

catalytic material under operative conditions. To recreate actual conditions in a catalytic reactor, and to be able to study many catalytic processes, require a robust and flexible system. We have developed a facility at the Swiss-Norwegian beam lines (SNBL) at the European Synchrotron radiation Facility (ESRF), where operating (flow) conditions up to 20 atm. and 900C in variable and switchable gas mixtures may be achieved. The system will be used for in situ powder diffraction as well as for XAS studies. A mass spectrometer is available for analysis of exhaust gases and a Raman spectrometer has been installed for combined in situ experiments. Results from studies of catalytic materials at operating conditions will be given.

Keywords: *in situ*, catalysis, operating conditions

## MS.18.4

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### *In situ* simultaneous Raman/XRPD study of solid-state reactions at non-ambient conditions

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Materials containing disordered moieties and/or amorphous or liquid-like phases or showing surface- or defect-related phenomena constitute a problem for their characterization using X-ray powder diffraction (XRPD), and in many cases Raman spectroscopy can provide useful complementary information. We have designed and realized a novel experimental set-up for simultaneous *in situ* Raman/High-resolution XRPD experiments to take full advantage of the complementarities of the two techniques in investigating solid-state transformations at non-ambient conditions. The invaluable added value of the proposed experiment is the perfect synchronization of the two probes with the reaction coordinate and the elimination of possible bias caused by different sample holders and conditioning modes used in *in-situ* but separate approaches. A gas blower allows studies from RT to 700K and 100K can be reached using a nitrogen cryostream. The experimental setup flexibility allows the addition of ancillary devices, such as a UV-lamp used to study photoreactivity or DAC to study high pressure regime. The set-up was tested on three solid-state transformations: i) the kinetics of the fluorene:TCNQ solid-state synthesis, ii) the thermal swelling and degradation of stearate-hydrocalcite nanocomposites, iii) the photoinduced 2+2 cyclization of (E)-furylideneoxindole. The reported experiments demonstrated that, even though the simultaneous Raman/XRPD experiment is more challenging than the separated ones, high resolution XRPD and Raman data can be collected. Concerning the obtained results, Raman gave information on surface reactivity and on flexible and disordered organic moieties hydration states while XRPD gave information on bulk properties and on stiff inorganic moieties.

Keywords: *in-situ* time-resolved powder diffraction, reaction mechanisms, raman spectroscopy

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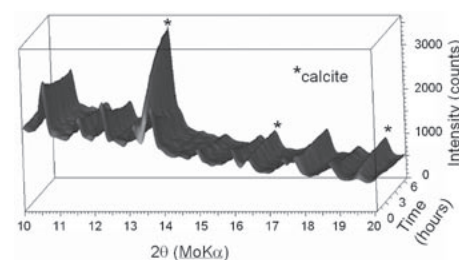
### Application of a high-pressure CO<sub>2</sub> cell to time-resolved studies with a lab powder diffractometer

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A gas-cell design for laboratory diffractometers rated to 12.4 MPa and 200 °C has been certified and constructed to the latest pressure vessel design codes [1]. The gas of interest in this case is CO<sub>2</sub> which is supercritical above 7.4 MPa and 31 °C. The temperature/pressure behaviour of CO<sub>2</sub> adds significant complications to the experimental application. The cell has been coupled with MoK $\alpha$  radiation and the Bruker Vantec PSD to enable time resolved studies to be conducted on a laboratory diffractometer. The snap-shot mode of the detector has been used to study the crystallization of poly-lactic acid (PLA) and PLA-clay composites under CO<sub>2</sub> pressure. Additionally, the carbonation of wollastonite has been studied as an initial model system for potential application to CO<sub>2</sub> sequestration studies. Given the sluggish kinetics of many sequestration reactions under milder conditions, restricted beamtime allocations at synchrotrons could be seen as a practical disadvantage for comprehensive studies versus a laboratory diffractometer.

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Keywords: gas-solid reactions, *in-situ* powder diffraction, time-resolved powder diffraction

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### Evolutionary crystal structure prediction and its applications to materials at extreme conditions

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Crystal structure prediction on the basis of just the chemical formula has long been considered a formidable or even insoluble problem. Several methods have recently been proposed to tackle this problem, among which the evolutionary algorithm USPEX (Universal Structure Predictor: Evolutionary Xtallography [1-3]) proved to be particularly efficient and reliable. Key ingredients of this method (selection, variation operators, redundancy control and constraint techniques) and its current developments will be discussed. Applications of this methods so far are quite numerous and include several technologically important systems and many materials of mainly fundamental interest (high-pressure phases of hydrogen,

nitrogen, oxygen, boron, alkali metals, calcium, CaCO<sub>3</sub> and MgCO<sub>3</sub>, CO<sub>2</sub> and CH<sub>4</sub> - [1,3-9]), some of which will be presented in this talk.

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Keywords: high pressure, phase transitions, density functional theory

## MS.19.2

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### Theoretical prediction and characterization of high pressure structures and properties of calcium

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This study employed a combination of theoretical techniques to predict the structure and properties of calcium IV and V at high pressures. Structural predictions for calcium in the pressure range 120 – 160 GPa were obtained with a genetic algorithm and with a pseudo-random search method. The X-ray diffraction pattern of the resulting structures are in excellent agreement with recent experimental results. Phonon and electron-phonon calculations were performed with plane-wave density functional methods to investigate the stabilities and potential superconductivity. The proposed structures are both found to be superconducting and the calculated T<sub>c</sub> values are close to those observed for Ca-IV and V. Theory indicates a superconducting transition at 25 K for the structures obtained in this study, in excellent agreement with experiment. Analysis of a recent theoretically predicted structure indicates that this structure may be unstable at high pressures

Keywords: *ab initio* calculations, calcium, high pressure studies

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### Polymorphism and structural phase transitions in crystals: Computer simulations by metadynamics

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The talk will present the recently developed algorithm for simulation of structural phase transitions in crystals[1,2]. The new approach is based on the general metadynamics algorithm[3] and searches for low-energy pathways leading from one crystal structure to another. It enables also simulation of complex reconstructive transitions with transformation pathways proceeding via several intermediate states, resulting in substantially improved predictive power. The applications of the algorithm will be demonstrated on several systems, with focus on silica[4] and carbon dioxide. We performed an extensive study aimed at investigation of structural transformations in silica and demonstrated that starting from  $\alpha$ -quartz it is possible to find nearly all silica polymorphs observed in the range of pressures from zero to several Mbar. We also investigate pressure-induced phase transitions of  $\alpha$ -cristobalite [5]. In carbon dioxide we study the interesting mechanisms of transformation of molecular phases to polymeric phases at high pressure. The results demonstrate that the new method is far more efficient than previous ones and for the first time the study of complex structural transformations with many intermediates is within the reach of molecular dynamics (MD) simulations.

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Keywords: polymorph prediction, structural transformations, computer simulation

## MS.19.4

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### First-principles calculations of pressure induced magnetic transition in siderite FeCO<sub>3</sub>

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Rhombohedral siderite FeCO<sub>3</sub> has been studied by using density functional theory (DFT) with the generalized gradient approximation (GGA). In order to take into account the strong on-site Coulomb interaction U present in FeCO<sub>3</sub>, we also performed the GGA + U calculations. We observed a pressure-induced magnetic transition (high spin  $\rightarrow$  low spin) at pressures of 15 GPa and 28 GPa, which were underestimated with respect to the experiment, for the GGA and GGA + U calculations, respectively. This phase transition was with a volume collapse of 10% around, also accompanied by an