Electron crystallography applied to a "real" sample: the structure of Mn_2O_3 solved by precession electron diffraction

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Abstract – Electron crystallography is a useful tool for structure determination in cases where X-ray diffraction is not sufficient, e.g. multi-phase (nanometre-sized) powders. The feasibility of different methods of electron crystallography has been shown on many different materials. In this contribution we apply the method of precession electron diffraction on a "real" sample. The structure of a Mn_2O_3 impurity in a nanometre-sized powder of MnO_2 was solved by direct methods. The influence of experimental parameters and the treatment of the obtained data are discussed.

1. Introduction

The emerging electron crystallography is a powerful tool for the determination of the atomic structures of crystals. Many examples have been shown in which electron crystallography has been able to solve even complex structures correctly (for recent examples see [1]). However, compared to X-ray crystallography it remains a delicate and time consuming method. Therefore it finds its real application in cases where X-rays are not sufficient to solve the structures. Prominent examples are multi-phase powders constituted of nanometre sized grains. In this work we present one of these "real" cases.

2. Sample

The sample studied is a nanometer-sized powder of MnO_2, which is interesting for applications in batteries, but which contained a few percent of an unexpected phase [2]. Powder X-ray diffraction showed the expected peaks of the β-MnO_2 phase and a few additional peaks not consistant with this phase. However, these peaks were insufficient for a phase determination. Figure 1 shows the secondary phase particle amongst clusters of MnO_2 crystals and the corresponding X-ray powder diffraction pattern.

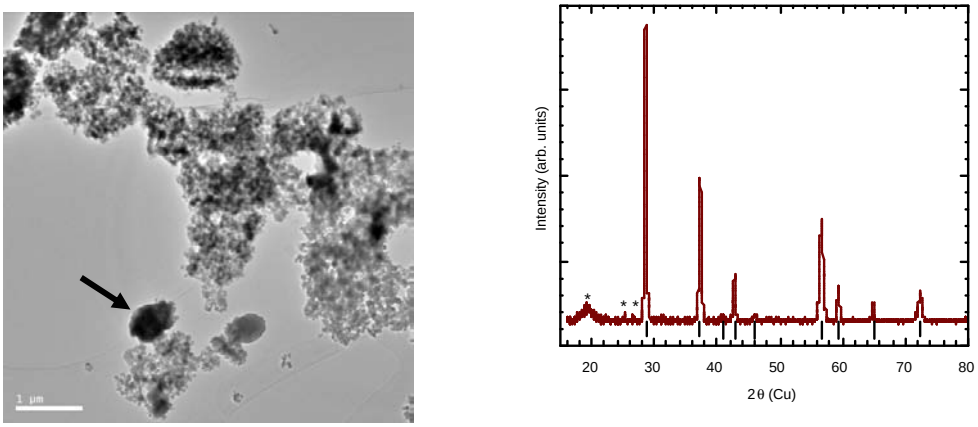

Figure 1 *– (left) TEM micrograph showing clusters of MnO_2 crystals and a single particle of Mn_2O_3 (arrow). (right) X-ray powder diffraction pattern: peaks not due to MnO_2 are marked by **

3. Experimental

The electron diffraction was performed in a Philips CM300ST equipped with a GATAN Slowscan CCD camera and the "spinning star" precession device. Using selected area electron diffraction (SAED) we identified the minority phase to be pseudo-cubic α-Mn_2O_3 with cell parameter a = 9.4 Å and space group *Ia3*.
For the structure determination a total of 17 zone axes covering the asymetrical unit of the cubic cell were recorded in classical SAED conditions and in precession mode with different precession angles up to 4°. The intensities of the reflections corresponding to real space distances d > 0.8 Å were measured using the ELD program of the CRISP package [3]. The intensities of equivalent reflections in each single EDP were merged and then the data sets corresponding to a same precession condition were merged using the program Triple (CRISP). After an additional merging of symetry equivalent reflections in these data sets we obtained the intensities of 196 independant reflextions in the complete data set.
The data were used as input for the SIR97 [4] program for structure determination. Since the diffracting crystal was not very thin we assumed the measured intensities to be proportional to the structure factor amplitude [5].

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4. Discussion

The importance of the precession technique for electron diffraction in order to obtain diffracted intensities close to those expected in kinematical theory becomes evident just by optical inspection of the EDPs. Figure 2 shows the [1 1 1] zone axis obtained by classical SAED (left) and by the precession technique with a precession angle of 2° (right). In SAED the intensities are very homogenous (except for a hexagon of slightly more intense reflections) and decrease with increasing diffraction vector modulus. In the precession EDP where multiple diffraction is reduced the differences in the intensities of different reflections are much more pronounced.

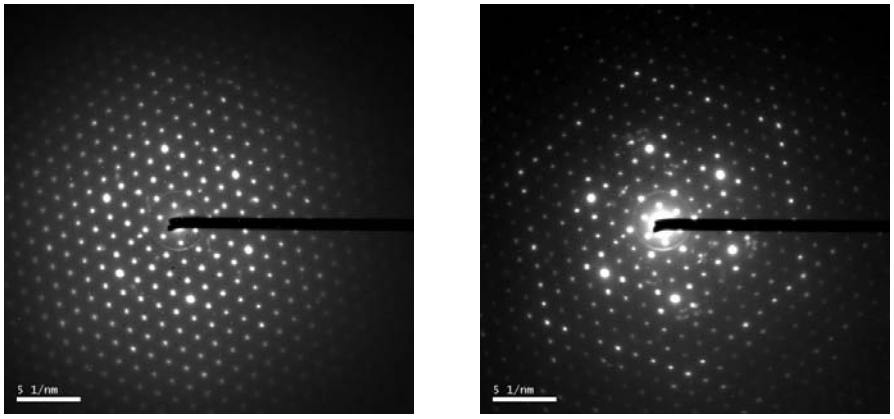

Figure 2 *–Electron diffraction patterns of the [1 1 1] zone axis obtained by SAED (left) and the precession technique (right)*

The better quality of the precession electron diffraction (PED) data also becomes evident when merging symmetry equivalent reflections or when merging intensities from different zone axes. Merging the intensities of different zone axes obtained in SAED yielded R factors between 10 % and 20 %. The R factors for merging the same zone axes obtained with a precession angle of 2° were between 4 % and 12 %. Consequently it was no surprise that the PED data was more suitable for structure determination by direct methods. The SIR97 program using the PED data yielded three predominant peaks in the electron density map corresponding to the 3 independent atoms of the structure. The spurious additional peaks are of much weaker intensity (table 1). The peaks in the electron density map obtained from the SAED data are of essentially the same height and it is impossible to determine the real atom positions.

Results of SIR97 with PED data					Results of SIR97 with SAED data				
Atom	Height	x	y	z	Atom	Height	x	y	z
Mn 1	2400	0.500	0.000	0.500	O 1	686	0.231	0.028	0.223
Mn 2	1405	0.250	-0.273	0.500	Mn 2	546	0.424	0.000	0.250
O 3	676	0.376	-0.159	0.416	O 3	533	0.330	0.040	0.165
O 4	414	0.247	-0.279	0.457	O 4	476	0.393	-0.139	0.199
Q 5	361	0.434	-0.066	0.566	O 5	458	0.132	0.132	0.132
O 6	345	0.209	-0.296	0.492	O 6	343	0.000	0.000	0.000
O 7	316	0.208	-0.208	0.292	Q 7	339	0.501	0.073	0.239
O 8	300	0.500	-0.250	0.423	O 8	303	0.004	0.004	-0.003
Final residual value = 25.42%					Final residual value = 34.89%				

Table 1 *– Comparison of the electron density peaks obtained by PED and SAED*

5. Conclusion

We have shown that electron crystallography can solve the structure of a minority phase in a nanometric powder sample. While the data obtained in SAED was not suitable for use in direct methods, the precession electron diffraction technique yields intensities close enough to kinematical theory to solve the structure unambiguously.

6. References

[1] *Proceedings of the Electron Crystallography School 2005, ELCRYST 2005: New Frontiers in Electron Crystallography*, Ultramicroscopy **107** (June-July 2007) 431-558

[2] Chr. Poinsignon, E. Djurado, H. Klein, P. Strobel, F. Thomas, *Electrochemical and surface properties of nanocrystalline beta-MnO_2 in aqueous electrolyte*, Electrochimica Acta, **51**, (2006) 3076-3085

[3] http://www.calidris-em.com/

[4] http://www.ic.cnr.it/registration_form.php

[5] M. Gemmi and S. Nicolopoulos, *Structure solution with three-dimensional sets of precessed electron diffraction intensities*, Ultramicroscopy **107** (2007) 483-494