Experimental report

14/03/2025

Proposal: **5-24-702** **Council:** 10/2022

Title: Pressure studies of the structuralphase transition in ß-PbO2

Research area: Physics

This proposal is a new proposal

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Samples: PbO2

Instrument	Requested days	Allocated days	From	To
D20	3	2	07/06/2023	09/06/2023

Abstract:

We propose to revisit the pressure dependence of the structural transition in ß-PbO2. Recent experimental results obtained at D2B [Phys Rev. BB 103, 064109 (2021)] and recent DFT calculations show an unusual scenario of the pressure induced structure changes of ß-PbO2.

In earlier works the tetragonal (sp. gr. P4_2/mnm) crystal structure of beta-PbO2 at ambient conditions changed to an orthorhombic CaCl2-type (Pnnm) above 4GPa. Recent measurements at D2B show that at ambient conditions the crystal structure of beta-PbO2 is orthorhombic (CaCl2-type) with a small degree of distortion.

DFT calculations of the crystal structure of ß-PbO2 and SnO2 were done as a function of pressure with Quantum Espresso software by using the Perdew-Zunger potential. The orthorhombic deformation parameter r(ab)=2(a-b)/(a+b) is constant (and positive) below 2GPa, then it crosses zero near 5GPa. Similar calculations for SnO2 show a gradual increase of r(ab) without any change of sign. We would like to study this transition in ß-PbO2 with small steps of pressure between 0 and 7 GPa at D20. This experiment can provide new information about the electronic and elastic properties of rutile-type dioxides.

In this study we have used one commercial powder sample of rutile-type β-PbO_2 provided by Acros, Lot A0414657 which was studied as sample S1 in [1]. Neutron powder diffraction (NPD) patterns were measured by using the instrument D20 at ILL Grenoble. The powder β-PbO_2 sample was kept at RT and the pressure was applied in a Paris Edinburg pressure cell. The Ti-Zr encapsulating gasket was filled with the β-PbO_2 powder sample mixed with a pressure transmitting medium, i.e. a deuterated 4:1 methanol-etahanol mixture. In order to improve the statistical accuracy of our NPD patterns we have not added any pressure calibrant. We used the $V(p)$ relation determined in earlier β-PbO_2 XRD pressure studies [2]. The measurements were done at increasing pressure values: 0; 0.5; 1.5; 2.8; 4.8 and 6.0 GPa. The NPD measurements were done at two wavelengths 1.543 Å and 2.417 Å. The wavelengths values were adjusted by using the results of our earlier NPD measurements with the same β-PbO_2 sample at ambient conditions using D2B at ILL [1]. Due to geometric limitations of the pressure cell useful NPD patterns could be measured for $10^\circ \leq 2\theta \leq 115^\circ$, where 2θ is the scattering angle.

The NPD and XRD patterns were analyzed using two methods. First by fitting pseudo-Voigt functions to individual Bragg peaks in order to obtain their 2-theta positions, intensities and peakwidths. Second by Rietveld analysis [3] of the whole NPD patterns by using Jana2006 software [4]. The fits with the tetragonal model of β-PbO_2 were of much worse quality so the $CaCl_2$-type orthorhombic structure (space group $Pnnm$) was assumed. Due to the limited 2-theta range in the pressure experiment only isotropic atomic displacements factors U_{iso}^{Pb} and U_{iso}^{O} were used. The pressure dependence of the orthorhombic unit cell constants and unit cell volume is given in Fig. 1.

Earlier PbO_2 x-ray powder diffraction pressure studies [2] reported the rutile-to-$CaCl_2$ transition at 3.8 GPa, while present results suggest an orthorhombic structure at ambient pressure. The results of the present study between 4 and 6 GPa agree with those from [2]. Based on previous studies on rutile-type materials using a Landau approach, r_{ab} should couple to thermodynamic variables T and P (and stress). In the case of a second-order transition, the square of r_{ab} exhibits a linear dependence on T or P, see e.g. NiF_2[5]. β-PbO_2 is different in that significant anisotropic peak broadening is present at ambient P and T indicating the presence of orthorhombic microstrain. On pressure increase, coupling to P is weak and then is close to linear between 2.8 and 6.0 GPa.

The integral breadths observed with NPD show a characteristic broadening of the peaks

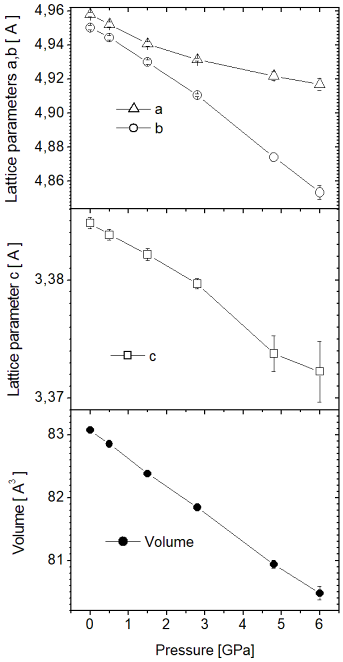

FIG. 1. Pressure dependence of the orthorhombic unit cell constants a, b (upper panel), c (middle panel) and unit cell volume (lower panel) determined by Rietveld analysis of NPD patterns for rutile-type β-PbO$_2$ at neutron wavelength of 1.543 Å, see text.

with $h \neq k$ while peaks with $h = k$ remain narrow even at high pressures as shown by NPD patterns in Fig. 2. The $h \neq k$ peaks (210) and (211) get broadened by $\sim 30\%$ between 0 and 2.8 GPa while the (111) and (220) peaks only by $\sim 5\%$.

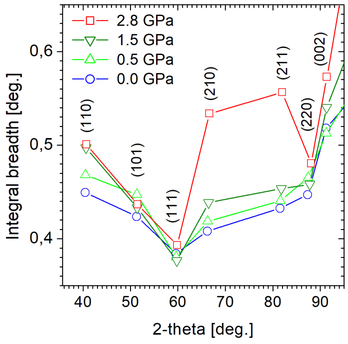

FIG. 2. Integral breadths of selected Bragg peaks obtained from NPD patterns of β-PbO$_2$ obtained at different pressures using neutron wavelength 2.417 Å. At each pressure there is a characteristic hkl-dependent broadening indicating the orthorhombic symmetry.

ACKNOWLEDGMENTS

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