemical shift of SiKα as a function of O/Si ratio in various silicate minerals based on the SiKα in quartz as a standard. The values of O/Si ratio such as 2, 2.5, 3, 3.5 and 4 correspond to the structure of silicate anions such as SiO$_2$, Si$_2$O$_5^{2-}$, Si$_3$O$_9^{2-}$, Si$_2$O$_7^{6-}$ and SiO$_4^{4-}$ respectively. The relation between O/Si ratio in minerals and the chemical shift of SiKα is almost linear. The results indicate that the polymerization degree of silicate may be estimated by measuring the chemical shift of SiKα in various silicates. In this study quartz was chosen as the standard for SiKα measurement, and the chemical shift is calculated from the difference between in quartz and in sample. No obvious difference was observed between crystal and amorphous silica. However the chemical shift of crystal and amorphous state in the composition of Na$_2$SiO$_5$ show the different values as seen in Fig.1. It may be considered that in amorphous state at the composition of O/Si=2.5 the structure of glass consists of not only...
Si$_2$O$_5$N$^{2n-}$ but also the mixture state of Si$_2$O$_7^{6-}$ and Si$_n$O$_{3n}$.$^{2n-}$. This may correspond to the fact that the infra-red spectra$^6$ of glass in this composition exhibit two peaks. There seems to be strong correlation between the energy of SiKa and the polymerization degree of silicates.

Now, the polymerization degree of silicate in the glass will be discussed through the measurement of SiKa in Na$_2$O and PbO-SiO$_2$ systems. Fig.2 shows the relationship between the content of Na$_2$O or PbO and the chemical shift of SiKa. As seen in the figure the chemical shift of SiKa becomes larger with increasing the Na$_2$O or PbO content. In R$_2$O-SiO$_2$ (R=Li,Na or K) systems larger chemical shift was observed for smaller value of Z/r of R$^+$ (Z:valence, r:ionic radius) or larger basicity of the oxide. It may be concluded that there exists distinct relationship between the chemical shift of SiKa and the polymerization degree of silicate anion. Maekawa et al.$^7$ reported that mixing the SiO$_2$ with R$_2$O results in a relative decrease of the positive charge on the Si atom compared with that of pure SiO$_2$. The results of this study are consistent with above paper, even though they did not mention about any difference in the chemical shift of SiKa according to the kind of R$_2$O in R$_2$O-SiO$_2$ systems.

Some studies$^2$-$^3$ have been carried out on the chemical shift of AlKa to investigate the coordination number of Al ion in the glass or crystal. Fig.3 shows the chemical shift of AlKa in some minerals or compounds containing the Al ion, where the metallic Al is used for standard. The Al ion contained in feldspar and orthoclase is in tetrahedral site, and shows rather small chemical shift. On the other hand, when Al$^{3+}$ ion is in octahedral site as seen in kaolinite, Al$_2$O$_3$, muscovite, tourmaline and so on, the chemical shift seems to be larger. Al$^{3+}$ ion is in both octahedral and tetrahedral sites in muscovite and the chemical shift of AlKa is in the intermediate position of orthoclase and Al$_2$O$_3$. The full width of half maximum of AlKa in muscovite is larger than that in orthoclase and Al$_2$O$_3$. The chemical shift of AlKa in cryolite in which the ligands are F$^-$ ion is larger than that in Al$_2$O$_3$. Even though Al$^{3+}$ ion in Al$_2$O$_3$ is in octahedral site, the chemical shift is almost the same as in muscovite. The ligands of Al$^{3+}$ in Al$_2$O$_3$ are oxygen ions only, whereas in kaolinite, Al$_2$O$_3$, muscovite, etc. they are oxygen ions and (OH)$^-$ ions or other anion. This may be one of the difference between Al$_2$O$_3$ and Al$_2$O$_3$ etc. The measurement of chemical shift of AlKa will provide some idea about the coordination number or the kind of ligands especially in octahedral site.

The polymerization degree of silicate anions have been studied by means of the infra-red absorption spectra$^6$, e.m.f method$^8$ or the experimental results on the physical properties of melts$^9$. Since the present work is mainly concerned with some findings on the relationship between the structure of silicate anions and the basicity, the methods of measuring the basicity has been investigated. Many papers have been published about e.m.f. measurement in oxygen concentration cells$^{10}$, CO$_2$ absorption into the molten salts$^{11}$ or determination of Fe$^{2+}$/Fe$^{3+}$ ratio in the glasses$^{12}$. None of these basicities, however, was effective to apply to various glass systems in the same scale of basicity.

The optical basicity derived from the nephelauxetic effect of Pb$^{2+}$ ion in quenched glasses has the possibility of showing the Lewis and new scale of basicity in glasses.

Fig.3 The chemical shifts of AlKa in minerals and compounds containing Al.
Fig. 4 shows the relation between the optical basicity and the chemical shift of SiKa in various silicate systems. As seen in this figure the linear relationship indicates that the polymerization degree of silicate anions will be determined by the optical basicity. In Fig. 4 the relation between the chemical shift of SiKa and the structure of silicate anion obtained in Fig. 1 was introduced.

In Fig. 5 the chemical shift of AlKa in oxide glasses containing 10mol% Al2O3 are shown in terms of optical basicity. The samples used here are silicate, borate and phosphate systems. In silicate systems the chemical shift of AlKa is small and comparable with orthoclase.

Borate is more acidic in optical basicity, chemical shift of which is more like that in w-Al2O3. Phosphate is considered to be more acidic and the chemical shift of AlKa are larger than that in w-Al2O3.

It is difficult to measure the optical basicity for the opaque or colored glasses, but the estimation of it may be possible from the values of the isomer shift of Fe in Mössbauer spectra(13). When the optical basicity is measured directly or estimated by means of the chemical shift of SiKa and AlKa or of the isomer shift of Mössbauer spectra, it would be a new scale of basicity for oxide glasses.

4. Conclusion.- The relation between the optical basicity and the polymerization degree of silicate anions and the coordination number of Al3+ in glasses were investigated by measuring the chemical shift of SiKa and AlKa with a use of double crystal type X-ray fluorescent analyser. The polymerization degree of silicate anions becomes smaller with increasing the chemical shifts of SiKa in negative direction. The oxygen coordination number of Al3+ ion becomes larger with increasing the chemical shift of AlKa. The relationship between the chemical shift of SiKa or AlKa and the optical basicity has been clarified in oxide glass systems.