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Structure of Ba₁₀Ge₅₀ from electron diffraction/X-ray powder diffraction data Wilder Carrillo-Cabrera
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Ba₁₀Ge₅₀ (earlier called BaGe₅) forms from high-temperature Ba₈Ge₄₃ 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. Ba₁₀Ge₅₀ 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 Ba₁₀Ge₅₀ 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 Ba₁₀Ge₅₀ 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 Ba₈Ge₄₃ by crystallographic slip and further reconstruction, stuffing extra atoms (2 × Ba + 7 × Ge) between the shifted structural slabs. Thus, Ba₁₀Ge₅₀ can be regarded as a structure intermediate between that of clathrates I and II. Ba₁₀Ge₅₀ is a charge-balanced Zintl phase with a covalent framework of four-bonded neutral (4b)Ge⁰ atoms and three-bonded (3b)Ge⁻ anions with Ba²⁺ cations filling 83 % of the closed (pentagon dodecahedra) or open germanium cages in the structure: [Ba²⁺]₁₀[(3b)Ge⁻]₂₀[(4b)Ge⁰]₃₀. The structure determination of the intermediate Ba₁₀Ge₅₀ 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.

[1] W. Carrillo-Cabrera, S. Budnyk, Yu. Prots, Yu. Grin, *Z. Anorg. Allg. Chem.* 2004, 630, 2267.

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Refinement of structural parameters of PbTiO₃ by Convergent-Beam electron diffraction. Roland Schierholz^a, Kenji Tsuda^b and Hartmut Fuess^a
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PbTiO₃ 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 PbTiO₃, due to Pb-O covalency. Experimentally the charge density in PbTiO₃ 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)

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Crystal structure solution via precession electron diffraction data: the BEA algorithm Giovanni Luca Cascarano^a, Carmelo Giacobazzo^{a,b}, Benedetta Carrozzini^a. ^a*Istituto di Cristallografia, CNR, Bari, Italy.* ^b*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.