

MS21-P6 Comprehensive Analysis of Disorder in NaLaF₄: an Efficient Up-Conversion Phosphor

Ruggero Frison¹, Thomas Weber², Tara Michels-Clark³, Michal Chodkiewicz⁴, Christina Hoffmann⁵, Andrei Savici², Anthony Linden¹, Hans-Beat Bürgi^{1,6}

1. Department of Chemistry, University of Zurich, CH-8057 Zurich
2. X-ray platform, Department of Materials, ETH Zurich, CH-8093 Zurich Switzerland
3. Lawrence Berkeley National Laboratory, Berkeley, CA 94720, USA
4. Biological and Chemical Research Centre, Department of Chemistry, University of Warsaw, Zwirki i Wigury 101, 02-089 Warszawa, Poland
5. Neutron Sciences Directorate, Oak Ridge National Laboratory, Oak Ridge, TN 37831, USA
6. Department of Chemistry and Biochemistry, University of Bern, CH-3012 Bern Switzerland

email: ruggero.frison@uzh.ch

NaLaF₄ is an efficient up-conversion phosphor [1] belonging to the family of rare earth-doped sodium lanthanide tetrafluorides where the nature of the photoactive sites can unambiguously be explained only in terms of a microscopic model of disorder [2]. X-ray and Neutron Diffuse Scattering (XDS, NDS), as *k*-space probes, provide statistically reliable data on atomic pair correlation functions and thus on deviations from the average periodic structure. Using high quality XDS and NDS datasets from the distinctive, planar diffuse scattering of NaLaF₄, we calculated the 3D-Difference Pair Distribution Function (3D- Δ PDF), identified the various types of disorder and derived an abstract model of interatomic vectors [3]. It was then possible by means of Monte Carlo (MC) simulations to build and optimize large model crystals providing a specific atomistic disorder model for NaLaF₄, whose Fourier transform gives an excellent fit to the experimental diffuse scattering. The distinct contrast displayed by the various atomic species with the two radiation types provides a better sensitivity to the different pair-wise correlations ultimately yielding more robust results.

- [1] T. Kano, H. Yamamoto, Y. Otomo, *J. Electrochem. Soc.* (1972) 119, 1561-1564. J.F. Suyver, J. Grimm, K.W. Krämer, H.U. Güdel, *J. Lumin.* (2005) 114, 53-59. A.Sarakovskis, J. Grube, A. Mishnev, M. Springis, *Opt. Mat.* (2009) 31, 1517-1534. [2] A. Aebischer, M. Hostettler, J. Hauser, K. Krämer, T. Weber, H.U. Güdel, H.B. Bürgi, *Angew. Chem. Int. Ed.* (2006) 45, 2802-2806. [3] T. Weber, A. Simonov, *Z. Krist.*, (2012) 227, 238-247.

Keywords: photo-active materials, disorder, diffuse scattering

MS21-P7 Unraveling Two-Dimensional Polymerization Propagation from Diffuse Scattering

Gregor Hofer^{1,2}, Martin Kröger³, A. Dieter Schlüter¹, Thomas Weber²

1. Laboratory of Polymer Chemistry, ETH Zurich, CH-8093 Zurich, Switzerland
2. X-Ray Platform D-MATL, ETH Zurich, CH-8093 Zurich, Switzerland
3. Polymer Physics, ETH Zurich, CH-8093 Zurich, Switzerland

email: gregor.hofer@mat.ethz.ch

A recent advance in polymer chemistry is two-dimensional polymerization [1]. This is achieved by pre-organizing trifunctional monomer molecules through crystallization followed by exposure of the crystal to intense light. This external trigger propels a thermally reversible photochemical reaction and genuine long-ranged ordered two-dimensional polymerization is accomplished.

The monomer molecules used in this study [2] crystallize in the chiral and polar space group *R*3. Polymerization occurs in the *ab*-plane of the crystal. Despite large structural changes during polymerization and depolymerization, the space group is preserved in this single-crystal-to-single-crystal transformation. Both, polymerization and depolymerization can be frozen in time by simply removing the crystal from the triggering source thus creating a disordered monomer/polymer single crystal. The highly polar solvent molecule 2-cyanopyridine is incorporated into the structure in an orientationally disordered manner. This disorder is altered by the polymerization reaction.

This contribution will address two-dimensional polymerization propagation by means of real crystal structure analysis. Three imaginable propagation models with different distributions of bonded monomer moieties are presented in Figure 1. Unlike Bragg scattering, diffuse scattering [3] is sensitive to the distribution of these bonded monomer moieties. High-resolution synchrotron measurements were done to record the diffuse scattering during the polymerization and depolymerization. Several different diffuse scattering features were observed and will be presented and qualitatively interpreted. The newly developed 3D- Δ PDF method [4] and Monte Carlo simulations will be employed to model the real structure. The combined results will reveal the type of polymerization propagation. Furthermore, additional aspects caused by the polymerization will be discussed, such as the overall change in the electric dipole momentum caused by the reorientation of the solvent molecules or the crystal quality.

- [1] Payamyar, P., King, B. T., Öttinger, H. C., & Schlüter, A. D. (2016). *Chem. Commun.*, 52, 18-34.

[2] Kory, M. J., Wörle, M., Weber, T., Payamyar, P., van de Poll, S. W., Dshemuchadse, J., Trapp, N., Schlüter, A. D. (2014) *Nat. Chem.*, 6, 779-784.

[3] Welberry, T. R. & Weber, T. (2016). *Cryst. Rev.* 22, 2-78.

[4] Weber, T., Simonov, A. (2012) *Z. Krist.*, 227, 238-247.