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Disproportionation of Q_m ($0 \leq m \leq 4$) species in partially devitrified $Li_2Si_2O_5$ glasses with small amounts of P_2O_5

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Abstract The effect of addition of small amounts of P_2O_5 in the lithium disilicate glasses results in the scavenging of lithium metal ions by a phosphate group, Li_3PO_4. As a consequence of the scavenging, the silicate network partially repolymerises. The phosphate group remains intact during heat treatment of the optically clear, X-ray amorphous and slightly nucleated base glasses. However, the relative amounts of the silicate species, Q_m ($0 \leq m \leq 4$), are dependent on the state of the glasses. These amounts, in the optically clear and X-ray amorphous, do not change with heat treatment but they do change, i.e. disproportionation occurs in the slightly nucleated and milky coloured glasses. The disproportionation follows the relation $2Q_3 \rightarrow Q_2 + Q_4$ which is evident from the relative intensity of the different peaks.

Introduction

Phosphorus pentoxide is one of the best nucleating agents that enhances the rate of nucleation in lithium silicates. Small amounts of phosphorus play an important role in the formation of glass ceramics by controlled devitrification of the base glass [1]. This nucleating property of phosphorus must reflect the local order of the silicate species, generally represented by Q_m ($0 \leq m \leq 4$), where m represents the number of bridging oxygen surrounding each Q, i.e. silicon. The ^{29}Si and ^{31}P nuclei in lithium phosphosilicate glasses have been investigated by using NMR [2, 3]. The Si^{4+} environment has also been looked up with the help of Raman spectroscopy [4] on these parent glasses.

Numerous studies [5–9] have been carried out on the effect of P_2O_5 addition in Li_2O–SiO_2 glass ceramic system. There has been considerable speculation about the physical and chemical processes that occur during conversion from glass to glass ceramics by means of heat treatment. TEM study of partially crystallized lithium phosphosilicate glasses [6] of compositions $30Li_2O \cdot 69SiO_2 \cdot 1P_2O_5$ and $31.5Li_2O \cdot 67.5SiO_2 \cdot 1P_2O_5$ has led to five models of phase separation where the authors have possibly observed the formation of $Li_2Si_2O_5$, SiO_2, Li_3PO_4, $Li_4P_2O_7$, $LiPO_3$, P_2O_5 and the presence of P_2O_5 in the precipitated silica. In the partially crystallized state the volume fraction of these compounds were so small that they could not be identified by using XRD. In a further study [8] of the same composition the authors did observe lithium disilicate crystals along with crystals of either different composition or different structures, which they assumed to be phosphates.

Harper and McMillan [10] and Hing and McMillan [11] observed a considerable change, upto 10^6 times higher, of nucleation density by choosing optimum nucleation temperature in the similar system. Later the researchers at Sandia National Laboratory [9] have found Li_3PO_4 in a highly crystalline Li_2O–SiO_2–P_2O_5 system and predict the growth of other phases epitaxially on the top of Li_3PO_4 crystals.

However, in the partially crystalline lithium phosphosilicate system the type of phases form during heat treatment are not very clear. As MAS NMR reflects direct information about the local order of Si^{4+} and its

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quantitative measurement in the lithium phosphosilicate system [2]; here we have used the technique to reveal the type and mechanism of formation of silicate phases in the partially devetrified Li_2O-$2SiO_2$-P_2O_5 glasses.

Experimental

Glass preparation

Lithium disilicate glasses with nominal 1.0, 2.0 and 5.0 mol% P_2O_5 were prepared from analytical grade Li_2CO_3 and Li_3PO_4 together with SiO_2, as described previously [2], by melting them at 1300 °C. The heat treatment sequence of the glasses is shown in Fig. 1. 0.1 mol% $MnCO_3$ was also added to reduce the ^{29}Si T_1 relaxation time, since this is typically 10 minutes in an undopped sample. Experiments showed that there was no difference in intensity ratio of the different Si peaks due to the addition of such a small amount of $MnCO_3$. All the samples were chemically analysed using wet chemical analysis [12] and the amounts of phosphorous in the base glasses are presented in Table 1. Slightly visible opalescence was observed in lithium disilicate glass with 4.3 mol% (analysed amount) P_2O_5.

NMR experimentation

The ^{29}Si broad line NMR and MAS NMR spectra were recorded on a Bruker MSL 360 spectrometer operated at 71.53 MHz. $\pi/4$ rf pulses with 120 s (LSP1, LSP2) and 90 s (LSP4) delays were employed to obtain unsaturated signal.

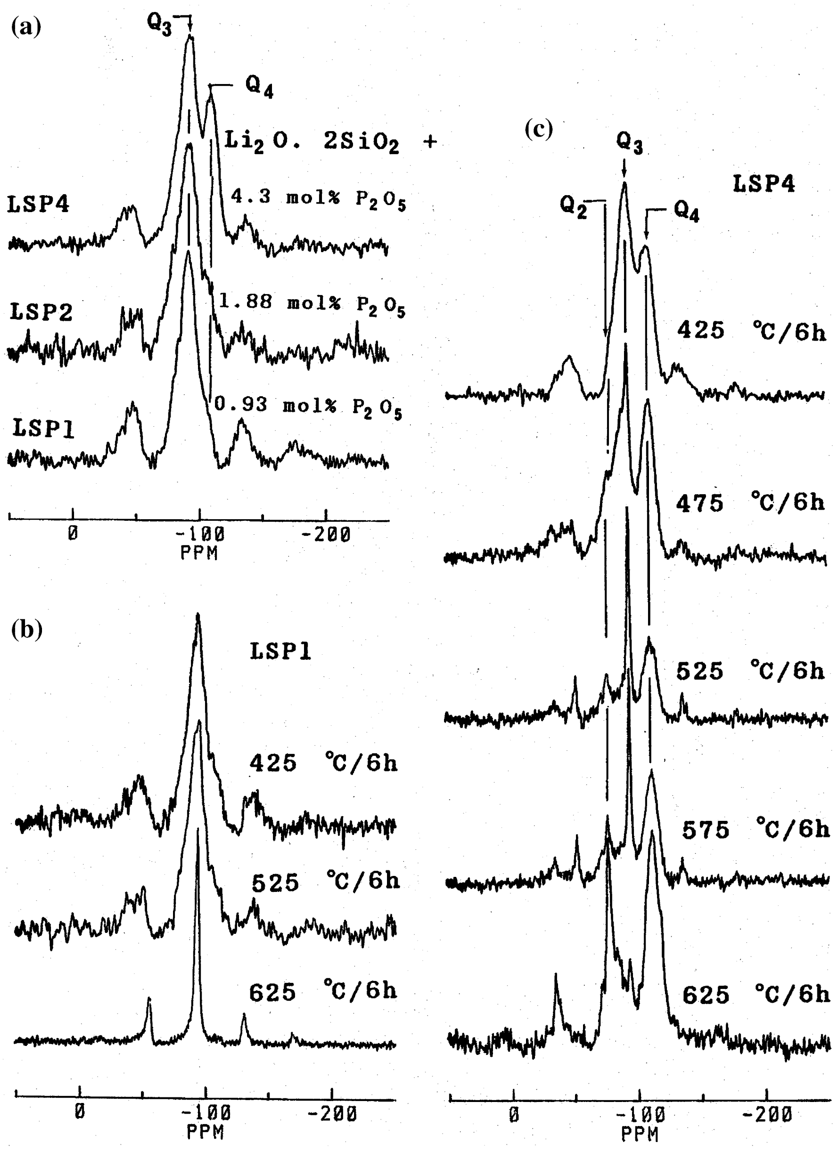

Fig. 1 ^{29}Si spectra of lithium disilicate with various amounts of P2O5 (**a**) base glasses, (**b**) LSP1 and (**c**) LSP4 heat treated at various temperatures

Table 1 ^{29}Si and ^{31}P spectral parameters and relative amounts of the species of lithium disilicate glasses and glass ceramics with the small amounts of P_2O_5

Sample	Amount of P_2O_5 (mol%) ± 4%	Heat treatment T°C/th	^{29}Si chemical shift parameter (ppm)						Values of Q_4/Q_3		^{31}P CS parameters (ppm)		Values of the Q_4/Q_3 ratio	
			Q_4		Q_3		Q_2				CS	FWHM	Theo. ± 0.05 [14]	Expt. ± 0.05
			CS	FWHM	CS	FWHM	CS	FWHM	Theo. ± 0..03	Expt. ± 0..03				
LSP1	0.93	NHT*	–108.0	7.2	–91.6	18.6	–	–	0.14	0.12	+9.7	7.0	0.14	0.08
LSP2	1.88	NHT	–109.1	10.1	–92.5	18.6	–	–	0.26	0.22	+9.7	7.0	0.26	0.22
LSP4	4.30	NHT	–111.4	12.4	–93.6	18.8	–	–	0.73	0.36	+10.4	7.0	0.73	0.36
LSP1		425/6	–108.7	8.5	–92.3	16.1	–	–	–	–	+10.0	7.0	0.14	0.10
		475/6	–108.3	9.6	–92.5	14.5	–	–	–	–	–	–	-	-
		525/6	–110.2	10.4	–93.2	14.0	–	–	–	–	–	–	-	-
		575/6	–110.6	12.1	–93.6	4.0	–	–	–	–	+10.1	3.0	0.14	0.07
LSP4		425/6	–111.3	12.5	–93.7	18.5	–	–	–	–	–	-	-	-
		475/6	–111.8	13.2	–94.4	10.0	–77.9	9.8	-	–	+10.4	4.5	-	-
		525/6	–111.7	13.0	–94.5	3.2	–76.4	9.6	-	–	+10.5	5.0	-	-
		575/6	–112.3	12.1	–94.7	2.7	–76.8	5.9	-	–	+10.4	3.2	-	-

NHT = No Heat treatment

Samples were spun at 3–4 kHz and tetramethylsilane was used as a reference. The ^{31}P MAS NMR was carried out using the same spectrometer operated at 145.78 MHz. $\pi/2$ pulse with 20s delays were applied to collect all the ^{31}P resonance with respect to 85% H_3PO_4. An exponential line broadening of 50 Hz for the ^{29}Si and 10–20 Hz for the ^{31}P was applied during the processing of the spectra.

Results

^{29}Si NMR in base glasses

The spectra for ^{29}Si in the lithium disilicate compositional range (LSP1,LSP2 and LSP4) with different amounts of P_2O_5 are shown in Fig. 1. The LSP1 and LSP2 spectra generally consist of two isotropic overlapping peaks, one corresponding to Q_4 [13–18] as a spherically symmetric unit, has no spinning sidebands (ss) and the other corresponding to Q_3 near axially symmetric and therefore associated with ss. Visual examination of the spectra shows that the Q_4 resonance increases in intensity as the amounts of P_2O_5 increases. A least square fit of them to two Gaussians was carried out to obtain the chemical shifts, full width at half maximum and area under the respective species. However, the spectrum of LSP4 contains two overlapping isotropic Q_4 and Q_3 peaks, and a submerged shoulder corresponding to Q_2 environment. This Q_2 is not conspicuous in the spectrum and the calculated amounts of the various species are erratic. The spectrum was however fitted to two Gaussians and all the NMR parameters are summarized in Table 1 together with the observed (Q_4/Q_3) ratio. The chemical shifts for both Q_4 and Q_3 become more negative as the concentration of P_2O_5 increases. The FWHM of the Q_4 resonance also increases by amounts greater than the experimental error.

^{29}Si NMR in heat treated glasses

The ^{29}Si spectra of the LSP1 and LSP4 glasses as a function of heat treatment are shown in Fig. 1b and c, respectively. The chemical shifts of the Q_3 and Q_4 species in LSP1 change with heat treatment and approach the value similar to their crystalline form. The sample LSP4 was initially glass-in- glass phase separated and the chemical shifts of the species do not change with heat treatment. However, the FWHM in all the samples changes with heat treatment and are summarized in Table 1.

^{31}P NMR in base and heat treated glasses

The spectra for ^{31}P in the LSP1, LSP2 and LSP4 glasses are shown in Fig. 2a. Only one phosphorous site is observed for all phosphorous concentration with a chemical shift of ~10 ppm. The FWHM of all the samples remain unchanged due to increase of P_2O_5 concentration.

The spectra of heat treated LSP1 and LSP4 glasses are shown in Fig. 2b and c respectively. As in the base glasses these spectra also show a single peak with a chemical shift of ~10 ppm. The FWHM of LSP1 is the same as in base glasses but it is different in LSP4. The spectral parameters for both base and heat treated glasses are presented in Table 1.

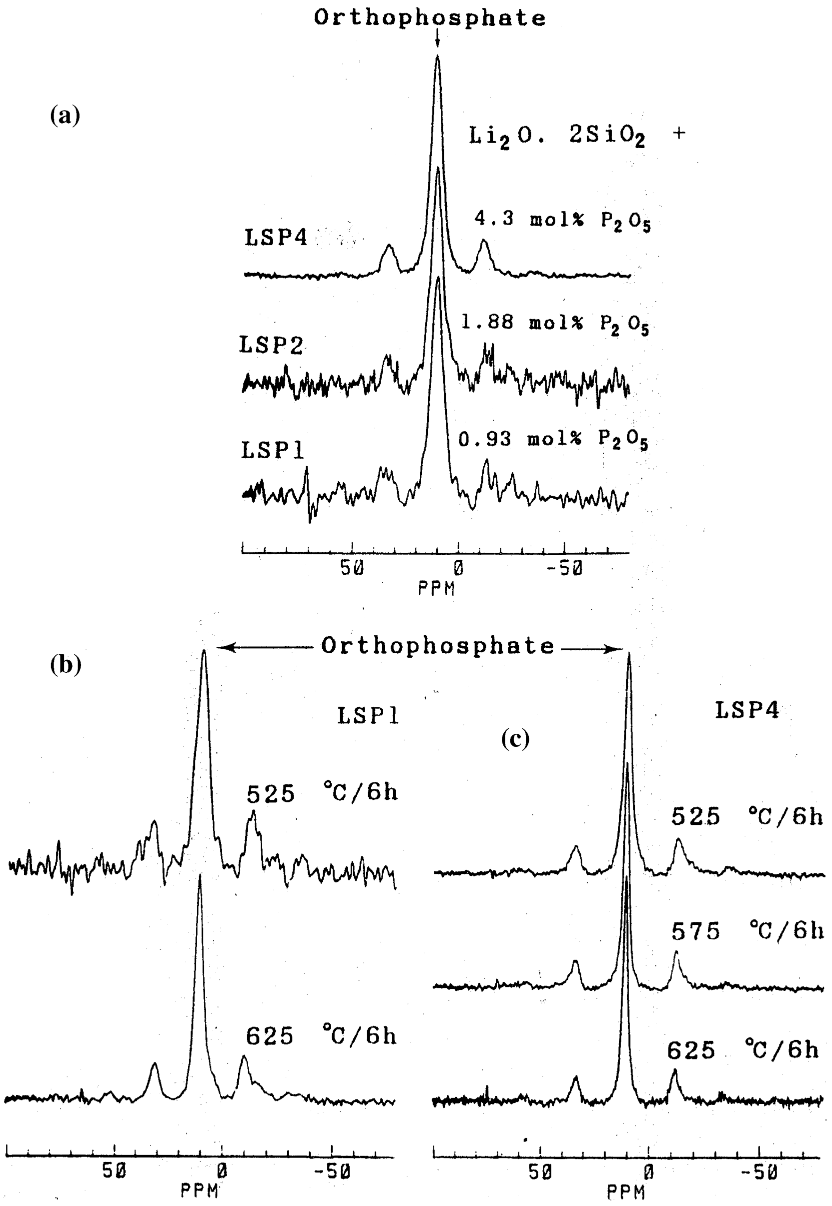

Fig. 2 ^{31}P spectra of lithium phosphosilicate glass and glass ceramics (**a**) base glasses, (**b**) LSP1 and (**c**) LSP4 heat treated at various temperatures

Discussion

^{29}Si base glasses

For a simple binary system $Li_2O \cdot 2SiO_2$ the major species present in the sample is the Q_3 unit [19]. However, Q_2 and Q_4 species also form in the disilicate compositional range [19–21]. The situation is somewhat different on addition of P_2O_5, even 1.0 mol%, to the Li_2O. $2SiO_2$ glass system (Fig. 1a). A more prominent Q_4 resonance is observed along with a Q_3 resonance and the former increases at the expense of the latter due to the increase of P_2O_5 in all the lithium phosphosilicates.

As predicted by Dupree et al. [2] the P_2O_5 reacts with Li^+ ion and forms Li_3PO_4. In lithium phosphosilicates, some of the Li^+ ions scavenged by the phosphorous from the Q_3 site, reducing the effective concentration of lithium in the silicate matrix. The ^{31}P spectra of all the samples (including the heat treated ones), resembling the environment Li_3PO_4, are similar to those presented by Dupree et al. [2] (Fig. 2a–c). In fact the number of oxygen per phosphorous is 2.5 in P_2O_5 but none of them are non bridging oxygen. Therefore, in order to form an environment like Li_3PO_4, phosphorous has to extract 1.5 oxygen atoms from the Q_3 portion of the glass [2]. This results in three additional Q_4 tetrahedra per phosphorous and the polymerisation of SiO_4 units increases with the increase of P_2O_5 resulting in an increase in intensity of the Q_4 resonance.

Chemical shift depends not only upon the nearest and next nearest neighbours but also on the amounts of the

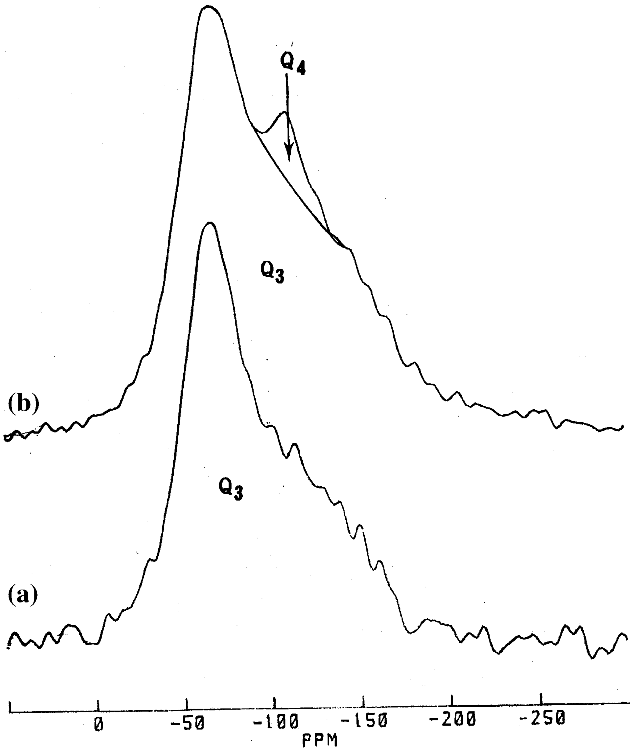

Fig. 3 Comparison of the ^{29}Si static spectra of crystalline (**a**) $Li_2O \cdot 2SiO_2$ and (b) $Li_2O \cdot 2SiO_2 \cdot 1P_2O_5$

modifier content. The observed variation in chemical shift with increasing P_2O_5 reflects the change in the effective number of modifier ion. The polymerisation of the SiO_4 network should move the chemical shift of both the Q_3 and Q_4 resonance as a function of P_2O_5 content towards the more shielded side, i.e. more negative. This is indeed the case as seen in Table 1.

The experimental Q_4/Q_3 ratios (Table 1) of all the samples, except LSP4, are consistent with the binary model [14] representing the presence of Q_4 and Q_3 as the significant species. The inconsistency regarding the ratio Q_4/Q_3 in LSP4 indicate the presence of another major species possibly Q_2. Fitting of another Gaussian for Q_2 environment lead to the decrease of Q_3, which would make the experimental Q_4/Q_3 closer to the theoretical value. It could be true that the presence of Q_2 accelerates the nucleation process resulting the base glass opalescence.

^{29}Si Heat treated glasses

The striking differences between the two sets of spectra (Fig. 1b, c) are the formation of Q_2 units along with Q_3 and Q_4 species in LSP4 due to heat treatments. There is no evidence of formation of Q_2 in LSP1 because of devitrification and the relative amounts of Q_3 and Q_4 remain almost constant. However, the amounts of Q_2 and Q_4 in LSP4 glass ceramics increases and that of Q_3 decreases (Fig. 1c) as a result of disproportionation $2Q_3 \rightarrow Q_2 + Q_4$. The rate of disproportionation increases with the increase of heat treatment temperature. This could be equally true if the sample is held at a particular temperature, which is high enough to disproportionate Q_3, for a different length of time.

Comparison of the static spectra of crystalline $Li_2O \cdot 2SiO_2 \cdot 1P_2O_5$ and $Li_2O \cdot 2SiO_2$ (Fig. 3) clearly reveals the presence of SiO_4 tetrahedra in the former. Therefore it can be concluded that Q_2 species may not be present in LSP1 which could accelerate the disproportionation $2Q_3 \rightarrow Q_2 + Q_4$ in the glass LSP1. Alternatively by looking at the ^{29}Si spectra of heat treated $32Li_2O.63SiO_2.4P_2O_5$ (LSP4; Fig. 1c) it is clear that Q_3 units convert to Q_2 and Q_4 as a result of aforesaid disproportionation. This indicates the presence of early nucleation of $Li_2O \cdot SiO_2$ (Q_2) in LSP4 which is small in amount to give the well resolved Q_2 line shape in the LSP4 base glass.

^{31}P NMR in base and heat treated glasses

Comparison of the peak position (10 ppm) with crystalline material [22, 23] suggests that the environment of phosphorous is like Li_3PO_4. From the single peak in both the glass and glass ceramics, it can be inferred that the ^{31}P environment does not change due to heat treatment. The relatively narrower line in the heat treated LSP4 sample represent the crystallinity of Li_3PO_4 units.

Conclusion

Addition of P_2O_5 up to 5 mol% in lithium disilicate system indicates that phosphorous itself does not participate in the silicate network but increases the polymerization of the Q_4 species by the effective removal of modifier cations. Thus amounts of Q_3 decreases and those of Q_4 increase with the increase of P_2O_5. In case of heat treated glasses disproportionation like $2Q_3 \rightarrow Q_2 + Q_4$ occurs only when early nucleation of Q_2 forms during cooling process of glass melt.

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