

# Local structure of iron ions in aluminosilicate glasses

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Iron is the key element to affect the coloration of glass in UV and near-infrared regions. From an energy point of view, the sheet glass, for example, has to be tailored to have optimized optical absorption to improve energy-saving of house and building. Glass coloration has been well known to depend on oxidation and coordination states of iron, and precise understanding of the iron speciation and its correlation with glass structure promote to add new functionality to glass.

This study gives our focus on aluminosilicate glass system, especially magnesium aluminosilicate glass. Since  $\text{Al}^{3+}$  and  $\text{Mg}^{2+}$  have close ionic radius to those of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$ , respectively, site distribution of Fe is of particular interest in this glass system. The purpose of this study is to understand the local environment of Fe ions in magnesium aluminosilicate glasses by measuring the optical absorption spectra as functions of glass composition and temperature.

$33(\text{MO or M}_2\text{O})\text{--}12\text{Al}_2\text{O}_3\text{--}55\text{SiO}_2$  (mol%) (M: Na, Mg, Ca, Ba) was picked up and named as NAS, MAS, CAS and BAS, respectively. These composition were checked by micro probe analysis. Optical absorption spectra of glasses were measured at room temperature and at low temperature (30 K~). All absorbances were corrected and absorption from sample was extracted. Electron paramagnetic resonance (EPR) spectra were collected in order to get additional information on  $\text{Fe}^{3+}$  about site distortion.

Figure 1 shows optical absorption spectra of MAS, CAS and NAS. There are significant change on the  $\text{Fe}^{2+}$  band ( $4000\text{ cm}^{-1} \sim 18000\text{ cm}^{-1}$ ),  $\text{Fe}^{3+}$  band ( $21000\text{ cm}^{-1} \sim 27000\text{ cm}^{-1}$ ) and tail of huge band, due to charge transfer from oxygen ions to iron ions, which overlapped  $\text{Fe}^{3+}$  bands at higher wavenumber. In absorption spectra at low temperature,  $\text{Fe}^{3+}$  bands can be seen clearer than those at room temperature and it can be extracted by gaussian fitting of UV-edge.  $\text{Fe}^{2+}$  bands and extracted  $\text{Fe}^{3+}$  bands were compared with crystalline samples having  $\text{Fe}^{2+}$  or  $\text{Fe}^{3+}$  sites with several kinds of coordination number (4 or 5 or 6). Both of the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  bands obtained from glasses can be represented by the bands of only 4 and 5 coordinated sites. Based on these considerations was done by Gaussian functions. From comparison of band intensity, it was found that the average coordination number of  $\text{Fe}^{2+}$  sites decreases with optical basicity of glasses decreasing and, in contrast, the average coordination number of  $\text{Fe}^{3+}$  increases. From EPR measurement, it was found that  $\text{Fe}^{3+}$  sites were most distorted in MAS (with lowest basicity) and lowest distorted in NAS glass (with highest basicity). This result supposed the fact that the average coordination number of  $\text{Fe}^{3+}$  increases with optical basicity decreasing. Because lower coordinated sites are indeed less subject to be distorted than higher coordinated sites.

Comparing the trend about coordination number as a function of optical basicity with that of silicate glasses, the average coordination number shows the different trend with optical basicity. it would be related to the structure of matrix structure of aluminosilicate glass. With optical basicity decreasing, it was found that the degree of Al avoidance decreases [1]. This means that the proportion of Al-O-Al bonding increases and Al-rich cluster is formed [2] (Figure 2). This deviation from average structure can cause the difference in the basicity in micro scale in glass. Higher basicity leads to oxidized species of Fe sites, larger distortion of sites and difference in coordination number.

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[2] A. R. Allu, Structure and Crystallization of Alkaline-Earth Aluminosilicate Glasses: Prevention of the Alumina-Avoidance Principle. *J. Phys. Chem. B*, pp 4737-4747 2018.

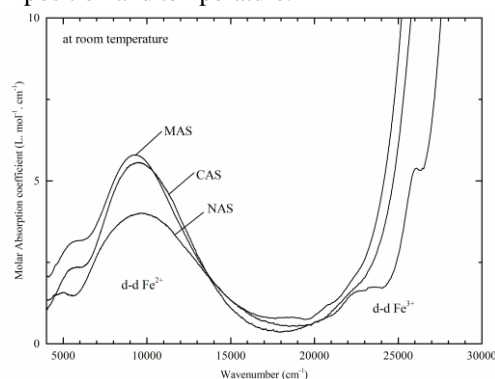


Figure 1. Optical absorption spectra at room temperature

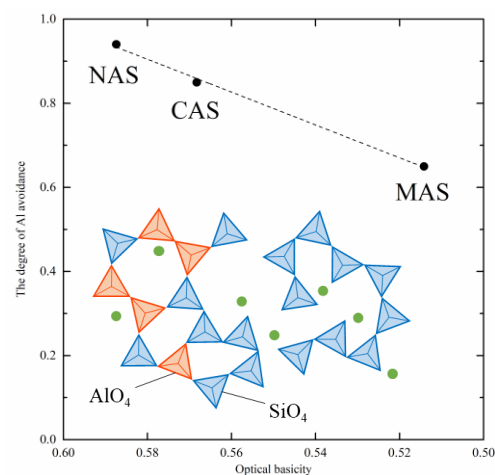


Figure 2. The degree of Al avoidance with optical basicity