

MS39-01 The interplay between x-ray powder and electron diffraction: the case of experimental petrology. Mauro Gemmi, “Center for Nanotechnology Innovation@NEST, Istituto Italiano di Tecnologia, Pisa, Italy.
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Multiphase powder samples, containing unknown crystalline phases, require a multi-technique approach to be investigated. Powder x-ray diffraction gives a global information on the sample but, because of the peak overlapping, is unable to identify all the phases, if some of them are unknown. Electron diffraction is complementary to x-ray, each powder grain can be investigated as a single crystal.

Experimental petrology is a perfect field to exploit the combination of these two techniques. The output of a high pressure – high temperature experiment, which simulates conditions of the earth interior, is a capsule of less than 1mm³ containing micrometric grains of several phases.

We will show here a combined investigation of electron and x-ray diffraction of samples having different composition in the MgO-Al₂O₃-SiO₂-H₂O system, at P,T condition around 5GPa and 700 °C, a model system for a subducted slab. After a preliminary screening of the sample with the electron microprobe to identify the composition of the larger crystal grains, x-ray laboratory data have been used to check if new unknown phases are present. Those samples showing an x-ray patterns with peaks that could not be indexed have been investigated with the TEM. Three new unknown phases have been identified. The big step forward made by electron diffraction as a structure solution technique due to precession electron diffraction [1] and automated electron diffraction tomography (ADT) [2] allows to use TEM as a single crystal diffractometer with a high chance of success in the structure solution. Two out of three of the identified phases have been solved with ADT. The first phase having ideal composition of Mg₂Al(OH)₂AlSi₂O₆ is a new type of hydrous pyroxenes (HAPY) containing water as OH group. Since it has been discovered at 5.4 GPa and 720°C, it can promote the H₂O transport beyond the chlorite breakdown [3]. A second experiment done with a bulk composition tuned on the chemical composition given by the structure solution gave a sample with HAPY as the main phase. A synchrotron radiation diffraction experiment on this sample allows the refinement of the structure. A second phase of unknown chemical composition has been solved with ADT. It is a monoclinic phase made up of a stacking of octahedral layer of brucite type with tetrahedral layers of isolated SiO₄ tetrahedra, a topology completely unknown among minerals. The third identified phase could not be solved, since it is disordered. However, the 3D reconstruction of its reciprocal space with ADT, indicates that this phases is formed by a disordered stacking of octahedral brucite layers and tetrahedral layers.

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MS39-02 Electron microscopy as seen through the eyes of a powder diffractionist. Lynne B. McCusker, Christian Baerlocher, *Laboratory of Crystallography, ETH Zurich, 8093 Zurich, Switzerland*,
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Electron microscopy has always been viewed by powder diffractionists as a valuable complementary technique that can be used in difficult situations. For example, a selected area electron diffraction (SAED) pattern can be very useful in resolving unit cell and space group ambiguities, which are common in powder diffraction. Scanning electron microscopy (SEM) images can be used to check for the presence of impurities, which can confuse the interpretation of a powder diffraction pattern, or to see the crystallite morphology, when a preferred orientation of the crystallites in the powder sample is suspected. If it is possible to record a high resolution transmission electron microscopy (HRTEM) image of the material, additional information can be gleaned (e.g. the presence and nature of stacking faults or point defects, which are difficult to characterize with powder diffraction data, or the channel system of a microporous material, which can be useful in the elucidation of the structure from powder diffraction data). It was not until 2006, however, that powder diffractionists recognized that electron microscopy data could also be used actively in the structure determination process [1]. An HRTEM image is a projection of the potential of the structure, and a Fourier transform of this image yields not only the amplitudes, but also the phases of the structure factors of the reflections contributing to that projection. Although a potential map is different from an electron density map, the two are closely related and the phases obtained from the HRTEM image are good estimates of the corresponding phases for the X-ray diffraction case. In other words, the HRTEM image can be used to obtain some starting phase information for structure determination from powder diffraction data. In the solution of three complex zeolite structures, the use of such phases in conjunction with high-resolution powder diffraction data was crucial to the structure determination [1-3]. Of course, it is not always possible to record a good HRTEM image, especially if the sample is beam sensitive. To circumvent this problem, the much simpler precession electron diffraction (PED) technique can be applied. The intensities measured using a PED attachment, while not completely kinematic, suffer much less from multiple diffraction that do those measured in a normal SAED experiment. As a result, reflections that are weak in a PED pattern can also be expected to be weak in the X-ray powder pattern and this information can be used to improve the estimation of the relative intensities of overlapping reflections. Furthermore, the intensities in the PED data have proven to be sufficiently reliable that it is possible to apply the charge-flipping algorithm [4] to estimate phases for the reflections in the projection, and these can be used in the same way as those obtained from an HRTEM image [5]. The fact that less-than-ideal PED intensities could be used for phase retrieval led to the idea of trying to do the same thing with intensities derived from a powder diffraction pattern. Indeed, it proved to be possible to obtain reliable phases from low-resolution, 2-dimensional subsets of the full 3-dimensional data [6]. This approach was applied successfully to the zeolite SSZ-82, which could not be solved directly from the powder diffraction data [7]. The complementarity of X-ray powder diffraction and electron microscopy data is a treasure that will continue to be mined by structural crystallographers.

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MS39-03 SU-66: Combining X-ray powder diffraction, electron diffraction and IR spectroscopy. A. Ken Inge,^a Tom Willhammar,^a Lynne B. McCusker^b and Xiaodong Zou^{*a} ^a*Berzelii Center EXSELENT on Porous Materials and Department of Materials and Environmental Chemistry, Stockholm University, SE-106 91 Stockholm, Sweden.* ^b*Laboratory of Crystallography, ETH Zurich, CH-8093 Zurich, Switzerland.*
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Crystalline open-framework materials such as zeolites and related oxides are of interest for their ability to size- and shape-selectively accommodate guest species in their pores and channels. Their properties relating to ion-exchange, sorption and catalysis allow for applications such as cracking of crude oil, water softeners, heating/cooling devices, catalysts for organic synthesis, and CO₂ capture. Open-framework germanates are of interest for their ability to form architectures with extra-large pores (≥14-rings), even if small organic guest species are used as structure directing agents. The majority of open-framework germanates are an assembly of large cluster building units, which in turn promotes the formation of structures with large pores. Thus, germanates are an excellent example of scale chemistry, i.e. frameworks with large pores can be constructed by using large clusters compared to a structure with the same topology but with smaller building units.¹ Many elegant germanate frameworks are composed of clusters built of multiple coordination polyhedra types. The Ge₁₀(O,OH)₂₇ (Ge₁₀) cluster for example is built of GeO₄ tetrahedra and GeO₆ octahedra, and is found in structures such as mesoporous SU-M with 30-ring channels.² Structure determination of germanates is often impeded by a number of factors. These include the difficulty in synthesizing sufficiently large crystals for single crystal X-ray diffraction, the tendency of having large unit cells that enhance peak overlap in X-ray powder diffraction (XRPD) patterns, and beam sensitivity under a transmission electron microscope.

SU-66 is a new open-framework germanate solved by a novel combination of techniques to overcome the mentioned issues. Prior to structure determination the cluster type was identified by comparing its infrared spectrum (IR) with spectra of germanates built of various cluster types. The region in the IR spectrum of SU-66 corresponding to Ge-O vibrations had strong resemblance of structures built of Ge₁₀ clusters. Once the cluster was identified, the unit cell and space group were determined by XRPD. However due to the poor figure of merit, the unit cell and reflection conditions were reconfirmed by selected area electron diffraction. Structure determination was performed by inserting two Ge₁₀ clusters, the unit cell parameters, space group, and the XRPD pattern into a simulated annealing parallel tempering algorithm in the program FOX.³ SU-66 has extra-large 26-ring channels and is one of the more complicated framework structures solved by XRPD. Additional studies show that other complicated framework structures can be solved in a similar way, even with rather poor quality XRPD data.

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