

PSD Mini Symposium on

Spectroscopy and Diffraction

Tuesday, November 13, 2018

10:00 to 11:45, WBGB 019

10:00 Element specific nonlinear XUV transient grating spectroscopy

Rok Bohinc, G. Pamfilidis, F. Bencivenga, F. Capotondi, A. Simoncig, E. Pedersoli, R. Mincigrucci, C. Masciovecchio, L. Foglia, R. Cucini, T. Feuerer, A. Cannizzo, H.M. Frei, Z. Ollmann, J. Rehault, C. Milne, J. Szlachetko, A. A. Maznev, and Gregor Knopp

10:30 Amorphous calcium carbonate crystallization in air: the role of impurities

Jacinta Xto, J. Johnston, C. Borca, J.A van Bokhoven and T. Huthwelker

11:00 Coffee break

11:15 Insight in the mechanochemical synthesis and structural evolution of hybrid organic-inorganic guanidinium lead(II) iodides

Manuel Wilke, N. Casati

Element specific nonlinear XUV transient grating spectroscopy

R. Bohinc¹, G. Pamfilidis¹, F. Bencivenga², F. Capotondi², A. Simoncig², E. Pedersoli², R. Mincigrucci², C. Masciovecchio², L. Foglia², R. Cucini², T. Feuerer³, A. Cannizzo³, H.M. Frei³, Z. Ollmann³, J. Rehault⁴, C. Milne¹, J. Szlachetko¹, A. A. Maznev⁵, and Gregor Knopp¹

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Extending the methodologies of nonlinear optics to the X-ray regime is a promising and exciting avenue in the light of the recent development of X-ray free electron lasers. For the first time, space, time, and energy resolved XUV-transient grating experiments on Si_3N_4 recorded around the Si $L_{2,3}$ -edge have been realized. The observed signal decays have been assigned to ultrafast charge carrier dynamics driven by Auger recombination and electron diffusion. The increase of the XUV energy above the absorption edge resulted in a shortening of the signal decay, which could be connected to an increase in the initial charge carrier density. The possibility to combine the X-FWM approach with the atomic selectivity provided by XUV/X-ray photons may in future open up the way for a manifold of studies on ultrafast processes and correlations with chemical sensitivity.

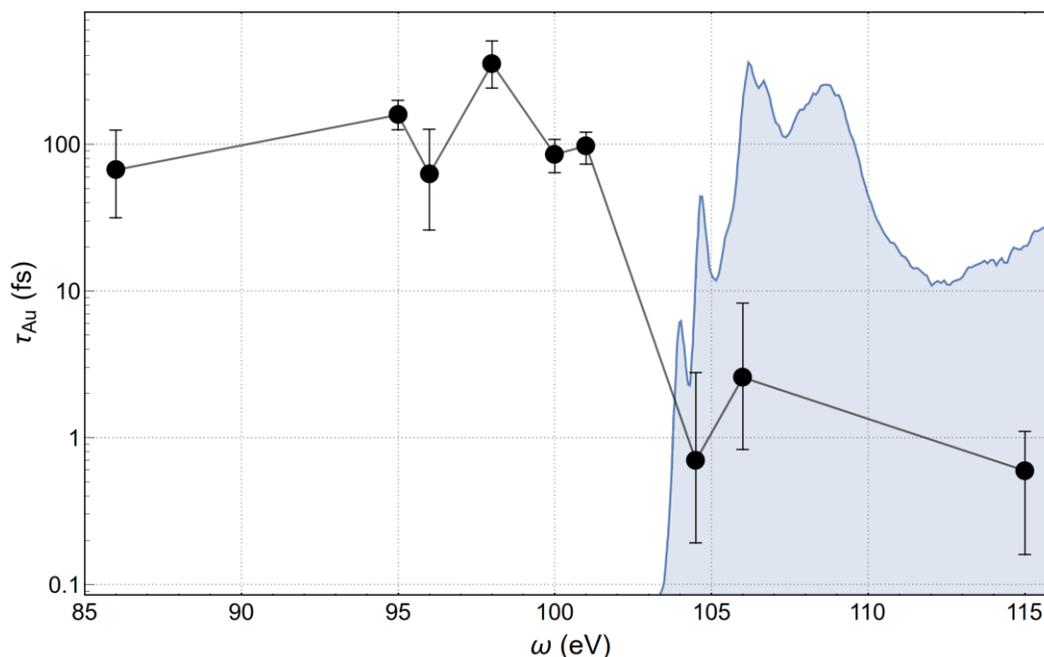


Figure 1: Fitted Auger lifetime decay (black) along with the Si $L_{2,3}$ XUV-absorption spectrum of $\gamma\text{-Si}_3\text{N}_4$ (blue).

Amorphous calcium carbonate crystallization in air: the role of impurities

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Amorphous calcium carbonate is the first solid phase that forms during the nucleation of calcium carbonate. The impeccable ability of biominerals to form functional calcium carbonate materials has been associated with their ability to control the crystallization of this amorphous phase. However, for man, this is still a huge challenge particularly because the mechanisms governing amorphous calcium carbonate crystallization are still evasive. In air, dry amorphous calcium carbonate has been found to gradually crystallize when exposed to humidity, the reason why this happens is unclear. Herein using in situ X-ray absorption spectroscopy and infrared spectroscopy we show that impurities, otherwise assumed to be spectator ions play a critical role in this process. Most salts involved in the synthesis of amorphous calcium carbonate are deliquescent and are often trapped in the ACCs owing to the very fast synthesis procedures. These trapped salts (NaCl/unreacted CaCl₂) when exposed to certain levels of humidity absorb water and dissolve, this results in a localized solution that facilitates the dissolution of ACCs and their subsequent crystallization in air.

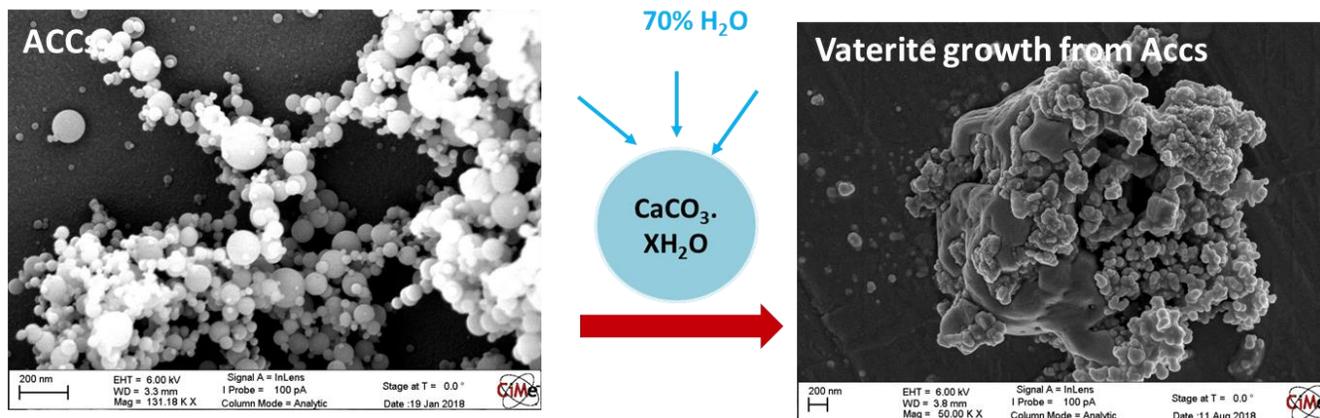


Figure 1: Amorphous calcium carbonate (ACCs) before and after exposure to humidity.

Insight in the mechanochemical synthesis and structural evolution of hybrid organic-inorganic guanidinium lead(II) iodides ¹

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Mechanochemistry is increasingly used for solid state reactions because of its advantages like high yields, high conversion rates, the easy handling, the small produce of waste and the good energy consumption, for which it belongs to green chemistry. ^{2,3} Nevertheless, the mechanisms behind mechanochemical reactions are still under investigation. Recently, setups were developed for monitoring mechanochemical reactions *in situ* using X-ray diffraction⁴, Raman spectroscopy⁵ or both combined.⁶ In all setups the originally steel made milling jar is replaced by a plastic jar.

Here we present the *in situ* investigation of the formation of a series of organic-inorganic hybrid materials from mechanochemical synthesis. The compounds are constructed by guanidinium-, lead(II)- and iodide-ions, with the formula $(C(NH_2)_3)_nPbI_{2+n}$ ($n = 1, 2, 3, 4$). For the *in situ* investigations a new setup, developed at the MS beamline is used.⁷ Due to the gained high quality data an automatic quantitative analyses of the time-resolved powder patterns was possible and revealed intermediate formations, solid-solid phase transitions and reactions between the guanidinium lead(II) iodides during the syntheses. We consider these discovered pathways to be linked to the respective structural features of the different compounds.

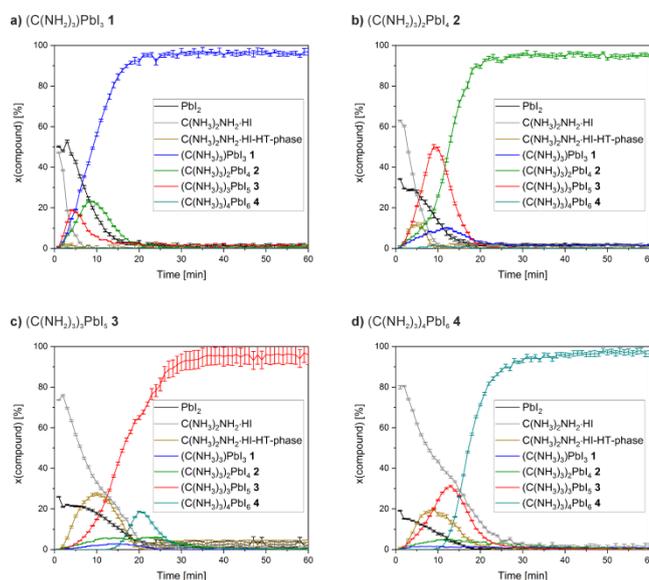


Figure 1: Time-resolved change of the amount of the given compounds for the *in situ* investigation of the synthesis of a) $(C(NH_2)_3)PbI_1$, b) $(C(NH_2)_2)_2PbI_4$ **2**, c) $(C(NH_2)_3)_3PbI_5$ **3**, and d) $(C(NH_2)_3)_4PbI_6$ **4**.

- [1] M. Wilke et al. *Chem. - Eur. J.*, **accepted**, (2018)
- [2] A. A. L. Michalchuk et al. *Crystengomm* **15**, 6403 (2013).
- [3] S. L. James et al., *Chem. Soc Rev.* **41**, 413 (2012).
- [4] T. Friscic et al., *Nat. Chem.* **5**, 66 (2013).
- [5] D. Gracin et al., *Angew. Chem. Int. Ed.* **53**, 6193 (2014).
- [6] L. Batzdorf et al., *Angew. Chem. Int. Ed.* **54** 1799 (2015).
- [7] V. Ban et al., *Anal. Chem.* **89**, 13176, (2017).