Experimental report

01/11/2022

Proposal: 1-10-47 **Council:** 4/2020

Title: Improved sample environment for insitu neutron powder diffraction: Temperature calibration and simultaneous Raman spectroscopy

Research area: Chemistry

This proposal is a new proposal

Main proposer: Raphael FINGER

Experimental team: Thomas HANSEN

Local contacts: Thomas HANSEN

Samples: Si
Pd
PbSO4

Instrument	Requested days	Allocated days	From	To
D20	2	2	05/06/2021	07/06/2021

Abstract:

Solid gas reactions are getting high attention due to far-reaching applications, e. g. the synthesis of functional materials and gas storage. A sapphire single-crystal gas pressure cell has been developed and used successfully for the study of hydrogenation reactions and pathways.

To maximize data quality and sample temperatures, thinner walled sample holder will be tested, reducing the contribution to the diffraction data and allowing a higher heating efficiency. Further, newly developed and validated gas pressure cells will be calibrated for the sample temperature with Pd and Si powder using a new pyrometer.

Additionally, simultaneous in situ Raman spectroscopy should be coupled with in situ neutron diffraction, using sapphire single-crystal gas pressure cells. This offers a complementary technique to in situ neutron diffraction, helping distinguish functional groups in crystal structures, e.g. OH-, NH2-, NH2-. Further, amorphous intermediate phases could be characterised, enabling new science. The proposed coupling has the advantage of probing exactly the same state of matter, instead of performing two different measurements.

Improved sample environment for *in situ* neutron powder diffraction using sapphire single-crystal cells: Temperature calibration and simultaneous Raman spectroscopy (experiment 1-10-47)

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Objectives

The first aim of this study was to test new gas-pressure cell designs for *in situ* neutron powder diffraction investigations for solid-gas reaction, especially their temperature calibration. The second aim was to develop methods for simultaneous neutron powder diffraction and Raman spectroscopic investigations using gas-pressure cells.

Experimental Details

All experiments were conducted at D20 (λ = 187 pm) by Dr. Thomas C. Hansen (ILL). Due to COVID-19 regulation user access was restricted. Because of this, the originally planned calibrations using laser heating were not performed and the first aim (see above) was abandoned.

Results and Discussion

$PbSO_4$ was used as a test material for the simultaneous neutron powder diffraction and Raman spectroscopic measurements. Issues with γ radiation produced by the neutron beam had to be resolved by proper shielding of the Raman spectrometer in order to avoid artefacts. $PbSO_4$ powder was filled into the sapphire single-crystal holder of a user supplied gas-pressure cell [1], which was mounted on the neutron diffractometer D20. Raman spectra were recorded with a portable spectrometer QEPRO (Ocean Optics, Germany) equipped with a Hamatsu CCD array detector. Excitation was realized with a CW diode laser with 100 mW and a wavelength of 532 nm (Innovative Photonics Solutions, United States of America). A 200 µm glass fibre connected to a heat resistant (up to 773 K) Raman probe head allowed for transmission of the 105 µm wide laser beam (divergence 15°) and collection of the scattered light. The probe head was covered with a neutron-absorbing varnish to avoid neutron activation (Fig. 1). The latter was made from gadolinium oxide powder and clear lacquer. The gas pressure cells based on sapphire single-crystals [1] proved to be well suited for both neutron diffraction and Raman spectroscopy as both simultaneous measurements yielded high quality data in accordance with literature (Fig. 1). The scientific results were published recently [2]. The complementarity of both methods will allow a complete characterization of materials and reaction pathways in *in situ* and operando measurements in the future.

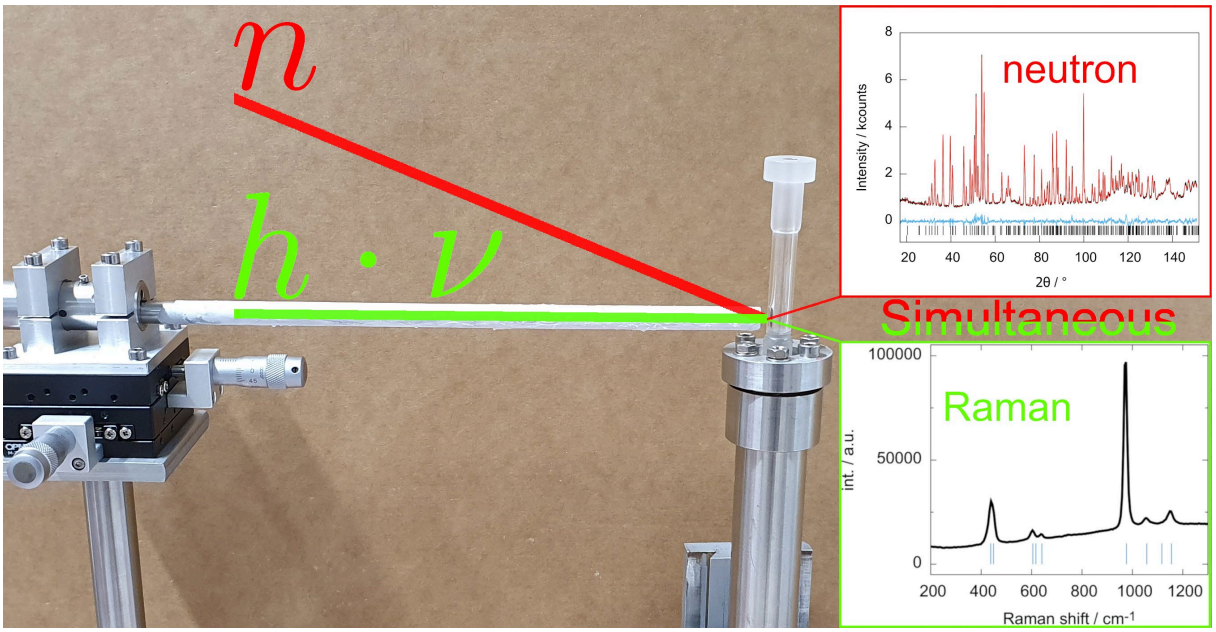

Fig. 1: Simultaneous neutron powder diffraction and Raman scattering is realized in a gas-pressure cell [1] for *in situ* measurements on D20 (data on $PbSO_4$ shown as an example).

Literature

[1] R. Finger, N. Kurtzemann, T. C. Hansen, H. Kohlmann, Design and use of a sapphire single-crystal gas-pressure cell for in situ neutron powder diffraction, *J. Appl. Crystallogr.* **2021**, *54*, 839–846; doi.org/10.1107/S1600576721002685.

[2] R. Finger, T. C. Hansen, H. Kohlmann, Simultaneous neutron powder diffraction and Raman spectroscopy – an approach of combining two complementary techniques, *Z. Kristallogr.* **2021**, *236*, 325-328; doi.org/10.1515/zkri-2021-2051.