Ph.D. DISSERTATION

Structural study of minerals and inorganic crystals

Ildikó Cora

Supervisor: Prof. István Dódony, D.Sc.

Eötvös Loránd University
Doctoral School of Earth Sciences
Program of Geology and Geophysics

Head of the Doctoral Program: Prof. Andrea Mindszenty, D.Sc.

2013
Introduction and the aims of the thesis

In our technology-based 21st century world our knowledge about materials plays a distinguished role. Revealing their atomic-scale structures makes it possible to manipulate the matter on an atomic scale, engineer their properties, and assure their quality. In structural crystallography single crystal X-ray diffraction still has hegemony beside e.g. electron beam techniques. The crystal size is the main limiting factor in its applicability. Nanotechnology - the mainstream research trend nowadays - mainly applies and requires the electron beam techniques. It was a challenging question of the last decades to determine the structure of submicron-, nanometer-sized single crystals. Now it is possible with the recently developed precession electron diffraction technique in combination with diffraction tomography. These techniques are also available in Hungary.

In my Ph.D. thesis I determined and refined the crystal structure of minerals and inorganic crystals. The topic of the first two parts of my thesis is the crystal structure determination. I provided a short background of the process of structure determination (intensity data processing and basics of structure determination) then I presented it in practice. I determined and refined the crystal structure of wulfenite from Mežica and synthetic aluminum-di and –dodecaborides using single crystal X-ray diffraction, and also the crystal structure of submicrometer-sized clay minerals as kaolinite from Mád and celadonite/glauconite from Úrkút; as well as apatite from Erdösmecske using precession electron diffraction dataset.

In the third and last part of my Ph.D. thesis I applied Patterson-method for crystal structure identification. For widespread application I wrote software for automatic calculation of Patterson-maps. I used Patterson-maps for easier differentiation between mica polytypes and polymorphs.
Methods

In structural crystallography single crystal X-ray diffraction still has hegemony beside e.g. electron beam techniques. We applied single crystal x-ray diffraction technique for crystal structure determination of the Medical wulfenite, aluminium-di and –dodecaborides. The measurements were achieved in the Single Crystal X-ray Diffraction Laboratory of Institute of Organic Chemistry Research Centre for Natural Sciences HAS with Professor Mátyás Czugler.

Transmission electron diffraction gives some advantages over x-ray methods, primarily because the scattering is stronger (also a disadvantage), and submicro-, nanometer sized materials are easily examinable, when single crystal X-ray diffraction fails.

However, the quality of intensities from conventional electron diffraction is usually too poor for structure determination due to multiple scattering (dynamical diffraction). In the precession electron diffraction (PED) technique, the beam is deflected prior the specimen to form a tilted illumination condition which reduces dynamical diffraction. Intensities acquired by this technique are (quasi)kinematical and are suitable for structure determination. However, for structure determination we need a 3-dimensional diffraction dataset that can be realised using diffraction tomography. With the combination of precession electron diffraction and diffraction tomography, the crystal structure of submicrometer sized materials (such as clay minerals) can be achieved.
Thesis of the dissertation and conclusions

I determined the crystal structure of minerals and inorganic crystals from diffracted intensity dataset produced by single crystal x-ray method and the recently developed precession electron diffraction combined with diffraction tomography.

Structure determinations achieved using *single crystal X-ray diffraction*:

1. The hemimorph *wulfenite from Mežica* crystallizes in the I-4 space group. The crystalchemical reason for its different symmetry is the chemical ordering, i.e. the 2-2 plumbum and molibdenum cation positions are not identical in their occupancy.
2. I determined and refined the crystal structure of AlB$_2$ and γ-AlB$_{12}$ crystals synthetised by Richárd Orbán.

Structure studies applying *precession electron diffraction* dataset:

3. The crystal structure of submicron-sized single crystal of *kaolinite from Mád* was determined and refined.
4. Structure determination and refinement was achieved on *apatite from Erdősmecske*. The studied crystal showed $P6_3$ symmetry I localized the poor amount of CO$_3^{2-}$ ion in two possible stuctural positions. In both cases the plane of the CO$_3$-group is perpendicular to the c axis.
5. During structure determination procedure I found two possible homologous structure models for *celadonite/glauconite from Úrkút*. From the two possible structure models I prefer the non-mica type, because it is in accordance with the observations of Edelman and Favejee (1940) and Dódony *et al.* (2013) on smectites. They concluded that smectites do not has mica-type but tridimite/cristobalite-type tetrahedral layer.
6. I wrote a software in Wolfram Mathematica for calculation of Patterson-maps using experimental intensity data, projected charge density map or atomic positions. The program was converted to the widespread Python language.
7. I calculated Patterson-maps of the so-called TTM mica using reconstructed projected charge density map and diffracted intensity data. The two calculated Patterson-maps were similar that confirmed its modelled crystal structure.
8. I selected properly mica polytypes form ICSD for calculation of their Patterson-maps. These polytypes can be distinguished based on their P-maps.
9. I set up the models of six different 1 TOT layer thick (1M) dioctahedral polymorphs and I compared them based on their calculated diffraction pattern and Patterson-maps in [001] direction.

The crystal structure of apatite from Erdősmecskes in [001] projection.

Calculated difference Fourier-map of Erdősmecskes apatite at z=0.216. The arrow shows one of the possible positions of the C in the structure.
References


Dódony, I., Németh, T., Kovács Kis, V. (2013): Silica/smectite association in chloropel, kézirat


List of publications related to the dissertation

Publications:


Presentations on international conferences:


Poster presentations on international conferences:

Presentations on conferences in Hungary:


