Technical Note

ESR spectra of Fe^{3+} Ions in lead silicate slags†

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

KEY WORDS (Electron Spin Resonance) (Lead Silicate) (State Analysis) (Fe^{3+} Ion)

Lead silicate glass has been widely investigated by various spectroscopic methods[1)–3)] in order to elucidate the structure of silicate glass and its melt. On the other hand, the clarification of state of iron in slags is very important in iron- and steel-making and in some welding processes using fluxes[4)–6)]. In this study, state of ferric ions in lead silicate glasses was investigated by electron spin resonance (ESR) spectroscopy.

Reagent grade SiO_2, PbO and Fe_2O_3 were used for preparing glass specimens. The mixtures of these reagents were melted in platinum crucibles at the temperatures 100°C higher than their liquidus temperatures in an electric furnace. Fe_2O_3 addition was fixed to be 0.5mol% in every glass. After being held for 1 hr in air, they were cooled. ESR spectra were measured with X-band method using a spectrometer of Varian E-109 type. Relative quantity of Fe^{3+} ions related to each resonance was approximately estimated by $I(\Delta H)^2$, where I and ΔH are the peak-to-peak height and width of the resonance.

ESR spectra of Fe^{3+} ions in lead silicate glasses are shown in Fig. 1. Two resonances are observed near g=2.0 (H=3400 G) and g=4.3 (H=1600 G), respectively. A shoulder is observed near g=6.0 (H=1050 G). According to the previous papers[7)–10)], the g=4.3 and g=6.0 resonances arise from Fe^{3+} ions in a rhombic and axial crystal fields, respectively. The g=2.0 resonance can arise from two sorts of origins, that is, from dipole-dipole interacted Fe^{3+} ions and Fe^{3+} ions in an axial crystal field. Further, it is indicated that the g=2.0 resonance due to dipole-dipole interaction between Fe^{3+} ions begins to be observed at the content of Fe_2O_3 more than 1 mol%. As shown in Fig.1, the intensity of the shoulder near g=6.0 has a tendency to increase with increasing the intensity of the g=2.0 resonance. Accordingly, it is reasonanble to assign the g=2.0 resonance not to dipole-dipole interacted Fe^{3+} ions but to Fe^{3+} ions in an axial crystal field. Figure 2 shows the composition dependence of the relative quantities of Fe^{3+} ions related to the g=2.0 and g=4.3 resonances. The relative quantity of Fe^{3+} ions related to the g=4.3 resonance, $r_{g=4.3}$, is nearly constant at the content less than about 50mol% and it increases with increasing PbO content when PbO content is over 50 mol%. This shows that Fe^{3+} ions have a tendency to prefer rhombic crystal field to axial one with increasing PbO content. The observa-

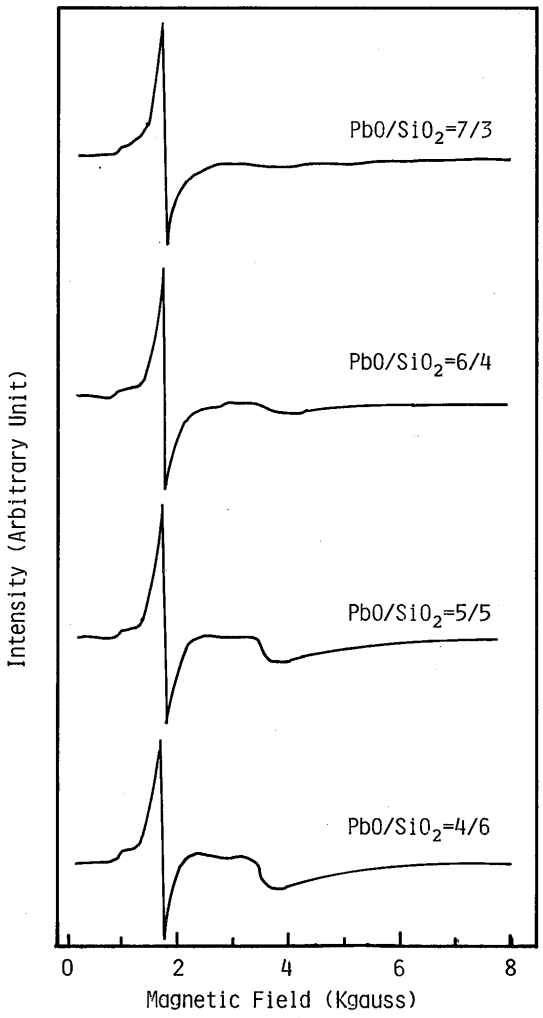

Fig. 1 ESR spectra of Fe^{3+} ions in lead silicate glasses

† Received on September 30, 1982
* Professor
** Instructor
*** Graduate Student

Transactions of JWRI is published by Welding Research Institute of Osaka University, Ibaraki, Osaka, Japan

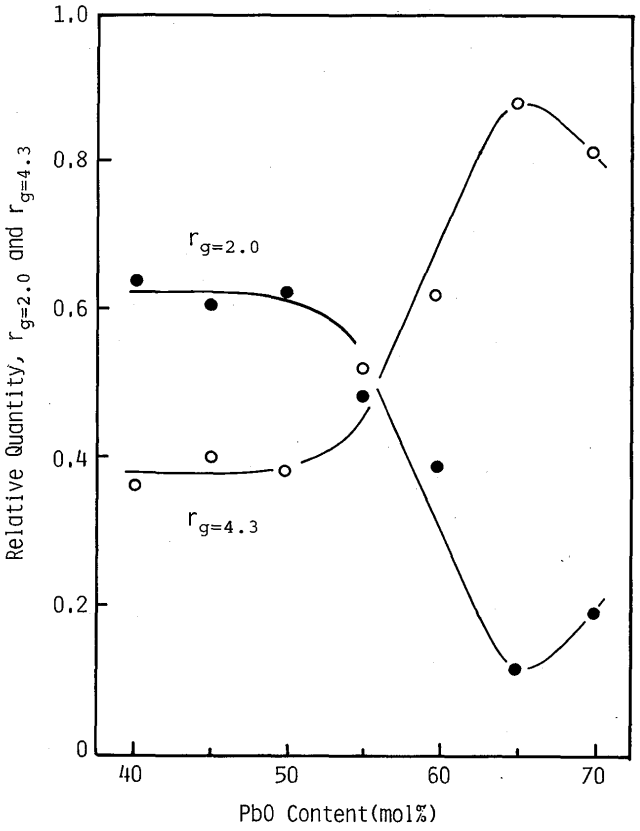

Fig. 2 Dependences of relative quantities, $r_{g=2.0}$ and $r_{g=4.3}$ upon PbO content.

tion of the tendency at the PbO content more than 50 mol% suggests that the increase of Fe^{3+} ions in a rhombic crystal field is closely related to the change of network structure to linear chain structure in lead silicate glass. The relation between state of Fe^{3+} ion and silicate structure will be investigated in near future.

References

1) B. Piriou and H. Arashi; High Temp. Sci. , 13 (1980), p299.
2) M. F. Mydlar, N. J. Kreidl, J. K. Hendren and G. T. Clayton; Phys. Chem. Glasses, 11(1970), p196.
3) M. Leventhal and P. J. Bray; Phys. Chem. Glasses, 6(1965), p113.
4) F. D. Richardson, Physistry of Metallurgy (Academic Press, London 1974), Vol. 2, p. 346.
5) O. A. R. Kay, A. Mitchell and M. Ram; J. Iron St. Inst., 208 (1970), p.141.
6) S. Nakano, K. Tamaki and J. Tuboi; J. Japan Welding Soc., 46 (1977), p.68 (in Japanese).
7) T. Castner, G. S. Newell, W. C. Holten and C. P. Slichter; J. Chem. phys., 32 (1960), p. 668.
8) C. R. Kurkjian and E. A. Sigety; Phys. Chem. Glasses, 9(1963), p. 73.
9) D. Loveridge and S. Parke; Phys. Chem. Glasses, 12 (1971), p.19.
10) D. M. Moon, J. A. Aitken, R. M. MacCrone and G. S. Cieloszyk; Phys. Chem. Glasses, 16(1975), p.91.