Structural Inequivalence of the Ion-Damage–Produced Amorphous State and the Glass State in Lead Pyrophosphate

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The detailed structural changes that occur during ion-beam–induced amorphization of a solid have been experimentally determined for the first time using single-crystal surfaces of lead pyrophosphate that were implanted with varying doses of Pb^{3+} ions. For all Pb-implant doses, the structure of the amorphous layer produced by ion bombardment was found to be significantly different than the structure of lead pyrophosphate glass prepared via thermal quenching.

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The present work addresses one of the most fundamental questions concerning the structural makeup of amorphous materials: What is the relationship between the microscopic structure of the material and the method used to produce the amorphous state? Detailed structural information for either the amorphous, the partially disordered, or the glass state of some phosphate solids can be obtained by means of the modern technique of high-performance liquid chromatography (HPLC).[1-7] Accordingly, this method is ideally suited for addressing the above question in the case of phosphate materials. In fact, the HPLC method was recently used[7] to study the detailed structural changes that occur during the thermally induced transition from a lead pyrophosphate glass to the homogeneous crystalline solid. At this time, although the method is limited to phosphates, it appears that no other technique is capable of providing such detailed structural information regarding the type and distribution of anions present in an amorphous or glassy solid. Additionally, the HPLC technique is sufficiently sensitive to permit the study of the structure of very thin (~200 nm) amorphous layers produced by ion implantation of single-crystal surfaces.

The phosphate solids of interest here are composed of PO_4 tetrahedra that are corner connected to form chains of varying length. These chains can be thought of as phosphate anions that bond to metal cations to form either the charge-neutral amorphous solid or a glass. In a given crystalline phosphate solid usually only one type of phosphate anion is present, but, in an amorphous material or glass with the same composition, both longer and shorter phosphate chains are present.[5-7] In the present case of the $Pb_2P_2O_7$ composition, HPLC can be used to determine quantitatively the relative concentration of each type of phosphate chain (anion) present in the disordered or crystalline solid.[7] Although the technique of HPLC is widely applicable to a large class of metal phosphates, the present work will focus only on lead pyrophosphate $Pb_2P_2O_7$. Lead pyrophosphate was chosen for the present study for several reasons. Large single-crystal plates of $Pb_2P_2O_7$ ($\sim 2\times 2\times 0.2$ cm^3) can be easily grown by slowly cooling (~1 °C/h) a melt of the appropriate amounts of PbO and P_2O_5 from 900 to 700 °C. Large single-crystal surfaces increase the HPLC signals for the extremely thin amorphous surface layers produced by ion bombardment. Additionally, if a melt with the $Pb_2P_2O_7$ composition is thermally quenched between two cold copper plates, a homogeneous lead pyrophosphate glass is formed, and the structural properties of this glass can then be directly compared with the structure of the amorphous layer produced by ion bombardment.

Lead pyrophosphate crystallizes in the triclinic space group $P\bar{1}$ and consists of pyrophosphate anions (i.e., two corner-linked PO_4 tetrahedra) bonded in the solid via surrounding lead cations.[8] The pyrophosphate groups are arranged in the form of sheets that are stacked to form a highly micaceous and easily cleaved crystal. Laue back-reflection x-ray measurements confirmed that the large crystal faces in these as-grown crystals were perpendicular to the *c* axis and parallel to the pyrophosphate sheets.

The entire surface of freshly cleaved or "as-grown" lead pyrophosphate crystals was implanted ~10° off of the *c* axis with Pb^{+3} ions at 540 keV/ion with doses ranging from 10^{11} to 5×10^{15} ions/cm^2. For the highest implant dose, this represents an average change in the lead concentration in the implant profile of only 4%. The implantation process results in a Gaussian-shaped distribution of implanted lead ions centered approximately 50 to 100 nm below the surface. The actual damaged surface layer, however, typically extends about 100–200 nm into the crystal because of "knock on" processes.[9] The $Pb_2P_2O_7$ crystals were implanted at liquid-nitrogen temperatures to prevent thermal recrystallization due to ion-beam heating, and no buildup of charge on the crystals was noted during implantation. For similar phosphate materials, it has been found that an implantation dose of between 10^{13} and 10^{14} ions/cm^2 is sufficient to render the near-surface region amorphous as determined by ion channeling and x-ray diffraction.[10]

Only the large faces (*c* axis) of the lead pyrophosphate crystals were implanted with lead. All other remaining faces of the crystals were masked using silver paint so that these surfaces were not affected when the crystals were analyzed by the HPLC technique. Although the surface area of these faces was quite small, these smaller faces (i.e., *a-c* or *b-c* surfaces) contributed to the chromatogram about an order of magnitude more, per unit surface area, than the larger faces (i.e., the *a-b* surfaces that are parallel to the cleavage direction).

The implanted, masked crystals were placed in a 1-cm^3 solution of 0.22*M* NaCl and $5\times10^{-3}M$ Na_4EDTA (EDTA denotes ethylenediamine tetra-acetic acid) until the amount of phosphorus in solution corresponded to the loss of a surface layer from the crystal approximately 100-nm thick. This process typically took between 15 to 30 min, but the exact time was determined for each implanted crystal since the dissolution rate of a heavily implanted layer was over 10 times faster than that of the as-grown, unimplanted crystal surface. Amorphous surface layers of approximately the same thickness were analyzed since, for a given implant dose, a variation of the local damage (and hence structure) with depth below the crystal surface could be resolved by the HPLC method. The structural analysis was carried out by injecting a small portion of the solution containing the phosphate anions from the implanted layer into the HPLC system.[5-7] The various anions were separated by an ion-exchange column that could resolve phosphate chains up to thirteen PO_4 tetrahedra in length (P_1, P_2, P_3, . . . ,P_{13}) as well as cyclic phosphate anions that are present in some phosphates. The resulting chromatograms consist of a series of peaks whose position corresponds to the type of phosphate anion (P_1, P_2, . . . ,etc.) and whose area is directly proportional to the amount of phosphorus contained in chains of that length. The HPLC system can be calibrated by analyzing various crystalline phosphate compounds with known structures. Both the residence time of individual phosphate anions on the column and the linearity of the detection signal with phosphorus concentration are calibrated using the crystalline standards.

A comparison of the chromatogram of a lead pyrophosphate glass produced by thermal quenching and that of a 100-nm-thick amorphous layer formed by ion implantation (10^{15} Pb^{+3} ions/cm^2) is shown in Fig. 1. Gross structural differences are obvious for the two materials. Relative to the glass, the percentage of P_2 is much lower for the ion-damaged layer which indicates that this layer is actually "more amorphous" or more disordered than the thermally quenched glass of the same composition. In addition, the glass has a much larger percentage of P_3 anions whereas the amorphous-implanted layer has significantly higher concentrations of P_1, P_4, and P_5 anions.

The chromatograms obtained from a 100-nm layer of the implanted lead pyrophosphate crystal surface are shown in Fig. 2 for various Pb^{+3} implant doses. The chromatogram at the top left of Fig. 2 is obtained from a freshly cleaved, unimplanted crystal surface. With the exception of a very small amount of P_1, the chromatogram consists of a single P_2 peak, corresponding to the

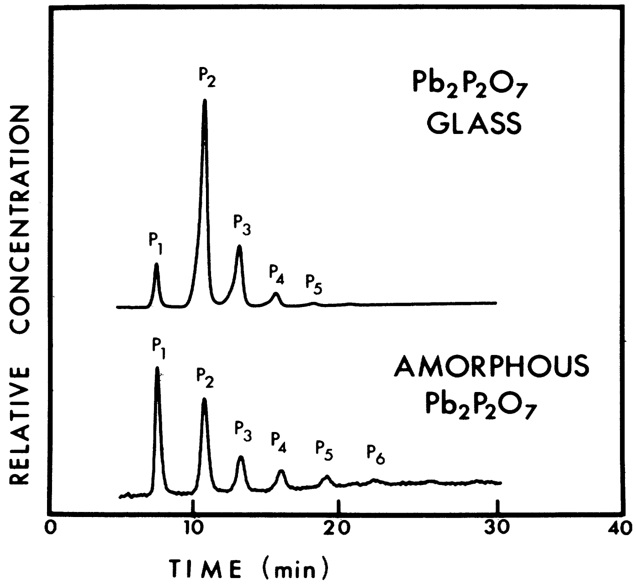

FIG. 1. Liquid chromatograms from a lead pyrophosphate glass produced by quenching the melt (top) and from a 100-nm-thick ion-damage–produced amorphous layer (bottom) on the surface of a lead pyrophosphate single-crystal implanted with 10^{15} Pb^{+3} ions/cm^2 at 540 keV/ion.

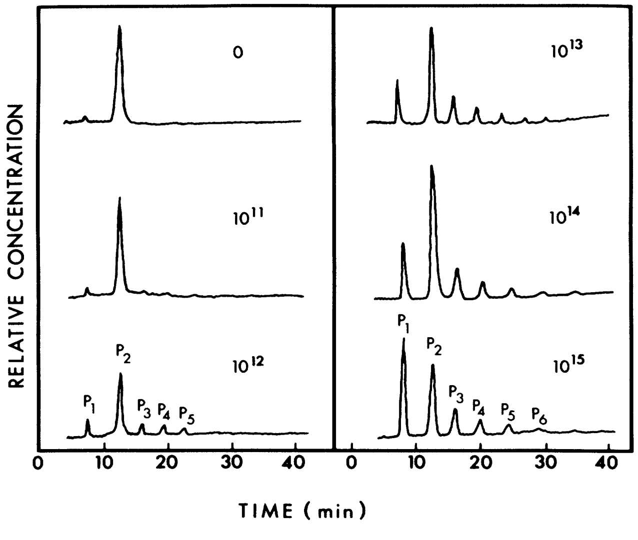

FIG. 2. Liquid chromatograms from 100-nm-thick layers on the surface of lead pyrophosphate single crystals that have been ion-implanted with various doses of Pb ranging from 10^{11} to 10^{15} ions/cm^2. The crystals were implanted with Pb^{+3} ions at 540 keV/ion with the doses indicated in the figure. The top left chromatogram was obtained from an unimplanted crystal and is shown for comparison.

presence of pyrophosphate anions in the solid crystal. This result, of course, is in agreement with the x-ray structural refinement for this material. For a relatively low lead dose of 10^{11} ions/cm^2, structural changes are already evident in the chromatogram; i.e., the concentration of P_1 is measurably larger and there is also a small but measurable amount of P_3. As the lead implant dose is further increased, the fractions of P_1 and P_3 in the surface layer increase significantly and still longer chains of phosphate anions are found. At a lead dose of about 10^{15} ions/cm^2, the chromatograms indicate that the damaged surface layer approaches a limiting amorphous structure and further increases in the implantation dose do not produce additional structural alterations.

The details of the structural evolution of the ion-damaged surface layer are illustrated in Fig. 3. Here the vertical axis corresponds to the percentage of total phosphorus present in each phosphate anion as the surface is exposed to increasing implant doses. These data provide a detailed map of the structural path followed by lead pyrophosphate as it is made amorphous with increasing doses of Pb^{3+}.

An important observation regarding the structural evolution of the ion-damaged-amorphous layer is that, regardless of the implant dose, the structure of this layer does not correspond to that of lead pyrophosphate glass prepared by thermal quenching of the melt. This point is illustrated by the data shown by the dotted lines in Fig. 3. Since it is not possible to reproduce the glass structure for any implantation dose, the ion-beam–amorphization process of lead pyrophosphate should not be viewed as equivalent to a thermal quench ($\sim 10^3$ K/sec) of the molten $Pb_2P_2O_7$ liquid.

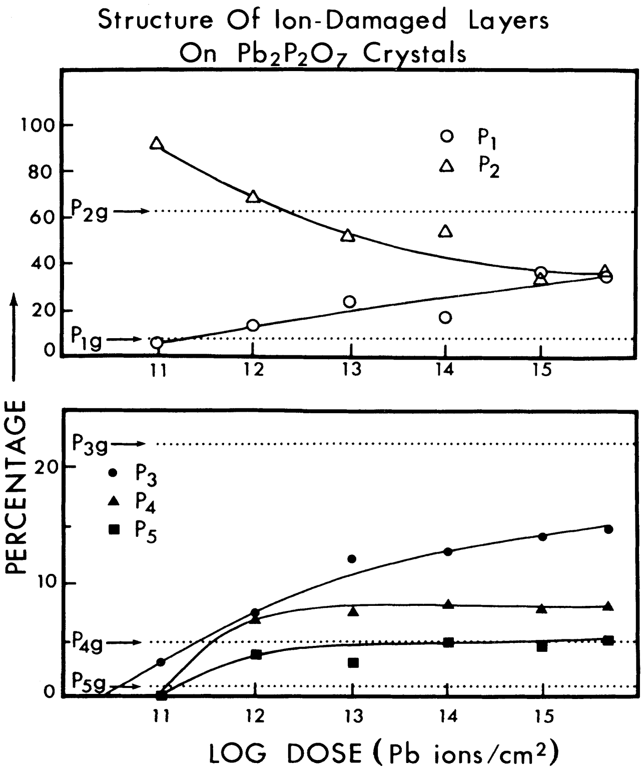

FIG. 3. The evolution with implant dose of the relative concentration of the five major phosphate anions in the ion-damaged layer. The corresponding concentrations of these same phosphate anions observed in a thermally quenched lead pyrophosphate glass are indicated by the dotted lines in the figure.

This finding differs from the results recently obtained by Lee *et al.*[11] on a different class of amorphous solids, i.e., amorphous metal alloys. Lee *et al.* used x-ray diffraction to show that the local atomic order was the same in amorphous Cu-Zr alloys regardless of whether the alloy was made amorphous by melt spinning, mechanical alloying, or irradiation by 2-MeV protons. Although the HPLC technique is more sensitive to intermediate-range order than is x-ray diffraction, the results of Lee *et al.* and those reported here clearly illustrate the danger of generalizing the properties found for a particular amorphous material to all classes of amorphous solids.

The mechanism by which longer phosphate anions are produced by ion implantation is not understood at this time. A relevant observation, however, is that for all except the highest implant doses, the average chain length of the phosphate anions in the damaged layers (as determined from the data in Fig. 2) remains near 1.95. If a very simple ionic model is assumed for an amorphous phosphate solid in which the charge on the phosphate chains is balanced by the charge on the metal cations, it is clear that for $Pb_2P_2O_7$ to remain a charge-neutral material, the average chain length must remain very near 2. In the ionic model, each phosphate chain of length n has a charge of $n+2$. It is easy to visualize why substantial amounts of P_1 are created in the implantation process since the 540-keV lead ion can easily sever any chemical bond including the bond between the two tetrahedra in a pyrophosphate anion. If, however, large amounts of P_1 are created without the formation of longer chains, then a substantial buildup of charge in the solid would occur. It may be this charge buildup that supplies the necessary energy for the formation of the observed longer chains. For those layers with very high Pb implant doses, the same basic argument holds—but the increase in the lead concentration (up to 4%) in the implant layer lowers the average chain length expected for the charge-neutral solid to about 1.8 rather than 2 (as is experimentally observed). For lead pyrophosphate glass, the average chain length is very near 2 (2 ± 0.02), and so for this material, formal charge neutrality is also preserved.

In summarizing, these results show that in the case of lead pyrophosphate, the amorphous ion-damage-produced state and glass state are structurally inequivalent—regardless of the implant dose. This finding indicates that for this material the ion-damage process should not be viewed as a mechanism that is equivalent to melting the material followed by a thermal quench of the molten liquid at rates in the range of $\sim 10^3$ K/sec.

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[1] J. R. Van Wazer, *Phosphorus and Its Compounds: Chemistry* (Interscience, New York, 1958), Vol. 1, Chap. 12.

[2] A. E. R. Westman and P. A. Gartaganis, J. Am. Ceram. Soc. **40**, 293 (1957).

[3] T. R. Meadowcroft and F. D. Richardson, Trans. Faraday Soc. **61**, 54 (1965).

[4] E. Thilo, Angew. Chem. Int. Ed. Eng. **4**, 1061 (1965).

[5] B. C. Sales, R. S. Ramsey, J. B. Bates, and L. A. Boatner, J. Non-Cryst. Solids **87**, 137 (1986).

[6] R. S. Brazell, R. W. Holmberg, and J. H. Moneyhun, J. Chromatogr. **290**, 163 (1984).

[7] B. C. Sales, J. O. Ramey, and L. A. Boatner, Phys. Rev. Lett. **59**, 1718 (1987).

[8] D. F. Mullica, H. O. Perkins, D. A. Grossie, L. A. Boatner, and B. C. Sales, J. Solid State Chem. **62**, 271 (1986).

[9] G. Carter and J. S. Colligon, *Ion Bombardment of Solids* (Elsevier, New York, 1968).

[10] L. A. Boatner and S. P. Withrow (unpublished).

[11] D. Lee, J. Cheng, M. Yuan, C. N. J. Wagner, and A. R. Ardell, J. Appl. Phys. **64**, 4772 (1988).