Co-ordination of Mg^{2+} in $MgO–P_2O_5$ glasses

Magnesium and zinc phosphate glasses are classified as being typical of the anomalous phosphate glasses by Kordes [1], that is, they show sharp minimums in the density – refractive index – and ultraviolet (u.v.) absorption edge–composition plots at metaphosphate composition [2]. The anomalous behaviour was attributed to the abrupt change of the co-ordination equilibrium of the metallic ion in the region of metaphosphate composition: octahedral or tetrahedral [1, 3]. Bogomolova *et al.* [4] found two kinds of VO^{2+} incorporated in the anomalous Zn or Mg phosphate glasses by electron spin resonance (ESR), whereas only a single kind of VO^{2+} was detected for the normal glass of $MO–P_2O_5$ (M=Ca, Sr, Ba and Pb). They concluded that two sites detected in ESR of VO^{2+} reflect the coexistence of 4- and 6-co-ordinated cations in the former glasses. However, the similar superposition in ESR spectra of VO^{2+} was observed also for cadmium phosphate glasses, despite being classified as normal phosphate glasses [5].

Recently, an empirical relation was established between the chemical shift of $K\alpha_{1,2}$ X-ray emission and the co-ordination number of Mg^{2+} in oxide crystals [6]. In the present article the method is used to elucidate the co-ordination structure of Mg^{2+} in $MgO–P_2O_5$ glasses.

The composition of the glasses were xMgO · $(100\text{-}x)P_2O_5$, where $x = 40, 45, 50, 54$ and 58 in mol%. The samples were prepared from $Mg_2P_2O_7$ and MgP_2O_6 crystals and $NH_4H_2PO_4$ reagent. $K\alpha_{1,2}$ emission of Mg^{2+} in the powdered glasses and MgO, which was used as the reference for chemical shift measurements, were measured alternatively on a high resolution instrument of the 2-crystal type (ADPx2) at room temperature. The other conditions for the emission measurements are given by Kawazoe *et al.* [6]

The chemical shifts of $K\alpha_{1,2}$ emission of Mg^{2+} in the glasses are given in Fig. 1 along with those

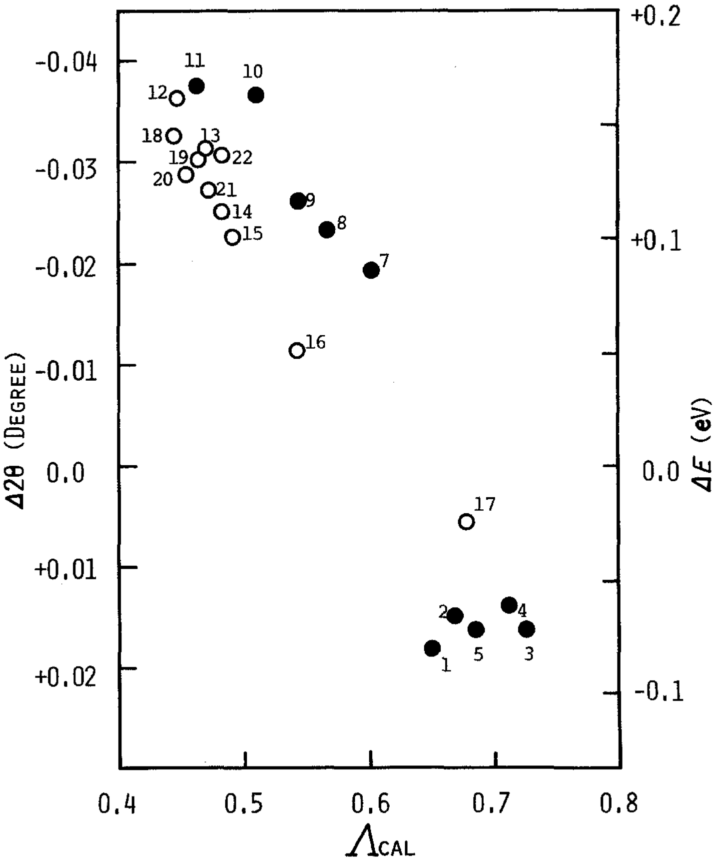

Figure 1 Relation between chemical shift of $MgK\alpha_{1,2}$ and the optical basicity of oxide crystals or glasses. Filled circles and open circles represent the results for crystalline oxides and glasses, respectively. In the following the figures in round brackets denote the known co-ordination number of Mg^{2+} in the crystals.
1: $MgAl_2O_4$ (4), 2: $Ca_2MgSi_2O_7$ (4), 3: $Li_{14}MgSi_4O_{16}$ (4), 4: $Li_{12}Mg_2Si_4O_{16}$ (4?), 5: Li_2MgSiO_4 (4?), 6: MgO (6), 7: $Mg_3B_2O_6$ (6), 8: $Mg_2B_2O_5$ (6), 9: $Mg_3P_2O_8$ (6 + 5), 10: $Mg_2P_2O_7$ (6 + 5), 11: MgP_2O_6 (6), 12: $5K_2O \cdot 5MgO \cdot 90B_2O_3$, 13: $10K_2O \cdot 10MgO \cdot 80B_2O_3$, 14: $5K_2O \cdot 25MgO \cdot 70B_2O_3$, 15: $5K_2O \cdot 30MgO \cdot 65B_2O_3$, 16: $20K_2O \cdot 20MgO \cdot 60B_2O_3$, 17: $25K_2O \cdot 25MgO \cdot 50SiO_2$, 18: $40MgO \cdot 60P_2O_5$, 19: $50MgO \cdot 50P_2O_5$, 20: $45MgO \cdot 55P_2O_5$, 21: $54MgO \cdot 46P_2O_5$ and 22: $58MgO \cdot 42P_2O_5$.

0022–2461/81/082318–02$02.20/0

for oxide crystals and some borate and silicate glasses. The horizontal axis of the figure is the calculated optical basicity of the matrix, which was proposed by Duffy and Ingram [7] to estimate Lewis basicity of oxyanionic crystals, glasses and solutions. The emission from 4-co-ordinated Mg^{2+} concentrates in the lower energy (higher $\Delta 2\theta$) region and that from 6-co-ordinated in the opposite region. It is clearly seen in the figure that all the emissions from the phosphate glasses with a composition ranging from $x = 40$ to 58 are located in the higher energy region. This suggests that 6-co-ordinated Mg^{2+} is predominant in the glasses. Since the line shape and the full-width at half maximum intensity (≈ 0.7 eV) were found to be almost identical for all the glasses and MgO (the reference crystal), the contribution from 4-co-ordinated Mg^{2+} seems to be negligible. Therefore, it is inferred that the abrupt change in the physical properties of $MgO-P_2O_5$ glasses around metaphosphate composition should not be attributed to the change in the co-ordination number of Mg^{2+}, as has been postulated. At present we have no convincing alternative explanation.

It may be interesting to note that there is a measurable difference between the peak energies for the metaphosphate glass and crystal, the emission from the crystal being at higher energy. This fact reveals that Mg–O bonding is stronger in the glass than in the crystal [6]. A similar phenomenon was also observed in the ESR spectrum of Cd^+ in CaP_2O_6 glass and β-CaP_2O_6 crystal [8].

References

1. E. KORDES, W. VOGEL and R. FETEROWSKY, *Z. Elektrochem.* 57 (1953) 282.
2. E. KORDES and R. NIEDER, *Glastech. Ber.* **41** (1968) 41.
3. E. KORDES and J. NAVARRETE, *ibid.* **46** (1973) 113.
4. L. D. BOGOMOLOVA, V. A. JACHKIN, V. N. LAZUKIN, T. K. PAVLUSHKINA and V. A. SHMUCKLER, *J. Non-Cryst. Sol.* **28** (1978) 375.
5. H. HOSONO, H. KAWAZOE and T. KANAZAWA, *ibid.* **37** (1980) 427.
6. H. KAWAZOE, H. KOKUMAI, T. KANAZAWA and Y. GOHSHI, *J. Phys. Chem. Sol.* in press.
7. J. A. DUFFY and M. D. INGRAM, *J. Non-Cryst. Sol.* **21** (1976) 373.
8. H. HOSONO, H. KAWAZOE, J. NISHII and T. KANAZAWA, *ibid.* in press.

Received 17 November
and accepted 12 December 1980

K. ISOZAKI
H. HOSONO
H. KOKUMAI
H. KAWAZOE
T. KANAZAWA
Department of Industrial Chemistry,
Faculty of Technology,
Tokyo Metropolitan University,
Fukasawa,
Setagaya-ku,
Tokyo 158,
Japan
Y. GOHSHI
Department of Industrial Chemistry,
Faculty of Engineering,
University of Tokyo,
Hongo,
Bunkyo-ku,
Tokyo 113,
Japan

The removal of surface silica and its effect upon silicon nitridation kinetics

It is well established that a thin (typically ~ 3 nm) native oxide layer covering the surface of silicon particles has a pronounced retarding effect on nitridation kinetics and that pretreatment of the powder with the object of removing the film leads to accelerated kinetics [1–3]. This letter presents the results of a brief study of the effects of pretreatments on the nitridation kinetics for high-purity silicon.

Silicon powder (~ 99.99 Si; Fe,Al ~ 100 ppm: < 8 μm) prepared from ingot was isostatically compacted (200 MPa) into cylinders (~ 1 cm diameter × 1 cm length) and nitrided in a controlled-atmosphere thermogravimetric balance. Both the powder preparation method and the balance are

0022–2461/81/082319–03$02.30/0