

First evidence for the coexistence of four-, five- and six-coordinated silicon in glasses prepared at ambient pressure

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Received (in Cambridge, UK) 1st August 2000, Accepted 11th September 2000

First published as an Advance Article on the web 2nd October 2000

At ambient pressure, a series of cadmium phosphosilicate glasses has been prepared in which, at certain phosphorus concentrations, the coexistence of four-, five- and six-coordinated silicon has been observed by ²⁹Si MAS solid state NMR spectroscopy.

In 1932 Zachariasen postulated that four coordinated silicon (Si^{iv}) is the building block of silicate glasses.¹ Indeed, several unsuccessful attempts were made subsequently to show that higher silicon coordination numbers would impose periodic long range order and consequent crystallinity.^{2,3} However, in 1987 a peak -213 ppm (characteristic of Si^{vi}) was first observed in the ²⁹Si NMR spectrum of a 1:2 alkali metal silicate glass containing >30 mol% P₂O₅ and prepared at ambient pressure.⁴ Other reports of higher coordination numbers (Si^v and Si^{vi}) occurring in alkali and alkaline-earth silicate glasses have appeared subsequently.^{5–8} Such knowledge of the local order of network forming silicon is needed to understand the physicochemical behaviour of silicate melts, magmas and plasmas at both ambient and high pressures.^{8–10} Generally, the transition of Si^{iv} to Si^v and to Si^{vi} is favoured at high pressures. We now report the first evidence of the coexistence of Si^{iv}, Si^v, and Si^{vi} in a series of cadmium phosphosilicate single phase glasses prepared at ambient pressure and which were wholly vitreous within the detection limit of X-ray diffraction.

The cadmium phosphosilicate single phase glasses were made using appropriate amounts of analytical grade CdCO₃, SiO₂ and P₂O₅. A 20 g batch of nominal composition for $x\text{CdO}\cdot(1-x-z)\text{SiO}_2\cdot z\text{P}_2\text{O}_5$ was mixed together in a glass bottle and shaken for 8 h to achieve a homogeneous mixture. Powder batches in an alumina crucible were heated to 1250 °C by an electric furnace for 2.5 h. In order to maintain ambient pressure the crucibles in the furnace were open to the atmosphere. The glass melt was splat cooled using two steel plates at room temperature to give $x\text{CdO}\cdot(1-x-z)\text{SiO}_2\cdot z\text{P}_2\text{O}_5$ as a transparent homogeneous glass which was wholly vitreous within the detection limit of X-ray diffraction and, on optical inspection, did not show any evidence of phase separation. The ratio

$x:(1-x-z)$ was kept constant at 1.5 while the value of z was varied between 0.50 and 0.70. The detailed composition of the samples and their nomenclature are given in Table 1.

All magic angle spinning (MAS) NMR spectra were obtained using a Chemagnetics AMX 300 Lite spectrometer operating at 59.61 MHz for ²⁹Si and 121.46 MHz for ³¹P. Pulses of 5 μs ($\pi/4$) followed by a delay of 120 s were employed for the investigation of the ²⁹Si nuclei; 1 μs ($\pi/4$) with a 20 s delay for ³¹P. The delays between pulses were chosen to ensure unsaturated signals. The samples were spun in 7.5 mm o.d. zirconia rotors at 6.5 kHz for ²⁹Si to put the spinning sidebands outside the -110 ppm to -215 ppm range. A higher rotational rate of ca. 14 kHz in 4.0 mm o.d. zirconia rotors was used for ³¹P nuclei. The chemical shifts and peak positions were measured with respect to TMS for ²⁹Si and 85% H₃PO₄ for ³¹P. The powdered samples were kept in a desiccator prior to spectral acquisition.

Fig. 1 shows the ²⁹Si spectra of CdSP1–CdSP4 and the NMR spectral parameters are presented in Table 1. Incorporation of phosphorus at >30 mol% is known to rupture Si–O–Si bonds in some alkali metal silicate glasses, leading to Si^{iv}–O–P and Si^{vi}–O–P bonds characterised by ²⁹Si resonances at -120 ppm and -213 ppm, respectively.^{3–7} The spectrum of CdSP1 ($z = 0.50$) glass showed an asymmetry on the high field side of the peak at -120 ppm suggesting the presence of a very small amount of a different species resonating at ca. -127.0 ± 1.0 ppm. This shift corresponds to an environment in which two adjacent silicon atoms are replaced by two phosphorus atoms while preserving the tetrahedral network.¹¹

The ²⁹Si NMR spectra obtained for the glasses of composition $0.55 \leq z \leq 0.70$ differed significantly from those glasses with both lower and higher values of z . For $z = 0.55$ a new resonance of low intensity at -165.0 ± 0.5 ppm, characteristic of Si^v, along with a Si^{vi} resonance at -213.0 ± 0.5 ppm were observed. Both of these resonances increased in relative intensity with further addition of P₂O₅ up to $z = 0.60$. The coexistence of four-, five- and six-coordinated silicon in glasses at atmospheric pressure is unprecedented. Moreover, in contrast

Table 1 Composition and spectral properties of the cadmium phosphosilicate base glasses

Sample	Nominal composition (mol%)			NMR spectral parameters (ppm) ± 0.5				Relative intensities (%)		
	CdO	SiO ₂	P ₂ O ₅	²⁹ Si chemical shift	²⁹ Si FWHM	³¹ P ^a chemical shift	³¹ P ^a FWHM	Si ^{iv}	Si ^v	Si ^{vi}
CdSP1	30.0	20.0	50.0	-118.4	17.5	-18.4	22.0	100.0	0.0	0.0
CdSP2	27.0	18.0	55.0	-119.0	16.4	-16.8	17.1	91.6 ± 3.5	2.8 ± 0.2	5.6 ± 0.3
				-164.5	13.4	-34.6	26.6			
				-213.2	10.7					
CdSP3	24.0	16.0	60.0	-119.4	17.4	-16.9	16.6	75.0 ± 3.0	7.1 ± 0.3	17.9 ± 0.8
				-165.0	13.1	-36.0	30.0			
				-212.8	10.4					
CdSP4	18.0	12.0	70.0	-119.6	17.2	-16.2	17.7	86.5 ± 3.5	3.9 ± 0.2	9.6 ± 0.5
				-165.1	12.8	-34.5	29.2			
				-213.6	11.3					

^a ³¹P chemical shifts and linewidths were obtained by deconvoluting the spectra.

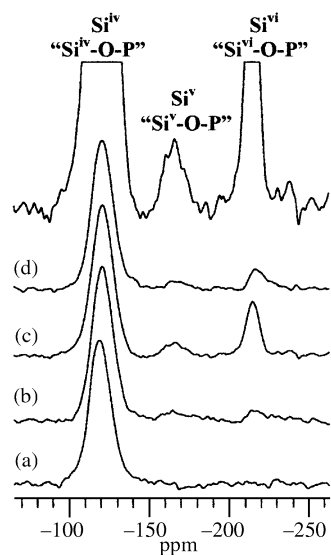


Fig. 1 ^{29}Si spectra of $x\text{CdO}\cdot(1-x-z)\text{SiO}_2\cdot z\text{P}_2\text{O}_5$ for $z =$ (a) 0.50, (b) 0.55, (c) 0.60 and (d) 0.70. The top spectrum is spectrum c $\times 8$ multiplication.

to alkali-metal phosphosilicate glasses, in the $\text{CdO-SiO}_2\text{-P}_2\text{O}_5$ system increasing z beyond 0.70 led to a decrease in the concentrations of the higher coordination number silicon environments. Integration of the unsaturated ^{29}Si NMR signals gave accurate measures of the $\text{Si}^{\text{IV}}:\text{Si}^{\text{V}}:\text{Si}^{\text{VI}}$ ratios in the splat cooled base samples (Table 1). The $\text{Si}^{\text{IV}}:\text{Si}^{\text{VI}}$ ratio remained constant at 0.42 ± 0.03 for those samples in which higher coordinated silicon could be detected.

The reported shift of -150 ppm for Si^{V} in a $\text{K}_2\text{Si}_4\text{O}_9$ glass⁸ is lower than that assigned to this environment in the cadmium phosphosilicate single phase glasses. We attribute this upfield shift to the silicon being surrounded by five oxygen atoms that are in turn bonded to phosphate species, phosphorus being of higher electronegativity.⁴ The Si^{VI} chemical shift, -213 ppm, observed for the cadmium phosphosilicate glasses corresponds almost exactly to that reported for SiP_2O_7 species.⁴⁻⁷

Although the glass melt had been maintained at ambient pressure, quenching *via* splat cooling might have led to the metastable retention of a coordination multiplicity which was appropriate only to high temperatures. As CdSP3 had the highest concentrations of Si^{V} and Si^{VI} , this sample was chosen to observe the effects of slow cooling of the melt. There was a successive diminution of the higher coordination number species with slower cooling rates, corresponding to the removal of structural defects in the glass on annealing. The decrease in Si^{V} abundance is consistent with similar observations for $\text{K}_2\text{Si}_4\text{O}_9$ glass.⁸ However, the decrease in the abundance of Si^{VI} contrasts with the situation for both phosphosilicate³ and alkali metal phosphosilicate systems where annealing leads to the transformation of Si^{IV} into Si^{VI} . This suggests that the cadmium phosphosilicate system has different thermodynamic properties to those of the alkali metal-based glasses. This could lead to different optical properties for the $\text{CdO-SiO}_2\text{-P}_2\text{O}_5$ glasses.

Fig. 2 illustrates the ^{31}P NMR spectra of the glasses and the corresponding spectral parameters are given in Table 1. The sample CdSP1 ($z = 0.50$) showed only one resonance at -18.0 ppm, characteristic of cadmium metaphosphate species, accompanied by asymmetry on both the low and high field sides of the peak. That at lower field is due to the presence of cadmium pyrophosphate, whereas that at higher field may be due to a small amount of phosphosilicate species in which the silicon is four-coordinated. This could be the same species causing the asymmetry in the Si^{IV} peak of the ^{29}Si spectrum. With increasing

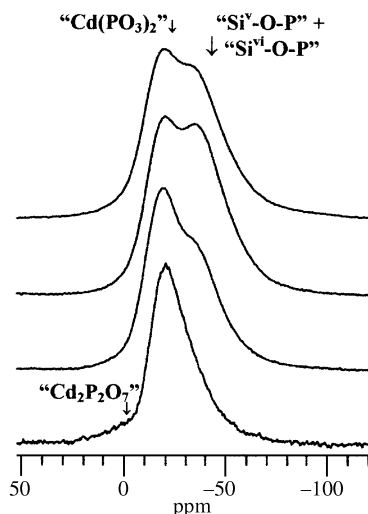


Fig. 2 ^{31}P spectra of $x\text{CdO}\cdot(1-x-z)\text{SiO}_2\cdot z\text{P}_2\text{O}_5$ for $z =$ (a) 0.50, (b) 0.55, (c) 0.60 and (d) 0.70. Only the isotropic band is shown for clarity.

P_2O_5 concentration another distinct resonance at -35.0 ppm, characteristic of phosphosilicate species with higher Si coordination numbers,⁴ and a metaphosphate peak at *ca.* -16.0 ppm were observed. Relative to the metaphosphate peak, the former increased in intensity for CdSP2 and CdSP3 but then decreased for CdSP4. This change in intensity is consistent with that observed for the ^{29}Si resonances of the phosphosilicate species.

In general, we would expect two ^{31}P resonances corresponding to $\text{Si}^{\text{V}}\text{-O-P}$ and $\text{Si}^{\text{VI}}\text{-O-P}$ environments, but such was not observed. However, the linewidth of the resonance at -35.0 ppm (FWHM *ca.* 30.0 ppm) was far greater than that reported for $\text{Si}^{\text{VI}}\text{-O-P}$ species (17.0 ppm) in alkali metal phosphosilicate systems.⁴ This substantiated the presence of peaks attributable to $\text{Si}^{\text{V}}\text{-O-P}$ species within the envelope of the resonance at -35.0 ppm. The unresolved spectral data suggest that the chemical shift difference between the two ^{31}P local orders is smaller than the difference in the linewidth of the resonances.

Further experiments are being performed to determine the variation of Si^{V} and Si^{VI} concentrations with CdO content. The thermodynamical and optical properties of the glasses are also being investigated and will be presented elsewhere.

We thank the Association of Commonwealth Universities in the United Kingdom for the award of a Commonwealth Fellowship (M. G. M).

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