High-pressure phase of $LaPO_4$ solved with single crystal x-ray diffraction

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With a high refractive index and low shear moduli, $LaPO_4$ monazite has a great potential as a host material for solid state lasers [1] and is a promising candidate as oxidation-resistant layer in ceramic composites [2, 3]. In addition, due to the crystal-chemical similarity between lanthanide and actinide elements, it is being intensively investigated for its use in the conditioning of radioactive waste [4]. One of the fundamental properties of lanthanide orthophosphates that is still not completely understood is their stability at extreme conditions. While a significant effort has been invested in the high-pressure study of orthophosphates with zircon-type structure ($I4_1/amd$), in monazite-type ($P2_1/n$) orthophosphates their lower symmetry and higher stability with respect to increasing pressure has limited the number of high-pressure structural studies to just one powder x-ray diffraction study [5]. Lacomba-Perales et al. [5] have shown that $LaPO_4$ undergoes a structural phase transition to an orthorhombic phase (proposed to be a barite-type structure with space group *Pnma*) at around 26 GPa and also that within the lanthanide orthophosphates $LaPO_4$ is the one with the lowest phase transition pressure. Solving the high-pressure phase of $LaPO_4$ would therefore provide insight into the pressure behavior of the family of monazite orthophosphates and is the goal of the present study.

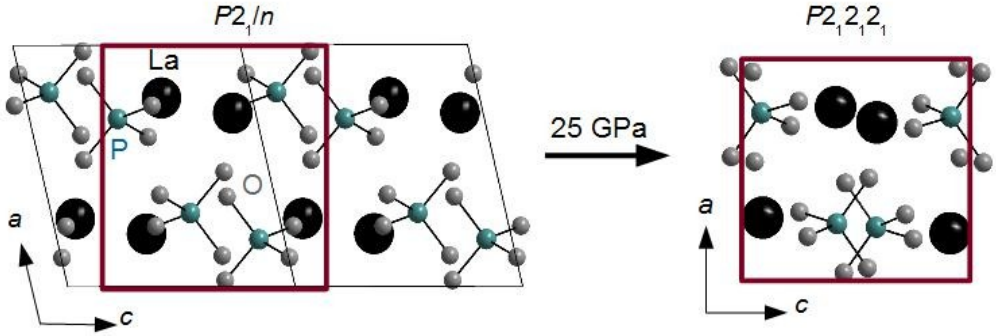

Figure 1. Projections along the [010] direction of the monazite-type structure (left) and of the post-barite-type structure (right) of $LaPO_4$ as derived from our experiments at 27 GPa. Comparable sections of the crystal structures are highlighted in red.

Single-crystal *x*-ray diffraction experiments of $LaPO_4$ have been performed at different pressures up to 31 GPa at the P02.2 Extreme Conditions Beamline at PETRA III (DESY, Hamburg). We have found that $LaPO_4$ transforms at 26 GPa from the monazite-type structure to an orthorhombic structure in good agreement with Ref. 5. However, our structural solution has shown that instead of a centrosymmetric barite-type structure, the high-pressure phase of $LaPO_4$ is an acentric structure similar to the post-barite structure proposed by Santamaría-Pérez et al. for $BaSO_4$ [6]. The acentricity of the high-pressure phase of $LaPO_4$ has been proven by second harmonic generation (SHG) experiments, which show the emergence of SHG above 25 GPa. *Ab*

initio calculations confirm the structural phase transition from the monazite-type to the post-barite-type structure at 21 GPa in $LaPO_4$. However, the calculations also predict an additional phase transition at 10 GPa to a barite-type structure not observed experimentally.

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