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# Effect of Heat-treatment on ESR Spectra of $\text{Fe}^{3+}$ Ions in Lead Silicate Slags<sup>†</sup>

Nobuya IWAMOTO\*, Yukio MAKINO\*\* and Hirosuke MIKAMI\*\*\*

## Abstract

*Effect of heat-treatment on the local environment around  $\text{Fe}^{3+}$  ions was investigated by ESR spectroscopy. Relaxation of distorted lattice around  $\text{Fe}^{3+}$  ions was most remarkably observed in the lead silicate slags containing 55 mol%  $\text{PbO}$ . The phenomenon is attributed to the formation of the less polymerized silicate anions.*

KEY WORDS: (ESR) ( $\text{Fe}^{3+}$  ions) (lead silicate slag)

## 1. Introduction

Lead silicate system has been much interested for the structural study of glasses because the system can be vitrified in a wide compositional region. Until now, structural investigations on lead silicate glasses have been performed with various methods such as X-ray diffraction<sup>1)-3)</sup>, NMR<sup>4)</sup>, Raman scattering<sup>5),6)</sup> and chromatography<sup>7),8)</sup> and much information on atomic arrangements of lead, silicon and oxygen or on the ionicity of lead has been obtained. On the other hand, many structural studies on ferric ions in silicate glasses or slags have been reported with electron spin resonance (ESR)<sup>9),10)</sup>, optical absorption<sup>11),12)</sup> and Mössbauer spectroscopies<sup>13),14)</sup>. However, the investigation on the state of  $\text{Fe}^{3+}$  ion in lead silicate glass or slag has scarcely been performed. Some investigators take interest in the electric conduction or relaxation in lead silicate glasses containing  $\text{Fe}_2\text{O}_3$ <sup>15),16)</sup>. Momo et al. studied the temperature-dependence of ESR spectra of  $\text{Fe}^{3+}$  ions but systematic study on compositional dependence of ESR spectra was not performed<sup>17), 18)</sup>.

In the previous study,<sup>19)</sup> the compositional dependence of ESR spectra of  $\text{Fe}^{3+}$  ions at room temperature in lead silicate slags was reported. In this study, the effect of heat-treatment on ESR spectra of  $\text{Fe}^{3+}$  ions in the same slags was studied to examine the change of the environment around  $\text{Fe}^{3+}$  ions as the continuation of the previous structural investigation on  $\text{Fe}^{3+}$  ions in lead silicate slags.<sup>19)</sup>

## 2. Experiments

Details for the preparation of glassy slags, measurement of ESR spectra and estimation of relative quantities of  $\text{Fe}^{3+}$  ions related to each resonance were given in the pre-

vious paper.<sup>19)</sup> Heat-treatments of lead silicate slags were performed at 100°C, 300°C and 500°C for 1 hr, 3 hr and 5 hr in air.

## 3. Results

ESR spectra of  $\text{Fe}^{3+}$  ions in lead silicate slags heat-treated at 300°C and 500°C for 3 hr are shown in Figs. 1

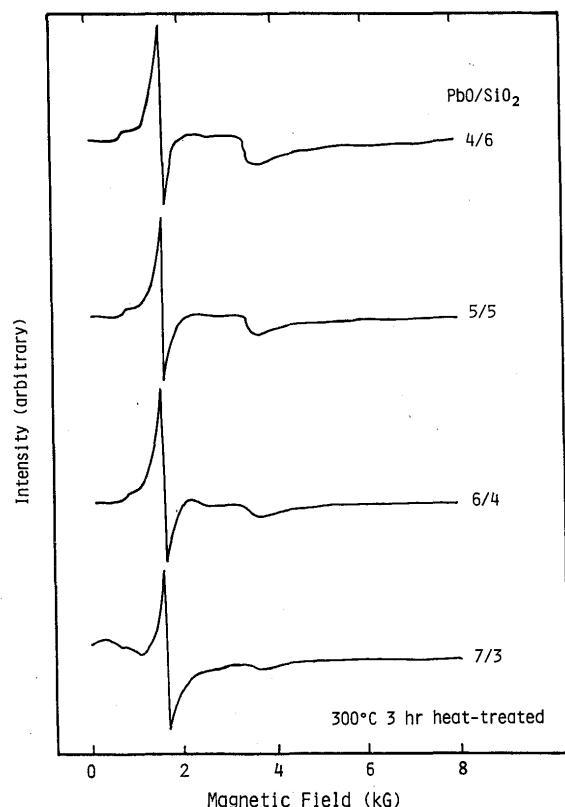


Fig. 1 ESR spectra of  $\text{Fe}^{3+}$  ions in lead silicate slags heat-treated in air at 300°C for 3 hr.

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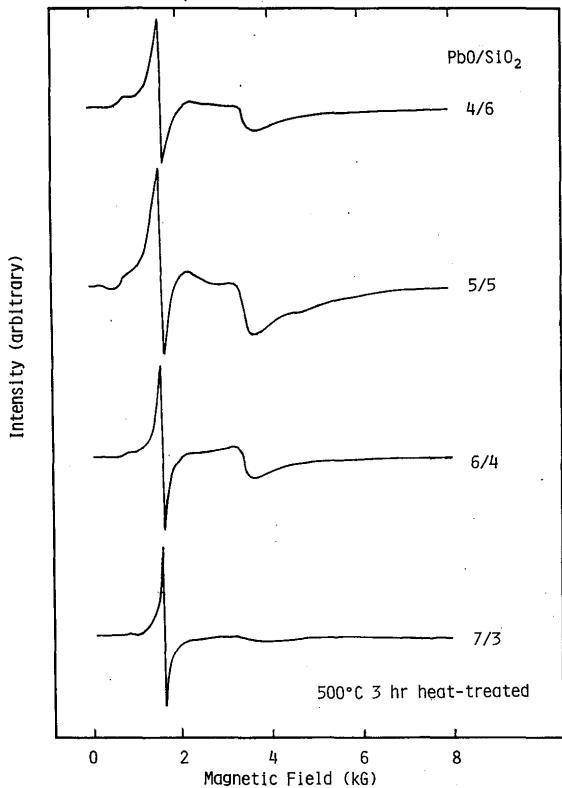


Fig. 2 ESR spectra of  $\text{Fe}^{3+}$  ions in lead silicate slags heat-treated in air at  $500^\circ\text{C}$  for 5 hr.

and 2. The clear increase of the  $g = 2.0$  (about 3400 G) resonance is observed in the slags containing about 55 mole%  $\text{PbO}$  with increasing the temperature in the heat-treatment. Figure 3 shows the relation between relative quantity of the  $g = 2.0$  resonance ( $r_{g=2.0}$ ) and  $\text{PbO}$  content. In the slags heat-treated at  $300^\circ\text{C}$ ,  $r_{g=2.0}$  value increases most remarkably in the slag with  $\text{PbO}/\text{SiO}_2 = 55/45$ . A maximum is also observed at the same composition in the slags heat-treated at  $500^\circ\text{C}$  for 3 hr. Typical X-ray diffraction patterns of heat-treated lead silicate slags having  $\text{PbO}/\text{SiO}_2 = 50/50$  are given in Fig. 4. As shown in this figure, typical amorphous pattern was observed in the slag heat-treated at  $300^\circ\text{C}$ . Same results were obtained in the slags with other compositions. These X-ray diffraction patterns are omitted. The dependence of linewidth of  $g = 4.3$  resonance ( $\Delta H_{g=4.3}$ ) on  $\text{PbO}$  content is shown in Fig. 5. The values of  $\Delta H_{g=4.3}$  in the glassy slags showed about 100 gauss irrespective of heat-treatment. The values of  $\Delta H_{g=4.3}$  in the crystallized slags, even in the partly crystallized slags, decreased and showed about 90 gauss. Only in the slag with  $\text{PbO}/\text{SiO}_2$  heat-treated at  $500^\circ\text{C}$  for 1 hr, a large value of  $\Delta H_{g=4.3}$  was obtained.

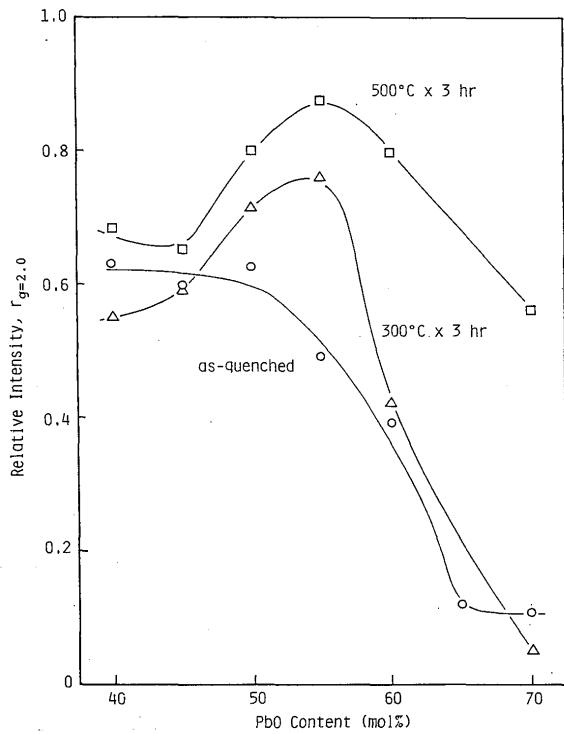


Fig. 3 Relation between relative quantity of the  $g = 2.0$  resonance ( $r_{g=2.0}$ ) and  $\text{PbO}$  content.

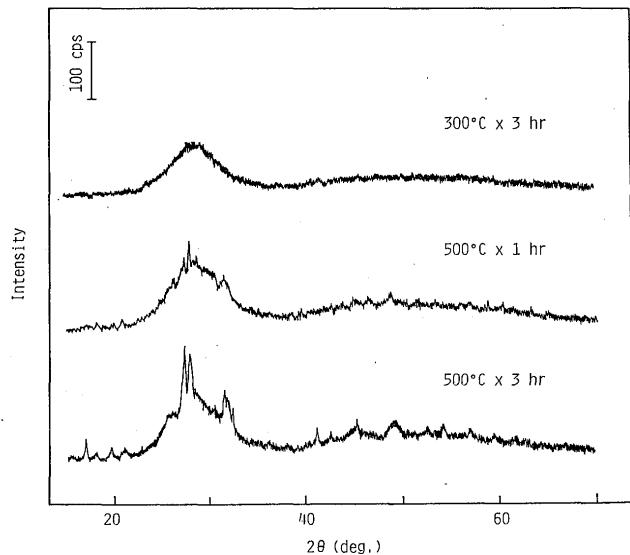


Fig. 4 Typical X-ray diffraction patterns of heat-treated silicate slags having  $\text{PbO}/\text{SiO}_2 = 50/50$ .

#### 4. Discussions

According to the previous papers,<sup>9,10,20</sup> three resonances are observed at about  $g = 2.0$  ( $\approx 3400\text{G}$ ),  $g = 4.3$  ( $\approx 1600\text{G}$ ) and  $g = 6.0$  ( $\approx 1050\text{G}$ ) in the glasses containing ferric ions. In most cases, the  $g = 6.0$  resonance is observed

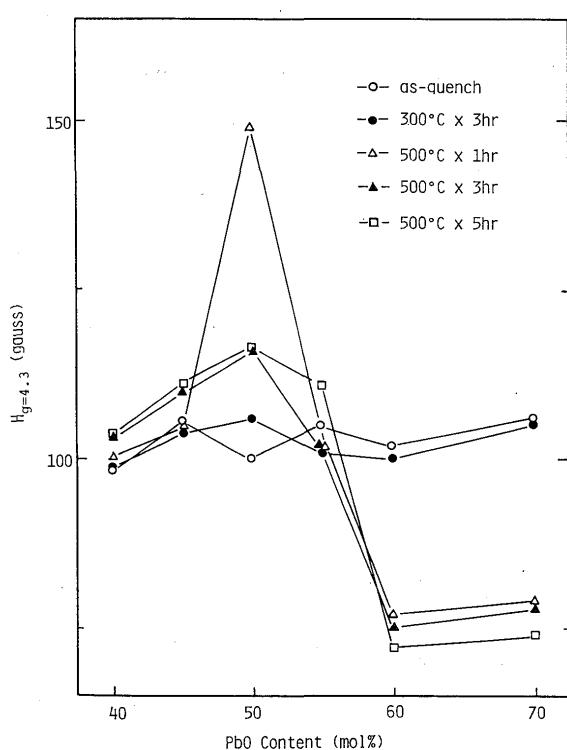


Fig. 5 Dependence of linewidth of the  $g = 4.3$  resonance ( $\Delta H_{g=4.3}$ ) on PbO content.

as the shoulder of the  $g = 4.3$  resonance. The  $g = 4.3$  and  $g = 6.0$  resonances can be assigned to  $\text{Fe}^{3+}$  ions in rhombic and tetragonal fields, respectively. The origin of the  $g = 2.0$  resonance is dependent upon  $\text{Fe}_2\text{O}_3$  content in oxide glasses. The resonance arises from dipole-dipole interacted  $\text{Fe}^{3+}$  ions in the glasses with more than about 1 mol%  $\text{Fe}_2\text{O}_3$  whereas it originates from  $\text{Fe}^{3+}$  ions in tetragonal fields in the glasses containing less than about 0.5 mol%  $\text{Fe}_2\text{O}_3$ .

Based on the interpretation on electron spin resonances of  $\text{Fe}^{3+}$  ions, it is considered that the increase of the  $g = 2.0$  resonance in the heat-treated lead silicate slags is due to the change of rhombic fields around  $\text{Fe}^{3+}$  ions. As shown in Figs. 1 and 2, the  $g = 6.0$  resonance is also observed and its intensity has an inclination to increase as the intensity of  $g = 2.0$  resonance increases. Therefore, the increase of  $g = 2.0$  resonance is mainly attributed to the formation of  $\text{Fe}^{3+}$  ions in tetragonal fields.

Though all slags remain still amorphous after the heat-treatment at  $300^\circ\text{C}$  for 3 hr, relative intensity ( $r_{g=2.0}$ ) of  $g = 2.0$  resonance shows remarkable increase only in the slags containing 50 and 55 mol% PbO. This supports that the heat-treatment relaxes the distortion of lattice around  $\text{Fe}^{3+}$  ions only in these slags which was introduced during cooling. Large relaxation of distorted lattice around

$\text{Fe}^{3+}$  ions in these is closely related to the structure of lead silicate slag. According to structural theory of slag,<sup>21), 22)</sup> there exists predominantly the network or sheet structure of  $\text{SiO}_4$  groups in lead silicate slags with more than about 50 mol%  $\text{SiO}_2$  and chain structure of  $\text{PbO}_4$  pyramids in the slags with PbO rich composition (more than about 65 mol%). In the composition range from 50 mol% to 65 mol% PbO, the concentrations of lower molecular polysilicate ions such as  $\text{SiO}_4^{4-}$  and  $\text{Si}_2\text{O}_7^{6-}$  increase with increasing PbO content.<sup>24)</sup> Accordingly, the large relaxation of distorted lattice around  $\text{Fe}^{3+}$  ions in the slags containing 50 or 55 mol% PbO is caused by the formation of the less polymerized silicate anions.

In the slags heat-treated at  $500^\circ\text{C}$  for 3 hr, the constituent ions in lead silicate slags can actively rearrange their positions during heat treatment. Accordingly, relative intensity of  $g = 2.0$  resonance increases rapidly in these slags except the slags containing PbO less than 45 mol%. No remarkable increment of  $r_{g=2.0}$  in the slags with 45 mol% PbO or less may be attributable to higher crystallization temperature. On the other hand, the effect of crystallization should be considered in the slags with PbO more than 50 mol%.<sup>25)</sup>

The reason why  $r_{g=2.0}$  shows a higher value in the slag with  $\text{PbO}/\text{SiO}_2 = 7/3$  heat-treated at  $500^\circ\text{C}$  for 3 hr is attributable to the broad linewidth (580 gauss) though the  $g = 2.0$  resonance apparently shows a very lower intensity as shown in Fig. 2. Accordingly, the effect of linewidth may be overestimated in the equation  $(\Delta H)^2 \cdot I$ , where  $I$  is the intensity of each resonance. Finally, the effect of dipole-dipole interacted  $\text{Fe}^{3+}$  ions may be considered to some extent, though the effect is expected to be small, because the dependence of the  $g = 2.0$  resonance on  $\text{Fe}_2\text{O}_3$  content are not examined in this study.

## 5. Summary

Effect of heat-treatment on ESR spectra of lead silicate slags containing 0.5 mol%  $\text{Fe}_2\text{O}_3$  was investigated. Even in the heat-treatment under the crystallization temperature, slight rearrangement of ions around  $\text{Fe}^{3+}$  ions was observed. The relaxation of distorted lattice due to heat-treatment was reflected in ESR spectra of  $\text{Fe}^{3+}$  ions and enhanced the formation of  $\text{Fe}^{3+}$  ions in tetragonal fields. The enhancement most remarkably occurs in the slags in which less polymerized silicate anions such as  $\text{SiO}_4^{4-}$  and  $\text{Si}_2\text{O}_7^{6-}$  are formed.

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