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S-character of Cd^+ centre in γ-irradiated alkali silicate glasses

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The s-character of Cd^+ centres and its fluctuation in γ-irradiated alkali silicate glasses were investigated using ESR spectroscopy. With increasing alkali content, the s-characters of Cd^+ centres in sodium and potassium silicate glasses decrease monotonically whereas the s-character in lithium silicate glasses shows a maximum and then decreases. The temperature effect on compositional dependence of the s-character of a Cd^+ centre is rarely observed in lithium silicate glasses. On the other hand, the temperature effect is clearly observed in sodium and it is suggested that local structures around Cd^+ centres in sodium and potassium silicate glasses is relaxed by annealing at room temperature.

1. Introduction

The state of $(ns)^1$ centres in glass has been widely studied using ESR spectroscopy [1–4]. Some investigators considered that the structure of $(ns)^1$ centres is a suitable probe ion for examining the structure of glass [5]. The s-character of Cd^+ centres in γ-irradiated oxide glasses was investigated by Feldmann *et al.* [6] and Imagawa [5]. Recently, detailed studies on Pb^{3+}, Tl^{2+} and Cd^+ centres were reported by Hosono *et al.* [7–9] and structural fluctuations of these centres, as well as s-characters, were elucidated by ESR spectroscopy. In some cases, it is suggested that the s-character of $(ns)^1$ centres can be related to basicity of the glass [5]. Close relations of the basicity of glass to its structure have been proposed from various standpoints [10–12]. The concept of basicity is useful for selecting a suitable composition of metallurgical slag and welding flux. Among various basicities, optical basicity using p-block ions is listed as an available one [13]. However, it is indicated that there exist some limitations in the oxide glasses containing metal ions which show high symmetry restricted covalency [14, 15].

In this study, the s-character of Cd^+ centres in γ-irradiated alkali silicate glasses was investigated using ESR spectroscopy based on the previous studies on oxide glasses [5, 7]. The relations between s-character and a few proposed basicities of these glasses are also discussed.

2. Experimental details

Reagent grade SiO_2, M_2CO_3 (M: Li, Na and K) and CdO were used for preparing glasses. These reagents were accurately weighed, mixed well in an agate mortar and pestle in acetone and dried well. The mixtures were melted in platinum crucibles at temperatures 100° C higher than their liquidus temperatures for 1 to 3 h, depending on viscosity. The initial content of CdO was 1 mol% in every glass. All glasses were produced by quenching in air. Pulverized glasses were irradiated by γ-rays from ^{60}Co for 2 h at a rate of 5.0×10^5 $R\,h^{-1}$ to produce Cd^+ centres. ESR spectra at room temperature were measured using a spectrometer of the Varian E-109 type and those at 173 K were measured using JEOL JES-PE-3X spectrometer. The reproducibility of ESR spectra due to the difference between spectrometers were

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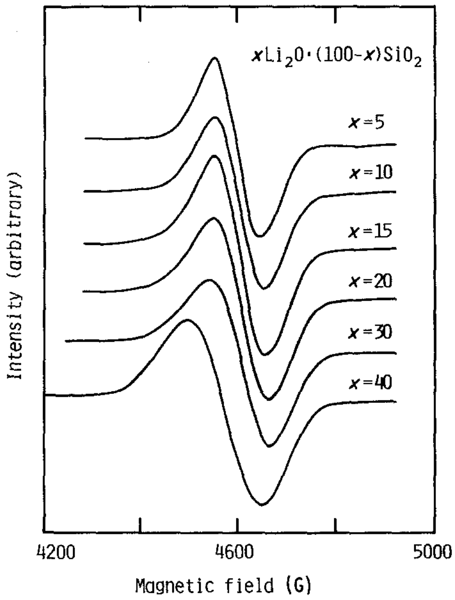

Figure 1 ESR spectra of signal II at room temperature in lithium silicate glasses.

checked in a few glasses. Modulation field strength was measured by proton resonator.

3. Results

Two resonances due to Cd$^+$ centres are observed near 3400 G (signal I) and 4500 G (signal II) in every alkali silicate glass. The dependence of signal II on glass composition is shown in Figs. 1 to 3. The positions of signal II in sodium and potassium silicate glasses shift to a lower field with increasing alkali content whereas, in lithium silicate glasses, the position shifts to a higher field up to about 30 mol% Li$_2$O and then to a lower field.

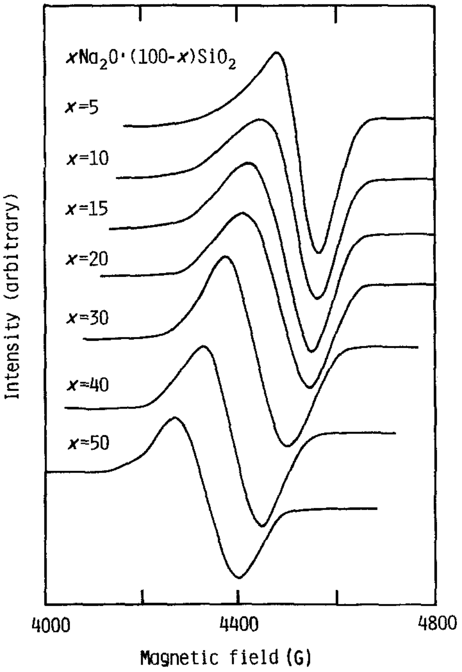

Figure 2 ESR spectra of signal II at room temperature in sodium silicate glasses.

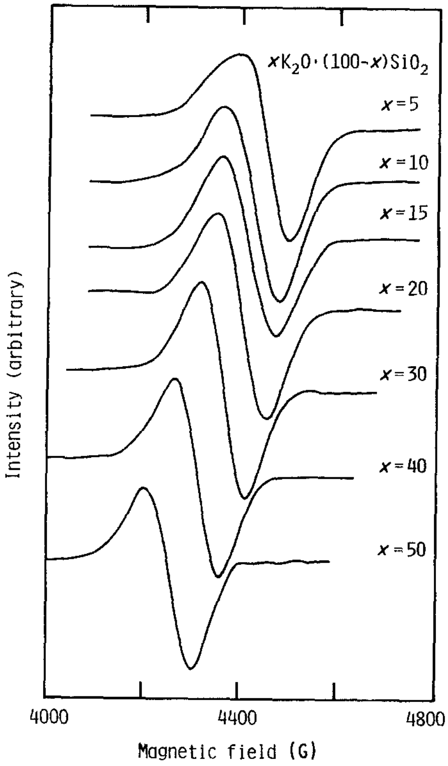

Figure 3 ESR spectra of signal II at room temperature in potassium silicate glasses.

The value of the s-character of Cd$^+$ centres in glasses was determined by the ratio of the hyperfine constant in glass and free ion, that is, A/A_{free}, where 0.4907 cm^{-1} was adopted as the A_{free} value of the Cd$^+$ ion [16]. The value of A in glass was determined by the following spin Hamiltonian, assuming g and A tensors are given by scalars (Breit–Rabi solution [17]),

$$\mathcal{H} = \beta H\cdot g\cdot S + I\cdot A\cdot S$$

that is, A is given by the equation

$$A = 2h\nu(h\nu - g_0\beta H)/(1 - 2h\nu)$$

where ν, h and g_0 are the microwave frequency, Planck constant and g-value which is determined by the position of the signal I due to non-magnetic nuclei Cd$^+$ ions.

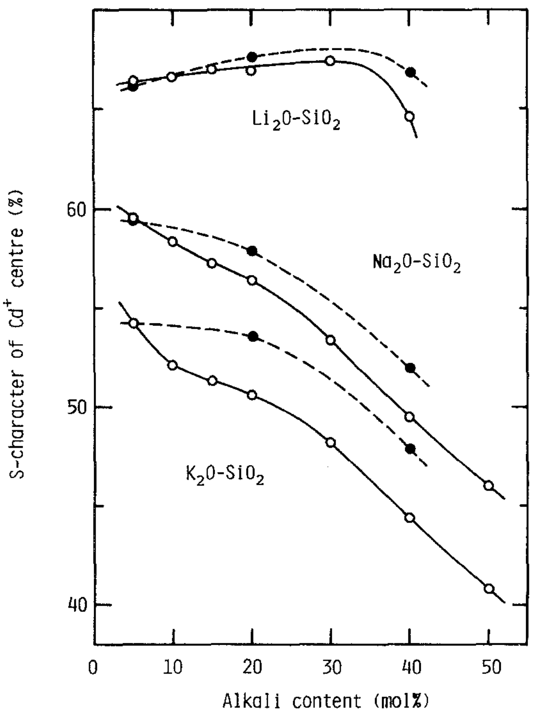

Figure 4 Dependence of the s-character of Cd$^+$ centres in alkali silicate glasses upon alkali content. (Solid and broken lines are the results at room temperature and 173 K, respectively.)

Fig. 4 shows the dependence of the s-character of Cd$^+$ centres in alkali silicate glasses upon alkali content; the s-character of Cd$^+$ centres measured at 173 K are also plotted in the figure. The s-character of the Cd$^+$ centre shows the highest value in the order lithium, sodium and potassium silicate glasses. With increasing alkali content, the s-character in sodium and potassium silicate glasses decreases monotonically whereas it increases slightly up to about 30 mol% Li_2O and then decreases in lithium silicate glasses. A slight difference between s-characters of Cd$^+$ centres measured at room temperature and 173 K is observed which becomes larger in the order lithium, sodium and potassium silicate glasses and/or with increasing alkali content.

Subsequently, structural fluctuation around the Cd$^+$ centre was considered from the change in linewidth of signal II and g-value of signal I. According to the previous paper [7], the fluctuation of the s-character of the Cd$^+$ centre can be estimated by the equation

$$\sigma_s = kg_0\beta(2h\nu + A)^2 \Delta H/A_{\text{free}}\cdot 1/2h^2\nu^2$$

where σ_s and ΔH are the fluctuation of the s-character of the Cd$^+$ centre and the linewidth of signal II, when the second order effects of g_0 and A and the contribution of the fluctuation of g-value to that of the s-character can be negligible.

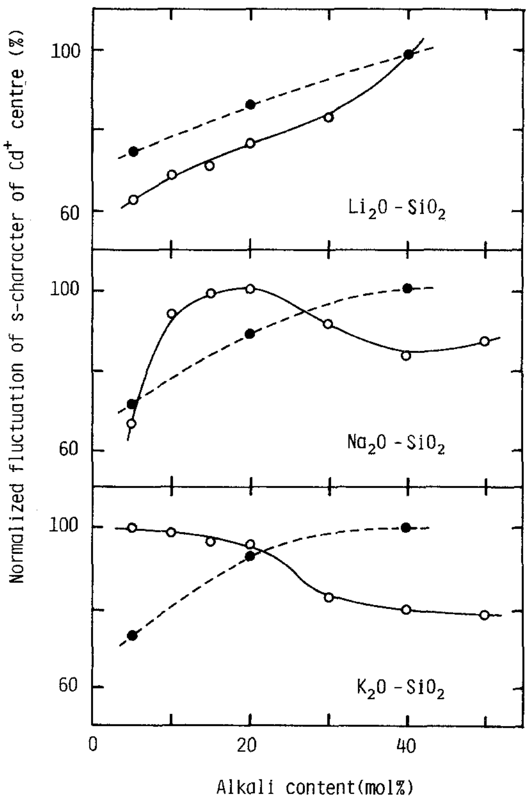

Figure 5 Dependence of the fluctuation of the s-character of Cd$^+$ centres upon alkali content. (Solid and broken lines are the results at room temperature and 173 K, respectively.)

The dependence of σ_s upon alkali content is given in Fig. 5. To examine the degree of relaxation at room temperature, the values of σ_s at room temperature are also plotted in Fig. 5. In lithium silicate glasses, similar dependences of σ_s upon alkali content are observed at room temperature and 173 K. On the other hand, quite different dependences of σ_s between room temperature and 173 K are observed in sodium and potassium silicate glasses.

4. Discussion

The s-character of (ns)^1 centres corresponds to the probability of the outermost electron of the centre being an (ns) electron, so that it is expected that the s-character of a Cd$^+$ centre is connected with the covalency of the Cd–O bond. Because the polarization of oxygen in oxide glass

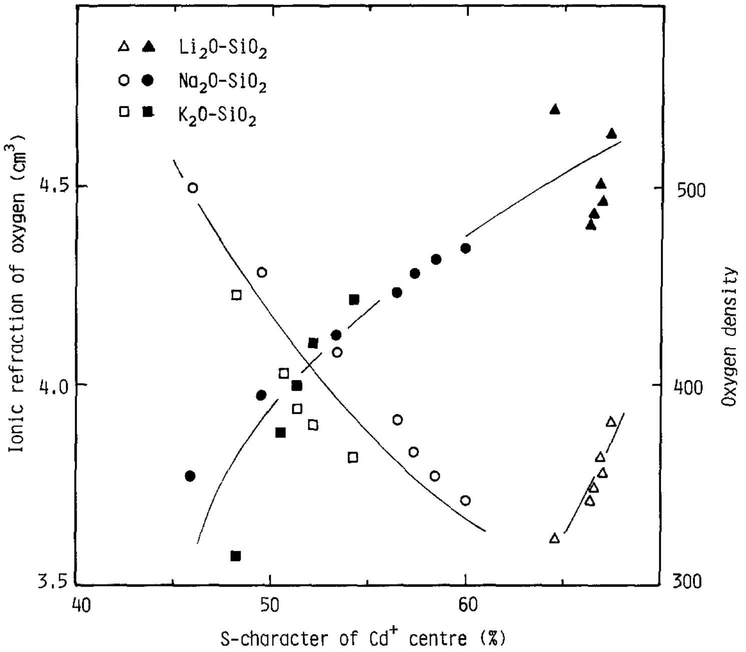

Figure 6 Relations of the s-character of Cd^+ centres to ionic refraction of oxygen (R_O) and oxygen density in alkali silicate glasses. Open and filled symbols are the data for R_O and oxygen density respectively.

is closely related to the average covalency of M–O bonds (M; constituent cations), the s-character of Cd^+ centres in oxide glass can be roughly estimated by ionic refraction of oxygen (R_O) in glass. The relation between the s-character of Cd^+ centres and R_O in alkali silicate glasses is given in Fig. 6. In the sodium and potassium silicate glasses, the s-character of Cd^+ centres decreases with increasing R_O whereas the value in lithium silicate glass increases as R_O increases. Therefore, the average chemical state of oxygens in oxide glass cannot be simply reflected in the s-character of the Cd^+ centre. The behaviour of the s-character of the Cd^+ centre in lithium silicate glasses seems to be attributable to phase separation [18] and/or oxygen packing behaviour of the glass [19].

The relation between the s-character of Cd^+ centres and oxygen density of alkali silicate glasses [19] is also plotted in Fig. 6. Although the plots of lithium silicate glasses are somewhat scattered, a sudden change of slope is not observed. Hosono *et al.* [20] indicated that densification by high pressure treatment weakens the Cd–O bond and the weakening may be caused by the increase in the coordination number of the Cd^+ centre. Because oxygen density is considered to be a measure of compactness of glass, the increase in oxygen density roughly corresponds to densification by high pressure treatment. Thus, it can be interpreted that the s-character of a Cd^+ centre increases with increasing oxygen density of the glass, which causes a weakening of the Cd–O bond.

As shown in Fig. 4, the temperature effect on the s-character of Cd^+ centres is more remarkably observed with increasing content of modifier oxide and ionic radius of modifier cation. The maximum discrepancy between the values measured at room temperature and 173 K was about 7% in $40K_2O \cdot 60SiO_2$ glass. The decrease in s-character of the Cd^+ centre at room temperature is attributed to structural relaxation due to the temperature effect. On the other hand, it is found from Fig. 5 that the compositional dependence of fluctuation of the s-character of Cd^+ centres is quite different from that of the s-character. The temperature in the measurement of the ESR spectrum strongly affects the compositional dependence of fluctuation of the s-character in sodium and potassium silicate glasses, although little temperature effect is observed in lithium silicate glasses. The results indicate that the s-character itself in sodium or potassium silicate glasses is not so markedly influenced by annealing at room temperature, but local structures around the Cd^+ centre are remarkably relaxed.

The relation between the s-character of a Cd^+ centre and theoretical optical basicity (Λ_{th}) is given in Fig. 7. The correlation between the s-character and Λ_{th} is not better than that between the s-character and R_O as shown in Fig. 6 and 7 and these relations depend on the glass system.

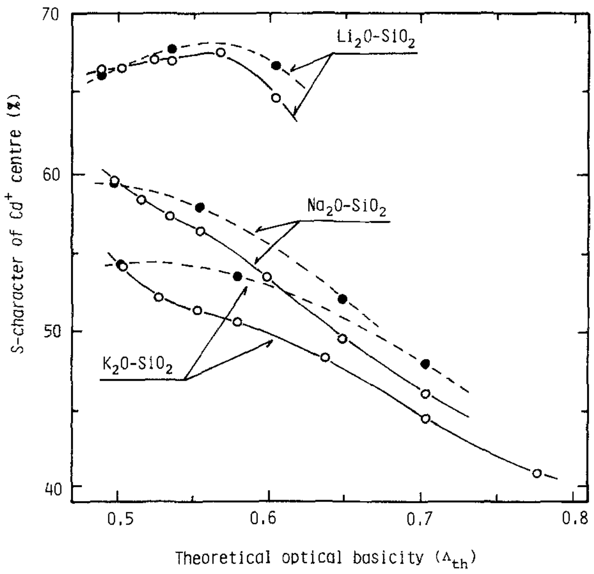

Figure 7 Relation between the s-character of Cd^+ centres and theoretical optical basicity (Λ_{th}).

Therefore, it is considered that the s-character of the Cd^+ centre is sensitively influenced by the species of modifier cation, even in glasses showing same basicity.

5. Conclusion

S-character of the Cd^+ centre in γ-irradiated alkali silicate glasses was determined using ESR spectroscopy. As alkali content increases, the s-character of a Cd^+ centre in sodium or potassium silicate glasses decreases monotonically and the value in lithium silicate glasses shows a maximum at about 30 mol% Li_2O and then decreases. From the compositional dependence of fluctuation of the s-character at room temperature and 173 K, it is seen that little structural relaxation around the Cd^+ centre occurs in lithium silicate glasses, whereas a clear relaxation is observed in sodium and potassium silicate glasses. It is found that the s-character of the Cd^+ centre to ionic refraction (R_O) or theoretical optical basicity (Λ_{th}) depends on glass composition, so that the s-character of the Cd^+ centre is sensitively influenced by the species of modifier cation, even in glasses having the same basicity.

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References

1. H. IMAGAWA, *J. Non-Cryst. Solids* 1 (1969) 335.
2. E. J. FRIEBELE, Proceedings of the International Congress on Glass, Prague, Vol. 3, edited by J. Götz (CVTS-Dům Techniky, 1977) p. 87.
3. H. HOSONO, K. KAWAZOE, J. NISHII and T. KANAZAWA, *J. Non-Cryst. Solids* **51** (1982) 217.
4. H. HOSONO, H. KAWAZOE and T. KANAZAWA, *ibid.* 55 (1983) 3.
5. H. IMAGAWA, *Phys. Chem. Glasses* **10** (1969) 187.
6. T. FELDMANN, A. TREININ and V. VOLTERRA, *J. Chem. Phys.* 42 (1965) 3366.
7. H. HOSONO, Y. ABE, H. KAWAZOE and T. KANAZAWA, *Yogyo-Kyokai-Shi (J. Ceram. Soc.* 92 (1984) 350.
8. H. HOSONO, H. KAWAZOE, J. NISHII and T. KANAZAWA, *J. Phys. Chem.* **86** (1982) 161.
9. *Idem, J. Non-Cryst. Solids* 44 (1981) 149.
10. F. IRMANN, *J. Amer. Chem. Soc.* **74** (1952) 4767.
11. A. PAUL and R. W. DOUGLAS, *Phys. Chem. Glasses* 9 (1968) 21.
12. M. G. FROHBERG and M. L. KAPOOR, *Stahl und Eisen* 91 (1971) 182.
13. J. A. DUFFY and M. D. INGRAMM, *J. Non-Cryst. Solids* 21 (1979) 373.
14. N. IWAMOTO, Y. MAKINO and S. KASAHARA, *ibid.*, 68 (1984) 379.
15. *Idem, ibid.*, 68 (1984) 389.
16. P. H. KASAI, *Phys. Rev. Lett.* **21** (1968) 67.
17. G. BREIT and I. I. RABI, *Phys. Rev.* **38** (1931) 2082.
18. E. M. LEVIN, "Phase Diagrams, Materials Science and Technology", Vol. 3, edited by A. M. Alper (Academic Press, 1970) Chp. 5, p. 143.
19. E. D. LACY, "The Vitreous State", (The Glass Delegacy University of Sheffield, 1955) p. 23.
20. H. HOSONO, H. KAWAZOE and T. KANAZAWA, *Solid State Commun.* 43 (1982) 769.

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