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Raman Spectroscopy of Calcium Phosphate Glasses with Varying CaO Modifier Concentrations

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Raman spectroscopy has been performed on a series of calcium phosphate glasses prepared from calcium dihydrogenphosphate and CaO in which the CaO content is varied from that of the metaphosphate stoichiometry, in which the mole ratio of CaO to P_2O_5 is 1.00, to a stoichiometry in which the mole ratio is 1.49. Investigation of the vibrational behavior provides insight into the effects of the CaO modifier on the depolymerization processes occurring in these phosphate glasses. Curve-fitting procedures are used to accurately identify peak positions and resolve overlapped bands in the spectra. Depolymerization of the phosphate chains is clearly observed in the vibrational spectra as indicated by shifts in the ν_s(POP), $\nu_s(PO_2)$, and $\nu_{as}(PO_2)$ vibrations. At the largest CaO modifier concentrations, distinct crystalline phases of α- and γ-$Ca_2P_2O_7$ are observed. Analysis of the Raman spectra for these systems suggests that crystallization occurs from the short chain regions of the glass.

Introduction

Phosphate glasses have been of interest for a variety of technological applications due to several unique properties.[1] They have been used as optical fibers in the UV region.[2] The long chains of metaphosphate glasses confer anisotropic characteristics to these fibers if properly prepared.[1] Important biological applications for phosphate glasses also exist. The mineral phase of bone and teeth consists mainly of hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$. Hench demonstrated that it was possible to fabricate calcium phosphate glasses that were biocompatible.[3,4] Both bone and dental implants are currently fabricated from these systems. Phosphate glasses also possess large thermal expansion coefficients and low melting temperatures, making them attractive for hermetic sealing to high expansion metals such as Al alloys.[5] The technological importance of these glasses requires that a detailed understanding of the molecular and structural chemistry associated with the synthetic stages and final products of these systems be developed in order for better glasses to be designed and implemented.

Phosphate glasses are composed of PO_4 tetrahedra which can be bonded to one (Q^1, $[P(OP)OP^-)_3]$), two (Q^2, $[P(OP)_2(O^-)_2]$), or three (Q^3, $[P(OP)_3(O^-)]$) other tetrahedra through the formation of P-O-P bonds at the corners of the tetrahedra.[6,7] The addition of metal cations such as Ca^{2+} to the glass in the amount of one metal cation to one P_2O_5 unit (the metaphosphate stoichiometry) changes the characteristics of the network from the three-dimensional random network of P_2O_5 to long chains of PO_4 tetrahedra possessing, on the average, two nonbridging oxygen atoms per tetrahedron. The classical picture of these glasses maintains that as higher concentrations of metal cations are added, the infinitely long phosphate chains are shortened. Q^1 terminal groups ($-PO_3^{2-}$) are thus formed by breaking bridging oxygens in the metaphosphate chain.[6-8]

On the basis of stoichiometric considerations, Van Wazer has described the average chain length ($\bar{n}$) or the number of P units in a chain in terms of the mole ratio of the metal cation to P_2O_5.[6] For the glasses of interest here, the relevant mole ratio is that of CaO to P_2O_5 and is given the notation $R = [CaO]/[P_2O_5]$. The average chain length is related to R according to the following equation:[6]

$$R = [CaO]/[P_2O_5] = (\bar{n} + 2)/\bar{n} \qquad (1)$$

Upon addition of a modifier metal cation, this relationship predicts that as R increases, $\bar{n}$ should systematically decrease in a continuous fashion. In general, this predicted behavior has been demonstrated for a variety of phosphate glasses.

Raman scattering has been successfully used for investigation of the molecular structure of phosphate glasses. Raman spectral studies of metaphosphate glasses reveal a medium-to-strong intensity band at 690-700 cm^{-1} for the ν_s(POP) vibration, a strong band at 1178-1168 cm^{-1} for the $\nu_s(PO_2)$ vibration, and a medium-to-weak band at 1260-1280 cm^{-1} for the $\nu_{as}(PO_2)$ vibration.[9-20] The posi-

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(1) Sales, B. C. *Mater. Res. Soc. Bull.* **1987**, *12*, 32.
(2) Wasylak, J.; Czerwosz, E. *J. Non-Cryst. Solids* **1983**, *56*, 117.
(3) Hench, L. L.; Splinter, R. J.; Allen, W. C.; Greenlee, T. K. *J. Biomed. Mater. Res. Symp.* **1972**, *2*, 117.
(4) Ogino, M.; Hench, L. L. *J. Non-Cryst. Solids* **1980**, *38*, *39*, 673.
(5) Wilder, J. A. *J. Non-Cryst. Solids* **1980**, *38*, *39*, 879.
(6) Van Wazer, J. R. *Phosphorous and Its Compounds*; Interscience: New York, 1958; Vol. 1.
(7) Zachariasen, W. H. *J. Am. Chem. Soc.* **1932**, *54*, 3841.
(8) Bezborodov, M. A.; Mazo, E. E.; Kaminskii, V. S. *Struct. Glasses* **1960**, *2*, 393.
(9) Bertoluzza, A.; Morelli-Bertoluzza, M.; Fagnano, C. *Rend. Accad. Naz. Lincei* **1973**, *54*, 944.
(10) Bertoluzza, A.; Morelli-Bertoluzza, M. A.; Fagnano, C.; Battaglia, M. A. *Rend. Accad. Naz. Lincei* **1976**, *61*, 269.
(11) Bobovich, Ya. S. *Opt. Spectrosc.* **1962**, *11*, 274.
(12) Morgan, S. H.; Magruder, R. H.; Silberman, E. *J. Am. Ceram. Soc.* **1987**, *70*, C378.
(13) Nelson, B. N.; Exarhos, G. J. *J. Chem. Phys.* **1979**, *71*, 2739.
(14) Rouse, G. B.; Miller, P. J.; Risen, W. M. *J. Non-Cryst. Solids* **1978**, *28*, 193.
(15) Fawcett, V.; Long, D. A.; Taylor, L. H. *Proc. Fifth Int. Conf. Raman Spectrosc.* **1976**, 112.

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tions of these bands are sensitive to length of the phosphate chains. As the number of shorter chains in the glass increases the presence of Q^1 groups is indicateed by growth of the $\nu_s(PO_3^{2-})$ band at ca. 1020 cm^{-1}.

Several recent investigations have been described in which the effect of modifier concentration on the resulting phosphate glass structure was evaluated with Raman spectroscopy.[12,14-16,18-21] Of relevance to the work described here is a report by Bertoluzza and co-workers. These investigators studied a series of calcium oligophosphate glasses of *R* values ranging from 1.13 to 1.65 that were prepared by rapid cooling of a melt of calcium metaphosphate and hydroxyapatite.[16] No crystallization was observed in the glasses formed by this method due to the very rapid cooling method used. Their Raman spectra were interpreted in terms of shortening of the phosphate chain length as *R* increased. No further quantitative information about relative amounts of various phases was presented. These researchers have presented similar Raman studies on sodium phosphate[9,10] and mixed sodium-calcium phosphate[22] glasses.

The work reported here was undertaken with the goal of investigating the change in molecular structure of calcium phosphate glasses resulting from the addition of varying amounts of CaO modifier. The glasses used in this study were cooled more slowly than those prepared by Bertoluzza and co-workers, and thus some crystallization is observed for higher CaO concentrations. Curve-fitting procedures are applied to the Raman spectra to resolve overlapping vibrational bands and aid in the identification of the different phases in these systems. Additionally, curve-fitting facilitates distinguishing the vibrational behavior of the shorter chain phosphate species and the resulting crystallization behavior of these systems.

Experimental Section

Sample Preparation. A series of calcium phosphate glasses were prepared from a mixture of $Ca(H_2PO_4)_2{\cdot}H_2O$ (Alfa, used as received) and CaO (Fisher Scientific, used as received) in which the concentration of the modifier was varied between 0 and 16 wt % in the original mixture. Melting was performed in air in covered Pt-Rh crucibles using a resistance-type box furnace at temperatures in the range 1300–1400 °C for 1 h. The fluid melts were quenched by pouring into a graphite mold and immediately transferred into an annealing furnace where they were annealed at ca. 540 °C, the glass transition temperature as determined by differential thermal analysis, for 15 min. The samples were then allowed to cool overnight in the furnace.

Glass Analysis. Calcium and phosphorus contents of the glass samples were determined by inductively coupled plasma–atomic emission (ICP-AE) spectroscopy to within ±1% accuracy. The mole ratio, $R = [CaO]/[P_2O_5]$, is determined from the ICP-AE results in order to predict the chain length of the phosphate glasses as a function of CaO modifier.

Residual water content of these glasses was determined with FTIR spectroscopy on a Beckman Model FT1300 FTIR spectrometer. Transmission spectra were obtained on bulk samples cut and polished (0.05 μm finish) into parallelepipeds of a thickness of ca. 5 mm. The amount of water was determined by using Beer's law from the following relationship:

Table I. Chemical Composition and H_2O Content of Calcium Phosphate Glasses

R	mol % CaO	mol % P_2O_5	H_2O content, mol/L
1.00	49.9	50.1	0.02
1.05	51.3	48.7	0.03
1.15	53.5	46.5	0.03
1.27	56.0	44.0	0.03
1.29	56.3	43.7	0.02
1.34	57.2	42.8	0.02
1.43	58.8	41.2	0.01
1.49	59.9	40.1	0.01

$$C = \frac{1}{\epsilon d} \log \frac{T_{3800}}{T_{3000}}$$

where *C* is the molar concentration, ϵ is the molar absorptivity of the ν(O–H) band at 3000 cm^{-1} (120 L/(mol cm)),[23] *d* is the sample thickness, T_{3800} is the transmission at 3800 cm^{-1} (background), and T_{3000} is the transmission at the ν(O–H) band at 3000 cm^{-1}. The water content results are shown in Table I.

X-ray Instrumentation. X-ray diffraction (XRD) structural analysis of these glasses was carried out on a General Electric XRD-5 diffractometer. Powdered samples (150 mesh) were placed on glass slides and scanned from 2θ = 15 to 60° at a rate of 2°/min by using monochromatic Cu Kα radiation. The source beam slit width was 3°, and the detector slit width was 0.1°.

Raman Spectroscopic Instrumentation. The Raman system used for spectroscopic studies consisted of a Spex 1403 double monochromator with 1800 grooves/mm holographically ruled gratings. The detection system was an RCA C31034A photomultiplier tube. The spectrometer is interfaced to a Spex Datamate minicomputer, which controls the monochromator and performs data acquisition and analysis. Data were transferred to a DEC LSI-11/23 computer system for curve fitting as described below. Laser excitation was provided by a Coherent Innova 90-5 Ar^+ laser at 514.5 nm. Laser power at the sample was typically 320–380 mW. Spectra of the glass samples were taken in frequency region between 350 and 1500 cm^{-1} at a spectral bandpass of 10 cm^{-1}. Spectra were acquired on powders of the glasses held in melting point capillaries.

Curve-Fitting Procedures. Curve-fitting software was written in-house[24] and provides for user-defined asymmetric Gaussian fits of up to nine overlapped spectral bands at one time. The user has the option of constraining any of the independent variables of peak frequency, left and right full width at half-maximum (fwhm), and intensity for each band to achieve the best fit. It was usually necessary to constrain as many parameters as possible in order to get a reliable fit of the Raman spectral data. Curve fitting was performed on two regions of the Raman spectral data, the ν_s(POP) region from ca. 630 to 850 cm^{-1} and the $\nu_s(PO_2)$ and $\nu_{as}(PO_2)$ region from ca. 950 to 1400 cm^{-1}.

The spectra from the low *R* value glasses are indicative of amorphous materials. These spectra were fit with a minimum number of asymmetric bands that could clearly be identified as either peaks or shoulders in the original spectra. In these fits, none of the parameters, position, fwhm, or intensity were constrained. The use of asymmetric profiles for the amorphous bands is justified by the fact that these bands reflect the total distribution of bonding environments in these amorphous materials, which is not expected to be symmetric. In the spectra from larger *R* value glasses, the number of bands attributable to the amorphous portion of the material was not changed, although their positions, intensities, and fwhm values were allowed to vary. In addition to the amorphous bands in the larger *R* value glasses, bands attributable to various crystalline phases of $Ca_2P_2O_7$ were observed. These bands are most clearly notable in the *R* = 1.49

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(16) Bertoluzza, A.; Battaglia, M. A.; Simoni, R.; Long, D. A. *J. Raman Spectrosc.* **1983**, *14*, 178.

(17) Exarhos, G. J. *Nucl. Instrum. Methods Phys. Res.* **1984**, *B1*, 498.

(18) Tallant, D. R.; Nelson, C.; Wilder, J. A. *Phys. Chem. Glasses* **1986**, *27*, 71.

(19) Sun, K.; Risen, W. M. *Solid State Commun.* **1986**, *60*, 697.

(20) Bertoluzza, A.; Fagnano, C.; Marinangeli, A.; Simoni, R.; Tinti, A.; Morelli, M. A. In *Biomaterials and Clinical Applications*; Pizzoferrato, A., Marchetti, P. G., Ravaglioli, A., Lee, A. J. C., Eds.; Elsevier: Amsterdam, 1987; p 511.

(21) Koudelka, L.; Klikorka, J.; Frumar, M.; Pisarcik, M.; Kello, V.; Khalilev, V. D.; Vakhrameev, V. I.; Chkhenkeli, G. D. *J. Non-Cryst. Solids* **1986**, *85*, 204.

(22) Bertoluzza, A.; Fagnano, C.; Fawcett, V.; Long, D. A.; Taylor, L. H. *J. Raman Spectrosc.* **1981**, *11*, 10.

(23) Arrigada, J. C.; Burckhardt, W.; Feltz, A. *J. Non-Cryst. Solids* **1987**, *91*, 375.

(24) LESSASOFT, University of Arizona, 1986.

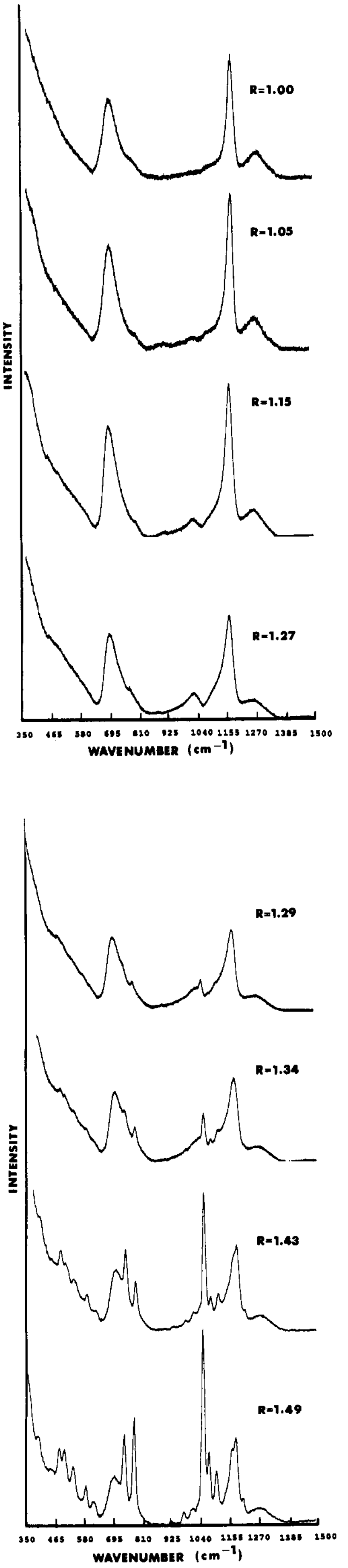

Figure 1. Raman spectra of calcium phosphate glasses (top) for R = 1.00 to R = 1.27 and (bottom) for R = 1.29 to R = 1.49.

Table II. Average Phosphate Chain Length as a Function of *R*

R	av chain length $\bar{n}$	R	av chain length $\bar{n}$
1.00	∞	1.29	6.9
1.05	40	1.34	5.9
1.10	20	1.43	4.7
1.15	13	1.49	4.1
1.27	7.4		

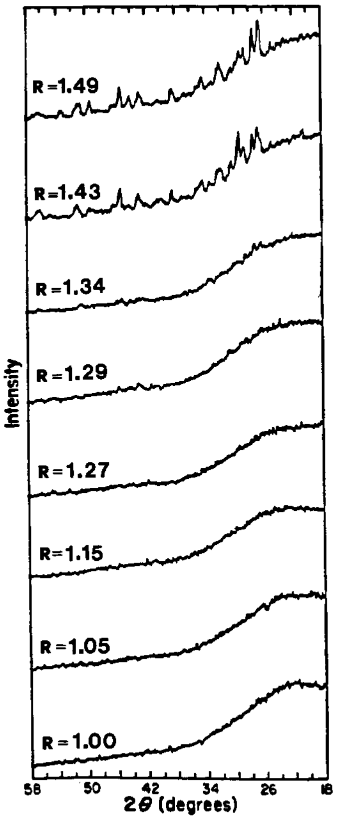

Figure 2. XRD results for calcium phosphate glasses.

material. In the fitting of the intermediate and large R value glasses (1.27 < R < 1.49) in which crystalline peaks could be identified, the positions and fwhm of these bands were constrained to those values measured on the crystalline bands in the R = 1.49 material. These constraints, in addition to assessment of the residuals and a realistic and acceptable visual fit of the spectra, were used as the criteria of acceptable fits of the spectra. Comparison of the relative intensities of the crystalline $Ca_2P_2O_7$ bands with those of the pure compounds in the literature was also used to assess the reliability of the final fits of the spectra of the larger R value glasses. For spectral regions containing more than nine spectral bands, several fits of the region were made to fit the bands present.

Results

Glass compositions having R values ranging from 1.00 to 1.49 were investigated in this study. Using eq 1 above to predict the average chain length, $\bar{n}$, based on stoichiometry for this series of glasses results in the chain length distribution shown in Table II. For the calcium metaphosphate glass (R = 1.00), the chain length is infinite, and for the glass with R = 1.49, the average chain length has decreased to a value of 4.1.

Raman spectra of these samples in the frequency region between 350 and 1500 cm^{-1} are shown in Figure 1. As will be discussed in greater detail below, these spectra exhibit the vibrational behavior characteristic of phosphate glasses at lower R values and of mixed glass and crystalline α- and γ-$Ca_2P_2O_7$ phases at higher R values. This behavior is consistent with the XRD results on these glasses shown in Figure 2. Prominent peaks associated with α-$Ca_2P_2O_7$ are observed at 2θ values of 27.5, 42.6, and 45.4 based on results in the literature.[25,26] Prominent peaks for γ-$Ca_2P_2O_7$ are seen at 2θ values of 26.7, 28.6, and 29.4 and are also consistent with data in the literature.[25,26] It is interesting to note that the first evidence of crystallization in these glasses is noted in the Raman spectrum of the R = 1.27 glass while clear evidence for the presence of crystalline phases cannot be seen in the XRD results until R values greater than or equal to 1.34 are reached.

Two frequency regions in the Raman spectra contain important information about the structure of these phosphate glasses. The frequency region between ca. 600 and 850 cm^{-1} contains bands associated with vibrations of the P–O–P chains. The frequency region between ca. 950 and 1400 cm^{-1} contains bands affiliated with $-PO_2-$ and $-PO_3^{2-}$ vibrations. For the calcium metaphosphate glass (R = 1.00), a band at ca. 695 cm^{-1} has been attributed to the ν_s(POP) vibration.[11,14] The bands at ca. 1175 and 1270 cm^{-1} are due to the $\nu_s(PO_2)$ and $\nu_{as}(PO_2)$ vibrations, respectively.[11,14]

The addition of a network modifier such as CaO causes depolymerization of the infinite phosphate chains resulting in a distribution of shorter chain length species whose average length is described by the values in Table II. Presumably, the presence of these species results in a $\nu_s(PO_3^{2-})$ band attributable to $-PO_3^{2-}$ terminal groups at ca. 1020 cm^{-1}. Qualitative evaluation of the spectra in Figure 1 indicates that the 1020-cm^{-1} band grows in intensity with increasing CaO content.

A more quantitative understanding of the changes occurring in the Raman spectra with variations in the CaO modifier concentration can be developed by consideration of Raman spectra that have been subjected to spectral decomposition procedures to resolve overlapped vibrational bands. Spectra in Figure 1 were subjected to these curve-fitting procedures in the frequency regions corresponding to the ν_s(POP), $\nu_s(PO_2)$, and $\nu_{as}(PO_2)$ vibrations. The results are shown in Figure 3 and are compiled with assignments in Table III.

In the ν_s(POP) region, two bands are observed at ca. 693 and 779 cm^{-1} for the long-chain amorphous phosphate glass. These bands increase in frequency as R increases. Additionally, bands at 738 and 775 cm^{-1} are observed at larger R values for the crystalline phases of γ- and α-$Ca_2P_2O_7$, respectively.[27,28]

The $\nu_s(PO_2)$ and $\nu_{as}(PO_2)$ bands of the amorphous chains are observed at ca. 1175 and 1270 cm^{-1}, respectively. As the CaO concentration is increased, these bands decrease in intensity first at the expense of the $\nu_s(PO_3^{2-})$ band of the terminal groups at ca. 1024 cm^{-1} and then at the expense of the crystalline $Ca_2P_2O_7$ bands. Bands for α-$Ca_2P_2O_7$ are observed in this region at 1005, 1072, 1102, 1162, and 1208 cm^{-1}. Bands from γ-$Ca_2P_2O_7$ are observed at 1046 and 1134 cm^{-1} in this region.

Discussion

The Raman spectrum of the metaphosphate glass (R = 1.00) exhibits two bands in the ν_s(POP) region and four bands in the $\nu_s(PO_2)$ and $\nu_{as}(PO_2)$ region. These bands have been fit to asymmetric profiles to reflect the asymmetric distribution of bonding schemes in these amorphous materials. The asymmetric band at 693 cm^{-1} is assigned to the ν_s(POP) of the long-chain phosphate species. It has been previously observed in similar phosphate glasses that as the chain length decreases, this band increases in frequency.[16] Thus, the asymmetry on the high-energy side of this band suggests an asymmetric chain length distribution toward shorter chains. Further evidence for this chain length distribution comes from the work of Van Wazer.[29] In solubility fractionation studies of sodium phosphate glasses with R values slightly greater than unity (Graham's salt), he found that ca. 95% of the chains were

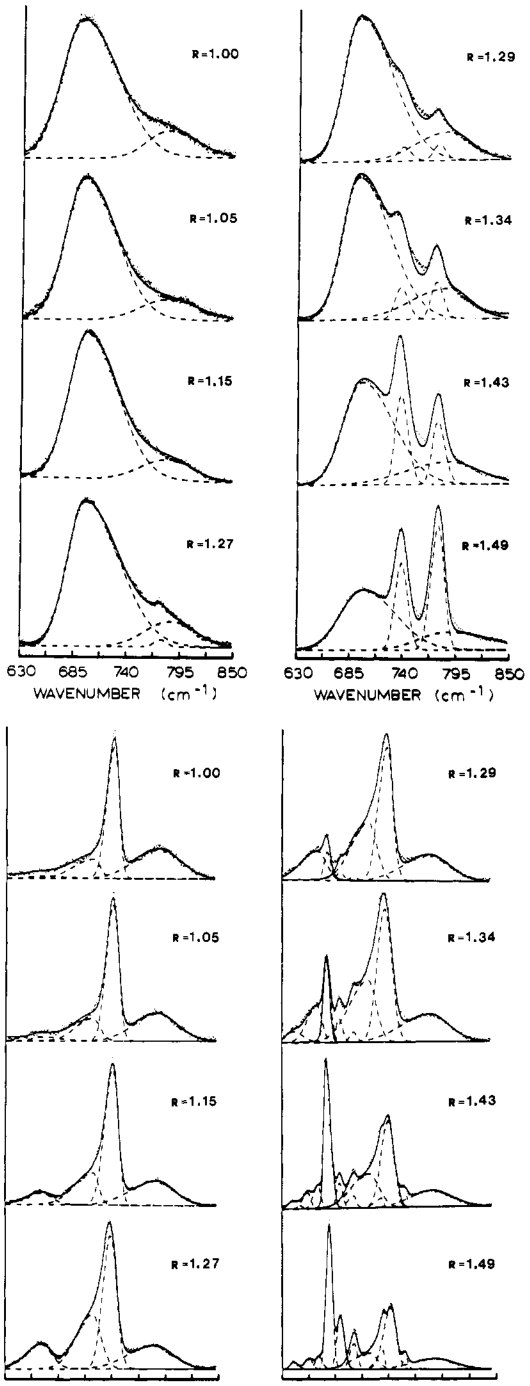

Figure 3. Curve-fitting results for calcium phosphate glasses as a function of R in the (top) ν_s(POP) and (bottom) $\nu_s(PO_2)$ frequency regions.

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[25] Ranby, P. C.; Mash, D. H.; Henderson, S. T. *Br. J. Appl. Phys.* **1954**, *Suppl. 4*, S18.

[26] McIntosh, A. O.; Jablonski, W. L. *Anal. Chem.* **1956**, *28*, 1424.

[27] Cornilsen, B. C.; Condrate, R. A. *J. Solid State Chem.* **1978**, *23*, 375.

[28] Cornilsen, B. C.; Condrate, R. A. *J. Inorg. Nucl. Chem.* **1979**, *41*, 602.

[29] Van Wazer, J. R. *J. Am. Chem. Soc.* **1950**, *72*, 647.

Table III. Raman Spectral Bands (cm^{-1}) and Assignments as a Function of *R*

1.00	1.05	1.15	1.27	1.29	1.34	1.43	1.49	assgnt
693	694	694	695	696	696	698	698	ν_s(POP), A[a]
				738	738	738	738	ν_s(POP), γ[b]
			775	775	775	776	776	ν_s(POP), α[c]
779	779	781	785	785	786	785	785	ν_s(POP), A
						921	921	ν_{as}(POP), γ
					974	974	972	ν_{as}(POP), α
1022	1024	1024	1026	1026	1026	1026	1026	$\nu_s(PO_3^{2-})$, A
				1046	1046	1048	1048	$\nu_s(PO_3^{2-})$, γ
				1074	1072	1072	1072	$\nu_s(PO_3^{2-})$, α
				1102	1102	1102	1101	$\nu_{as}(PO_3^{2-})$, α
1134	1134	1134	1134	1134	1134	1134	1134	A
1178	1176	1174	1170	1170	1170	1178	1178	$\nu_s(PO_2)$, A
						1208	1208	$\nu_{as}(PO_3^{2-})$, α
1274	1270	1268	1264	1262	1264	1267	1270	$\nu_{as}(PO_2)$, A

[a] A = amorphous phase. [b] γ = γ–$Ca_2P_2O_7$ phase. [c] α = α–$Ca_2P_2O_7$ phase.

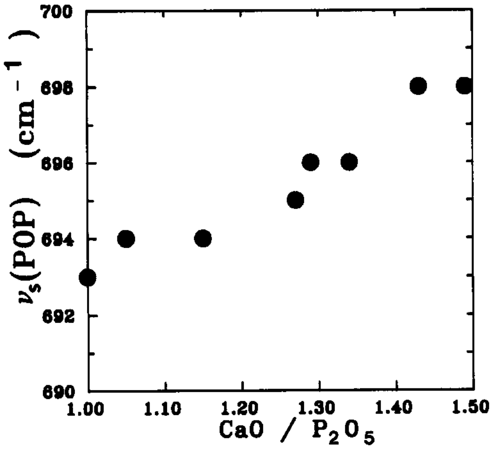

Figure 4. Frequency of the ν_s(POP) band as a function of *R*.

Table IV. Fwhm of ν_s(POP), $\nu_s(PO_3^{2-})$, and $\nu_s(PO_2)$ as a Function of *R*

	fwhm, cm^{-1}		
R	ν_s(POP)	$\nu_s(PO_3^{2-})$	$\nu_s(PO_2)$
1.00	135	154	61
1.05	123	127	61
1.15	119	129	66
1.27	124	130	69
1.29	118	147	76
1.34	116	75	73
1.43	122	38	68
1.49	132	35	62

between ca. 100 and 500 P units with an average P unit length of 193.

A second ν_s(POP) band is observed in the metaphosphate spectrum at ca. 779 cm^{-1}. This band has been observed previously[16] but not assigned. This band may be due to very short chain phosphate units or ring structures which are known to be increasingly important in the composition region between the ultraphosphate (pure P_2O_5) and metaphosphate compositions.[6] The higher frequency of this band relative to the band at ca. 695 cm^{-1} is consistent with shorter chains of phosphate units.

Four bands are observed at 1022, 1134, 1178, and 1274 cm^{-1} in the region of the spectrum containing vibrations of $-PO_3^{2-}$ and $-PO_2-$ groups. The band at 1022 cm^{-1} has been assigned to the $\nu_s(PO_3^{2-})$ vibration.[16,30,31] The band at 1134 cm^{-1} has been observed previously but not unequivocally assigned. Its presence is most often associated with the presence of long phosphate chains.[32] The bands at 1178 and 1274 cm^{-1} are due to the $\nu_s(PO_2)$ and $\nu_{as}(PO_2)$ vibrations, respectively.[9-20]

As CaO is added to the glass, several effects on the spectra in the ν_s(POP), $\nu_s(PO_2)$, and $\nu_{as}(PO_2)$ regions are observed. These effects can be divided into two groups, those occurring while the material remains largely amorphous ($R < 1.34$) and those observed for compositions in which significant crystallization occurs ($R > 1.34$). For the amorphous composition region, a slight increase in peak frequency of the main ν_s(POP) band from 693 to 696 cm^{-1} is observed between *R* values of 1.00 and 1.49 as shown in Figure 4. This effect of network modifier on phosphate glass structure has been observed previously and has been attributed to a decrease in the P–O–P bond angle as the average length of the phosphate chains decreases.[14,17] This increase in peak frequency is accompanied by a systematic decrease in fwhm of the band from ca. 135 to ca. 118 cm^{-1} as shown by the data in Table IV. This observation suggests that the P–O–P environment is becoming more homogeneous as the phosphate chains are depolymerized. Beyond this composition, however, where crystalline phases begin to form, the fwhm increases again to 132 cm^{-1}, suggesting that the remaining glassy part of the mixed amorphous–crystalline phase possesses a large distribution of amorphous P–O–P environments. The overall decrease in the intensity of this band as *R* increases indicates an overall decrease in the relative amount of the amorphous phase in these systems.

The intensity of the band at 779 cm^{-1} relative to that at 695 cm^{-1} is largely insensitive to *R* value in these glasses. This observation argues against assignment of this band to short-chain phosphate species which would be expected to increase in amount as CaO increases. Therefore, this band may be due to a small amount of ring phosphates whose concentration is relatively constant as the *R* increases.

Finally, for *R* values greater than ca. 1.34, new bands are observed in this region at ca. 738 and 775 cm^{-1}. These bands are due to γ- and α-$Ca_2P_2O_7$, respectively, and increase in intensity as *R* increases.

The $-PO_2-$ region of the spectrum, although somewhat more complex, also contains considerable information about the effect of CaO on the structure of these phosphate glasses. As *R* increases, the spectra in this region become more complex, indicating the existence of different phases in these glasses. The peak at 1175 cm^{-1} in the metaphosphate glass decreases in frequency as *R* increases, indicative of an increase in the average $-PO_2-$ angle with addition of modifier,[14,17,32,33] consistent with the contraction

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(30) Almeida, R. M.; Mackenzie, J. D. *J. Non-Cryst. Solids* **1980**, *40*, 535.

(31) Bartholomew, R. F. *J. Non-Cryst. Solids* **1972**, *7*, 221.

(32) Nelson, C.; Tallant, D. R. *Phys. Chem. Glasses* **1985**, *26*, 119.

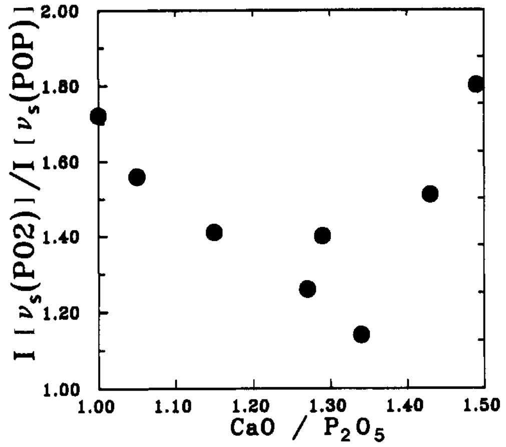

Figure 5. $I[\nu_s(PO_2)]/I[\nu_s(POP)]$ as a function of R.

of the chain indicated by the data in the ν_s(POP) spectral region. This effect has been observed previously and concluded to be the result of the removal of electron density from the nonbridging oxygens as more cations are added to the glass.[14,17]

Several additional observations can be made about the spectral behavior of this band as the CaO concentration is increased. First, as shown in Table IV, the fwhm of the $\nu_s(PO_2)$ band increases as R increases for the compositions in which the material remains largely amorphous. This behavior is opposite to that observed for the ν_s(POP) band and suggests that as the phosphate chains are shortened, a greater heterogeneity in the amorphous PO_2 environment exists giving rise to a broadened band. Second, the relative intensity of this band decreases as R increases consistent with depolymerization of the long phosphate chains to form shorter chain units in the glass phase.

The $\nu_{as}(PO_2)$ band shows similar behavior in the amorphous region as R increases. A decrease in the peak frequency from 1274 cm^{-1} for R = 1.00 to 1262 cm^{-1} for R = 1.29, a ratio just prior to significant crystallization in these systems, is observed. The relative intensity of this band decreases as expected as the depolymerization, and crystallization processes become important at larger R values.

The last amorphous band quantitatively evaluated in detail is the $\nu_s(PO_3^{2-})$ band observed at ca. 1020 cm^{-1}. In the amorphous region (R < 1.34), the frequency of this band increases slightly with R. Additionally, the intensity of this band increases with R as expected on the basis of an increasing number of chain termini with decreasing average chain length.

The crystalline phases grow progressively predominant in these systems as R increases. Although exact quantification of the relative amounts of the two crystalline phases cannot be determined without knowledge of the scattering cross sections for these species, the α-$Ca_2P_2O_7$ phase is the first to be observed in these systems, but the γ-$Ca_2P_2O_7$ phase grows more rapidly once it is observed at R = 1.29.

Several pieces of evidence support the assertion that these phases grow predominantly at the expense of the short chain phosphate units. Parameters indicative of increasing amounts of shorter chain phosphate units change with R in one direction until significant crystallization begins to occur at R > 1.34 at which point these parameters reverse their direction of change. For example, the fwhm of the ν_s(POP) band decreases and the fwhm of the $\nu_s(PO_2)$ band increases with R in the amorphous region, indicative of shorter phosphate chain formation. However, as can be seen by the data in Table IV, upon significant crystallization in these systems for R > 1.34, these fwhm values change in the opposite direction. Similarly, the frequencies of the $\nu_s(PO_2)$ and $\nu_{as}(PO_2)$ bands decrease with R to ca. 1.34, at which point they again increase. The fwhm of the $\nu_s(PO_3^{2-})$ band decreases drastically for R > 1.34 as can be seen by the data in Figure 4. Finally, the intensity ratio of the $\nu_s(PO_2)$ band to the ν_s(POP) band, which is indicative of the electron-withdrawing power of the cation and hence the degree of covalency of the Ca–O bond, generally decreases with R for values less than 1.34 and then increases for R > 1.34 as shown in Figure 5. These changes are interpreted to indicate loss of some of the short-chain component of the amorphous phase to crystallization. This conclusion is reasonable based on the chain length distributions found for phosphate glasses of similar R value by several researchers. Meadowcroft and Richardson found that ca. 83% of the chains were of seven or less P units in calcium phosphate glasses of R = 1.5.[34] Cripps-Clark and co-workers similarly found that ca. 80% of the chains were of seven or less P units in sodium phosphate glasses of R values between 1.4 and 1.5.[35] Thus, at high R values in these systems, a considerable number of short-chain phosphate species exist from which facile crystallization would be expected. Crystallization of the pyrophosphate from these short-chain forms is consistent with the observations of this study.

Conclusions

The effect of addition of increasing amounts of CaO modifier to calcium metaphosphate glasses has been followed in this study using Raman spectroscopy. Spectral decomposition of the resulting spectra allow development of a quantitative understanding of the depolymerization processes occurring in these systems. For R < 1.34, this process generates increasing numbers of short-chain phosphate species. At R > 1.34, α-$Ca_2P_2O_7$ begins to crystallize. As R is made progressively higher, crystalline γ-$Ca_2P_2O_7$ becomes the predominant crystalline phase in these systems. The pyrophosphate crystals appear to develop from the short-chain component of the amorphous material.

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(33) Chakraborty, I. N.; Condrate, R. A. *Phys. Chem. Glasses* **1985**, *26*, 68.

(34) Meadowcroft, T. R.; Richardson, F. D. *Trans. Faraday Soc.* **1965**, *61*, 54.

(35) Cripps-Clark, C. J.; Sridhar, R.; Jeffes, J. H. E.; Richardson, F. D. *Phys. Chem. Process Metallurgy*; The Richardson Conference, 1973; p 233.