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Thermal expansion of silico-phosphate glasses with small additions of Fe_2O_3: EPR and dilatometric studies

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Electron paramagnetic resonance (EPR) and dilatometric measurements in phosphosilicate glass have been made in order to elucidate an anomalous trend of the linear thermal expansion coefficient β when Fe_2O_3 was added to the composition. The $g \simeq 2$ and $g_{eff} \simeq 4.27$ EPR lines were attributed, respectively, to undistorted and octahedrally coordinated Fe^{3+} ions, and to Fe^{3+} ions in low symmetry (rhombic) sites. The Fe^{3+} ion distribution in the network at different temperatures has been explained by a model of chemical insertion and it has been proved that the Fe^{3+} ions have two kinds of role as network modifiers. A relationship has also been found between β and the amounts of Fe_2O_3 added in the range 0 to 12 wt %.

1. Introduction

Studies have been carried out to find out in which way the Fe^{3+} ions enter a phosphosilicate vitreous system (used for its bioactivity characteristics in contact with living tissues) showing an anomalous trend of the linear thermal expansion coefficient β for Fe_2O_3 additions of less than 4 wt %. Anomalous behaviour of physical parameters has been observed by other authors for vitreous systems containing Fe^{3+} and P^{5+} [1, 2].

2. Experimental details

The base glass had the composition [3]: 45 SiO_2, 6P_2O_5, 24.5 Na_2O, 24.5 CaO (in wt %). To this composition was added Fe_2O_3 in the range 0.2 to 12.0 wt %, corresponding to x mol g^{-1} of Fe^{3+} with $2.5 \times 10^{-5} \leqslant x \leqslant 150.0 \times 10^{-5}$.

The batches were fired in air in a platinum crucible into a programmed kiln. The program was formulated with an overall glass-making firing time of about 300 min distributed in the following manner:

(a) reaching 300° C in 20 min and held steady at this temperature for 15 min (to allow the evaporation of water from the powders to be as complete as possible);

(b) reaching 900° C in 45 min and held steady at this temperature for 20 min (to allow complete CO_2 removal since Na_2O and CaO were introduced as carbonates);

(c) reaching the range 1050 to 1100° C in 20 min and held steady at this temperature for 15 min (to help the initial synthesis reactions, to complete the removal of all the gases present and to obtain a sufficient amount of initial melt);

(d) reaching 1350° C in 60 min and held steady at this last temperature for 2 h to allow the complete homogenization of the melt.

The melts thus obtained were poured out into graphite moulds pre-heated to 600° C, then slowly cooled to room temperature. The thermal history of the glasses obtained and the methodologies by which they were prepared were accurately standardized.

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†It is with deep regret that we note the death of Professor G. L. Del Nero.

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TABLE I Weight per cent of Fe_2O_3 addition and the equivalent x mol g^{-1} of Fe^{3+}, linear thermal expansion coefficient $\beta \pm 2 \times 10^{-7}$, x_r mol g^{-1} of Fe^{3+} ions in lower symmetry sites ($x_c = x - x_r$), experimental parameter $y = x_r/x_c$.

Addition (wt%)	$x \times 10^{-5}$ (mol g^{-1})	$\beta \times 10^5$ (°C^{-1})	$x \times 10^5$ 350°C (mol g^{-1})	$x \times 10^5$ 167°C (mol g^{-1})	$x \times 10^5$ 20°C (mol g^{-1})	y 350°C	y 167°C	y 20°C
0	0	1.40						
0.2	2.5	1.39	2.4 ± 0.2	2.4 ± 0.2	2.4 ± 0.2	20.00 ± 1.5	28.00 ± 2.2	55.00 ± 3.5
0.5	6.23	1.45	5.5 ± 0.4	5.7 ± 0.5	6.0 ± 0.5	7.60 ± 0.6	11.00 ± 0.9	24.00 ± 2.0
1.0	12.5	1.45	10.0 ± 0.7	11.0 ± 0.7	12.0 ± 0.8	3.80 ± 0.3	5.60 ± 0.5	11.00 ± 0.9
2.0	25.0	1.43	16.0 ± 1.2	18.0 ± 1.2	21.0 ± 1.4	1.80 ± 0.2	2.60 ± 0.2	5.50 ± 0.5
3.0	37.6	1.42	20.0 ± 1.6	23.0 ± 1.8	29.0 ± 2.0	1.10 ± 0.1	1.60 ± 0.1	3.40 ± 0.3
4.0	50.1	1.38	22.0 ± 1.8	26.0 ± 2.1	34.0 ± 2.8	0.78 ± 0.06	1.10 ± 0.1	2.10 ± 0.2
8.0	100.0	1.39	20.0 ± 1.6	26.0 ± 2.2	41.0 ± 3.3	0.25 ± 0.02	0.30 ± 0.02	0.70 ± 0.06
12.0	150.0	1.39	21.0 ± 1.8	27.0 ± 2.1	40.0 ± 3.2	0.16 ± 0.01	0.22 ± 0.02	0.36 ± 0.03

The dilatometric tests were performed with an automatic Netzch dilatometer in a temperature range 20 to 500° C. The samples, 5 cm long, were obtained with an accurate lapping of the little rods obtained from the moulds. The $\beta = (1/L_0)(\mathrm{d}L/\mathrm{d}T)_p \simeq \alpha/3$ values are reported in Table I. EPR measurements were performed at X-band (9.008 GHz) at 350° C, 167° C, 20° C and −196° C. For the same Fe_2O_3 additions the EPR spectra at 20° C and at −196° C were identical. The line shape was Gaussian and the resonance spectrum of all the samples was interpreted as the overlapping of one symmetric signal with $g = 2.000 \pm 0.015$ and one non-symmetric signal with $g_{\mathrm{eff}} = 4.27 \pm 0.03$.

The $g \simeq 2$ signal was attributed to Fe^{3+} ions in undistorted octahedral coordination (O_h sites) and the $g_{\mathrm{eff}} \simeq 4.27$ signal to Fe^{3+} ions in axial symmetry sites with a rhombic component C_{2v} (perhaps also a distortion towards C_{3v} in some cases) [4–7]. The line-width of the $g \simeq 2$ symmetric signal $\Delta H_{\mathrm{pp}} = 600 \pm 50$ G does not depend on x or on the temperature; on the contrary the observed effective line-width of the non-symmetric signal depends on x and on temperature as summarized in Table II.

We called x_r the molar number g^{-1} of Fe^{3+} ions in low symmetry sites and x_c the molar number g^{-1} of Fe^{3+} ions in regular octahedral coordination. Using numerical methods [8] we computed the signal areas and we ascertained that $x_r + x_c = x$ for every x-value. We also obtained the $y = x_r/x_c$ parameter, and consequently:

$$x_r = xy/(y+1) \quad (1)$$

$$x_c = x/(y+1). \quad (2)$$

The Fe^{3+} ions appear to insert, in the two sites, in different ways; in fact x_r increases with x until a maximum value x_{rm} is reached, depending on the temperature, as shown in Fig. 1, and the Fe^{3+} ions in low symmetry sites are well distributed in the network since, at a given temperature, the effective ΔH_{pp} values of the non-symmetric signal show a quasi-linear increase with x_r. On the contrary, the undistorted octahedral sites are occupied by Fe^{3+} ions with cluster formation as suggested by the fact that the line-width of the symmetric signal does not depend on x and x_c [9].

3. Discussion

The EPR spectra show that Fe^{3+} inside the glass resides in two distinct sites, given the symbols when empty, $*_r$ and $*_c$. The occupation of these sites by the iron ions will be indicated by x_r and

TABLE II Experimental values of the effective linewidth ΔH_{pp} of the $g_{\mathrm{eff}} = 4.27$ EPR line.

$\times 10^5$	ΔH_{pp}(G) 350° C	ΔH_{pp}(G) 167° C	ΔH_{pp}(G) 20° C
2.5	70 ± 5	50 ± 4	40 ± 3
6.23	90 ± 7	70 ± 5	60 ± 5
12.5	110 ± 10	100 ± 10	90 ± 7
25.0	150 ± 12	140 ± 12	140 ± 12
37.6	170 ± 15	160 ± 15	180 ± 15
50.1	180 ± 15	180 ± 15	210 ± 15
100	170 ± 15	180 ± 15	250 ± 15
150	180 ± 15	180 ± 15	240 ± 15

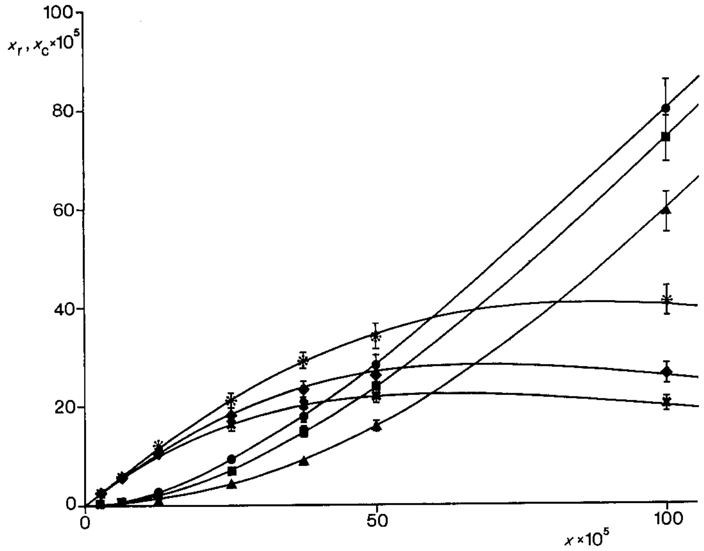

Figure 1 Experimental values of x_r (*, at 20°C; ◆, at 167°C; x, at 350°C) and of x_c (▲, at 20°C; ■, at 167°C; ●, at 350°C) and plot of Equations 1 and 2.

x_c (see Equations 1 and 2) and will depend on both temperature and Fe^{3+} concentration. Thus, if chemical equilibria take place, we may write:

$$Fe^{3+}_{fi} + *_r \rightleftarrows x_r$$

$$Fe^{3+}_{fi} + *_c \rightleftarrows x_c,$$

where Fe^{3+}_{fi} indicates the "free" ion, i.e. the Fe^{3+} not associated with a site. By eliminating Fe^{3+}_{fi} in the above equations we obtain:

$$x_c + *_r \rightleftarrows x_r + *_c,$$

where the reaction constant is given by†

$$K = x_r *_c / x_c *_r.$$

Thus, by setting

$$f(x) = *_c / *_r$$

and $y = x_r/x_c$, we obtain†

$$K = yf(x).$$

Figs. 2a and b show that data points can be fitted well with the choice $f(x) = \sinh(bx)$ or $f(x) \simeq bx$ for small x-values.

The best-values of b and K deduced with such a choice are:

for $T = 20°C$: $b = 2.50 \times 10^3$ and $K = 3.48$

for $T = 167°C$: $b = 2.44 \times 10^3$ and $K = 1.72$

for $T = 350°C$: $b = 2.38 \times 10^3$ and $K = 1.13$.

From the van't Hoff relation:

$$\Delta G^0 = -RT \ln K,$$

we obtain a free energy $\Delta G^0 = -5\,\text{kJ mol}^{-1}$. Such an endothermic heat of reaction is comparable with the energy for the free rotation of the tetrahedrons into the glass and with the changes in enthalpy associated with the changes of Fe^{3+} coordination.

The temperature-induced structural relaxation in a glass involves changes of the Fe^{3+} coordination [11, 12]. Unlike crystals, where such a change occurs in a narrow temperature range (phase transition), in glasses many coordination arrangements may coexist over extended temperature intervals and there is a continuous change, with temperature, of the population factors. These changes are driven by the structural relaxation of the glass network and can be predicted by the usual thermodynamic relations.

For a Fe_2O_3 content less than 4 wt %, a low symmetry rhombic coordination is favoured and x_r remains nearly constant when x is increased above 50×10^{-5}; assuming in a hypothetical model, as an orientative example, that the Fe^{3+} ions are associated with a site P^{5+} (Fig. 3), the low symmetry of these sites may be due to a distortion of the charges around the Fe^{3+} created by its dipole moment, by the P=O bonds and/or to the presence of alkaline ions [13, 14]. Our findings for $x \geqslant 50 \times 10^{-5}$ agree with the often made suggestion [15–21] that octahedral surroundings for Fe^{3+} are favoured when phosphate groups are present.

The dilatometric tests prove that the linear

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† The algebraic final formulation proposed for chemical equilibrium within a single phase remains formally the same with other approaches.

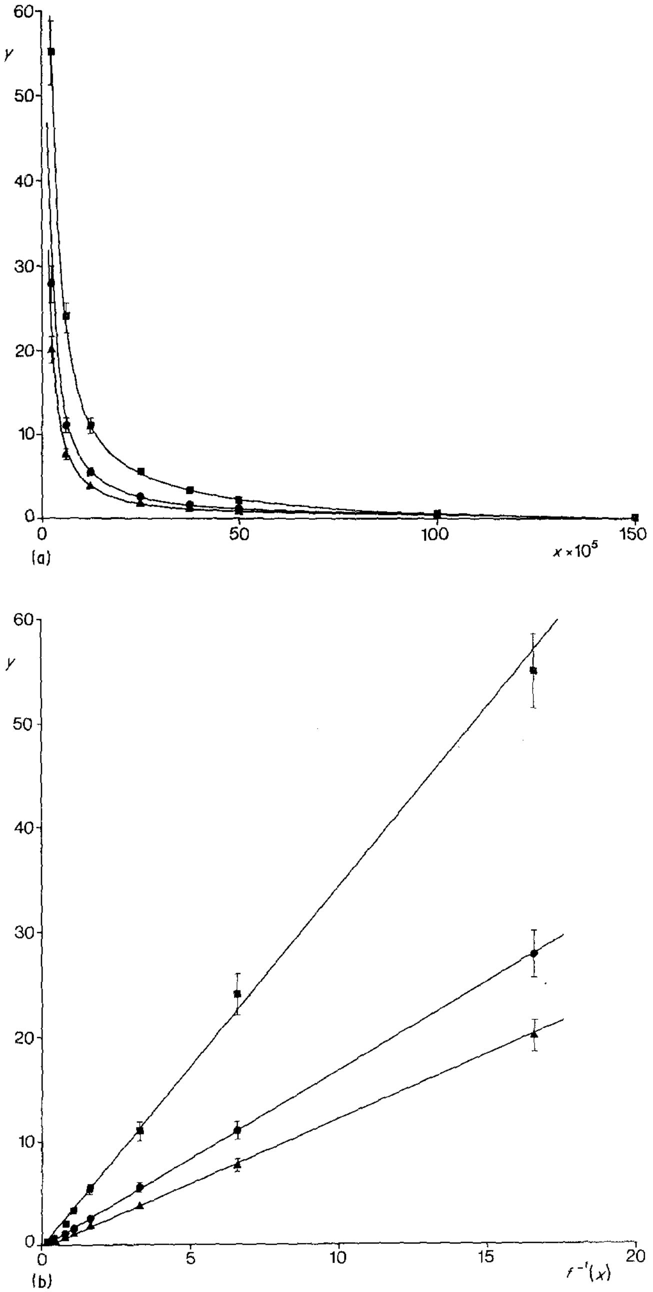
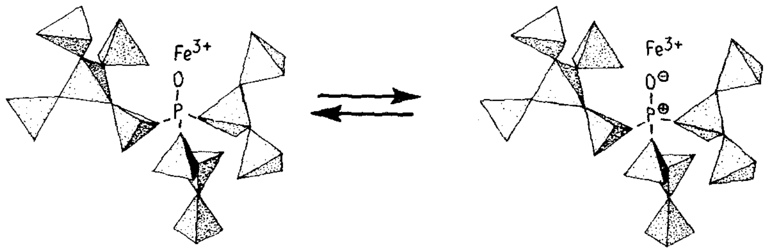


Figure 2 Best-fit curves of experimental values of y against x (a) and y against $f^{-1}(x)$ (b) at 20° C (■), at 167° C (●) and at 350° C (▲).

Figure 3 Interaction hypothesis between an Fe^{3+} ion and a neighbouring oxygen ion of a phosphatic group bonded with the silicate network (the SiO_4^{4-} groups are reported as tetrahedra).



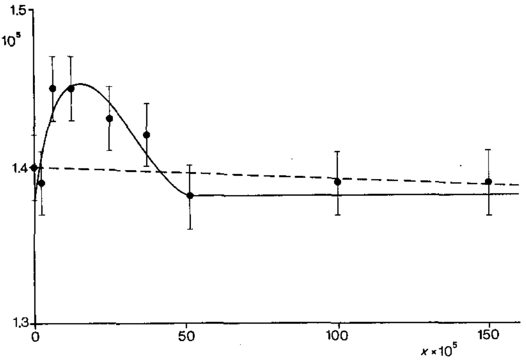


Figure 4 Experimental values of linear thermal expansion coefficient β of the doped glass: the dashed line is the trend of β against x according to Winkelmann and Schott. The continuous line is the plot of Equation 3.

thermal expansion coefficient β depends on the amount of Fe_2O_3. However, for $x < 50 \times 10^{-5}$ the relationship between β and x is not linear (see Fig. 4): while it is possible that some iron species exist which escape the EPR observation [22–29], it is believed that this phenomenon is related to the behaviour of the y-values.

It was therefore attempted to deduce a relationship between β and x: giving to Fe^{3+} ions in low symmetry sites the role of network modifiers inside a network substantially stable and assuming that the network is definitively filled in this manner when all the low symmetry sites, for a known temperature, are occupied and then it undergoes a continuous rearrangement of the network by the further additions of Fe_2O_3 (where new sites are created for Fe^{3+} at the higher symmetry coordination), the following empirical relation is suggested:

$$\beta = 40(\bar{x}_{rm} - \bar{x}_r)\bar{x}_r + 1.38 \times 10^{-5}, \qquad (3)$$

where $\bar{x}_{rm}$ and $\bar{x}_r$ are the average values calculated from Equation 1 around the test temperature of β.

Because the expansion coefficient for the glass system containing p wt% of Fe_2O_3 can be written, for the additive law:

$$\alpha = \sum_i p_i a_i - (p/100) \sum_i p_i a_i + pa,$$

where p_i are the wt% and a_i are the characteristic constants of original glass components, and a is the characteristic constant of Fe_2O_3, we obtain, from Equation 3:

$$a = 1.9 \times 10^{-6}(\bar{p}_{rm} - \bar{p}_r)\bar{p}_r/p + 4.14 \times 10^{-7}. \qquad (4)$$

We deduce, from Equation 4, that a reaches its constant value of $\sim 4 \times 10^{-7}$ when the rhombic sites are all occupied by Fe^{3+} ions.

4. Conclusions

The study of this phosphosilicate glass with Fe_2O_3 additions reveals that Fe^{3+} ions, on entering the glass network, reside in the following ways:

1. for addition of small amounts (< 4 wt%) of Fe_2O_3 a distorted rhombic coordination of Fe^{3+} predominates,
2. for higher Fe_2O_3 addition the rhombic sites are all occupied and the Fe^{3+} ions insert themselves into sites with regular octahedral coordination.

A relationship to evaluate the transition energy between the two coordination geometries was established and the dependence of β on the added Fe_2O_3 was qualitatively explained.

The system behaves according to the Winkelmann and Schott rule if the characteristic constant a of Fe_2O_3 is employed for Fe_2O_3 additions larger than 4 wt %.

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References

1. K. E. FOX, T. FURUKAWA and W. B. WHITE, *J. Amer. Ceram. Soc.* **64**, (1981) C42.
2. O. GZOWSKI, L. MURAWSKI, W. LIZAK, H. BINCZYCKA and J. SAWICKI, *J. Phys. D.* **14** (1981) L77.
3. L. L. HENCH, *Ceramurgia* **5** (1977) 253.
4. B. BLEANEY and K. W. H. STEVENS, *Rep. Prog. Phys.* **16** (1953) 108.
5. H. H. WICKMAN, M. P. KLEIN and D. A. SHIRLEY, *J. Chem. Phys.* **42** (1965) 2113.
6. T. KOMATSU and N. SOGA, *ibid.* **72** (1980) 1781.
7. C. M. BRODBECK and R. R. BUKREY, *Phys. Rev.* **B24** (1981) 2334.
8. C. B. AZZONI, G. L. DEL NERO, A. KRAJEWSKI and A. RAVAGLIOLI, *Lett. al Nuovo Cimento* **26** (1979) 55.
9. L. D. BOGOMOLOVA and E. K. HENNER, *J. Mag. Res.* **41** (1980) 422.
10. A. WINKELMANN and O. SCHOTT, *Ann. der Physik Chem.* **51** (1894) 735.
11. J. ROBERTSON, *Phys. Chem. Glasses* **23** (1982) 1.
12. A. C. WRIGHT and A. J. LEADBETTER, *ibid.* **17** (1976) 122.
13. T. CASTNER JR, G. S. NEWELL, W. C. HOLTON and C. P. SLICHTER, *J. Chem. Phys.* **32** (1960) 668.

14. D. LOVERIDGE and S. PARKE, *Phys. Chem. Glasses* **12** (1971) 19.
15. J. WONG and G. A. ANGELL, "Glass: Structure by Spectroscopy" (Marcel Dekker, New York, 1976).
16. R. J. EDWARDS, A. PAUL and R. W. DOUGLAS, *Phys. Chem. Glasses* **13** (1972) 137.
17. C. R. KURKJIAN and E. A. SIGETY, *ibid.* **9** (1968) 73.
18. E. BAIOCCHI, M. BETTINELLI, A. MONTENERO and L. DISIPIO, *Commun. Amer. Ceram. Soc.* **3** (1982) C39.
19. J. E. FENSTERMACHER, *J. Non-Cryst. Solids* **38/39** (1980) 239.
20. F. N. STEELE and K. W. DOUGLAS, *Phys. Chem. Glasses* **6** (1966) 246.
21. P. S. DANIELSON and J. W. H. SCHREURS, *J. Non-Cryst. Solids* **38/39** (1980) 177.
22. H. V. LAVER JR and R. V. MORRIS, *J. Amer. Ceram. Soc.* **60** (1977) 443.
23. A. K. BANDYOPADHYAY, M. RIBES, F. PERNOTL and J. ZARZYCKI, *Phys. Chem. Glasses* **23** (1982) 31.
24. G. A. C. M. SPIERINGS, G. M. G. JOCHEM and T. P. M. MEEVWSEN, *Glass Technol.* **22** (1981) 234.
25. J. A. DUFFY, *Phys. Chem. Glasses* **16** (1975) 22.
26. N. A. EISSA, A. N. SANAD, S. M. YOUSSES, S. A. EL-HENAWII and S. SH. GOMAA, *Acta Phys. Hung.* **48** (1980) 403.
27. V. N. MANK and L. S. SONKIV, "Geochemistry Topics", edited by Doklady (Scripta Publ. Co., New York, 1979).
28. G. LEHMANN, *Phys. Status Solidi* **B99** (1980) 623.
29. J. W. PARK and H. CHEN, *Phys. Chem. Glasses* **23** (1982) L107.

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