

Structural Alterations in the Amorphous-to-Crystalline Transformation of Lead Pyrophosphate

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The detailed structural changes that occur during the isothermal transition from a glass to a single-phase crystalline solid have been determined for the first time by use of the modern technique of high-performance liquid chromatography. Quantitative measurements of the evolution of the type and relative concentration of individual structural units present during the devitrification process were made on lead pyrophosphate glasses annealed below, at, and above the glass transition temperature.

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The relationship between the structural properties of the amorphous and crystalline phases of a solid and the intervening structural alterations that occur in the transition region between these phases are questions of considerable fundamental significance. While modern x-ray, neutron, and other diffraction techniques are capable of providing precise, detailed information regarding the structural properties of crystalline solids, even the most innovative applications of these same methods to amorphous materials provide only limited and rudimentary structural information. The technique of high-performance liquid chromatography (HPLC), however, can provide information about either amorphous or partially recrystallized phosphate solids on a scale and at a level of structural detail that is virtually impossible to achieve with any other currently available experimental technique.¹⁻⁶ The HPLC method is widely applicable and can be used to study a large class of metal phosphates where the metal cation can be, for example, an alkali metal, alkaline earth, transition metal, rare earth, or actinide.

The polyphosphate solids of interest here are composed of PO_4 tetrahedra that are corner linked to form chains of varying size. These chains represent phosphate anions that bond to metal cations to form the charge-neutral solid. In general, only one type of phosphate anion will be present in a crystalline solid, but, in a glass with the same chemical composition, phosphate anions consisting of both longer and shorter phosphate chains will occur. For many phosphate glasses, HPLC can be used to determine quantitatively the type (i.e., chain length) and the relative concentrations of phosphate chains present either in the "as-prepared" glass or at any stage of the devitrification process. Accordingly, it is possible to follow the structural evolution as the transition from the glassy to the crystalline state occurs as a result of isothermal annealing.

The structural alterations associated with the devitrification process induced by isothermal annealing were investigated for the composition $\text{Pb}_2\text{P}_2\text{O}_7$ (lead pyrophosphate). This material is particularly well suited to a study of this type since it can be easily prepared in ei-

ther the glassy or crystalline state by simply controlling the solidification rate from the melt. HPLC can then be used to determine the structural properties of both the end members of the system (i.e., glass and single crystal) in the as-prepared state as well as the intervening structural characteristics. During the devitrification process, the material must not form other phases, and both thermal and x-ray analyses show that this does not occur for $\text{Pb}_2\text{P}_2\text{O}_7$.

In performing an HPLC structural analysis, it is necessary to dissolve some of the solid phosphate in an aqueous solution. Previous work¹⁻⁶ has established that if this dissolution is carried out correctly, then the distribution of phosphate anions in solution will be the same as that present in the amorphous solid. This critical correspondence has been verified both by a number of experimental tests and from known properties of the phosphates. These include the following: (1) The stability of phosphate chains and rings with respect to hydrolysis reactions in neutral or high-pH solutions has been established. (2) Liquid-chromatography results yield exact agreement with the structural determinations of the phosphate anions present in crystalline phosphates (see the discussion below and Fig. 1). (3) Phosphate anions in the chromatography solution are not subjected to polymerization mechanisms. (4) The average chain length measured by HPLC is the same as that calculated on the basis of charge balance from the glass composition. (5) Experimentally, it is found that the average chain length of a crystalline phosphate and the average chain length determined by HPLC for a glass with the same composition are the same. (6) In the case of lead phosphate glasses, the distribution of phosphate anions as determined by HPLC and the distribution predicted by the theory of Parks and Van Wazer are in quantitative agreement. (7) Spectroscopic information including Mössbauer, EPR, and Raman results corroborate the HPLC findings, and, in particular, it is possible to predict the shape of the dominant Raman band from the HPLC measurements.⁵ Additional details regarding the correspondence between the liquid chromatogram and the structure of phosphate glasses are given in Ref. 5. It

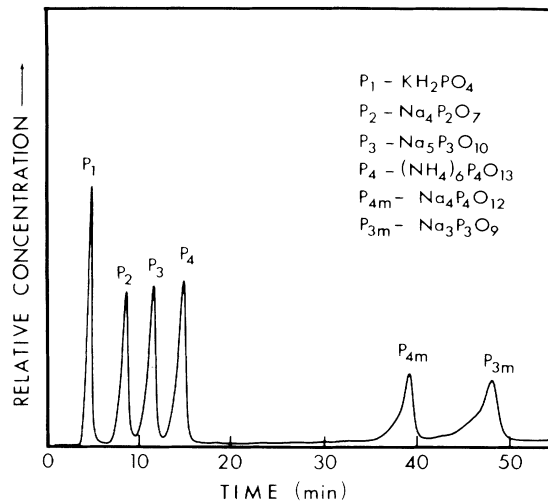


FIG. 1. Liquid chromatogram of a "standard solution" prepared by dissolving several crystalline phosphate compounds in an aqueous solution. Each of the phosphate compounds listed in the upper right of the figure contributes only one phosphate anion and is responsible for only one of the peaks in the chromatogram.

should be emphasized that it is the relatively unique dissolution mechanism of phosphate glasses in high- pH or neutral solutions that allows one to apply the HPLC technique to structural analysis, and that silicate and borate glasses dissolve in such a way that most of the silicate or borate anion structures present in the solid are destroyed or altered during the dissolution process and, hence, the HPLC technique does not work for glasses of this type.

Lead pyrophosphate was synthesized by melting and reacting appropriate amounts of PbO and $NH_4H_2PO_4$ for several hours in air. Large single-crystal plates of $Pb_2P_2O_7$ could be produced by slow cooling ($\approx 1^\circ C/h$) of the melt in the range from 900 to 700 $^\circ C$, and a homogeneous glass with the same composition could be prepared by quenching of the melt between cold copper plates. X-ray diffraction and polarized-light analysis verified the absence of crystalline material in the $Pb_2P_2O_7$ glass. $Pb_2P_2O_7$ consists of sheets of pyrophosphate (P_2) chains (i.e., two PO_4 tetrahedra in length).⁷ HPLC analysis of $Pb_2P_2O_7$ single crystals also shows that only P_2 chains are present when the crystals are dissolved in a high- pH solution, in exact agreement with the x-ray structure analysis.

The HPLC analysis of crystalline, glassy, and partially devitrified $Pb_2P_2O_7$ was performed by our dissolving ≈ 100 mg in an aqueous high- pH solution that was then injected into the HPLC system.⁵ Here the various phosphate anions were separated by an anion exchange column. Phosphate chains up to 13 PO_4 tetrahedra in length (P_1, P_2, \dots, P_{13}) could be resolved by the analytical column as well as cyclic anions. The resulting

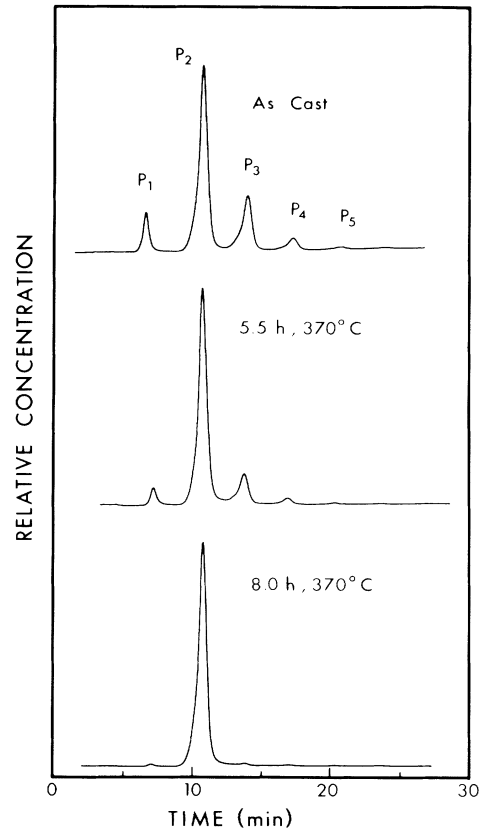


FIG. 2. Liquid chromatograms for (top) lead pyrophosphate glass as prepared; (middle) material at an intermediate state of the devitrification transition at 370 $^\circ C$; and (bottom) almost fully recrystallized $Pb_2P_2O_7$ after 8 h at 370 $^\circ C$.

chromatogram consists of a series of peaks whose position corresponds to the type of phosphate anion (i.e., P_1, P_2, \dots, P_{13}) and whose area is proportional to the amount of phosphorous contained in chains of that length. It should be noted that while HPLC does not provide structural information about the local environment of the metal cations (Pb in this case) in the solid, detailed information of this type has recently been obtained with extended x-ray-absorption fine structure.⁸

The chromatography system is calibrated by our dissolving various crystalline phosphates with known structures and then injecting the resulting solution into the HPLC system. Only one type of phosphate anion is known to be present in each crystalline compound from the established structure of the material. If only one crystalline compound is dissolved, then the chromatogram exhibits only one peak with a chain length corresponding to the known type of anion. If a number of crystalline phosphate compounds are dissolved in the solution, then a "standard" chromatogram can be produced. An example of the chromatogram obtained from crystalline phosphates with chains that are one, two, three, and four PO_4 tetrahedra in length plus two cyclic

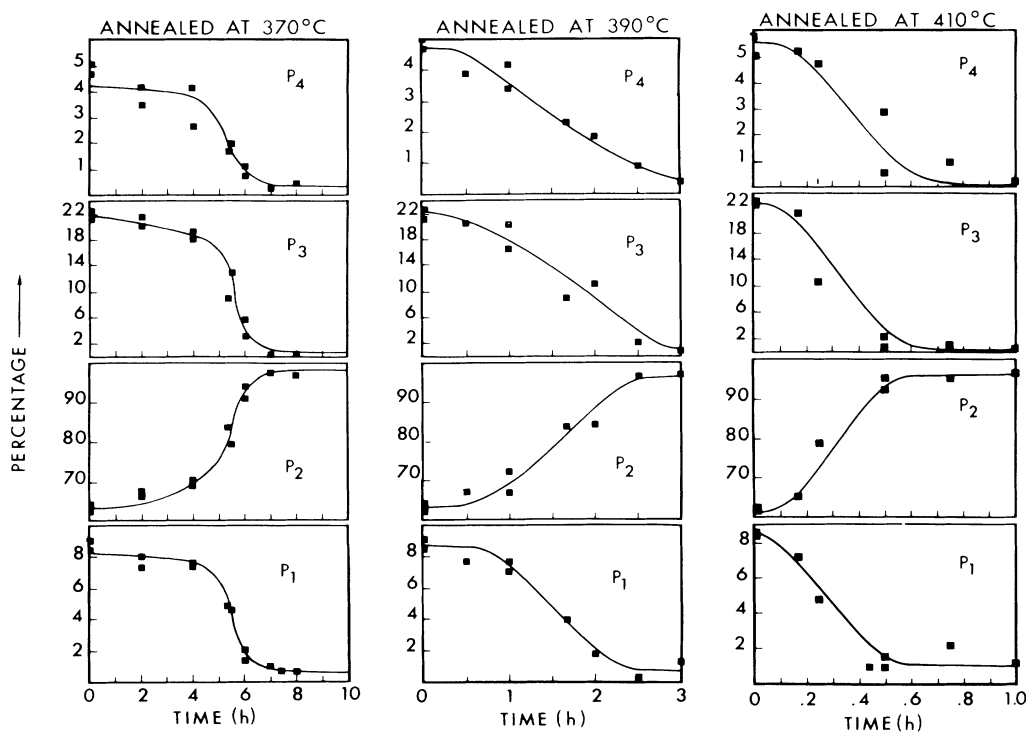


FIG. 3. The evolution with time of the relative concentration of the four major phosphate anions during the devitrification of $\text{Pb}_2\text{P}_2\text{O}_7$ at 370, 390, and 410°C. The vertical axis corresponds to the percentage of the total phosphorus contained in chains of that length.

anions trimetaphosphate and tetrametaphosphate is shown in Fig. 1.

The chromatogram obtained for a $\text{Pb}_2\text{P}_2\text{O}_7$ glass prepared by quenching the melt is shown at the top of Fig. 2. This chromatogram shows that the glassy phase consists of a large peak corresponding to chains that are two PO_4 tetrahedra in length (P_2 chains) as well as both longer and shorter phosphate chains. In this chromatogram, for the as-cast glass, the chains are labeled out to P_5 . The average chain length computed from this chromatogram is 2 ± 0.02 indicating that there is an exact charge balance in the glass between phosphate anions and lead cations. Scanning calorimetry measurements showed that the glass transition occurred at $\approx 390^\circ\text{C}$ with rapid recrystallization beginning near 440°C .

Lead pyrophosphate glass samples were isothermally annealed at temperatures above, at, and below the glass transition temperature by our placing the material in a scanning calorimeter and rapidly raising the temperature to the annealing point. The sample was then annealed in a nitrogen atmosphere for the desired time period, rapidly cooled to room temperature, and then placed in the chromatography solution. The middle chromatogram in Fig. 2 shows the result obtained for a partially devitrified lead pyrophosphate sample. A comparison of this chromatogram with that shown in the top trace for the as-cast glass shows that after 5.5 h at 370°C , the height

of the P_2 peak has increased relative to the peaks corresponding to orthophosphate (P_1) chains and to the P_3 and longer chains. By annealing of as-cast glass specimens for various time periods, the detailed structural evolution of the material can be mapped out as it transforms to the fully crystalline state and finally exhibits a chromatogram that consists of essentially only the P_2 peak. The chromatogram for a $\text{Pb}_2\text{P}_2\text{O}_7$ glass after 8 h at 370°C is shown at the bottom of Fig. 2 and, in this case, the recrystallization process is almost complete.

The details of the structural evolution during the amorphous-to-crystalline transformation for annealing temperatures of 370, 390, and 410°C are illustrated in Fig. 3. Here the vertical axis corresponds to the percentage of total phosphorus present in the form of each anion as the material transforms from the glassy state at $t=0$ to the crystalline state that is achieved when the fraction of chains longer or shorter than P_2 approaches zero. For the case of $\text{Pb}_2\text{P}_2\text{O}_7$ glass annealed below the glass transition temperature (i.e., at 370°C), the results in Fig. 3 show that the recrystallization process consists of an induction period during which the relative change in the percentages of the various phosphate chains is small. Following this induction period, there is a relatively rapid alteration of the ratios of the various phosphate anions until the P_2 unit associated with the crystalline state predominates. As shown in Fig. 3, in the case

of the anneal of 390°C, the induction period is significantly shorter than for the glass annealed at 370°C (i.e., < 1 h vs \approx 4 h at 370°C). For the case of the isothermal anneal above the glass transition temperature, Fig. 3 shows that the induction period has essentially disappeared and that the entire process of recrystallization is complete after about 30 min. At all three annealing temperatures, the end product of the devitrification process was single-phase polycrystalline lead pyrophosphate. The results illustrated in Fig. 3 provide a mapping of the structural path followed by lead pyrophosphate in transforming from the glassy to the crystalline state.

The process of devitrification of a glass is traditionally divided into two separate regimes; i.e., the nucleation of microcrystallites followed by the growth of macrocrystallites. The time period for nucleation is often treated as an induction period during which nothing occurs on a macroscopic scale. For example, devitrification data are often described by a modified Avrami equation of the form⁹⁻¹¹ $x(t) = 1 - \exp[-K(t - \tau)^n]$ where x is the volume fraction recrystallized at time t , K is a thermally activated rate constant for recrystallization, τ is the induction period for nucleation, and n is the Avrami coefficient that is used to determine the dimensionality of the controlling mechanism of recrystallization. For the devitrification data shown in Fig. 2, τ would correspond to about 3 h, and the value for n is close to 3 which would correspond to volume crystallization either on preexisting nucleation sites or for interface-controlled growth. This type of analysis, however, simply does not utilize much of the information that is obtained by HPLC analysis. For example, during the "induction period" the present results show that there are measurable changes in the concentrations of the phosphate structural units. These changes should be taken into account by any devitrification model. Additionally, there are clearly differences in the time dependence of the evo-

lution of individual phosphate anions. Also, while the rate of devitrification increases by a factor of 15 in going from 370 to 410°C it does not follow an Arrhenius law in this temperature region. Information of this type suggests that a more specific microscopic theory of the devitrification process is required to account for the details revealed by the HPLC technique, and in the case of many phosphate glasses, the technique provides the quantitative experimental basis for the formulation of such a theory.

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