

Structure–Property Correlations in Lithium Phosphate Glasses: New Insights from $^{31}\text{P} \leftrightarrow ^7\text{Li}$ Double-Resonance NMR

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Received October 6, 1999. Revised Manuscript Received March 28, 2000

The macroscopic properties of binary alkali phosphate glasses are characterized by the presence of unexpected minima in the glass transition temperatures at alkali concentrations near 20–25 mol %. In the present study, the structural origin of this behavior is explored on the basis of multinuclear single- and double-resonance NMR experiments. ^{31}P magic-angle spinning NMR spectra track the successive network depolymerization caused by Li_2O addition, while ^6Li chemical shifts indicate a lithium coordination number of four to five. The monotonic evolution of these spectra with increasing alkali content reveals that the nonlinear macroscopic behavior does not reflect any abrupt structural changes at the local level. In contrast, $^{31}\text{P}\{^7\text{Li}\}$ rotational echo double-resonance spectroscopy indicates substantial restructuring on longer distance scales, relating to the spatial arrangement of the lithium ions with respect to the phosphorus sites in the network. The data suggest that the average number of lithium atoms surrounding a phosphorus site increases abruptly near 20–25 mol % Li_2O , as the phosphate chains become cross-linked by electrostatic Li^+ –oxygen interactions.

Introduction

Phosphate glasses are technologically important materials with possible applications as metal to glass seals,^{1,2} fast ion conductors,³ and biomedical implants.⁴ A prerequisite for a controlled fine-tuning of these materials is an understanding of the macroscopic physical and chemical properties in terms of microscopic structural information. While there is an abundant literature on this topic, alkali phosphate glasses with a modifier content <50 mol % (ultraphosphate glasses) have been studied to a much lesser extent, partly because of their large hygroscopicity.^{5–8} A first systematic study conducted by Hudgens and Martin as a function of alkali oxide modifier content revealed an unexpected minimum in the glass transition temperature near 20–25 mol % M_2O ($\text{M} = \text{Na}, \text{Li}$).⁹ Since no other binary oxide glass system is known to show such a compositional dependence of T_g , it would be of great interest to provide a structural rationale for this be-

havior. Standard ^{31}P magic-angle spinning (MAS) NMR spectroscopy has revealed no particular abrupt changes of the local phosphorus coordination in this concentration range.^{7,10} With increasing modifier content, the spectra reflect the successive conversion of $\text{Q}^{(3)}$ to $\text{Q}^{(2)}$ to $\text{Q}^{(1)}$ phosphate units as the network is successively depolymerized. Furthermore, to date, no structural information on longer distance scales (medium-range order) has been able to provide any insights into the T_g behavior. For example, aspects of the $\text{Q}^{(n)}$ connectivity in phosphate glasses have been recently characterized on the basis of ^{31}P two-dimensional dipolar recoupling experiments.^{11–14} Using the radio-frequency driven recoupling technique (RFDR), Alam and Brow concluded that the linking of $\text{Q}^{(3)}$ and $\text{Q}^{(2)}$ units is statistical.¹⁰ In a similar vein, Hudgens and co-workers¹⁵ have discussed their Raman results on ultraphosphate glasses in terms of a π -bond delocalization on $\text{Q}^{(3)}$ species, resulting in a strengthening of the P–O–P linkages.

A complementary aspect of medium-range order in glasses concerns the spatial distribution of the modifier cations, which, as shown by Gaskell, can display a high degree of uniformity in oxide glasses.¹⁶ On the basis of X-ray and neutron diffraction experiments on alkaline

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Table 1. Batch Compositions and ^{31}P and ^6Li Isotropic Chemical Shifts of the Studied Glasses

glass no.	$x(\text{Li}_2\text{O})$		T_g/K	$\delta_{\text{iso}}(^{31}\text{P})/\text{ppm}$			relative area/%			$\delta_{\text{iso}}(^6\text{Li})/\text{ppm}$
	batch	from $Q^{(n)}$ ratio		$Q^{(1)}$	$Q^{(2)}$	$Q^{(3)}$	$Q^{(1)}$	$Q^{(2)}$	$Q^{(3)}$	
1	0.1	0.10	527		-33.6	-52.2		11	89	-1.15
1a	0.15		521							
2	0.2	0.18	516		-34.2	-51.0		22	78	-1.05
3	0.3	0.32	512		-30.8	-44.5		48	52	-0.85
3a	0.35	0.37	518		-28.7	-42.5		60	40	
4	0.4	0.40	550		-25.4	-34.6		66	34	-0.65
4a	0.45	0.50		-4.6	-23.0		1	99		
5	0.5	0.51	597	-4.5	-22.9		2	98		-0.45
5a	0.55	0.50		-4.9	-23.2		1	99		

earth phosphates, Hoppe postulated a sudden change in the mode of alkali metal binding to the phosphate network near modifier concentrations of 20–25 mol %.^{17–20} On the other hand, molecular dynamics simulations suggest that the T_g minimum is correlated with a high concentration of strained three-membered rings.²¹ However, none of the above studies present any experimental evidence for a compositional discontinuity in the medium-range order that would allow for a direct correlation with the T_g minimum observed. The spatial ordering of alkali ions in phosphate glasses has been the subject of several recent NMR papers.^{22,23}

In the present study, we introduce ^{31}P – $\{^7\text{Li}\}$ rotational echo double-resonance (REDOR) spectroscopy^{24,25} as a new tool for studying the spatial relationship between lithium and phosphorus in lithium phosphate glasses. This technique is sensitive to the dipole–dipole coupling strength between ^{31}P and ^7Li , hence providing information about cation–phosphorus internuclear distance distributions. Using this technique, we will show that at glass compositions near the T_g minimum an abrupt restructuring of the medium-range order takes place, resulting in an increased number of lithium atoms around each phosphorus site.

Experimental Section

Sample Preparation and Characterization. Lithium orthophosphate (Li_3PO_4) and lithium metaphosphate (LiPO_3) were purchased from Aldrich and used without further purification. Phosphorus pentoxide (P_2O_5 , Aldrich) was purified by sublimation following a procedure described by Hudgens and Martin.⁹ Glasses in the ultraphosphate region were prepared by grinding appropriate amounts of P_2O_5 and LiPO_3 together under an inert atmosphere and heating the material within evacuated sealed silica glass ampules at 900 °C for 24 h. Subsequently, the tubes were allowed to cool in the transfer chamber of the glovebox. Glasses with nominal compositions exceeding 30 mol % Li_2O were prepared by heating appropriate amounts of Li_3PO_4 , LiPO_3 , and P_2O_5 in alumina crucibles in

an induction furnace at ≈ 1000 °C. The melts contained a 20% excess of P_2O_5 to compensate for evaporation losses. In addition, 0.01 mol % MnCO_3 was added in some cases to shorten the long spin–lattice relaxation times of the ^{31}P nucleus. Glasses were prepared by rapid melt quenching on a water-cooled copper block. The nominal compositions of the prepared glasses are listed in Table 1.

Glass transition temperatures were determined using a Netzsch DSC-200 calorimeter. Thermogravimetric measurements carried out on a Netzsch STA-409 instrument confirmed the preparation of completely anhydrous glasses.

NMR Experiments. The ^{31}P and ^7Li NMR experiments were carried out on a Bruker CXP200 spectrometer, equipped with a Tecmag MacSpec pulse programmer. Spectra were recorded at resonance frequencies of 77.78 and 81.02 MHz for ^7Li and ^{31}P , respectively, using a 4 mm multinuclear MAS probe operated at typical spinning speeds of 10 kHz. The ^6Li MAS spectra were recorded using a Bruker CXP300 spectrometer at a resonance frequency of 44.16 MHz using a standard 7 mm MAS probe, operated at a spinning speed of 6 kHz. Chemical shifts are referenced to 85% H_3PO_4 and 1 M LiCl solution for ^{31}P and ^6Li , respectively. For ^7Li , solid LiCl was used as an external secondary reference ($\delta_{\text{iso}} = -1.06$ ppm relative to 1 M aqueous LiCl ²⁶).

Owing to the small difference in Larmor frequencies of ^{31}P and ^7Li , double-resonance experiments involving these nuclei cannot be conducted with standard NMR equipment. Therefore, the $^{31}\text{P}\{^7\text{Li}\}$ and $^7\text{Li}\{^{31}\text{P}\}$ REDOR experiments reported below utilized a special hardware setup described in detail elsewhere.^{27,28} These double-resonance experiments were conducted at a spinning frequency 10 kHz, using a 4 mm MAS probe. All of the measurements were conducted at room temperature. Temperature-dependent ^7Li NMR experiments on representative samples in the range from 298 to 90 K (constant line width of ≈ 9 kHz) confirmed that the ^7Li – ^{31}P dipolar interaction is not modulated by ionic motion of the lithium ions.

Results

Figure 1 shows the compositional dependence of the glass transition temperature T_g . While there is some discrepancy between our values and those of Hudgens and Martin,⁹ the general trend is the same, and the minimum in T_g at ≈ 20 – 25 mol % Li_2O is unambiguous.

The ^{31}P MAS spectra are collected in Figure 2. Shown is only the centerband region; spinning sidebands are omitted. The spectra clearly document the successive formation of $Q^{(2)}$ units at the cost of $Q^{(3)}$ units and then, at the point when all $Q^{(3)}$ is consumed, the conversion of $Q^{(2)}$ units into $Q^{(1)}$ units, as the lithium oxide content is increased. The presence of only two different PO_4 polyhedra in any given sample favors a distribution of

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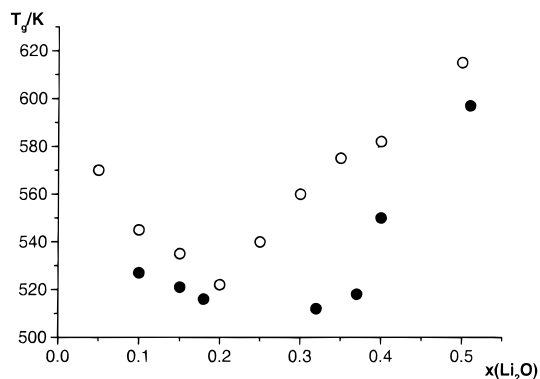


Figure 1. Glass transition temperature T_g as a function of x in glasses of composition $(\text{Li}_2\text{O})_x(\text{P}_2\text{O}_5)_{1-x}$: full circles, this work; open circles, values taken from ref 9.

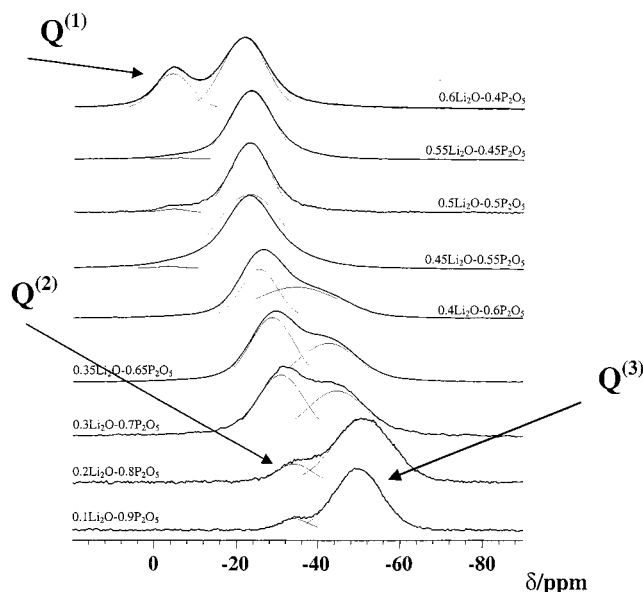


Figure 2. ^{31}P MAS NMR spectra as a function of x in glasses of composition $(\text{Li}_2\text{O})_x(\text{P}_2\text{O}_5)_{1-x}$. Shown are the centerband spectra only, together with their deconvolution into Q^n structural units.

the $Q^{(n)}$ units following the basic ideas of van Wazer²⁹ (binary model) and rules out a statistical distribution. Rather, Figure 3 illustrates quantitative agreement between the fractions of the $Q^{(n)}$ species and those predicted by the binary model. These results are in good agreement with previous studies.⁷

The quadrupolar coupling constant QCC as determined from the span of the spinning sidebands in the ^7Li MAS spectra (not shown) did not show any dependence on the modifier mole fraction and was in all cases determined to 180 ± 10 kHz. Possible changes in local environment were probed using ^6Li and ^7Li MAS NMR. Because of reduced dipolar and quadrupolar broadening effects, the isotope ^6Li ($I = 1$) is preferable to the ^7Li ($I = 3/2$) isotope, resulting in significantly enhanced spectroscopic resolution.^{23,26,30} In agreement with the results of Alam et al.,²³ Figure 4 reveals that the isotropic chemical shifts increase monotonically from

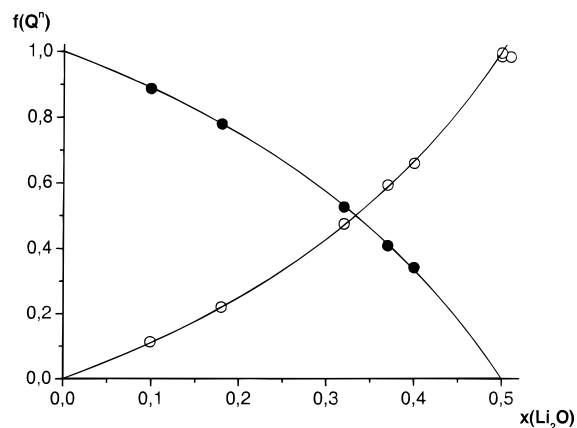


Figure 3. $Q^{(2)}$ and $Q^{(3)}$ species distributions as determined from the ^{31}P MAS NMR spectra (including spinning sideband contributions). Solid lines represent theoretical predictions according to the binary (van Wazer) model.

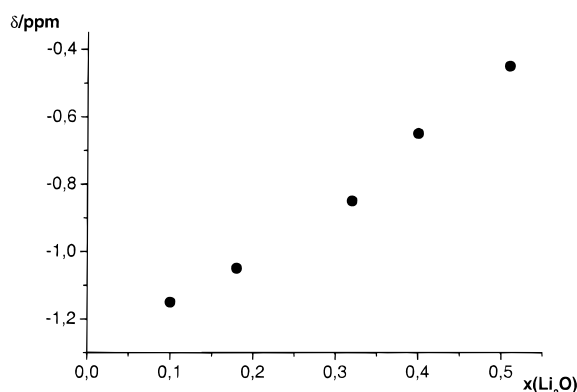


Figure 4. ^6Li NMR chemical shifts as a function of x in glasses of composition $(\text{Li}_2\text{O})_x(\text{P}_2\text{O}_5)_{1-x}$. Note the linear increase in the Li isotropic chemical shift (downfield shift) with increasing modifier content.

-1.2 to -0.4 ppm as the Li_2O content is increased from 10 to 60 mol %. This behavior parallels that of many other alkali-containing oxide glasses,³¹ reflecting the increased covalency of the Li^+ -oxygen bonding interaction.

REDOR Experiments. To monitor the heteronuclear dipolar coupling strength between the ^{31}P and ^7Li nuclei, $^{31}\text{P}\{^7\text{Li}\}$ and $^7\text{Li}\{^{31}\text{P}\}$ REDOR experiments were carried out. The pulse sequence used is shown in Figure 5. In short, a rotor-synchronized spin echo experiment on the observed nuclei (S) defines their full echo intensity S_0 . In a second experiment, π -pulses applied in the middle of the rotor period to the nonobserved nuclei (I) reintroduce the I-S dipole-dipole coupling, which would otherwise be averaged out under the conditions of fast magic angle spinning. As a result, the spin echo signal of the observed nuclei is attenuated, producing intensity S . The magnitude of the normalized difference signal $(S_0 - S)/S_0$ depends on both the strength of the dipolar coupling and the length of the dipolar evolution time NT_r , i.e., the product of the number of rotor cycles and the length of the rotor period.

Figure 6a shows the result of a $^{31}\text{P}\{^7\text{Li}\}$ REDOR experiment for a glass containing 30 mol % Li_2O . The

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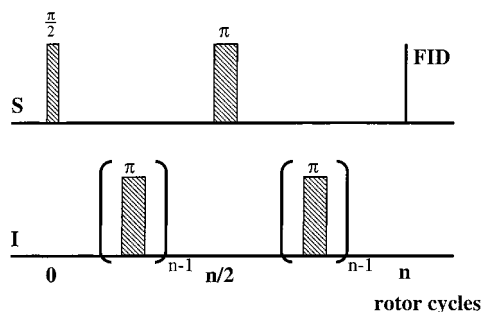


Figure 5. Schematic representation of the REDOR pulse sequence used in the present study.

top spectrum represents the result of a ^{31}P spin echo experiment, whereas the middle spectrum was obtained with the additional ^7Li π -pulses present. For each spectral component, the magnitude of the difference signal (Figure 6a, bottom) is a measure of the ^7Li – ^{31}P dipolar coupling strength. Note that the signal arising from the $\text{Q}^{(2)}$ units shows a larger REDOR difference intensity than that of the $\text{Q}^{(3)}$ units, indicating a stronger dipole–dipole coupling with ^7Li spins. The complete REDOR curves for this glass, obtained by systematically varying the number of rotor cycles, are summarized in Figure 6b. In this representation, the curvature at short evolution times is proportional to the dipolar second moment characterizing the heteronuclear ^{31}P – ^7Li dipole–dipole coupling.³² Inspection of Figure 6b confirms that the $\text{Q}^{(2)}$ units interact significantly more strongly with ^7Li than the $\text{Q}^{(3)}$ units do. Analogous results presented in Figure 7 for glass containing 60 mol % Li_2O reveal that the dipolar interaction $\text{Q}^{(1)}$ –Li is even stronger than the $\text{Q}^{(2)}$ –Li interaction.

Figure 8a,b summarizes the REDOR curves for the $\text{Q}^{(3)}$ and the $\text{Q}^{(2)}$ units measured in all the glasses of the present study. Note the significantly different curvatures of glasses containing 10 and 20 mol % Li_2O from those of all the other materials. Thus, the $^{31}\text{P}\{^7\text{Li}\}$ –REDOR experiments reflect a sudden increase in the ^7Li dipolar field experienced by the ^{31}P nuclei in the network occurring at Li_2O contents between 20 and 30 mol %. As discussed further below, this abrupt change in the spatial ordering of the lithium atoms around the phosphorus sites in the network provides the clue for explaining the compositional dependence in T_g observed in this glass system.

Figure 9 finally shows the results of $^7\text{Li}\{^{31}\text{P}\}$ REDOR experiments on the glass samples studied. Note that in this case no discontinuous changes are observed. All the glasses show more or less the same REDOR curvature, indicating that the strength of the dipolar field exerted by the ^{31}P spins at the ^7Li site remains constant throughout the compositional region studied.

Discussion

The solid-state NMR spectra presented here provide important information about both short- and medium-range order in lithium phosphate glasses. The ^{31}P MAS spectra track the depolymerization of the three-dimensional P_2O_5 network as the modifier concentration (Li_2O)

is increased. $\text{Q}^{(3)}$ structural units are successively converted to $\text{Q}^{(2)}$ units, decreasing the total number of P–O–P connectivities. No $\text{Q}^{(1)}$ structural units are detected unless all of the $\text{Q}^{(3)}$ polyhedra have been converted to $\text{Q}^{(2)}$ polyhedra. Thus, the depolymerization of the phosphate network follows van Wazer's equations:

$$f(\text{Q}^{(3)}) = 1 - x/(1 - x) \quad (1a)$$

$$f(\text{Q}^{(2)}) = x/(1 - x) \quad (1b)$$

where $f(\text{Q}^{(n)})$ denotes the relative fraction of the $\text{Q}^{(n)}$ species. Concomitantly, the isotropic chemical shift values for the $\text{Q}^{(n)}$ structural units are found to increase with increasing modifier content, reflecting a decrease in the mean bond order (decrease in π -bonding character). The continuous evolution of chemical shifts further suggests that in these glasses the $\text{Q}^{(2)}$ and $\text{Q}^{(3)}$ species do not form separate cluster domains, as was also confirmed by 2D ^{31}P RFDR MAS experiments.¹⁰ While the depolymerization process can explain the initial decrease of T_g at modifier contents below 20 mol % Li_2O , the subsequent T_g increase at higher alkali oxide concentrations remains unexplained by these data.

The ^6Li chemical shifts reflect the compositional evolution of the short-range order of the lithium ions. On the basis of lithium silicate model compound work, Xu and Stebbins proposed a linear correlation of ^6Li isotropic chemical shift and mean coordination number.³⁰ Thus, any abrupt change in the LiO_n coordination environment should manifest itself in the chemical shift/modifier content dependence. In contrast, Figure 4 shows a monotonic linear relationship, suggesting a mean coordination number between four and five.²³ Again, the ^6Li NMR data provide no evidence for a change in the network structure in the compositional region of the T_g minimum.

While the ability of ^{31}P and ^6Li MAS NMR experiments to characterize the short-range order in the studied phosphate glasses is well-proven, medium-range order information is only available on the basis of the REDOR results. The $^7\text{Li}\{^{31}\text{P}\}$ REDOR curves give no evidence of any significant change in the average number and distance of phosphorus atoms near lithium, as a function of Li_2O content. This result is consistent with a Li–O–P connectivity that remains constant throughout the glass-forming region. More information is obtainable when analyzing the $^{31}\text{P}\{^7\text{Li}\}$ REDOR curves. Since a $\text{Q}^{(1)}$ PO_4 unit requires two Li^+ cations locally for charge compensation, a $\text{Q}^{(2)}$ unit requires one, while no charge compensation is necessary for a $\text{Q}^{(3)}$ unit, the ^7Li local field experienced by these $\text{Q}^{(n)}$ units is expected to decrease in the order $\text{Q}^{(1)} \rightarrow \text{Q}^{(2)} \rightarrow \text{Q}^{(3)}$. Inspection of Figures 6 and 7 reveals that this expectation is clearly confirmed by the experimental results.

The most important information, however, is contained in Figure 8a,b. The REDOR curvatures for the $\text{Q}^{(2)}$ units of lithium phosphate glasses containing 10 and 20 mol % Li_2O are more or less identical, then show an abrupt increase at 30 mol % Li_2O , and subsequently increase only slightly toward higher modifier contents. A completely analogous trend is observed for the $\text{Q}^{(3)}$ structural units. The abrupt increase in the magnitude of the ^{31}P – ^7Li dipole–dipole coupling between 20 and 30 mol % Li_2O reflects a drastic change in the spatial

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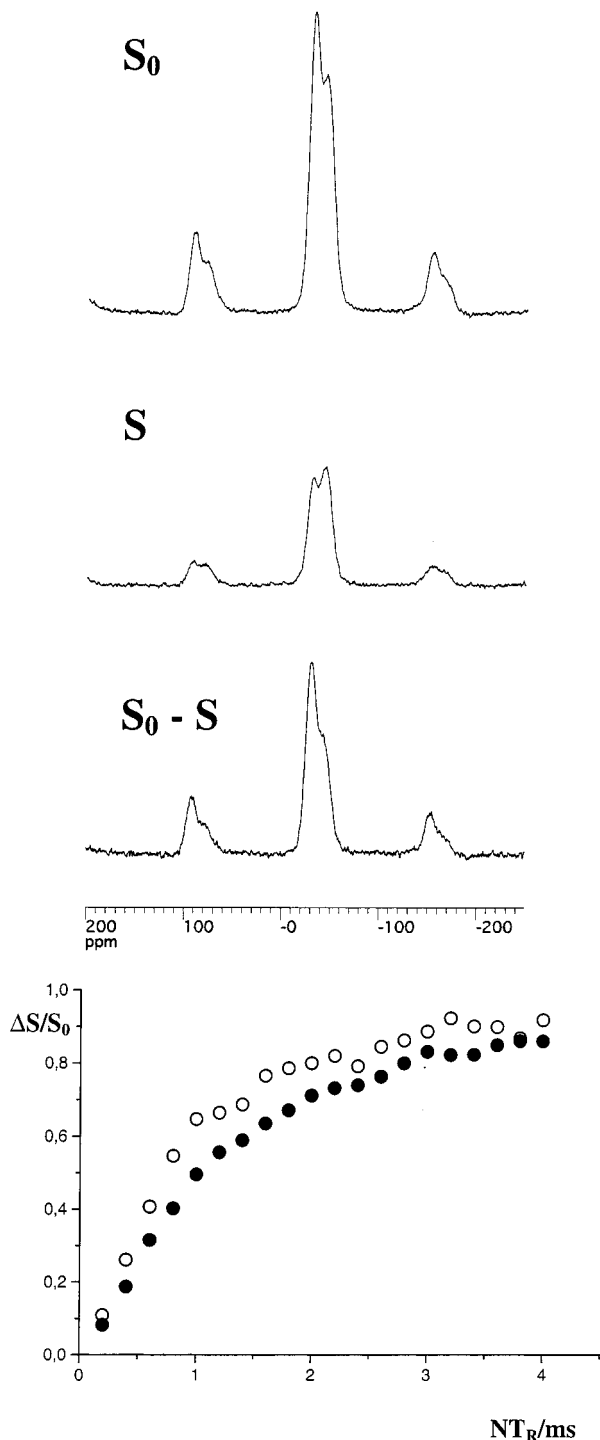


Figure 6. $^{31}\text{P}\{^7\text{Li}\}$ REDOR results for glass $(\text{Li}_2\text{O})_{0.3}(\text{P}_2\text{O}_5)_{0.7}$. (a, upper) Representation of the spectra: top, ^{31}P MAS spin echo experiment; middle, $^{31}\text{P}\{^7\text{Li}\}$ REDOR; bottom, REDOR difference spectrum. Experimental details: ν_{MAS} 10 kHz; 90° pulse lengths 6 and 4 μs for ^{31}P and ^7Li , respectively; 20 rotor cycles. (b, lower) Normalized REDOR intensity $\Delta S/S_0$ vs dipolar evolution time NT_r for the $Q^{(2)}$ (open circles) and $Q^{(3)}$ resonances (full circles).

arrangement of lithium in relation to the phosphate network. In principle, this effect could be due to either a decrease in the mean $^{31}\text{P}-^7\text{Li}$ internuclear distance or an increase in the mean number of Li cations surrounding the $Q^{(n)}$ PO_4 polyhedra. The first explanation is ruled out on the basis of the ^6Li MAS and the $^7\text{Li}\{^{31}\text{P}\}$ REDOR results, as these experiments would

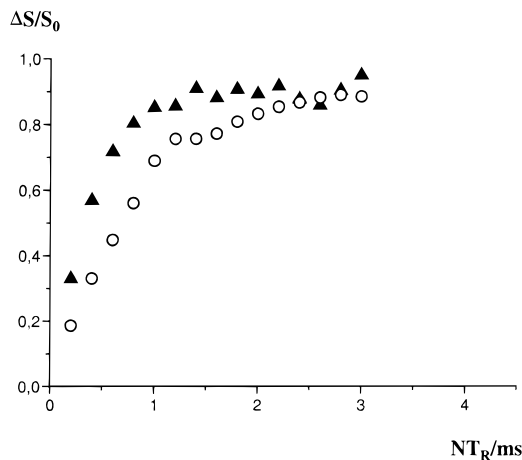


Figure 7. Normalized REDOR intensity $\Delta S/S_0$ vs dipolar evolution time NT_r for the $Q^{(2)}$ (open circles) and $Q^{(1)}$ resonances (full triangles) for glass $(\text{Li}_2\text{O})_{0.6}(\text{P}_2\text{O}_5)_{0.4}$.

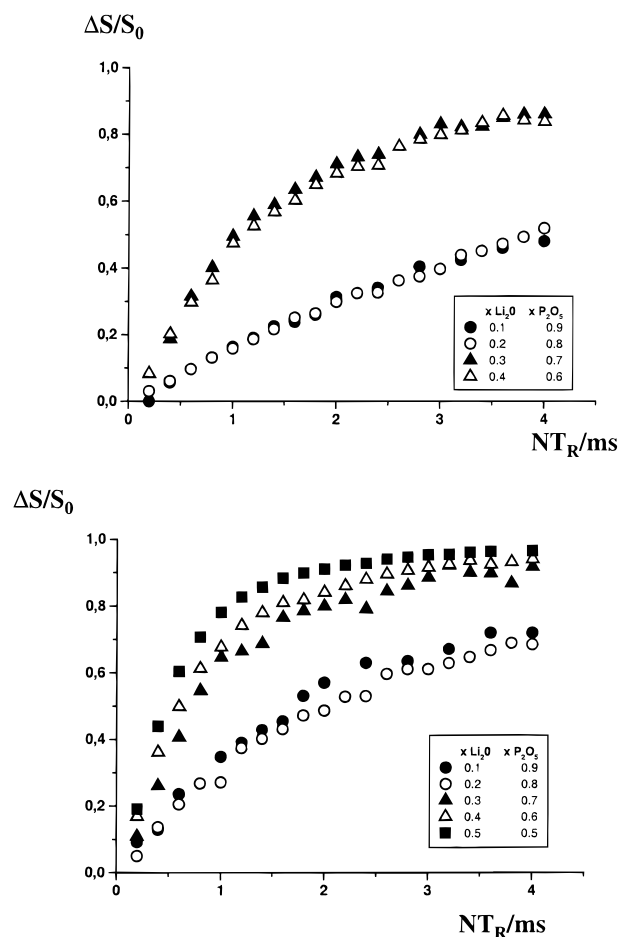


Figure 8. Compilation of the normalized $^{31}\text{P}\{^7\text{Li}\}$ REDOR difference intensities $\Delta S/S_0$ vs dipolar evolution time NT_r for the (top) $Q^{(3)}$ resonances and (bottom) $Q^{(2)}$ resonances for all of the glasses studied.

respond very sensitively to a change in the $^7\text{Li}-^{31}\text{P}$ internuclear distances. Therefore, we conclude that the dominant change involves the number of Li cations present in the vicinity of a $Q^{(2)}$ PO_4 polyhedron. A possible scenario for this structural transformation is sketched in Figure 10. This scenario was first proposed by Hoppe to describe changes in the packing densities in alkaline earth phosphate glasses.³³ Mueller and co-workers have discussed this model to explain composi-

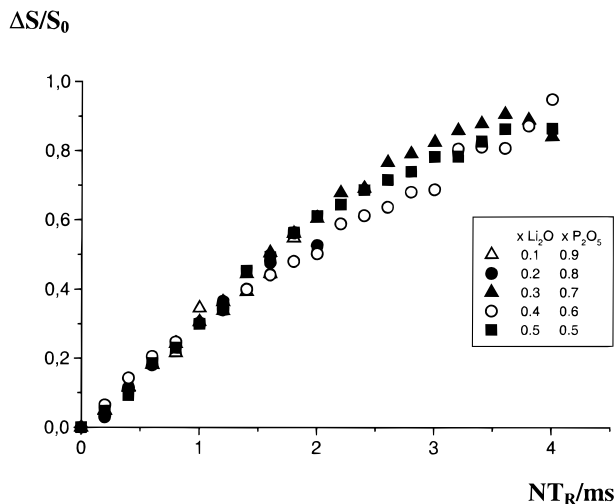


Figure 9. Compilation of the normalized ${}^7\text{Li}\{{}^{31}\text{P}\}$ REDOR difference intensities $\Delta S/S_0$ versus dipolar evolution time of the REDOR experiments for all of the glasses studied.

tional trends in ${}^{23}\text{Na} \rightarrow {}^{31}\text{P}$ CP transfer rates in sodium phosphate glasses.²² In glasses with modifier contents ≤ 20 mol % Li_2O the Li ions are fairly isolated from each other and interact with a single $\text{Q}^{(2)}$ structural unit in the network by utilizing two nonbridging oxygen atoms (Figure 10a). This binding mode constitutes edge-sharing between the $\text{Q}^{(2)}\text{PO}_4$ and the $\text{Li}-\text{O}_n$ polyhedra. At higher Li concentrations, however, a given $\text{Q}^{(2)}$ phosphate unit can attach to two different Li cations, and vice versa (Figure 10b). This rearrangement explains the dramatic change seen in the ${}^{31}\text{P}\{{}^7\text{Li}\}$ REDOR experiment. Furthermore, since the P–O–P connectivity corresponds to statistical linking of the $\text{Q}^{(2)}$ and $\text{Q}^{(3)}$ structural units,¹⁰ it appears plausible that the $\text{Q}^{(3)}\text{--}{}^7\text{Li}$ interaction is subject to the same compositional changes as the $\text{Q}^{(2)}\text{--}{}^7\text{Li}$ dipolar interaction. This expectation is borne out by the results collected in Figure 8a.

All of the other spectroscopic observations are consistent with the proposed model. Regardless of modifier content, no significant compositional change is expected for the dipolar field experienced by the ${}^7\text{Li}$ nuclei due to surrounding ${}^{31}\text{P}$ nuclei. Indeed, no significant changes are observed by ${}^7\text{Li}\{{}^{31}\text{P}\}$ REDOR spectroscopy (Figure 9). Furthermore, since the proposed change in binding mode involves no change in the lithium coordination number, the local oxygen environment of the Li^+ ions is affected very little, in accord with the monotonic compositional dependence of the ${}^6\text{Li}$ chemical shifts observed.

Assuming that the lithium ions are dominantly coordinated by the nonbridging oxygen (NBO) atoms in the network (i.e., both the neutral $\text{P}=\text{O}$ and the anionic $\text{P}-\text{O}^-$ species), the structural rearrangement occurring near 20–25 mol % Li_2O can be considered a direct consequence of Li^+ adopting a coordination number of four to five. In glasses with composition $(\text{Li}_2\text{O})_x(\text{P}_2\text{O}_5)_{1-x}$ the number of these NBOs is given by

$$n(\text{NBO}) = \{f(\text{Q}^{(3)}) + 2f(\text{Q}^{(2)})\}(1-x) \quad (2)$$

Substitution of the $\text{Q}^{(n)}$ species concentrations by eq 1 indicates that in phosphate glasses the number of

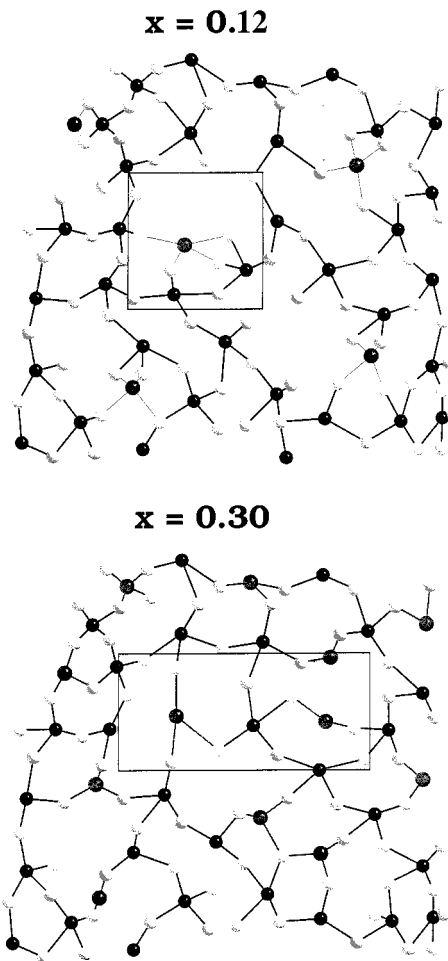


Figure 10. Proposed medium-range order for $(\text{Li}_2\text{O})_x(\text{P}_2\text{O}_5)_{1-x}$ glasses for the compositional ranges: (top) $x = 0.2$ and (bottom) $x = 0.3$.

NBOs remains unity independent of modifier content. Therefore, the modifier concentration $x \leq 0.2\text{--}0.25$ marks the limit up to which the formation of isolated LiO_n ($4 \leq n \leq 5$) is possible; beyond this limit, the LiO_n polyhedra must approach one another and share common nonbridging oxygen atoms. At that point, the chainlike connection of one phosphate $\text{Q}^{(2)}$ unit to two different LiO_n polyhedra becomes the structure-determining feature. Assuming that a reduction of the mean lithium coordination number of 4–5 is unlikely, then a further increase in the modifier content leads to a contact between adjacent LiO_n polyhedra.^{23,33} The structural changes lead to successive cross-linking of phosphate chains, resulting in the experimentally observed increase in the glass transition temperature above 20–25 mol % Li_2O .

Conclusions

Multinuclear single- and double-resonance NMR studies have been carried out on glasses in the system $x\text{Li}_2\text{O}(1-x)\text{P}_2\text{O}_5$, with the goal of clarifying the structural origins of the unexpected minimum in the glass transition temperature T_g at $x = 0.2\text{--}0.25$. While single resonance ${}^6,{}^7\text{Li}$ and ${}^{31}\text{P}$ NMR studies show that this behavior is unrelated to short-range order, the ${}^{31}\text{P}\{{}^7\text{Li}\}$ REDOR results indicate pronounced changes in the strength of the dipole–dipole coupling between the

phosphorus $Q^{(n)}$ structural units and the modifier cation Li^+ . These findings are consistently explained by a change in the intermediate range order at a $Q^{(2)}$ site. On the basis of all of the experimental evidence, we propose that the reconstruction of the network occurring near 20–25 mol % Li_2O involves the rearrangement of the Q^2-Li connectivity from a geometrically challenging edge-sharing PO_4LiO_n connection to a more favorable chainlike $Li-O-P-O-Li$ arrangement, which dominates at higher modifier concentrations. Most likely, the concomitant cross-linking of the polyphosphate chains

by electrostatic interactions with lithium ions is responsible for the T_g increase observed in this compositional region.

Acknowledgment. This work was supported by the Ministerium für Forschung und Wissenschaft, Nordrhein-Westfalen. The authors thank T. M. Alam and R. K. Brow (ref 23) as well as K. T. Mueller and co-workers for preprints of their manuscripts (ref 22).

CM990623F