NON-CONVENTIONAL DIAGNOSTICS OF MICROCRYSTALLINE MINERAL PHASES BY TEM

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Introduction

Microcrystals show a large variety in regards of structural ordering, phase heterogeneity and phase interrelations. Grainy mono-phase and multi-phase systems, crystal twins, phase changes due to displacements in the atomic structure, phases resulting from solid solution decomposition etc. make diagnostics by conventional Transmission Electron Microscopy Images (TEMI): Selected Area Electron Diffraction Images (SAEDI), Dark Field Images (DFI) and Bright Field Images (BFI), difficult, even impossible in certain cases. In such cases phase identification relates to synchronous investigation of local information obtained by every possible TEMI: in diffraction mode (Electron Diffraction Images (EDI): SAEDI and Convergent Beam Diffraction Image (CBDI)), DFI, BFI, High Resolution Image (HRI) and Energy Dispersive X-ray Spectra (EDS) from an area comparable to the electron beam spot (from 0,001 to 3 square micrometers in the Microprobe operation mode and from 80 to 8000 square nanometers in Nanoprobe operation mode). Modern digital methods of atom structure modeling, digital image processing and digital image simulation are used. In the present work some peculiar diagnostics cases are presented: of microcrystalline lead molybdate and manganese oxides phases.

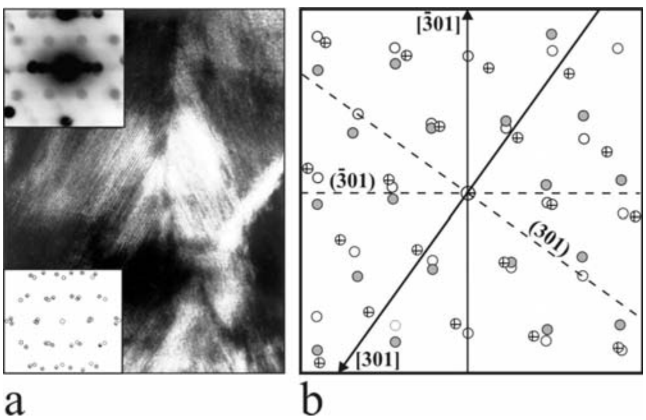

Fig. 1. (a) Manganese oxide – pyrolusite crystal twin. CBEDI is shown in the upper left corner. In the lower left corner CBEDI diagram form Fig. 1b is shown in a scale corresponding to experimental EDI scale; (b) CBEDI diagram of pyrolusite crystal twinning in respect to both possible twin planes (301) and (-301).

A study on manganese oxide crystal twin

Figure 1a shows a crystal twin of manganese oxide determined by EDS. SAEDI performed on one twin part definitely identifies (Dimov, Iamakov, Bozhilov, 1994) pyrolusite laying on a {010} face perpendicularly to the electron beam. In CBEDI, obtained from the intermediate region of the twin (from both parts simultaneously) an image is observed of several overlaying plane point sets. Pyrolusite has a rutile type structure with crystals elongated along [001], tabular in respect to {010} and with characteristic twins to (301) types twin plane (Костов, 1973). The EDI is not characteristic of a twin structure composed of two point sets (Hirsch et al., 1977), it is more complicated and reflects twinning in respect to both observable planes in that direction – (301) and (-301) (Fig.1b). Characteristic lines of diffraction maximums are observed, lined in mirror symmetry in respect to the twin planes shown by dotted lines (perpendicularly to inverse space plane vectors). In phase contrast mode (200) atom planes are visualized with d= 0.22 nm. CBEDI orientation in Fig.1a coincides with the orientation of the phase contrast image. A coincidence is observed between directions of the twin plane visualized as a phase contrast line in HRI and of the twin line in CBEDI diagram. Figure 1a shows a good correspondence between the diagram and the experimental EDI.

A study on synthetic lead molybdate

In many cases phases that have been synthesized for optical purposes are determined as ideal monocrystals. Studied by TEM, various polycrystal aggregates, grainy and defective structures are observed in the samples. A typical example is lead molybdate $PbMoO_4$ synthesized in CLMC.

Figure 2 shows a polycrystalline molybdate aggregate. Separate grains are evident. The polycrystalline character displays in SAEDI too, thus phase identification is not possible. From the region shown in large scale, CBDI was obtained. Two point sets of inverse lattice planes of lead molybdate with indexes (110)* and (001)* are observed and with regard of them identification has been performed.

Figures 3a and 3b show respectively a monocrystal and SAEDI in [100] direction. Figure 3c shows a phase contrast image. Along with ideal structure, there are regions where phase contrast cannot be visualized due to increased diffraction contrast. Digital processing has been performed of the region marked (Димов, 2002).

Figure 4a shows the background corrected image. Corrected image amplitude is shown on Figure 4b. The triple atom plane set observed is presented by three plane waves. The phase contrast image suffers of noise from inevitable fluctuations of Poisson character as a result of artifacts like pollution and non-linearity of the detector and of the image’s analog-to-digital converter. Those artifacts have relatively random character and contribute to a nearly uniform background that is presented in image amplitude as additional to the harmonic maximums of lower amplitude, which can be easily eliminated by level discrimination. Figure 4c shows amplitude with discriminated random fluctuations used as mask. Figure 4d shows filtrated image. As a result of filtration, atomic plane sets are visualized. Dislocations are observed that deform structure in the intermediate region and transform it in a small angle boundary, which alters diffraction and phase contrast around the defect. The small angle boundary has been modeled (Fig. 3d) (Димов, 2002, Dimov et al, 2003). There is good correspondence between simulated and experimental images.

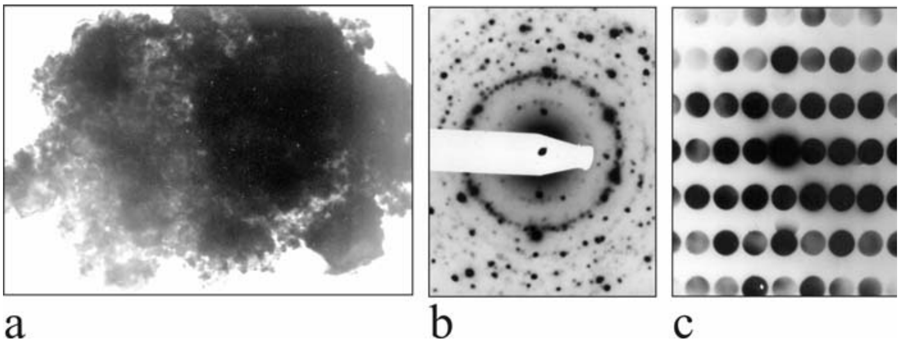

Fig. 2. BFI (a), EDI (b) and CBEDI (c) of polycrystalline $PbMoO_4$ aggregate. Single grains of aggregate can be seen.

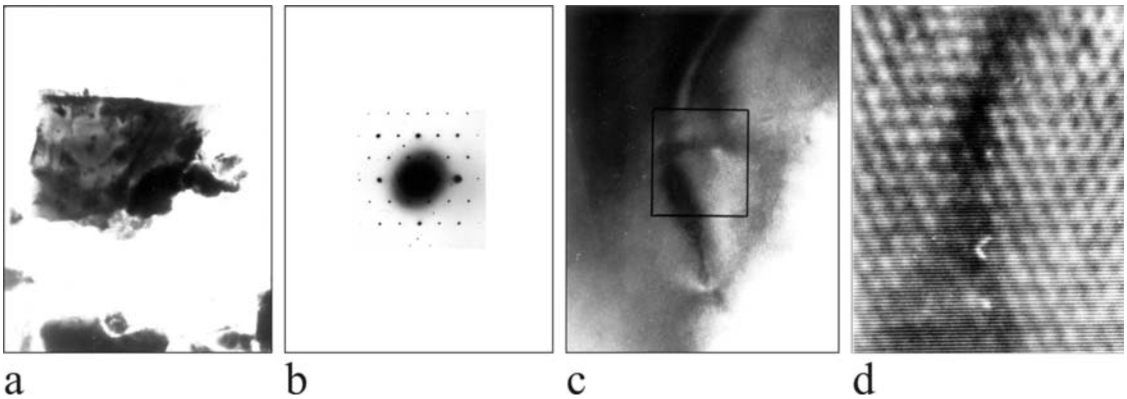

Fig. 3. BFI (a), EDI (b), experimental phase contrast image (c) and simulated phase contrast image (d) of lead molybdate Pb MoO_4 monocrystal.

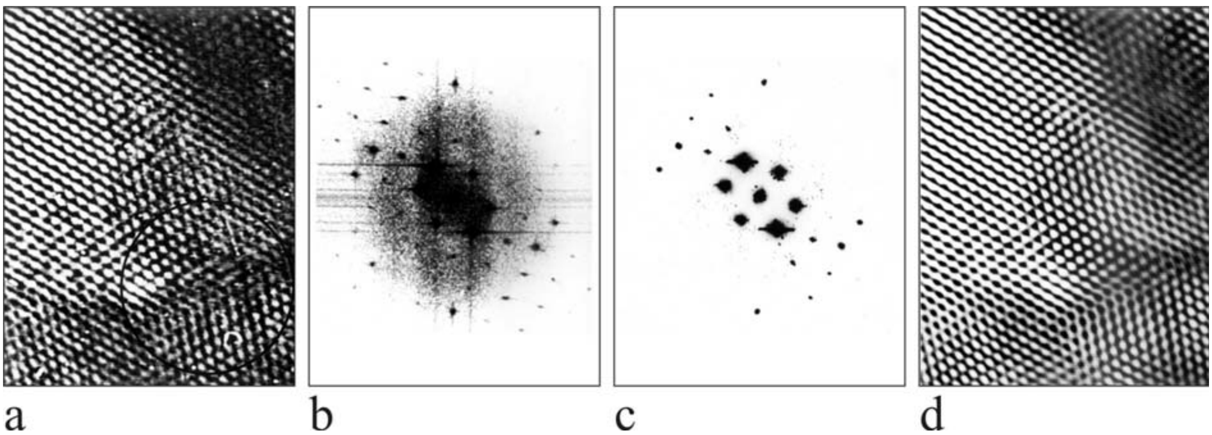

Fig. 4. (a) Background corrected image of marked defect region; (b) Amplitude of Fig. 4a image; (c) Amplitude of Fig 4b image with random fluctuations eliminated. It is used as a mask for diffraction contrast filtering of Fig. 4a image; ***(d)*** Filtered image of the defect region. Diffraction contrast influence has been reduced.

A study on natural calcium-manganese oxide

Figure 5a shows an aggregate with a complex, nearly polycrystalline CBEDI that does not allow for identification of the phase studied. EDS analysis of the aggregate determines Ca and Mn composition. Circle measurement in the EDI determines spacing distances d_1=0.49 nm and d_2 =2.59 nm. HRI study found that isolated regions can be observed (Figure 5a, regions 1, 2, 3) where moirй sets are visualized. Digital image processing was performed to smooth background and normalize contrast, than Fourier filtering was applied to eliminate non-periodic noise. Two single and one double sets with different periods have been distinguished (Fig. 5b), resulting from

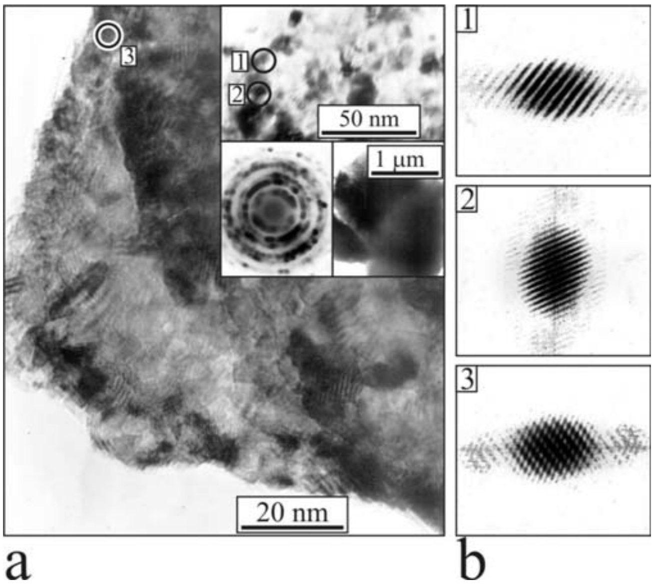

Fig. 5. (a) Diffraction contrast image of calcium-manganese oxide. In the upper right corner zoomed crystal regions, entire particle in lower scale and CBEDI are shown; (b) Regions 1, 2 and 3 after Fourier transformation processing.

grains with random orientation, which form a polycrystalline aggregate that has been identified as manganese oxide (neotokite – pisolite).

Conclusion

Simultaneous crystal twinning in respect to two planes has been found in pyrolusite. In a synthetic lead molybdate monocrystal considered ideal, polycrystalline aggregate of grainy phase texture was identified. A defect region was visualized with dislocations implanted, which had caused a small angle boundary and had altered phase and diffraction contrast of molybdate. Natural calcium-manganese oxide was studied and identified as a neotokite – pisolite aggregate. Identifications have been performed using both conventional diagnostics and non-conventional methods – HRTEMI and CBEDI, as well as SAEDI modeling and computer simulation of phase and diffraction contrast images.

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