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Diffuse scattering study of γ -pigment red 170

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Pigment Red 170 is an economically important automotive coating in the paint industry, but subject to fading. Structurally it has four polymorphic forms namely the α , β , γ and δ -polymorph. Among them the γ -polymorph shows superior pigment properties. [1] It has been found that modifications of some of the molecule's substituents can affect the durability, but a rational approach to such modifications requires an understanding of the crystal structure of the pigment. Despite the importance of Pigment Red 170 in many industrial applications only a few structural studies have been carried out. [1,2] Only recently, Schmidt *et al.*, have determined the structures of the α - and γ -phases from a combination of X-ray powder diffraction and crystal structure prediction algorithms. [1,2] According to the description given, both phases have layer-like structures.

Single crystal data of the γ -phase have been collected by Schmidt on a sealed tube diffractometer. They show diffuse scattering. We have collected Synchrotron data from the same crystal and found that the observed rods of diffuse scattering are typical of faulted layer stacking. There is currently some uncertainty concerning the correct unit cell that should be used to describe the average structure. The Synchrotron data suggest a larger unit cell than that derived by Schmidt. We will describe our results from the attempts to derive the correct unit cell and solve and refine the average structure.

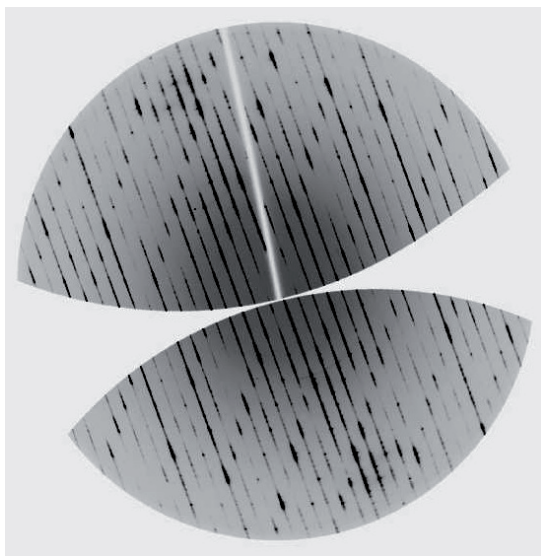


Fig. 1. The $h2l$ reciprocal lattice plane from the γ -phase of Pigment Red 170 collected on the BM01A beamline at SNBL (ESRF).

[1] M.U. Schmidt, D.W.M. Hofmann, C. Buchsbaum, H.J. Metz, *Angew. Chem. Int. Ed.* **2006**, *45*, 1313-1317. [2] W.D.S. Motherwell, H.L. Ammom, J.D. Dunitz, A. Dzyabchenko, P. Erk, A. Gavezzotti, D.W.M. Hofmann, F.J. J. Leusen, J.P.M. Lommerse, W.T.M. Mooij, S.L. Price, H. Scheraga, B. Schweizer, M.U. Schmidt, B.P. van Eijck, P. Verwer, D. E. Williams, *Acta Cryst.* **2002**, *B58*, 647-661.

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Real structure of $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($0.5 < x < 0.8$) phosphors by TEM and XRD

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Oxonitridosilicates (sions) such as $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ are known as efficient phosphors for pc-LED applications. The silicate layers consist of highly condensed SiON_3 tetrahedra interconnected by N^{3-} atoms while metal atoms are located between those layers. The emission wavelength can be tuned by changing the atomic ratio Ba: Sr, ranging from blue to yellow-green [1]. The corresponding crystal structures have been discussed controversially in the literature. The compounds exhibit a wide variety of real-structure effects like twinning, intergrowth and stacking disorder [2,3]. In order to determine complex structural phenomena in mixed Sr/Ba sions, a combination of electron microscopy and diffraction as well as X-ray diffraction methods has been employed successfully. For $\text{Sr}_{0.5}\text{Ba}_{0.5}\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$, diffuse intensities observed in X-ray powder and electron diffraction patterns are fully explained by simulations based on a model including stacking disorder as well as twin and anti-phase boundaries. The unexpected red-shifted luminescence can be understood based on the detailed knowledge of structural features.

For $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x \approx 0.25$), single-crystal X-ray data show that the crystal structure is a variant of that of $\text{BaSi}_2\text{O}_2\text{N}_2$; however, the metal atom layers are corrugated in a similar fashion as in $\text{SrSi}_2\text{O}_2\text{N}_2$ which otherwise exhibits a different structure. The Ba rich compounds exhibit disordered silicate layers and show pronounced diffuse intensities in diffraction patterns. Additional intergrowth of (pseudo)orthorhombic and triclinic domains in $\text{Sr}_{1-x}\text{Ba}_x\text{Si}_2\text{O}_2\text{N}_2:\text{Eu}^{2+}$ ($x \approx 0.25$) is evident in HRTEM images, SAED patterns and reciprocal lattice sections calculated from X-ray data. The structures of the individual domains are corroborated by HRTEM simulations based on structure models developed from single-crystal data combined with information from electron diffraction. Experimental luminescence spectra show two maxima which correspond to the two different structure types building up the intergrown domains.

[1] V. Bachmann, C. Ronda, O. Oeckler, W. Schnick, A. Meijerink, *Chem. Mater.* **2009**, *21*, 316-325. [2] O. Oeckler, F. Stadler, T. Rosenthal, W. Schnick, *Solid State Sci.* **2007**, *9*, 205-212. [3] J. A. Kechele, O. Oeckler, F. Stadler, W. Schnick, *Solid State Sci.* **2009**, *11*, 537-543.

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Water-mediated hierarchal structure in room temperature ionic liquids

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Room temperature ionic liquids (RTILs) have been big subjects of environmental friendly "green chemistry". Almost zero vapor pressure in RTILs is one of outstanding features. We have already reported anomalous behaviors of N,N -diethyl- N -methyl- N -2-methoxyethyl ammonium tetrafluoroborate ([DEME][BF₄])-H₂O mixtures by simultaneous X-ray diffraction and DSC measurements.[1-5] In particular, at 1 mol% H₂O, two kinds of superstructures, volume

contractions and anomalous domain structures were observed. By substituting D₂O at fixing the water concentration, the anomalies disappeared gradually. On the other hand, the quenched mixtures of RTILs-H₂O show a curious “double glass transition”.[6-9] Bonding nature of hydrogen plays an important role both on crystal and glassy states.

Recently, we found hierarchical structure in the [DEME][BF₄]-H₂O system by small angle X-ray scattering, “prepeak” and principal peak on the X-ray diffraction and optical absorption in UV-vis region.[10] Even at liquid state, water-mediated heterogeneous fluctuations are dominant. Furthermore, nearly-free hydrogen bonded water in Raman spectra is detected below 80 mol% H₂O mixtures. Water network over the medium-range is key to comprehend the complicated behaviors.

- [1] Y. Imai, H. Abe, T. Goto, Y. Yoshimura, S. Kushiyama, H. Matsumoto, *J. Phys. Chem. B* **2008**, *112*, 9841-9846. [2] Y. Imai, H. Abe, T. Goto, Y. Yoshimura, Y. Michishita, H. Matsumoto, *Chem. Phys.* **2008**, *352*, 224-230. [3] Y. Imai, H. Abe, Y. Yoshimura, *J. Phys. Chem. B* **2009**, *113*, 2013-2018. [4] H. Abe, Y. Yoshimura, Y. Imai, T. Goto, H. Matsumoto, *J. Mol. Liq.* **2009**, *150*, 16-21. [5] H. Abe, Y. Imai, T. Takekiyo, Y. Yoshimura, *J. Phys. Chem. B* **2010**, *114*, 2834-2839. [6] Y. Yoshimura, T. Goto, H. Abe, Y. Imai, *J. Phys. Chem. B* **2009**, *113*, 8091-8095. [7] Y. Imai, H. Abe, T. Miyashita, T. Goto, H. Matsumoto, Y. Yoshimura, *Chem. Phys. Lett.* **2010**, *486*, 37-39. [8] Y. Imai, H. Abe, H. Matsumoto, O. Shimada, T. Hanasaki, Y. Yoshimura, *J. Chem. Thermo.* **2011**, *43*, 319-322. [9] Y. Yoshimura, H. Kimura, C. Okamoto, T. Miyashita, Y. Imai, H. Abe, *J. Chem. Thermo.* **2011**, *43*, 410-412. [10] M. Aono, Y. Imai, Y. Ogata, H. Abe, T. Goto, Y. Yoshimura, T. Takekiyo, H. Matsumoto, T. Arai, *Metal. Mater. Trans. A*, **2011**, *42*, 37-40.

Keywords: Hierarchical Structure, Hydrogen bonding, H/D effect

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Interpretation and analysis of diffuse scattering using Monte Carlo simulation

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Monte Carlo (MC) computer simulation of a model structure has become a powerful and well-accepted technique for aiding the interpretation and analysis of diffuse scattering patterns. The method consists of comparing diffraction patterns calculated from a computer model of the disordered structure with measured X-ray or neutron diffuse intensities. The advantage of the method is that it can be applied generally to all systems regardless of their complexity or the size of the atomic displacements that might be present. The only limitation is the extent to which the MC energy can be made to realistically represent the real system energy. At one extreme a very simplified model may be useful in demonstrating particular qualitative effects while at the other a quantitative and very detailed description of disordered structures can be obtained.

Over the last two decades the methodology has developed and improved enormously as a direct consequence of the (Moore's Law) increase in the power of computers (a factor of 10⁶). In early studies [1], two-dimensional (2D) models representing projections of a crystal structure were used, simulations could only be carried out for a limited number of MC cycles and only qualitative comparisons were made between the model and the observed data. Now it is possible to use fully 3D models of a sufficient size to allow good representation of statistical properties, sufficient MC cycles to ensure that equilibrium distributions are attained and realistic interatomic or intermolecular potentials. The

result is that models can be developed that give truly quantitative fits to observed diffuse scattering data and this allows detailed understanding of the mechanisms leading to the diffuse scattering [2].

In this paper we describe the advances that have been made and illustrate the progress using a variety of examples. These range from the different polymorphic forms of the pharmaceuticals benzocaine and aspirin, the flexible molecular compound *p*-(*N*-chlorobenzylidene)-*p*-chloroaniline, to a particularly interesting 19kDa viral protein example that exhibits frustration on a 73Å × 73Å triangular lattice.

- [1]. T.R. Welberry, R.L. Withers, *Physics and Chemistry of Minerals* **1990**, *17*, 117-24. [2]. E.J. Chan *et al.*, *Acta Crystallographica Section B-Structural Science* **2009**, *65*, 382-92.

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3D-PDF analysis of diffuse scattering from manganese Prussian Blue analog

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The metal substitutes of Prussian Blue are actively investigated because of their unique combination of magnetic and optical properties. All crystals in this family are disordered and disorder plays an important role for local physical properties like, for example, charge transfer. Information about the average structure alone is not sufficient for an understanding of such properties. By the use of X-ray diffuse scattering it is possible to obtain quantitative occupation correlations of disordered positions and accurate distances between atoms. Using this information one may build fragments of the real structure for modeling of physical properties.

In this work we present the results of direct three dimensional pair distribution function (3D-PDF) refinements of diffuse scattering from the manganese analog of Prussian Blue. The diffuse scattering was measured at the Swiss-Norwegian beam line at ESRF Grenoble. Qualitative analysis of the PDF showed presence of strong substitutional correlations and associated atomic displacements (the so called size effect). Direct 3D-PDF fitting is capable of refining all relevant correlation parameters. Explicit construction of a physical model is not required as it would be in case of the Monte Carlo refinements.

Keywords: diffuse, disorder, 3D-PDF

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Modeling diffuse scattering on supercomputers with ZODS

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Single crystal structure determination from Bragg diffraction has become a largely routine operation. The information obtained is limited, however: it is the average over time and space of all crystallographic