

## LOCAL AND LONG RANGE ORDERS IN TRANSITION METAL OXIDES AND SELENIDES AND METAL ORGANIC FRAMEWORKS STUDIED USING COMBINED TECHNIQUES (XRD AND IN-SITU RAMAN)

**P. Zajdel**<sup>1\*</sup>, **I. Kruk**<sup>2,3</sup>, **P.-Y. Hsieh**<sup>2,5</sup>, **W. van Beek**<sup>4</sup>, and **M.A. Green**<sup>2,5</sup>

<sup>1</sup> *Institute of Physics, University of Silesia, ul. Uniwersytecka 4, 40-007 Katowice, Poland*

<sup>2</sup> *NIST Center for Neutron Research, 100 Bureau Drive, Gaithersburg MD-20899, USA*

<sup>3</sup> *Department of Chemistry, University College of London, 20 Gordon Str, WC1H 0AJ London, UK*

<sup>4</sup> *Swiss-Norwegian Beamline, ESRF, Grenoble Cedex F-38043, France*

<sup>5</sup> *Materials Science & Engineering, University of Maryland, College Park MD-20742-6033, USA*

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*\*) e-mail: pawel.zajdel@us.edu.pl*

Constant development of synchrotron radiation sources opens up new avenues in investigation of local and long range structure of materials. On one side, it improves already existing techniques like powder diffraction (XRD) by increasing their angular and time resolutions. On the other hand, the increased signal to noise ratio allows to extract new useful information from the same data, like the Pair Distribution Function (PDF) encoded in the background of XRD.

Unfortunately, the long time needed for such „one-shot” experiments makes them unusable for regular use. The solution to this problem is the use of combined techniques to obtain the equivalent information in a shorter time, while maintaining the correlation between the studied properties and the external stimulus like the temperature or pressure.

While the XRD remains the method of choice for the long range structure, the local properties can be obtained using different techniques with Extended X-Ray Absorption Fine Structure (EXAFS) being the prominent example. However, when light elements (C, N, O, H) are involved, Raman spectroscopy is more advantageous.

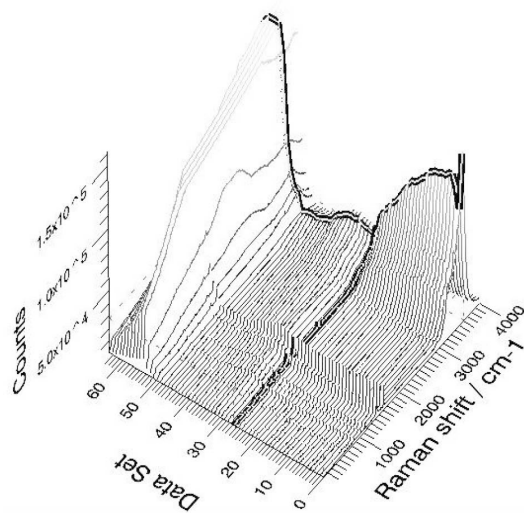


Figure 1. Evolution of Raman signal on heating up of holmium based MOF. The dark strips mark point where the first solvent molecule is lost. The sudden increase of signal at dataset 60 is due to decomposition of the compound.

The presentation will include results obtained for 3 classes of materials: seleno-spinels ( $\text{ZnCr}_2\text{Se}_4$ ), transition metal (TM) oxides and metal-organic frameworks (MOF). In particular, MOFs recently fueled rapid development of these combined techniques due to their possible applications as a storage material for use in the hydrogen based economy.

Research was conducted at the ESRF beamline BM1 (Swiss-Norwegian Beamline) [1] and consisted of simultaneous measurements of XRD and Raman spectra in the temperature range from 90 K to 700 K as well as under the gas pressure up to 20 bar.

For the chalcogenides and oxides we have searched for the signature of local deformations happening at temperatures higher than the critical temperature of the long range structural transition. In the case of oxides the distortions were expected to appear due to Jahn-Teller effect, for selenides due to possible magnetostriction.

For the metal-organic materials the research aimed at finding the correlation between structural properties of the host framework and the amount of the guest species adsorbed inside it as function of the temperature and pressure.

In the first part the as-synthesized MOF was heated up in order to empty up the structure from the solvents used during the synthesis (Fig. 1). Here, Raman spectroscopy was used to monitor the disappearance of the signal from guest molecule and host-guest interactions. Such approach is much superior than the usual two step, „off-line” technique, when material is desolvated separately at high temperature, then transferred to different place where the XRD study is made at (usually) different temperature.

In the next step, while different gases were introduced to the empty system, the Raman spectra was used to monitor the interactions between host and the adsorbed gas while XRD patterns are used to verify the position of adsorption sites.

Additionally the time resolution of the order of minutes allowed to identify new intermediate phases and check the phase integrity upon cooling.

### References

[1] E.Boccaleri *et al.*, *J. Appl. Crystallogr.* **40**. (2007) 684.