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# Formation of Paramagnetic Center in Amorphous Lead Silicate during Crystallization†

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KEY WORDS : (Paramagnetic Center) (Amorphous) (Lead Silicate) (Crystallization)

Local structures of transition metal ions in amorphous oxides have extensively been interested by many investigators<sup>1)</sup>. Since Sands has reported the pioneering work using electron spin resonance (ESR) method<sup>2)</sup>, ESR has widely been used for clarifying local environments of various transition metal ions and other paramagnetic centers in amorphous oxides<sup>3),4)</sup>.

In the previous paper<sup>5)</sup>, we have reported high temperature ESR on ferric ions in amorphous lead silicates and it was suggested that dipolar interaction between ferric ions changes at the temperature between 673 K and 773 K. In the present study, formation of paramagnetic center in amorphous lead silicate containing ferric ions during crystallization was investigated by high temperature ESR method.

Details on specimen preparation and high temperature ESR experiment are shown in the previous paper<sup>5)</sup>. Typical ESR spectra of ferric ions in the same amorphous lead silicates are also given in the previous paper<sup>5)</sup>. **Figures 1 and 2** show the resonances of a paramagnetic center in the amorphous lead silicate which were measured at the high temperature between 239 K and 873 K, and at room temperature just after measuring each high temperature ESR spectrum. Though some difference was detected between the lineshapes of spectra measured at 473 K and room temperature, no other resonance is observed, except for broad resonance due to ferric-ferric dipolar interaction.

A new resonance appeared near 330 mT with increasing the temperature and the sharp resonance was most clearly observed at 773 K. After being over 773 K, the intensity of the resonance became very weak again. Comparing the high temperature ESR spectra with the room temperature ones, the resonance at room temperature was more sharply observed on account of temperature effect on ESR signal gain. The sharp resonance obtained at narrow scanning range is shown in

**Fig. 3.** The lineshape was almost symmetrical and linewidth was calculated to be 16 mT from peak-to-peak width in the ESR derivative curve. The g-value of the sharp resonance was estimated to be 1.990 from the microwave frequency and observed magnetic field.

Paramagnetic centers related to electronic defects and trace ions in amorphous silica and silicates has widely been investigated<sup>1)</sup>. Especially, electronic states of defects in amorphous silica has been studied in details by various methods<sup>6)</sup>. Because it is reasonable to assign the observed sharp resonance to electron-trapped center from the g-value, hole-trapped centers such as OHC and E centers should be eliminated from the candidate of the observed sharp resonance<sup>1)</sup>. Observation of complex lineshape in the spectra due to these centers also supports the strong rejection for assigning the observed resonance to these centers.

In the present study, as described in the previous paper<sup>5)</sup>, the specimen amorphous silicate contains iron ions added in the form  $\text{Fe}_2\text{O}_3$ . Accordingly, there is some possibility to observe other resonances due to ferric ions, in addition to three resonances arising from isolated ferric ions in rhombic and tetragonal fields and dipolar-interacted ferric ions. Up to the present, however, no sharp resonance originated from ferric ions has been observed near 330 mT in the amorphous oxides, though it is possible to observe a sharp resonance due to ferric ions in weak fields from the theoretical standpoints.

Defect center related to trivalent lead is likely to be plausible for an origin of the observed resonance<sup>7)</sup>. Though the asymmetric lineshape of the resonance arising from  $\text{Pb}^{3+}$  defect center has been observed in  $\gamma$ -irradiated lead silicate glasses, the g-value of the resonance ( $g_{\parallel} = 1.97$ ,  $g_{\perp} = 2.007$ ) is close to the value of the sharp resonance in the present work. The appearance of these resonances in same binary system (that is, in the lead silicate) seems to support the possibility of  $\text{Pb}^{3+}$

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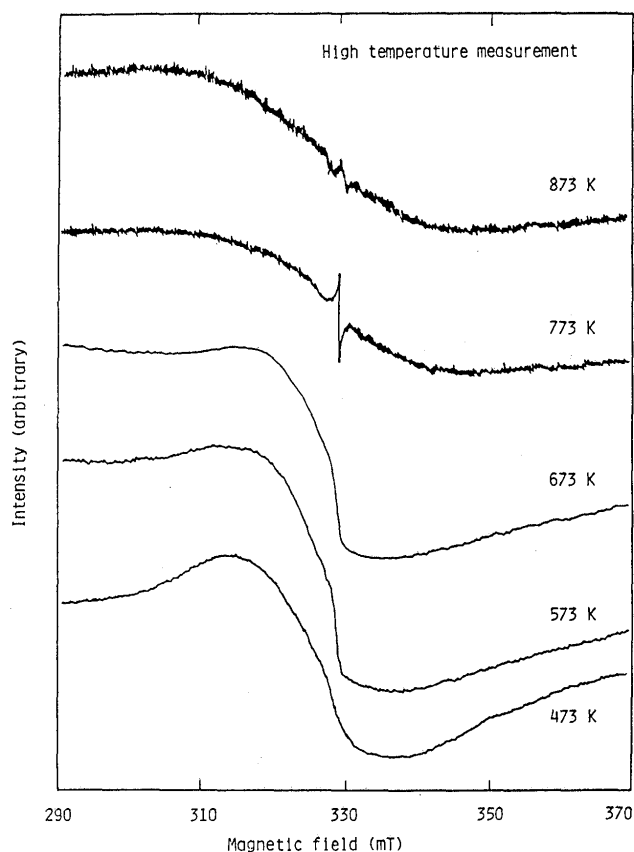


Fig. 1 High temperature ESR spectra of amorphous lead silicates ( $\text{PbO/SiO}_2 = 4/6$ ) containing 0.5 mol%  $\text{Fe}_2\text{O}_3$ .

defect center. However, conclusive assignment of the observed resonance in the premonitory stage of crystallization to  $\text{Pb}^{3+}$  defect center is not possible by several reasons. For example, no observation of another broad resonance located at a rather high field ( $\sim 550$  mT), though the intensity is very weak, is an important

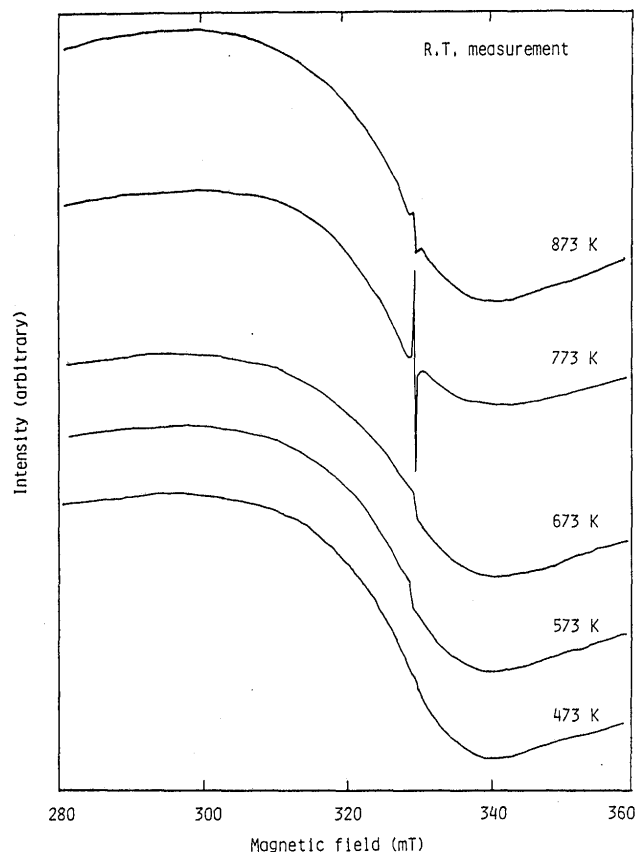


Fig. 2 ESR spectra at room temperature obtained from annealed amorphous lead silicates (0.5 mol%  $\text{Fe}_2\text{O}_3$ ,  $\text{PbO/SiO}_2 = 4/6$ ) just after measuring each high temperature ESR spectrum.

negative reason<sup>7)</sup>.

Symmetric lineshape of the observed resonance should be also considered because asymmetry is closely connected with fine structure of paramagnetic center. According to the previous work<sup>7)</sup>, the asymmetry of

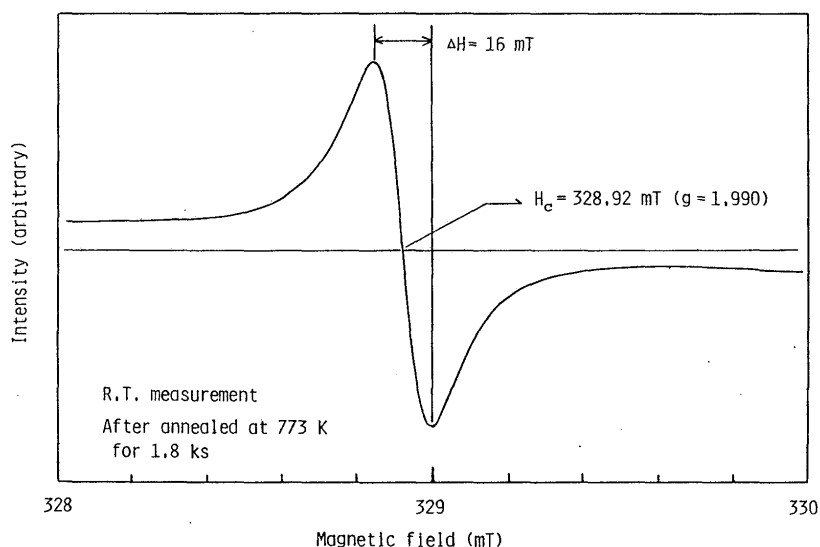


Fig. 3 ESR spectrum in narrow scanning range obtained from amorphous lead silicate which was heat-treated at 773 K for 1.8 ks in the high temperature ESR measurement.

lineshape and hyperfine structure appeared in the ESR spectra of  $\gamma$ -irradiated lead silicate glasses which were measured at liquid nitrogen temperature and at high PbO content. Our results was obtained from the measurements over room temperature, so that it seems to be reasonable to observe symmetrical lineshape on account of temperature effect. Accordingly, detailed measurements on the lineshape of the observed resonance below liquid nitrogen temperature is required for trustworthy assignment of the resonance.

The appearance of the observed resonance is likely to correspond to the premonitory stage of crystallization as being easily deduced from Figs. 1 and 2, and the results of the previous paper<sup>5)</sup>, in which it was shown that host amorphous silicate was not crystallized by heat treatment of 873 K for 7.2 ks in air. Accordingly, it is sure that Si-O and/or Pb-O bond breaking, or some atomic rearrangement of constituent ions is related to the

appearance of the observed sharp resonance. In the further investigation, qualitative analysis on ferric ions will be reported and connected with the formation of the electron-trapped center in the premonitory stage of crystallization.

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