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# High Temperature ESR Study on Ferric Ions in Amorphous Lead Silicates

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Local environment around ferric ion and  $\text{Fe}^{3+}\text{-Fe}^{3+}$  interaction in amorphous oxides have widely been investigated by various spectroscopic methods such as NMR<sup>1)</sup> and optical absorption<sup>2)</sup> techniques. ESR of  $\text{Fe}^{3+}$  ions in oxide glasses has been also much interested by many investigators<sup>3)</sup> since Castner *et al.*<sup>4)</sup> observed ESR of  $\text{Fe}^{3+}$  ion in oxide glasses. In general, three resonances have been observed near  $g=2$ ,  $g=4.3$  and  $g=6$  in the ESR spectrum of many amorphous oxides containing ferric ions. According to previous results<sup>5)-8)</sup>, the  $g=4.3$  resonance is assigned to an isolated ferric ion in a tetrahedrally distorted coordination. The  $g=2$  resonance at a smaller content of  $\text{Fe}_2\text{O}_3$  than about 1 mol% is attributed to an isolated ferric ion in an axially distorted octahedral or tetrahedral environment. With increasing  $\text{Fe}_2\text{O}_3$  content, the resonance arises from the dipole-dipole interaction between ferric ions. The  $g=6$  resonance can be assigned to the same origin as the  $g=2$  resonance at a small  $\text{Fe}_2\text{O}_3$  content.

High temperature ESR of ferric ions in amorphous oxides has not so widely investigated. Momo *et al.*<sup>9),10)</sup> have reported on the high temperature ESR of ferric ions in some vitreous matrix including  $\text{PbO-SiO}_2$  glass. With increasing temperature in measuring ESR spectrum, they observed the faster decrease of the intensity of  $g=4.3$  resonance than that expected simply on the basis of the Boltzmann distribution law, and it was suggested that rapid decrease of  $g=4.3$  resonance arises from some atomic rearrangement in a high temperature.

The first purpose of the present study is to clarify local rearrangement around ferric ions in amorphous lead silicate using ESR spectroscopy. Secondly, our interest is focused on the clustering behaviour of ferric ion in amorphous matrix and detection of average cluster size using ESR spectroscopy.

Amorphous lead silicates ( $\text{PbO/SiO}_2 = 4/6$ ) containing 0.5 mol%  $\text{Fe}_2\text{O}_3$  were prepared by melting mixtures of reagent grade  $\text{SiO}_2$ ,  $\text{PbO}$  and  $\text{Fe}_2\text{O}_3$  powders in platinum crucible at the temperature of 100K higher than the

liquidus for 1.8ks in air. After quenching in air, the amorphous block was taken out of platinum crucible and pulverized using agate pestle and mortar. Pulverized specimens evacuated silica tubes at a low vacuum of 1 Pa order were mainly used for ESR measurement. In some experiments, ESR spectra were measured using pulverized specimens in unevacuated silica tubes. High temperature ESR spectra were measured using same specimen at every 100K interval in the temperature range from 373 to 973K. Every spectrum was measured within 1.8ks. Whenever each high temperature ESR spectrum was measured, specimen was cooled once in the resonant cavity and room temperature ESR spectrum of the annealed same specimen was measured before measuring ESR spectrum at next higher temperature.

Typical ESR spectra of ferric ions in the amorphous lead silicate at high and room temperatures are shown in Figs. 1 and 2. No effect of evacuating specimen in silica tube on ESR spectrum was basically observed. Comparing room- and high-temperature ESR spectra, maximum peak of derivative curve of the  $g=2$  resonance was more clearly observed with increasing temperature up to 673K. Besides, the  $g=2$  resonance is likely to be more intense with increasing temperature. As the maximum peak of the  $g=2$  resonance becomes clear, linewidth of the resonance becomes narrower up to 673K as shown in Fig. 3.

After the temperature in the measurement of ESR spectrum exceeded 673K, the maximum peak of the  $g=2$  resonance disappeared and the linewidth of the resonance showed similar value to those obtained from all room temperature measurements. Thus, linewidth of  $g=2$  resonance changed clearly at the temperature between 673 and 773K. According to our XRD results, host amorphous silicate was not crystallized by heat treatment of 873K for 7.2ks in air. Therefore, high temperature ESR spectra obtained below 773K can be interpreted without considering the effect of crystallization.

Though linewidth of ESR depends on the concentrations of magnetic ions, the linewidth can be interpreted

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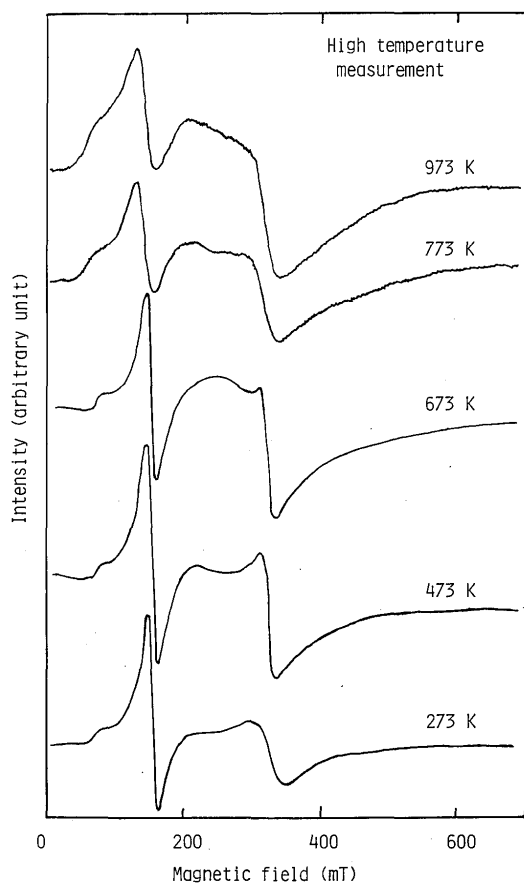


Fig. 1 ESR spectra of ferric ions in amorphous lead silicate ( $\text{PbO/SiO}_2 = 4/6$ ) at various temperatures.

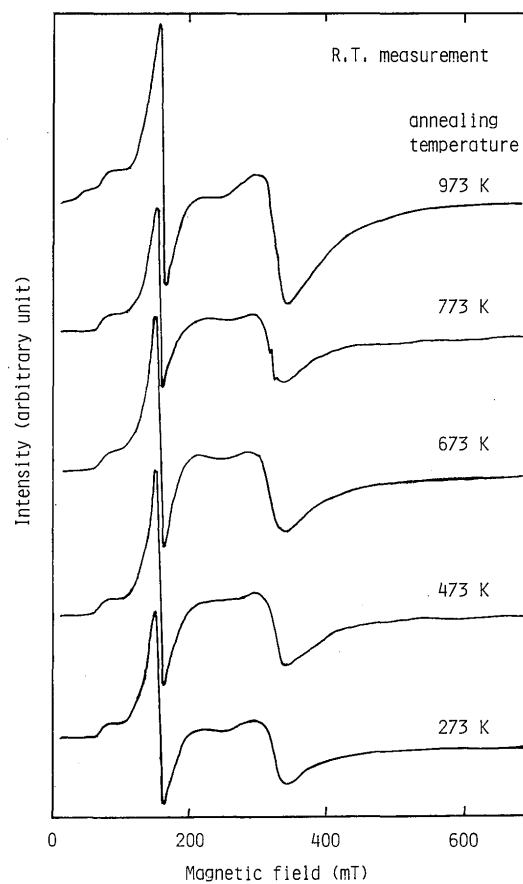


Fig. 2 ESR spectra of ferric ions in amorphous lead silicate ( $\text{PbO/SiO}_2 = 4/6$ ) at room temperature ( $= 293 \text{ K}$ ) after measured at each high temperature.

as follows<sup>11</sup>);

- (a)  $T < \theta_D$  ( $\theta_D$ ; Debye temperature)  
Linewidth is determined by (1) dipole-dipole interaction and (2) exchange interaction.
- (b)  $T > \theta_D$   
Linewidth is also affected by ionic motion, ionic diffusion and ion interchange.

Our results below 673K can be interpreted by exchange interaction and dipole-dipole interaction because host amorphous silicate was not crystallized below 673K. Linewidth become broader by dipole-dipole interaction and narrower by exchange interaction, so that linewidth of the  $g=2$  resonance below 673K can be attributed to the increase of exchange interaction or decrease of dipole-dipole interaction.

In the crystallization processes of some sodium silicate glasses containing  $\text{Fe}^{3+}$  ions, the decrease of linewidth was observed though the glasses contain a large amount of  $\text{Fe}_2\text{O}_3$  than those in the present study<sup>12</sup>). In the sodium silicate glasses, it has been also indicated that narrowing of linewidth arises from the decrease of site distortion around  $\text{Fe}^{3+}$  ions from cubic symmetry, which might be

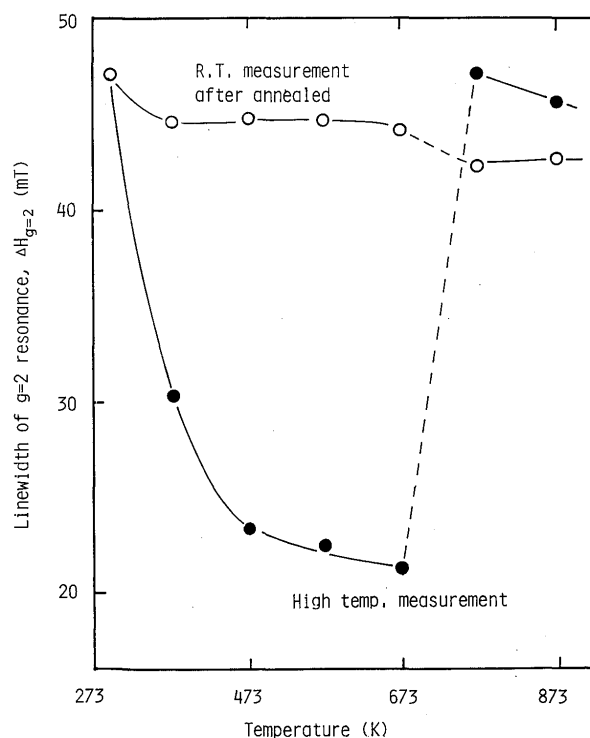


Fig. 3 Dependence of linewidth of the  $g = 2$  resonance upon temperature.

removed during crystallization. In the high temperature ESR below 673K, we should assume ionic diffusion or ion interchange if the exchange interaction between ferric ions is the main cause for narrowing the linewidth of the  $g=2$  resonance.

As shown in Fig. 3, however, narrowing of the  $g=2$  resonance was reversibly observed below 673K. Therefore, the narrowing may originate from temperature averaging of dipole-dipole interaction. Further, less effect of exchange interaction on the narrowing of linewidth can be supported by the decrease of exchange integral value with increasing temperature.

In the  $g=2$  resonances in the high temperature ESR spectra above 773K, linewidths showed similar values to those in room temperature measurements and maximum peak of derivative curve of the  $g=2$  resonance disappeared. These phenomena suggest the occurrence of ionic motion between ferric ions and atomic rearrangement in the host lattice. With disappearing the maximum peak of  $g=2$  resonance in the high temperature experiments, the  $g=2$  resonance in the room temperature measurement after annealed above 873K displayed a remarkable maximum peak. The result seems to be attributed to the increase of dipole-dipole interaction between ferric ions, which occur as the result of ionic diffusion during high temperature measurement.

In summary, the change of lineshape of the  $g=2$  re-

sonance between 673K and 773K is likely to arise from clustering of ferric ions, which can not be detected by XRD method. In the further study, it is desired to clarify cluster size of ferric ions and local environment around isolated ferric ions which produce  $g=4.3$  resonance.

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