

Pressure-induced transformations in palmierite-type $\text{Pb}_3(\text{P}_{1-x}\text{As}_x\text{O}_4)_2$: An X-ray single crystal study

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Lead phosphate-arsenate solid solutions of the palmierite structure type are improper ferroelastics. Similar to complex perovskite-type relaxor ferroelectrics, ferroic nanoregions occur at temperatures well above the temperature of macroscopic para-to-ferroelastic $R\bar{3}m$ to $C2/c$ phase transition and they give rise to a specific pattern of diffuse diffraction maxima at positions forbidden by the symmetry of the paraelectric phase, but allowed in the ferroelastic phase. The diffuse maxima have therefore been interpreted as arising from nanoregions whose local structure resembles that of the ferroelastic phase. The nanoregions are purely dynamic in pure lead phosphate, but have a static component once the material is doped with As. Further, our recent temperature-dependent Raman scattering investigation on mixed crystals [1] showed that, for intermediate compositions, this material exhibits a multi-step phase transformation with two well-separated characteristic temperatures of transformation for the arsenate and phosphate complexes; ‘two-mode behaviour’. On cooling, the PO_4 tetrahedra remain dynamically disordered until the macroscopically determined phase transition temperature T_c , while the AsO_4 tetrahedra become ferroelastically distorted well above T_c . The same symmetry change is known to occur in pure $\text{Pb}_3(\text{PO}_4)_2$ at pressures of ~ 1.9 GPa [2,3], but the diffuse scattering has not been characterised in detail, and it has not been measured at high pressures for members of the solid solution. We have now performed high-pressure single-crystal X-ray diffraction measurements on samples of two critical compositions, $\text{Pb}_3(\text{PO}_4)_2$ and $\text{Pb}_3(\text{P}_{0.2}\text{As}_{0.8}\text{O}_4)_2$ (designated “As80”) at the DESY/HASYLAB F1 beam line to determine the high-pressure transition behaviour and to compare it to the high-temperature behaviour.

Crystal plates, formed by the dominant $(001)_{\text{trigonal}} = (100)_{\text{monoclinic}}$ cleavage, less than $15 \mu\text{m}$ thick to overcome the severe absorption, and less than $100 \mu\text{m}$ across, were loaded in diamond-anvil cells of the Boehler-Almax design. This design has the anvils supported by tungsten carbide seats that do not contribute to the background scattering in diffraction patterns, and therefore allow weak diffuse scattering from the sample to be measured. A 4:1 methanol-ethanol mixture was used as a pressure-transmitting medium to ensure hydrostatic conditions, as the ferroelastic transition is very sensitive to applied shear stress. Data were collected with a monochromatic beam of $\lambda = 0.5000 \text{ \AA}$, and a MarCCD 165 detector at a sample-to-detector distance of 100 mm with a step width of 1° and 40 frames per measurement, and an exposure time of 120 s per frame. As the diffuse scattering became weaker at higher pressures, the exposure time was increased up to a maximum of 480 s per frame. The pressure was determined by the ruby-line luminescence method. Reciprocal-space sections were reconstructed by importing the raw data frames into the CRYDALISTM software from Agilent Technologies.

The structure of these compounds consists of composite layers of PO_4 and AsO_4 tetrahedra whose oxygen atoms provide octahedral coordination for Pb1 sites within the layers. The composite layers of Pb1 and tetrahedra alternate with double layers of Pb2 sites. In the aristotype phase with $R\bar{3}m$ symmetry both Pb atoms in principle should occupy high-symmetry fixed positions with site symmetry $\bar{3}m$ for Pb1 and $3m$ for Pb2. At room conditions, both samples are in the ferroelastic monoclinic phase with $C2/c$ symmetry, in which the both Pb atoms are displaced within their layers, and the tetrahedra are rotated and tilted. The diffraction patterns of both samples measured in the DAC at pressures below the ferroelastic phase transition show two classes of peaks. Weak super-lattice peaks indexed with $k + l = 2n + 1$ on the monoclinic unit cell contain only contributions from a single domain, and are therefore sharp. The much stronger main Bragg peaks with indices $k + l = 2n$ are broadened because they contain contributions from two or all three domain orientations that arise from the $R\bar{3}m$ to $C2/c$ symmetry reduction.

Previous diffraction measurements have shown that the pure phosphate sample undergoes the $C2/c$ to $R\bar{3}m$ phase transition at 1.9 GPa, as indicated by optical observation and precise unit-cell parameter measurements [2]. The new data collected at F1 show that the weak superlattice peaks remain sharp below the phase transition pressure; therefore there is no significant development of structural disorder prior to the macroscopic phase transition. This conclusion is supported by our complimentary Raman measurements that show that the local structural distortions of the tetrahedra, as measured by the splitting of PO_4 bending modes, exhibit exactly the same second-order behaviour as the spontaneous strain. The superlattice diffraction peaks become diffuse above the transition pressure, indicating local disorder in the structure.

Previous structure determinations by neutron diffraction showed that this is due to the local displacements of Pb2 atoms within the structure from their high-symmetry positions in the $R\bar{3}m$ phase [3]. The diffuse scattering persists up until the pressure (3.0 – 3.5 GPa) at which neutron diffraction showed that the displacements of the Pb2 are completely suppressed. We can therefore conclude that the diffuse scattering arises in pure Pb phosphate from the same type of ferroic nanoregions that are present at high temperature.

The phase transition pressure of the As80 sample is reduced to ~1 GPa, but otherwise the diffraction patterns at high pressures show the same basic behaviour as that of the pure phosphate (Fig. 1). Below the transition the superlattice reflections are sharp, and they become diffuse above the transition and gradually decrease in intensity until at 2.9 GPa they were no longer detectable even with the longest exposures possible. In contrast to the high-pressure behaviour of the pure phosphate, but exactly analogous to the high-temperature behaviour of As80 [1], Raman spectra show splitting of the AsO₄ bending modes far above the transition.

In general, the new diffuse scattering and complimentary Raman measurements indicate that at the atomic structural level, the high-pressure behaviour is very similar to that at high temperatures. In pure phosphate, the distortions of the PO₄ tetrahedra follow the overall macroscopic behaviour of the material, and the diffuse scattering in the paraelastic phase is due to ferroic nanoregions defined by the correlated displacements of Pb2 atoms. In As80, the nanoregions involve not only Pb2 displacements but distortions of the AsO₄ tetrahedra. This clearly shows that the 2-mode behaviour apparent at high temperatures also occurs at high pressures in lead phosphate-arsenate solid solutions of the palmierite structure type

The new experimental data also revealed a new phase transition in both materials at higher pressures that is unrelated to the ferroelastic phase transition. A full characterisation of this previously unreported transition requires further work.

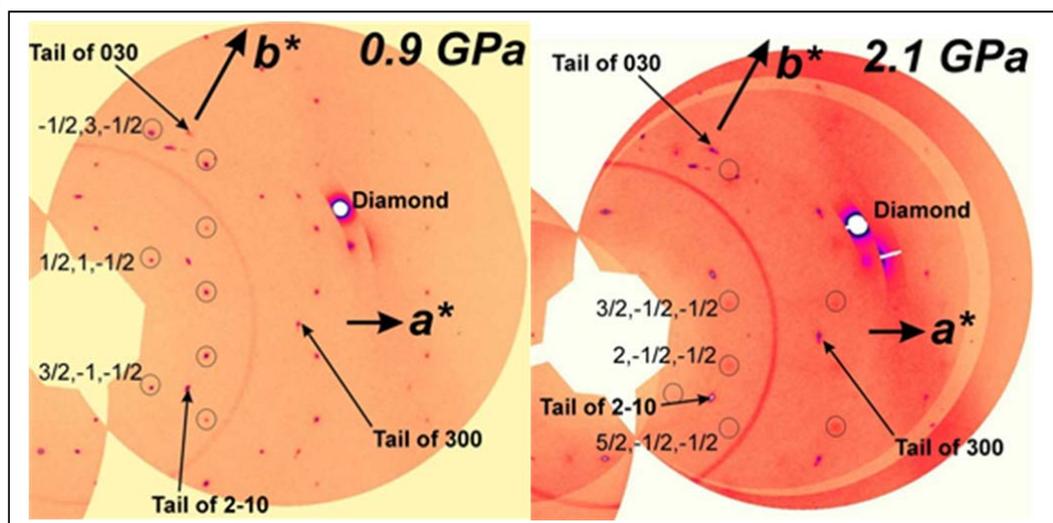


Fig 1. Reciprocal-space-layer sections $hk\ 1/2$ reconstructed in $R\bar{3}m$ from synchrotron single-crystal X-ray diffraction data of the As80 sample at P=0.9 (120 s /frame) and 2.1 GPa (480 s /frame). Positions of some super-lattice spots that occur in triplets around the tails of Bragg spots are indicated by circles. At 0.9 GPa, just below the macroscopic ferroelastic phase transition, the superlattice spots are allowed by the $C2/c$ symmetry and are strong and sharp. At 2.1 GPa, more than 1 GPa above the transition, these superlattice spots are forbidden by the $R\bar{3}m$ symmetry, but some are still present as diffuse maxima. This indicates that the structure still contains nanoregions with local distortions with the monoclinic pattern.

Acknowledgements

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References

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