

# Structure determination of nano-crystals with precession 3D electron diffraction tomography in the transmission electron microscope

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## INTRODUCTION

Rapidly developing nanotechnology urgently needs analytical tools to characterize nanocrystals. The transmission electron microscopy (TEM), where strong efforts have been dedicated in recent years towards the construction of aberration correctors in order to achieve sub-Angstrom resolution in imaging may give detailed atomic structure information but only in projection. If we want to have access to the full 3D atomic crystal structure information a complementary technique is required.

A possible alternative for 3D structure determination is furnished by electron diffraction (ED), which does not suffer from the resolution limitations imposed by the spherical aberration of the objective lens. Unfortunately electrons interact with matter some orders of magnitude strongly than X-rays and tend to scatter several times while traversing through a specimen. Multiple diffraction events, known also as dynamical effects, modify the final intensities of the reflections, so that such data cannot straightforwardly be used for structure solution.

Recently, the precession electron diffraction (PED) technique was developed as an approach to reduce dynamical effects in electron diffraction patterns [1]. This method is based on the precession of the incident electron beam, which is inclined away from the optical axis of the TEM and precesses on a cone surface having the vertex fixed on the sample. Due to the high precession frequency (100 Hz), the resulting PED pattern recorded is the sum of ED patterns produced by the precessing beam sequentially. Due to beam precession, reflection intensities are integrated over diffraction conditions that are far from perfect zone axis orientation, therefore dynamical effects in PED patterns are reduced.

PED has been used for ab-initio structure determination and many structures were solved by this approach from collecting zonal axis (ZA) patterns [2, 3]. Although the collection of ZA PED patterns has proved to be an effective approach for structure determination, it has severe limitations, among which the lack of data completeness is the most important.

Very recently a new technique using 3D

electron diffraction tomography combined with precession has filled this gap; it is now possible to collect ED data for any crystal, without any prior knowledge of the specimen crystal symmetry by just tilting the sample (manually or automatically) along any arbitrary axis [4]. This article describes the principle of the technique and gives a few illustrative new application examples of ab-initio 3D structure determination.

## MATERIALS AND METHODS

This new tomography technique in reciprocal space is based on a collection of PED patterns at different tilt angles during specimen tilt, similar to how it is done in real space tomography, therefore the method is called 3D diffraction tomography (derived from the Greek *tomo* (τομή) = cut or slice; and *grapho* (γραφώ) = record).

The principle of the method is sampling the reciprocal space in small steps without any prior information on the orientation of the crystal. The only essential requirement is that the data are collected from the same crystal. In such a way high-index crystallographic zones are typically recorded through a tilt around an arbitrary axis. As the information about the angular relationship between the diffraction patterns is available, the three-dimensional reciprocal volume can be reconstructed (Figure 1).

3D diffraction tomography can be performed in any TEM using a standard single tilt or tomography holder (manual tilting in our case). An efficient sampling depends on the crystal symmetry, the higher the symmetry the smaller the minimum required range, however a tilting range of the specimen from  $-60^\circ$  to  $+60^\circ$  along the goniometer axis with a tilting step of  $1^\circ$  is an optimal compromise. Thus, a total tilt wedge of  $120^\circ$  can be recorded, providing 121 diffraction patterns that are usually enough for structure determination. However, it is clear that when the highest tilting range is used, more reciprocal space is covered providing enhanced precision in structure solution. Although for crystal structure determinations a tilt of at least  $-45^\circ$  to  $+45^\circ$  is recommended, a tilt of  $15^\circ$  to  $+15^\circ$  is enough for cell parameter determination.

Data acquisition is performed as follows: (i) select a suitable transparent single crystal or an area of a crystal; (ii) tilt the crystal to the negative limits of the tilting range (e.g.  $-60^\circ$ ); (iii) acquire a PED pattern using the available CCD camera; (iv) tilt the crystal  $1^\circ$ ; (v) track the crystal or the targeted area back under the beam; the crystal usually moves a bit even if it is at the correct eucentric height; (vi) repeat steps (iii) to (v) up to the highest possible positive tilting limit to complete acquisition (Figure 2). This procedure can be completed in 60-90 min with the most

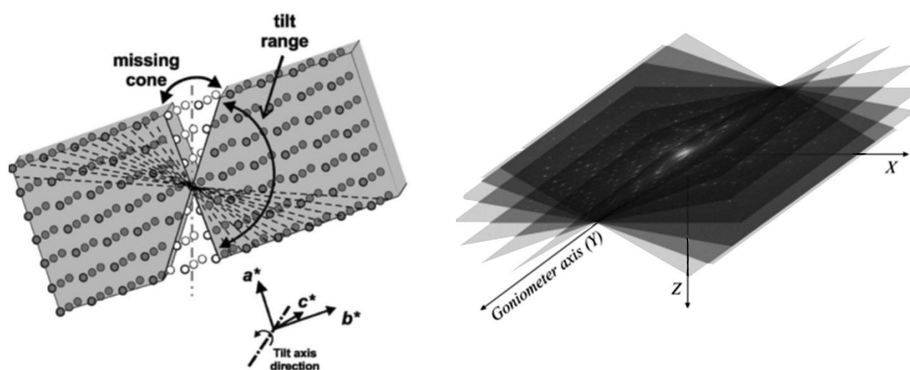
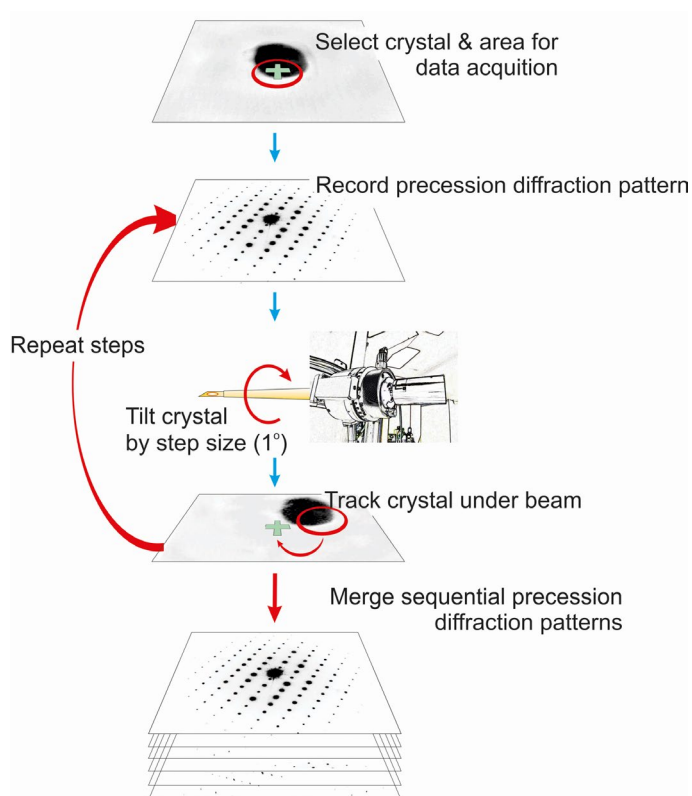


Figure 1

Principles of electron diffraction tomography data processing. See text for detailed explanation. (Courtesy of T. Gorelik, E. Mugnaoli and U. Kolb, University of Mainz.)



**Figure 2** Schematic representation of electron diffraction tomography procedure. See text for a detailed explanation.

time consuming step being the crystal tracking under the beam, which in our TEM must be done manually by the operator.

The diffraction patterns collected in such a way (tilts every  $1^\circ$ ) may suffer from gaps in the reciprocal space reconstruction between the tilt steps. PED helps to overcome this problem [5]. Using a precession angle equivalent to the tilt step, the precession movement makes the Ewald sphere sweep through the missing space between the ED patterns, allowing the intensities falling between subsequent recorded patterns to be integrally recovered and measured precisely.

In this work a Digistar P1000 (NanoMEGAS) [6] precession unit connected to a Zeiss Libra 120 TEM operating at 120 kV with an in-column Omega filter was used. A 16 bit 2k x 2k CCD camera bottom-mounted for electron-diffraction data recording was also used.

PED data (precession angle  $1^\circ$ ) for 3D tomography were collected in parallel illumination (Köhler mode) with the smallest condenser aperture available to minimize the illuminated area, in our case a  $19\ \mu\text{m}$  or  $5\ \mu\text{m}$  apertures which corresponded to an illuminated area on the sample of  $600\ \text{nm}$  or  $150\ \text{nm}$ , respectively. All the data collections were energy filtered, with the outer slit of the omega filter set to a width of 15 eV and centered on the zero-loss peak. In this way most of the inelastic scattering was filtered out.

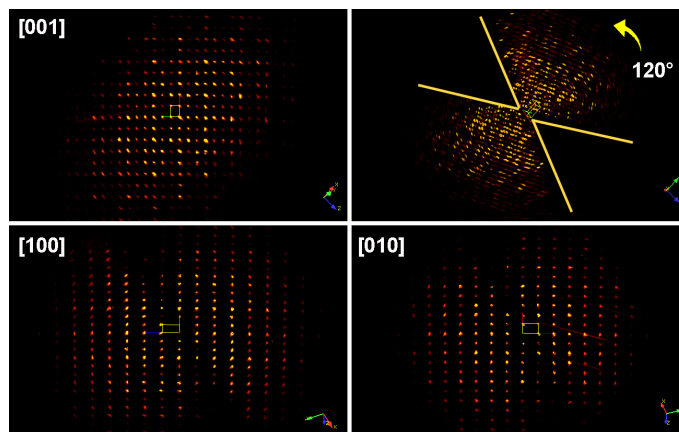
The ADT3D software package (developed by Prof. Ute Kolb's group in Mainz [4] and distributed by NanoMEGAS [6]) was used for processing the diffraction tomography

**Figure 4** (Top) 3D reconstruction of the reciprocal space obtained on  $\text{Y}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$  with ADT3D software. The space is visualized along a direction slightly inclined from the [010] zone axis. (Bottom) Structural model of  $\text{Y}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$  obtained from electron tomography data. O is red, Cu is blue, Ba is green and Y is yellow.

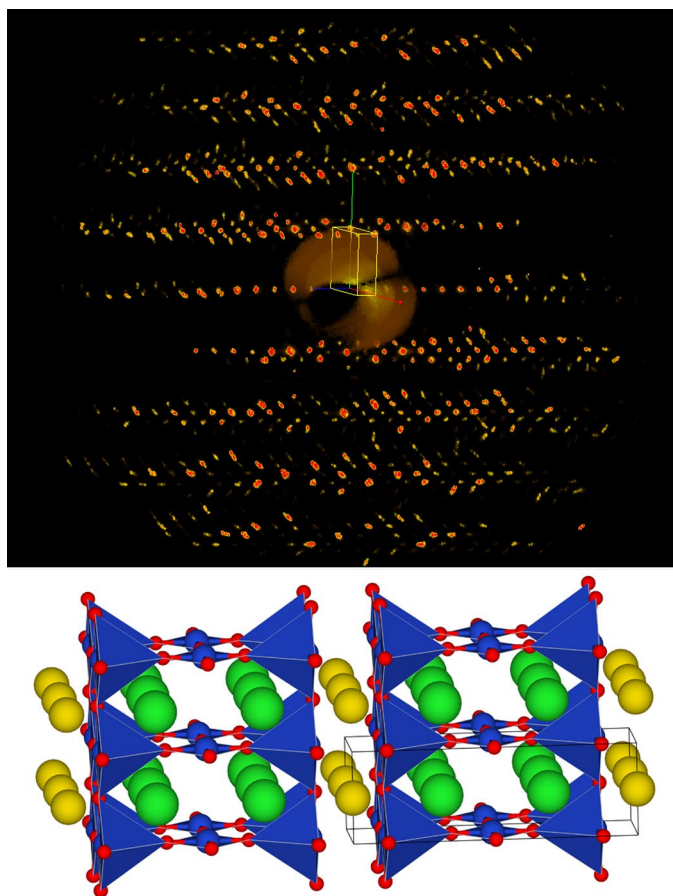
data presented here [7]. The procedure for the automatic 3D reconstruction of reciprocal space, unit cell parameters determination (accuracy 2–4 %) and  $hkl$  intensity determination is described elsewhere [4, 5].

## RESULTS

In this work we present the structure determination of three known structures, hemimorphite ( $\text{ZnSi}_2\text{O}_7(\text{OH})_2 \cdot \text{H}_2\text{O}$ ), mayenite ( $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ ) and the Y123 superconductor of nominal composition  $\text{Y}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$ . While



**Figure 3** 3D reconstruction of the reciprocal space obtained on hemimorphite with ADT3D software. The projection along the three fundamental zone axes [100], [010] and [001] are reported. In the top right box the view of the data collection along the goniometer tilt axis is shown.



the first two structures have been chosen just as test examples, for the Y123 superconductor, although it has a known structure, this is the first time that it has been studied by electron diffraction tomography. In our study a  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  polycrystalline sample (with  $x=0.3$ ,  $y=6.99$ ) was synthesized by solid state reaction methods [8].

Hemimorphite is orthorhombic space group *Imm2*, mayenite is cubic space group *I-43d*, and  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  is orthorhombic with space group *Pmmm*. The extinction group of each

structure can be determined from the electron data collection. Details of the data collections on the three samples and the estimate of their unit cell parameters are shown in Table 1.

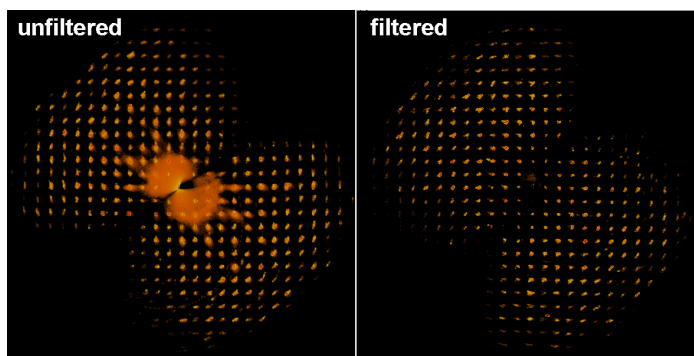
The 3D reconstruction of the hemimorphite reciprocal space performed by ADT3D is shown in Figure 3. The projections along the three main crystallographic axes are displayed and a fourth view along the tilt axis is added to appreciate the portion of the reciprocal space that is missing. It is worth to recall that such a view is impossible to obtain on the analyzed crystal, since it is parallel to the sample plane,  $90^\circ$  from the optical axis of the TEM.

The reflection intensities extracted by ADT3D have been processed with the direct methods software SIR2008 [9]. As can be seen from Table 1 the number of integrated reflections is very high giving a coverage of the reciprocal space of at least 80% up to a resolution of  $0.9 \text{ \AA}$ , in the case of high symmetry space groups, a completeness hardly achievable with zone axis patterns. Due to the completeness of the reflection data sets and to the reduced dynamical character of the scattering, because of the simultaneous effect of precession and random crystal orientation, the three structures can be solved. In the structure solution no previous knowledge of the symmetry was used, except for the extinction group directly derivable from the integrated reflections. Among all the possible space groups compatible with the extinction group only the correct space group gives a chemically meaningful solution.

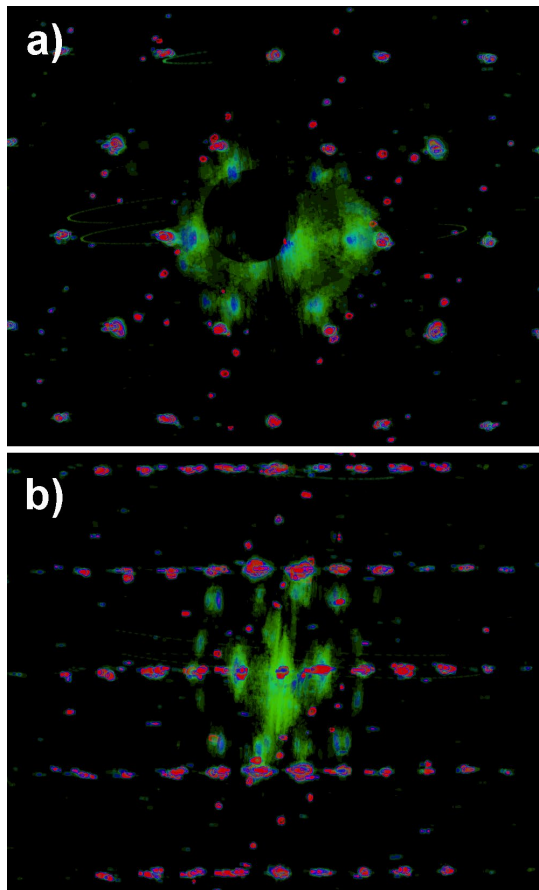
The solutions obtained in this way are compared with the reference structures [10–12] in Table 2. As can be seen all the structures have been solved with a maximum error in the position of the atoms of  $0.21 \text{ \AA}$ . The structural model of  $\text{Y}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$  obtained with electrons is reported in Figure 4 together with its reconstructed reciprocal space viewed along an oblique direction close to  $[010]$  in order to appreciate the 3D character of the data collection. For the current Y123 sample we found only Y in the structure. In a future work, the exact occupancy refinement of the Y/Pr site will be reported by electron crystallography methods in  $\text{Y}_{1-x}\text{Pr}_x\text{Ba}_2\text{Cu}_3\text{O}_y$  ( $x=0.0\text{--}1.0$ ) samples where yttrium has been substituted by praseodymium [8].

All data collections that have been used for the structure solution are energy filtered on the zero-loss peak. The advantages of filtering out the inelastic scattering is evident from Figure 5, where a comparison between the reconstructed reciprocal space of mayenite with and without energy filtering is displayed. In the unfiltered data the background of inelastic electrons is partially masking weak peaks at low scattering angles and the reflections are more broadened [13].

The 3D precession diffraction tomography method is not only effective for ab-initio structure solution but is also a very powerful tool for visualizing additional details of the electron scattering. In the case of a disordered structure that exhibits a strong diffuse scattering, the 3D reconstruction allows us to detect the 3D shape of the diffuse scattering and its location with respect to the Bragg peaks. As an example, the reconstruction of the reciprocal space of the mineral cesarolite ( $\text{PbMn}_3\text{O}_6(\text{OH})_2$ ) is shown in Figure 6.



**Figure 5**  
3D reconstruction of the reciprocal space of a mayenite crystal viewed along  $[001]$  direction. Energy unfiltered (left) and filtered (right) data collections are displayed. The two data collections can be directly compared since they are taken on the same crystal and in the same experimental conditions.



**Figure 6**  
3D reconstruction of the reciprocal space of a cesarolite crystal. (a) Projection along the 3 fold axis. (b) Projection obtained by rotating the reciprocal space  $90^\circ$  along the vertical direction of (a). Purple: the Bragg reflections. Green-blue: the halo of diffuse scattering due to crystal disorder.

## CONCLUSIONS

The crystal structure of  $\text{Y}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$  has been solved for the first time using 3D precession diffraction tomography. The structure determination of  $\text{Y}_{0.8}\text{Pr}_{0.2}\text{Ba}_2\text{Cu}_3\text{O}_7$  is only the first step towards a future more detailed study of the substitution of Pr for Y in the starting material, and its influence on the superconductor properties in comparison to structural variations.

The completeness of the three structure solutions presented here demonstrates that electron crystallography can be efficiently applied to structural studies of several nanomaterials of high technological interest. Electron diffraction tomography and precession electron diffraction, together with the use of efficient and user-friendly software, provide the TEM community with a powerful and efficient tool for structural studies of a variety of materials including nanometer-scale crystals that are difficult to study by conventional X-ray

techniques. More than 45 different nanomaterial structures (with both known and unknown structures) have been solved (such as catalysts, polymers, pigments, minerals, complex oxides, metals, alloys, etc) in the last 2–3 years with 3D diffraction tomography coupled with precession diffraction. The technique is easy to implement on any TEM [6] working at 120–300 kV and the minimum size of crystals that can be studied may vary from 250 nm down to 25 nm (depending on the TEM electron source, LaB<sub>6</sub> or FEG).

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<b>Hemimorphite</b>
Collected PED patterns: 121 Angular range: -60° to +60° Reciprocal space coverage: 80% at 0.9 Å resolution Collected reflections (unique): 1238 (336) Unit cell: a = 8.266 Å (8.367); b = 10.841 Å (10.730); c = 5.091 Å (5.115) R <sub>val</sub> = 25.5%
<b>Mayenite</b>
Collected PED patterns: 110 Angular range: -60° to +49° Reciprocal space coverage: 95% at 0.9 Å resolution Collected reflections (unique): 1509 (110) Unit cell: a = 11.89 Å (1.9921) R <sub>val</sub> = 27.4%
<b>Y123</b>
Collected PED patterns: 116 Angular range: -55° to +60° Reciprocal space coverage: 65% at 0.9 Å resolution Collected reflections (unique): 1071 (245) Unit cell: a = 3.76272 Å (3.814); b = 3.83 Å (3.8812); c = 11.50964 Å (11.6395) R <sub>val</sub> = 35.4%

**Table 1**

Details of the 3D diffraction tomography data collection. The unit cell parameters obtained with ADT are reported together with those of the reference structure in parenthesis. R<sub>val</sub> is the agreement factor reported by SIR2008 at the end of the solution process.

Hemimorphite		Reference structure (X-ray and neutron diffraction)			3D precession diffraction tomography			
Atoms	Label	X	Y	Z	X	Y	Z	Δ(Å)
Zn	Zn	0.2047(1)	0.1613(1)	0	0.205	0.160	0	0.02
Si	Si	0	0.1465(2)	0.5076(5)	0	0.141	0.529	0.12
O	O1	0.1604(8)	0.2055(1)	0.6363(4)	0.152	0.217	0.657	0.18
O	O2	0	0.1669(2)	0.1938(4)	0	0.156	0.204	0.12
OH	O3	0.3050(2)	0	0.0410(6)	0.289	0	0.073	0.21
O	O4	0	0	0.5912(6)	0	0	0.601	0.05
H <sub>2</sub> O	O5	1/2	0	0.5195(13)	1/2	0	0.491	0.15
<b>Mayenite</b>		<b>Reference structure</b>			<b>Electron</b>			
Atoms	Label	X	Y	Z	X	Y	Z	Δ(Å)
Ca	Ca	0.89096(5)	0	3/4	0.902	0	3/4	0.14
Al	Al1	0.01866(3)	0.01866(3)	0.01866(3)	0.018	0.018	0.018	<0.02
Al	Al2	1/4	7/8	0	1/4	7/8	0	-
O	O1	0.18556(3)	0.18556(3)	0.18556(3)	0.184	0.184	0.184	0.03
O	O2	0.44182(4)	0.15035(3)	0.03677(4)	0.439	0.148	0.041	0.06
<b>Y<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub></b>		<b>Reference structure</b>			<b>Electron</b>			
Atoms	Label	X	Y	Z	X	Y	Z	Δ(Å)
Ba	Ba	0.5	0.5	0.1850(2)	0.5	0.5	0.1874	0.05
Y/Pr	Y	0.5	0.5	0.5	0.5	0.5	0.5	-
Cu	Cu1	0	0	0	0	0	0	-
Cu	Cu2	0	0	0.3565(5)	0	0	0.355	<0.02
O	O1	0	0.5	0	0	0.5	0	-
O	O2	0	0	0.1566(23)	0	0	0.160	<0.02
O	O3	0.5	0	0.3776(21)	0.5	0	0.382	0.06
O	O4	0	0.5	0.3765(21)	0	0.5	0.383	0.06

**Table 2**

Comparison between the reference structures obtained with other techniques (X-ray and neutron diffraction) and the 3D diffraction tomography solutions for the three investigated structures. The reference structures are taken from [10], [11] and [12] for hemimorphite, mayenite and Y<sub>0.8</sub>Pr<sub>0.2</sub>Ba<sub>2</sub>Cu<sub>3</sub>O<sub>7</sub> respectively. In the last column (Δ) the shift of the atomic positions between the two models is reported.

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## BIOGRAPHY

Mauro Gemmi obtained his PhD in physics from the University of Bologna in 2000 with a thesis on structure solution with electron diffraction data. After one year as a post doc at the Structural Chemistry Department of Stockholm University, he became responsible for the transmission electron microscopy lab at the Earth Science Department of Milan University from 2002 to 2010. In 2008 he was an invited scientist at CNRS Institut Néel, Grenoble, and since 2010 he has been responsible for transmission electron microscopy and nanocrystallography research at the Center of Nanotechnology Innovation@NEST, a centre of the Italian Institute of Technology in Pisa, Italy. His research interests include the development of new electron diffraction methods for solving unknown crystal structures, nanotexture analysis with TEM, TEM characterization of nanowires and nanostructures, and interaction between nanomaterials and biological systems.



## ABSTRACT

We show the application of the novel precession 3D electron diffraction tomography to the structure solution of nanocrystals. This technique is an alternative approach to structure solution when, for specific reasons like for example a multi-phase sample or a low crystallinity sample, the conventional x-ray diffraction approaches fail. The details, the characteristics of the technique and the possibility of its implementation on a standard TEM are discussed. As test examples, three known crystal structures are solved with this technique.

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