

**FA4-MS24-T01**

**Structure of Ba<sub>10</sub>Ge<sub>50</sub> from electron diffraction/X-ray powder diffraction data** Wilder Carrillo-Cabrera  
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Ba<sub>10</sub>Ge<sub>50</sub> (earlier called BaGe<sub>5</sub>) forms from high-temperature Ba<sub>8</sub>Ge<sub>43</sub> phase (clathrate I, stable at 770–800 °C) by annealing at 450–600 °C [1]. It crystallized in the form of thin layers assemblages (1–3 μm thick layers). The solution of its crystal structure from single crystal X-ray data is then a challenge. Ba<sub>10</sub>Ge<sub>50</sub> has now been characterized by a combination of electron diffraction and X-ray powder diffraction methods. Powder particles or FIB thin cuts (FEI Quanta 200 3D dual beam) were used for the electron diffraction study performed on Philips CM20 and Tecnai 10 electron microscopes. A preliminary structure solution based upon electron diffraction data only was attempted without success, because perhaps the intensity electron data suffered of too strong dynamical effects. The final determination of the crystal structure (orthorhombic space group *Pmna*, no. 57; *a* = 10.7242(7), 9.2873(8), 14.7905(11); *Z* = 1) was a consequence of a detailed crystal chemical analysis. However, key features like crystallographic relationships to neighbouring phases and space group determination both derived from electron diffraction data played an important and crucial role. Several features indicated that Ba<sub>10</sub>Ge<sub>50</sub> can be an orthorhombic derivative of the cubic clathrate II structure. Accordingly, an initial ideal structure model was built up. The final structure model (a minority Ge position is 50% occupied and a neighbouring Ge position splits in two sites) was refined by the Rietveld Method using X-ray powder diffraction data. On one hand, the crystal structure of Ba<sub>10</sub>Ge<sub>50</sub> can be described as a heavily defect clathrate II structure with (2×) Ba and (18×) Ge vacancies per unit cell. On the other hand, it can also be derived from the clathrate I structure Ba<sub>8</sub>Ge<sub>43</sub> by crystallographic slip and further reconstruction, stuffing extra atoms (2 × Ba + 7 × Ge) between the shifted structural slabs. Thus, Ba<sub>10</sub>Ge<sub>50</sub> can be regarded as a structure intermediate between that of clathrates I and II. Ba<sub>10</sub>Ge<sub>50</sub> is a charge-balanced Zintl phase with a covalent framework of four-bonded neutral (4b)Ge<sup>0</sup> atoms and three-bonded (3b)Ge<sup>-</sup> anions with Ba<sup>2+</sup> cations filling 83 % of the closed (pentagon dodecahedra) or open germanium cages in the structure: [Ba<sup>2+</sup>]<sub>10</sub>[(3b)Ge<sup>-</sup>]<sub>20</sub>[(4b)Ge<sup>0</sup>]<sub>30</sub>. The structure determination of the intermediate Ba<sub>10</sub>Ge<sub>50</sub> clathrate is important, because it contributes to the understanding of the phase transition of the hydrated clathrate I to clathrate II under high pressure, which might happen by reconstructive crystallographic shear or slip.

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**Keywords: electron diffraction, Ba<sub>10</sub>Ge<sub>50</sub>, crystal structure**

**FA4-MS24-T02**

**Refinement of structural parameters of PbTiO<sub>3</sub> by Convergent-Beam electron diffraction.** Roland Schierholz<sup>a</sup>, Kenji Tsuda<sup>b</sup> and Hartmut Fuess<sup>a</sup>  
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PbTiO<sub>3</sub> is used as a component in a variety of ferroelectric and relaxor materials with perovskite structure. Calculations by Cohen [1] suggested, the tetragonal phase is stabilized in PbTiO<sub>3</sub>, due to Pb-O covalency. Experimentally the charge density in PbTiO<sub>3</sub> has been studied by x-ray powder diffraction confirming the results by Cohen [2,3].

To observe data from a single crystalline area we use Convergent-Beam Electron Diffraction (CBED). Energy filtered 2-dimensional data sets including first-order Laue zones were collected for 14 different incidences around the five zone axis [00-1], [100], [110], [101], [111]. These data sets are used for a refinement of structural parameters such as atomic positions, anisotropic temperature factors and low order structure factors using the program *mbfitpack* [4]. Due to the conversion from electron to x-ray structure factors [5], low order structure factors can be refined with higher accuracy from electron diffraction. We will show the reconstructed 3-dimensional charge density, and discuss the results in comparison to literature.

[1] R. E. Cohen *Nature* 358 (1992) 136-138. [2] Y. Kuroiwa *et al. Phys. Rev. Lett.* 87 (2001) 217601. [3] H. Tanaka *et al. Phys. Rev. B* 74 (2006) 172105. [4] K. Tsuda and M. Tanaka *Acta Cryst. A* 55 (1999) 939-954. [5] J. C. H. Spence and J. M. Zuo *Electron Microdiffraction* New York: Plenum (1992)

**Keywords: CBED, PbTiO<sub>3</sub>, charge density**

**FA4-MS24-T03**

**Crystal structure solution via precession electron diffraction data: the BEA algorithm** Giovanni Luca Cascarano<sup>a</sup>, Carmelo Giacobazzo<sup>a,b</sup>, Benedetta Carrozzini<sup>a</sup>. <sup>a</sup>*Istituto di Cristallografia, CNR, Bari, Italy.* <sup>b</sup>*Dipartimento Geomineralogico, Università di Bari, Italy.*  
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The strong interaction of the electrons with the matter is responsible of many beam dynamical scattering effects, which cause strong deviations of the diffraction intensities from the kinematical values, and therefore a limited capacity of precisely determining the values of the structural parameters. *PED* techniques [1] reduce the number of reflections which are simultaneously excited and therefore allow to describe the scattering by few beam approximations. Usually 2-dimensional reflections from few well oriented zone axis are collected. More recently [2,3] the *ADT* (automated diffraction tomography) technique has been developed which, in combination with *PED*, allows much larger completeness values. We have studied the statistical features of *PED* and *ADT* amplitudes with particular attention to the effects they produce on the efficiency of the phasing procedures, specifically on Direct Methods approaches. A new algorithm, denoted *BEA*, is proposed: once an even imperfect structural model is available, the *best* amplitude among the equivalent reflections is used to improve the model. It is shown that *BEA* is able to provide more complete structural models, to make the phasing process more straightforward and to end with crystallographic residual much better than those usually obtained by electron diffraction.

- [1] R. Vincent, P.A. Migdley, *Ultramicroscopy* 53 (1994) 271-282.  
 [2] U. Kolb, T. Gorelik, C. Kübel, M.T. Otten, D. Hubert, *Ultramicroscopy* 107 (2007), 507-513. [3] U. Kolb, T. Gorelik, M.T. Otten, *Ultramicroscopy*, 108 (2008), 763-772.

**Keywords: electron diffraction, precession diffractometry, direct methods**

#### FA4-MS24-T04

**Structure of molecular crystals solved by automated electron diffraction.** Tatiana Gorelik, Enrico Mugnaioli, Andrew Stewart, Galina Matveeva, Ute Kolb. *Institute of Physical Chemistry, University of Mainz, Germany.*  
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Organic materials ranging from pharmaceuticals to pigments and polymers are essential part of everyday life. Molecular packing within these materials is a basis for understanding and controlling the functionality of the compound. Therefore structural investigations on molecular crystals are of great importance both for industrial applications and fundamental research.

Of particular interest is the structure of nano sized organic crystals; these crystals can either be confined in size on purpose (to suit better their applications) or exist only as nano crystalline domains. Crystal structure of nano phases often differ from that of larger crystals exhibiting different polymorphs [1]; a situation when a structure determined from a larger crystal via single crystal X-ray diffraction does not fit the X-ray powder profile of the nano material occurs much more often than is commonly perceived. Therefore techniques for structural analysis of molecular nano phases are of increasing importance in the age of nanotechnology.

Electron diffraction can provide structural information from a single crystal with a size down to 20 nm. Electron crystallography of organic materials has a long history going back to 50s [2]. Molecular crystals were always attractive for electron crystallography due to minimal effects associated with dynamical scattering. Nevertheless the method is not widely spread due to experimental difficulties connected with the beam damage. To overcome these limitations automated procedures for data collection optimizing the total electron dose distribution were created [3, 4].

The quality of automatically collected electron diffraction data sets turned out to be sufficient to perform ab-initio structure solution and even detect water molecules incorporated into molecular packing. Structure solution of organic crystals of various classes based on automatically collected electron diffraction data will be presented.

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**Keywords: electron crystallography, ab-initio structure determination, molecular crystals**

#### FA4-MS24-T05

#### Measuring electron scattering factors by large angle rocking beam electron diffraction (LARBED).

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The strong interaction of fast electrons with matter is viewed by many as both a blessing – the analysis of tiny volumes may yield excellent diffraction data – and a curse – even in thin samples dynamical scattering theory should be applied – at the same time.

Although it is, at least in principle and for moderately thin samples, possible to invert the dynamical scattering and extract scattering factor amplitudes and phases directly from diffraction data [1] it is common practice to treat electron diffraction data with kinematic scattering theory and use existing direct methods, iterative phasing algorithms, or information from HRTEM images to reconstruct the phase information. For this purpose the precession electron diffraction (PED) technique [2] has been of great help.

In contrast to PED, the LARBED technique [3] aims to preserve the information about the angle of incidence. Figure 1 shows first the LARBED acquisition principle, and also the benefit of having diffraction discs with a diameter much larger than the distance between two neighboring diffraction spots: The 2-dimensional rocking curves allow (a) all the symmetry information available from CBED patterns is available even for samples with very large unit cell and/ or very low thickness, (b) very accurate determination of structure factor amplitudes and sample thickness is made possible by fitting kinematical rocking curves to the data, (c) forbidden reflections may easily be identified [3], and (d) dynamical theory may be applied to retrieve the structure factor phases directly from the data [3].

In this presentation I will focus on aspects (a) and (b): the quantitative determination of structure factor amplitudes from LARBED patterns.

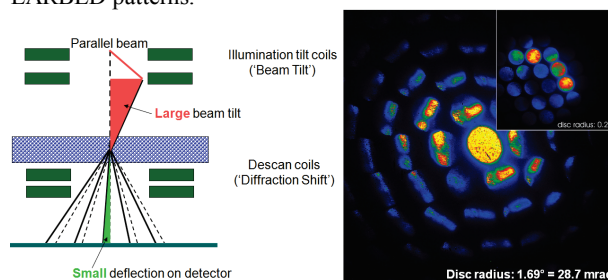


Figure 1 Left: diagram illustrating the LARBED experimental setup. The large beam tilt is above the sample is scaled down to a size avoiding overlapping diffraction discs. Right: LARBED pattern of Si (110). While the inset shows the diffraction discs without applying any de-scan, the scale of the diffraction discs in the large diffraction pattern has been reduced 6.25 fold to produce the same size discs.

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**Keywords: quantitative electron diffraction, CBED, dynamical electron scattering**