Experimental report

03/09/2022

Proposal: 5-23-747 **Council:** 4/2020

Title: Symmetry of the topological semimetal phase in beta-PbO2: neutron diffraction study

Research area: Physics

This proposal is a new proposal

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Samples: PbO2

Instrument	Requested days	Allocated days	From	To
D2B	1	1	15/02/2021	16/02/2021

Abstract:

Recent DFT studies discussed the possibility of a topological Dirac semimetal phase in beta-PbO2. The rutile-type crystal structure of beta-PbO2 is tetragonal (P42/mnm). Recent studies [4] suggest the existence of an orthorhombic (Pnnm) structure also.

The tetragonal beta-PbO2 structure can host a 3-dimensional topological Dirac semimetal phase while the orthorhombic structure can be only a topological insulator as shown by symmetry analysis and DFT calculations. The crutial difference is due to the presence of the symmetry operation {4001|¿,¿,¿}(fourfold rotation about [001] and translation by ¿,¿,¿) in the space group. This operation is present in the tetragonal phase and absent in the orthorhombic phase. DFT calculation presented in recent papers lead to different conclusions about the crystal structure and the electronic properties of beta-PbO2. Chen et al. suggest a topological phase transition with the orthorhombic phase below 200K and the tetragonal one above 200K. On the other hand Peng et al. suggest a stable tetragonal structure at all temperatures. These contradicting views can be elucidated by neutron diffraction.

The results of the proposal 5-23-747 have been published in Phys Rev. B103, 064109 (2021). Please find below a brief summary with the main conclusions.

Orthorhombic symmetry and anisotropic properties of β-PbO_2

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The structural and electronic properties of the rutile-type oxide β-PbO_2 (plattnerite) are studied by neutron and synchrotron radiation diffraction and first-principles density functional theory (DFT) calculations. Both diffraction measurements and DFT calculations show that β-PbO_2 has a $CaCl_2$-type orthorhombic structure (space group *Pnnm*) instead of the widely accepted β-PbO_2 rutile-type tetragonal structure (space group $P4_2/mnm$). This symmetry lowering in β-PbO_2 is a robust effect observed at ambient pressure at temperatures between 100 and 400 K. The orthorhombic symmetry rules out the possibility of a semimetallic symmetry-protected state in β-PbO_2. Both diffraction measurements and DFT calculations show an anisotropy of thermal expansion, atomic vibrations, and elastic constants of β-PbO_2 along the [100] and [010] directions.

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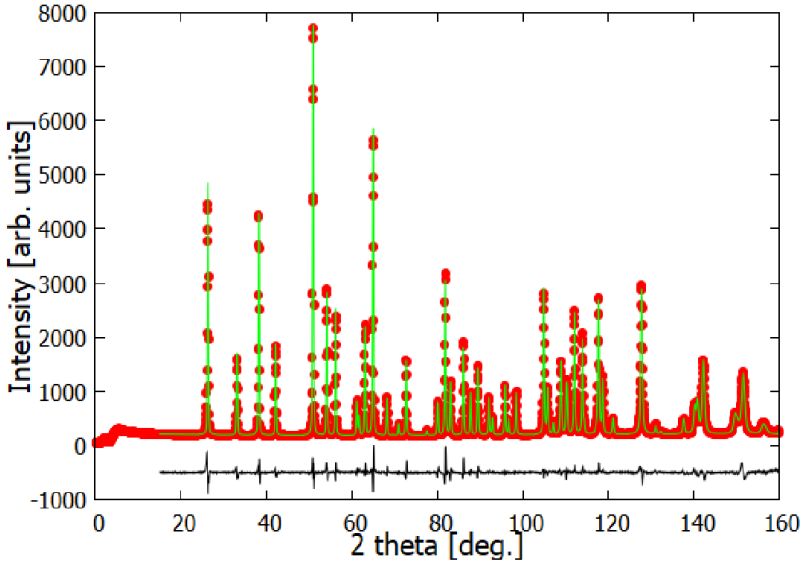

IV. CONCLUSIONS

Neutron and SR diffraction studies as well as DFT calculations demonstrate that β-PbO_2 has an orthorhombic $CaCl_2$-type structure at temperatures from 100 to 400 K. The recent DFT calculations from [4] suggesting a phase transition from the insulating low-symmetry phase to the semimetal high-symmetry phase at 200 K are not supported by our results. Our studies highlighted different thermal expansion coefficients and different anisotropic displacement parameters along the a and b directions ($a > b$) in β-PbO_2. DFT calculated frequencies of the Raman active phonon modes agree with the experimental results from [57]. Calculations evidence that β-PbO_2 is softer in the b direction than in the a direction ($a > b$) as $C_{11} > C_{22}$. This result is also consistent with the larger thermal expansion along b axis than along the a axis and the anisotropic displacement parameters being larger in the b direction than in the a direction (U_{22}[Pb] > U_{11}[Pb]). From these observations one can expect the anisotropy of other physical properties of β-PbO_2, e.g., thermal and ionic conductivity and the hydrogen diffusion process. It is also possible to expect similar anisotropic properties of other rutile-type systems, e.g., β-MnO_2 and MnF_2 [33].