

Composition- and temperature-dependent diffraction study of palmierite-type $\text{Pb}_3(\text{P}_x\text{V}_{1-x}\text{O}_4)_2$

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Pure palmierite-type lead-orthophosphate has been extensively studied as model system for discontinuous improper ferroelastic phase transitions. With increasing impurity contents, kation- and anion-diluted crystals usually show drastic renormalization effects of the transition temperature, a change to continuous transition behaviour and the stabilization of precursor-clusters above the critical temperature [1, 2].

The system $\text{Pb}_3(\text{P}_x\text{V}_{1-x}\text{O}_4)_2$ has been studied by powder diffraction (neutron, X-ray), spectroscopical and dielectric methods [3, 4]. In comparison to pure lead-orthophosphate, it displays a complex sequence of composition- and temperature-dependent phase transitions. Phosphorus-rich crystals ($x > 0.7$) show a phase transition from a paraelastic high-temperature phase with symmetry R-3m to a ferroelastic phase with space group A2/a (C2/c). Evidence for a further transition was found using Raman-spectroscopy [1]. Vanadium-rich crystals ($x \neq 0.3$) undergo a sequence of phase transitions from a paraelastic-paraelectric phase (R-3m) across a ferroelastic-antiferroelectric phase with symmetry $\text{P}2_1/\text{c}$ to a ferroelastic-ferroelectric low-temperature phase α ($\text{P}2_1$). Moreover, an intermediate phase with symmetry A2/a exists between γ and β .

Temperature-dependent single crystal studies of selected chemical compositions ($x=0.7, 0.6, 0.3$) were done at beamline F1 (HASYLAB/DESY) using a wavelength of 0.71 Å (sample-detector distance: 40 mm) and an on-line CCD-detector system. Room temperature studies were performed for all three compositions. Low-temperature data were collected with a $\text{N}_2(1)$ -cryostat for $x=0.7$ (280 K, 265 K, 240 K, 175 K) and $x=0.3$ (175 K). The measurements were carried out using omega-scans with a step width of 0.1° in different phi- and chi-positions up to a resolution of 0.52 \AA^{-1} . Scans which showed diffuse intensities above T_c were collected at least twice to avoid oversaturation of strong Bragg-reflections at longer exposure times. Each data set was subsequently scaled against the primary beam intensity, corrected for sample external scattering (background frames) and identical scans were finally added up to give overall exposure times between 10 sec above T_c and 5 sec below T_c .

The CCD-data of samples with $x=0.7$ show an overall rhombohedral symmetry of the paraelastic high-temperature phase, however broad diffuse intensities are clearly visible even 40 K above T_c (ca. 260 K) (Figure 1). A similar effect can be observed for samples with composition $x=0.3$. For a detailed characterisation of the diffuse scattering, selected reciprocal regions were reconstructed from pre-processed raw data. Reconstructed reciprocal areas around $(-1 \ 2 \ 12)$ for samples with $x=0.7$ are shown in figure 2 as a function of temperature. Above T_c the diffuse maxima are centered around symmetry-allowed Bragg-reflections of the paraelastic HT-phase and must be indexed by half integers. The diffuse scattering shows a slight anisotropic spatial distribution in reciprocal space with an elongation along a^* , indicating a higher degree of disorder along $[111]_{\text{rh}}$. On cooling from room temperature to 265 K the diffuse scattering maxima sharpen slightly with an accompanied increase in intensity. This effect results from small (ca. 50 Å), dynamic precursor-clusters of the monoclinic ferroelastic LT-phase in an overall paraelastic matrix. The trigonal arrangement around the rhombohedral reflections corresponds to a set of three orientational states of displaced Pb-atoms along the monoclinic axis, separated by 120° between the individual precursor-clusters. On further cooling to 245 K, below the ferroelastic transition point, the trigonal symmetry of the matrix is broken, a preferential orientation of the binary axis is chosen and the diffuse maxima above T_c become Bragg reflections of static ferroelastic domains. Reconstructed reciprocal images at 175 K show a further splitting of Bragg reflections. This effect is caused by an additional phase transition which has only been found by Raman-spectroscopical methods till now.

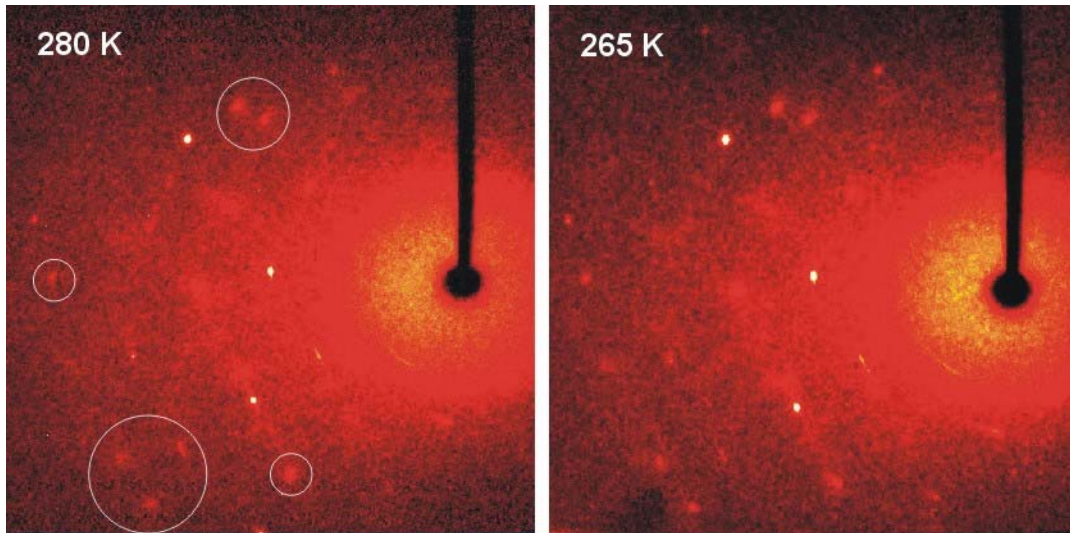


Figure 1: CCD-frames of a sample with composition $x=0.7$ at 280 K and 265 K. Selected precursor-induced diffuse intensities encircled in left image.

Figure 2: Temperature-dependent reconstructed reciprocal maps around $(-1\ 2\ 12)_{\text{th}}$. From left to right: 280 K, 265 K, 245 K, 175 K

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References

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