

Review

Crystal Structures from Powder Diffraction: Principles, Difficulties and Progress

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Abstract: The structure solution from powder diffraction has undergone an intense evolution during the last 20 years, but is far from being routine. Current challenges of powder crystallography include ab initio crystal structure determination on real samples of new materials with specific microstructures, characterization of intermediate reaction products from in situ, in operando studies and novel phases from in situ studies of phase diagrams. The intense evolution of electron diffraction in recent years, providing an experimental (precession) and theoretical (still under intense development) solution to strong dynamic scattering of electrons, smears the traditional frontier between poly- and single-crystal diffraction. Novel techniques like serial snapshot X-ray crystallography point in the same direction. Finally, for the computational chemistry, theoreticians hand-in-hand with crystallographers develop tools where the theory meets experiment for crystal structure refinement, which becomes an unavoidable step in the validation of crystal structures obtained from powder diffraction.

Keywords: powder diffraction; structure solution; X-ray diffraction; DFT calculations; electron diffraction

1. Crystal Structures from Powders: Where Are We Currently?

Crystal structure determination using powder diffraction (SDPD) started only three years after W.L. Bragg published four crystal structures (NaCl-type) from single crystal data [1]. Peter Debye and Paul Scherrer had solved in 1916 the structure of LiF [2] from X-ray powder diffraction data. The author has no intention to review the long and successful history of SDPD in this review; the reader can consult an excellent review by A.K. Cheetham, Chapter 2 in [3], by W.I.F. David in [4] or by W. Paszkowicz in [5]. The structure solution means in this article determination of the (average) 3D-periodic arrangement of the atoms in the crystal using mainly the information content of Bragg scattering in the diffraction pattern. The case of aperiodic crystals (modulated and quasicrystals), of short-range order (diffuse scattering), as well as of nano-crystals (crystals without measurable Bragg signals) will not be discussed here. The structure prediction, on the other hand, will be used in the sense of the determination of the 3D arrangement of the atoms in the crystal using mainly first-principle calculations, and any experimental observation, like the diffraction pattern, is used only for the validation of the predicted structural model.

1.1. Indexing: Still a Bottleneck

Despite an intense development of indexing algorithms in the last 20 years, the detection of the correct lattice may still be a bottleneck of the structure solution in the case of low resolution powder patterns or in the case of monoclinic and triclinic symmetry. A review of known indexing algorithms may be found in Chapter 7 of [3], Chapter 5 of [6] and Chapter 7 of [7]. Each crystallographer and each crystal may work better with a particular algorithm, but as is said in another excellent indexing

review [8]: “Powder indexing works beautifully on good data, but with poor data it will usually not work at all”. The author can only agree with that statement and add (unidentified source, but very probably R. Shirley): “Success of the indexing increases proportionally with the number of different applied indexing programs”. The author’s personal choice is the dichotomy algorithm (see [9] for a historical review) nicely implemented in the programs DICVOL04 [10], Fox [11,12] and X-Cell [13]. The advantage of the dichotomy algorithm is its speed (especially in Fox) and its robustness towards low data quality. Indexing is followed by space group determination, which is based on systematic extinction analysis supported by the knowledge of crystal physical properties, like piezoelectricity, the presence of which excludes centrosymmetric space groups. Fairly robust algorithms for space group determination are based on full pattern fitting (Le Bail or Pawley), available in most software packages.

The indexing can be quite difficult for the crystals lying on opposite ends of the symmetry scale:

Low-symmetry crystals: The indexing algorithm very often proposes for monoclinic crystals several solutions, which are hard to rank on the basis of usual criteria like expected cell volume (based on formula volume and the number of formulas in the cell, in agreement with Wyckoff site multiplicities) and figure-of-merit. A very strong criterion of the cell validity (not only for monoclinic crystals) is the observation of crystallographic extinctions. This means that a cell that shows an extinction of, for example, reflection 020 will rarely be the correct one, unless there is an explanation for it, like the use of X-rays for compounds where hydrogen is not only bonded to a molecule like a terminal ligand, but it is a crystal building element like an anion.

High-symmetry crystals: The indexing algorithms often find a sub-cell, which does not clearly show crystallographic extinctions. The failure of the indexing may not be in an erroneously-used impurity reflection or low precision of peak positions, but in too low of an upper limit for the cell volume. Do not be afraid of big cells! If one of the indexing solutions is a big cell with many crystallographic extinctions pointing clearly to one extinction symbol, it is highly probable that this is the correct one. Very nice examples are recent solutions of two metal borohydrides $KAl(BH_4)_4$ [14] and $Li_3Cs_2(BH_4)_5$ [15], both in the rare space group *Fddd*.

A particular difficulty is indexing of multiphase samples. Even if peaks of known phases are identified in the measured powder pattern, one is never sure that the remaining peaks belong only to one novel phase. An elegant solution, used for a long time in many laboratories, is what the author calls “decomposition-aided indexing” [16]: the in situ powder diffraction data are recorded while the sample is heated up to the disappearing of the peaks of one unknown phase (decomposition, melting, reaction). This allows the separation of the peaks of several novel phases.

As a final word about indexing powder patterns, we may use what the author always says to his students: “If you like your unit cell, then it is correct”. This means that all criteria, such as nice crystallographic extinctions, cell volume in agreement with the chemical formula and any relation to the unit cell of related compounds, must be valid simultaneously.

1.2. Fast and Low Noise Data: 2D-Detectors

The 2D-detectors developed for faster and better quality data collection for single crystals became very popular in powder diffraction. The speed of the data collection has opened the door for in situ studies involving fast (few seconds) structural changes (phase transitions, reactions) [17]. In addition to the excellent time resolution, highly accurate diffracted intensities (good powder average) and a lower sensitivity to preferred orientation are obtained by using 2D-detectors as the whole Debye–Scherrer ring is collected and not only a short segment of it determined by the window of the point or linear detectors. This leads to a very low statistical noise in the data (smooth powder pattern), allowing the detection of very weak peaks needed for correct indexing and space group determination. Logically, the next step is curved 2D-detectors, in the ideal case a sphere around the sample allowing high Bragg angles to be collected simultaneously with the low angle data, certainly a challenge for the developers.

1.3. Which Method for Structure Solution?

The structure solution methods may be generally divided into two groups: intensity extraction (IE)-based algorithms working in the reciprocal space (traditionally called reciprocal space methods) and pattern modelling (PM)-based algorithms working in the direct space (traditionally called direct space methods or global optimization methods) and using the chemical knowledge from that space. Hybrid methods iterating between both spaces are known as well, but a decisive criterion to classify a method is whether the method requires integrated intensities of individual peaks in a powder pattern (IE) or not (PM). A schematic view of possible SDPD roads is given in Figure 1. For a comprehensive review of the methods, see [3].

Powder diffraction uses the same methodology for the structure solution regardless of the nature of the compound to be investigated, but the careful selection of the solution algorithm according to the compound may considerably improve the success rate. The separation of compounds by the inorganic/organic boundary is of less importance for the diffraction than the knowledge of how the atoms build up larger building units and the crystal itself. This does not mean a particular difference for IE methods; however, it becomes important for PM. The structure solution algorithm working in the direct space has to know how to define basic structural units (BU) of the crystal, which are then manipulated (optimized) by the algorithm. A molecular/non-molecular boundary is therefore relevant for the choice of a structure determination method.

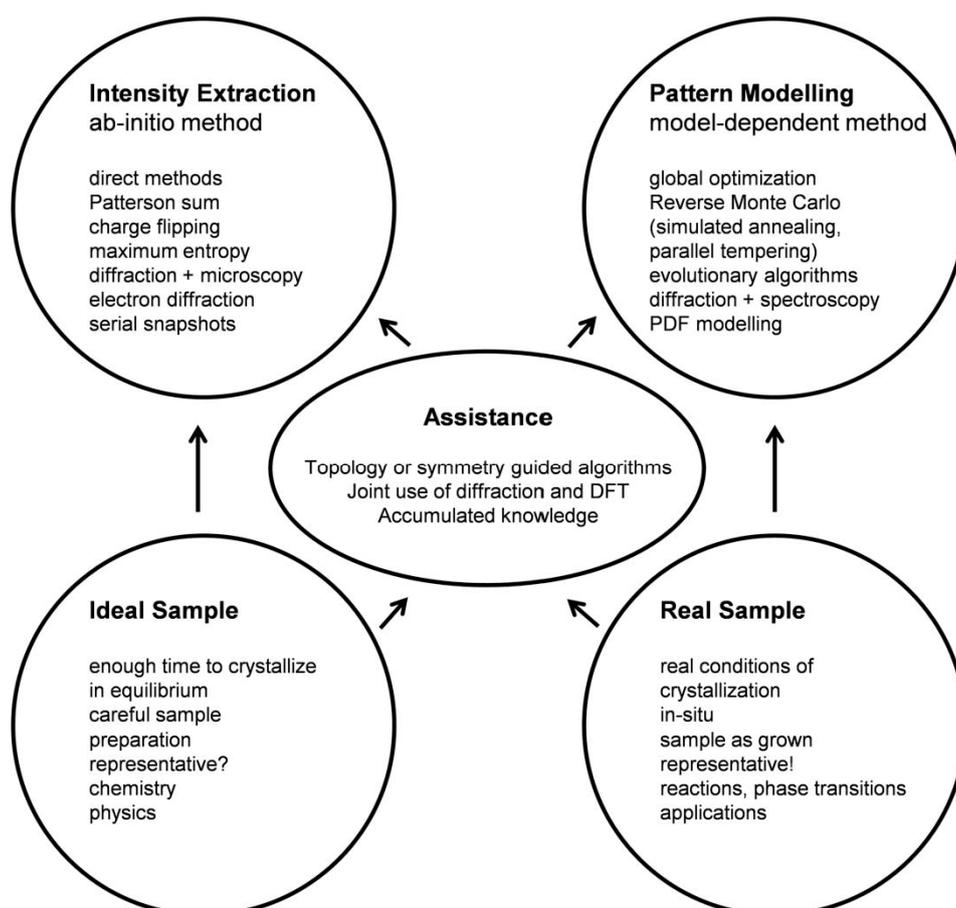


Figure 1. Schema of the structure determination from powder diffraction. While for the ideal sample, there is no need to proceed by assistance of and/or the use of pattern modelling, even if it this road is possible, the real sample has no other choice than to use assisted pattern modelling.

1.3.1. Methods Using Intensity Extraction

The methods that work with the integrated intensities extracted from the powder pattern are the choice when high resolution powder patterns are available, i.e., when an important fraction of reliable integrated intensities may be extracted down to $d \sim 1 \text{ \AA}$. For more specific criteria of what the high resolution pattern means, see Chapter 8 in [3]. Whenever the reliable intensities can be extracted, these methods should be used, because the long time evolution of direct methods (Chapters 10 and 11 in [3]), Patterson sum-based methods (Chapter 13 in [3]), charge-flipping (dual-space method) [18] and maximum entropy method [19], to name the most commonly used, has resulted in powerful tools. The resolution of the powder pattern is nowadays determined mostly by the quality of the sample: the crystals have to have enough time to crystallize, be in thermodynamic equilibrium, and the sample must be carefully prepared [20]. Such a crystal will be certainly used when studying the chemistry or physics of the compound, but the sample is not necessarily representative for a material from applications where, often, out of equilibrium conditions lead to metastable phases.

Several ideas were developed to assist (and improve) the extraction of integrated intensities from the powder pattern: those where no additional data must be collected, like the Patterson function (Chapter 12 in [3]), triplet relation based (Chapter 11 in [3]) or maximum entropy related (Chapter 14 in [3]) and those based on multiple datasets, like texture and thermal dilatation based (Chapter 9 in [3] and [21]).

1.3.2. Methods Using Pattern Modelling

When no reliable integrated intensities can be extracted from a powder pattern, then the only choice is modelling the pattern as a whole, i.e., a synthetic approach contrary to the analytical approach (intensity extraction). Such a situation is typical for real conditions of crystallization as found in many applied materials, in situ studies of reactions and phase transitions. The sample is as grown and is representative for the material. Often, a high time resolution is required to catch the intermediate or rapidly transforming phases. There is no need to extract the integrated intensities; low resolution powder data ($\sim 2 \text{ \AA}$) are often sufficient, and the methods work with patterns containing broadened, overlapped peaks. Any additional information about the atomic coordination and connectivity creating bigger BUs and leading so to a lower number of structural parameters to be determined is easily used. Generally, the pattern modelling methods differ in the algorithm of the global optimization, i.e., the algorithm that globally optimizes the structural model to make its calculated powder pattern better fit the observed one (diffraction cost function). Algorithms are known from the global optimization field of mathematics, and the simplest algorithms, like reversed Monte Carlo (RMC) in simulated annealing and parallel tempering mode or evolution algorithms, are used. For more information, see Chapter 15 in [3] or [22].

PM methods are also easily coupled with any other information aimed to identify the correct crystal structure: knowledge of the chemistry of the unit cell and bonding between the atoms is already actively used in construction and merging of BUs. Crystal energy on the level of electrostatic potentials (ab initio calculations are used for structure validation and prediction, rather than determination) is often coupled with the diffraction cost function (Chapter 15 in [3]). Crystal chemistry contains valuable knowledge accumulated by generations of solid state chemists and crystallographers. While it is mostly based on the observation of known crystal structures and empirical relations among them, it can be very useful in making a decision about which structural model is more probable. The active use of crystallographic databases (see www.iucr.org/resources/data) is highly recommended (author's opinion).

2. Molecular Compounds

A molecule or a complex anion is naturally a BU formed by strong intramolecular interactions (covalent) and packed by intermolecular interactions (dispersive, hydrogen or halogen-bond, π -, coordinating- and ionic-interactions) in the unit cell. No sharing of atoms between the molecules and complex anions occurs. This means that molecular crystals are ready to be easily treated by PM

methods. The BU is easily defined when the molecule or complex anion is known. It is probably not a surprise that one of the most complex molecular crystals solved ab initio from powder diffraction data was solved by RMC in parallel tempering mode. It contains 63 organic (non-hydrogen) atoms in the asymmetric unit, and active use of fragments' connectivity knowledge was essential in the structure solution [23].

The most important group of compounds treated with PM methods is probably pharmaceuticals, as they are typically available in powder form, and novel molecules are systematically synthesized. For a review about the powder crystallography of pharmaceuticals, see [24].

3. Non-Molecular Compounds: Extended Solids

Non-molecular compounds, also called extended solids, are constructed by bonds (ionic, covalent) that extend "infinitely" in three dimensions through a crystal. These non-molecular crystals usually crystallize with higher symmetries, and atoms often occupy special Wyckoff positions; building a model for the PM method is therefore not a straightforward procedure [25]. The presence of high-order symmetries leads to a fragmentation of BUs, as any group of atom (e.g., an octahedron) can be located on a symmetry element, so that only part of the atoms of a symmetry-constrained BU are truly independent. The actual arrangement in space of the BUs, relative to the symmetry elements of the unit cell, are a priori unknown. To cope with this, Deem and Newsam used a merging term in the cost function of their PM method [26], which has then evolved in a general and simple algorithm called dynamical occupancy correction (DOC) implemented in the PM program Fox [11].

One of the most important groups of materials that motivated many developments in SDPD is zeolites built up from SiO_4 tetrahedra. For a review, see [27]. Intense development of PM methods was started by zeolite research [26]. The texture method for integrated intensities extraction was developed on zeolite samples [21]. A nice topology-guided dual space method has been developed for zeolites [28], but the approach is easily modified to any other class of compound with a typical underlying topology.

Another group of polyhedral compounds important for SDPD evolution are (among others) oxides. As these are often real materials, PM methods have been intensively applied here. The most complex structure ever solved from powder diffraction (SDPD applied to proteins is usually based on detected isomorphisms) is $\alpha\text{-Bi}_2\text{Sn}_2\text{O}_7$, a 176-atom polyhedral compound, solved by an RMC search among subgroups of the pyrochlore space group $Fd\text{-}3m$ [29], an approach that can be called the symmetry-guided PM method.

Metal hydrides are rarely available as single crystals due to the method of synthesis and are another SDPD evolution engine [30]. The program Fox has been originally developed on demand from the hydrogen storage community, but has found much broader application [31]. Hydrides are close-packed compounds when formed by hydrogen gas absorption in intermetallic compounds, usually not well crystallized, and therefore, PM methods are used for SDPD. Another group of hydrides, the complex hydrides, contains a homoleptic complex anion with hydrogen as the ligand, a well-studied example being borohydrides. They are prepared typically by mechano-synthesis leading to fine powder excluding IE methods for SDPD. Borohydrides' powder crystallography is a nice example when powder diffraction needs to be assisted by other methods of characterization like various spectroscopies and by crystal chemistry tools (structural analogies between borohydrides and oxides) when facing relatively complex structures [32]. In general, the powder crystallography of metal hydrides is exciting as it provides for all types of crystallographic difficulties, like multi-phase samples, anisotropic line broadening, weak superstructures, pseudo-symmetry, local order in disorder, a weak scatterer close to a strong one, phase transitions and reactions [16].

4. Structure Validation: Help of Theoreticians

Computational chemistry provides information about the studied crystal, which is hardly accessible from powder diffraction. Ab initio calculations on the DFT level can be used at

three stages of SDPD: initial model building (mostly the optimization of a molecule), structure refinement (alternatively with Rietveld refinement) and post-experimental structure validation [33]. The last one helps to validate new structures, locate light hydrogen atoms, especially when using high-pressure diffraction data of limited quality, and even to correct the symmetry and some structural details [15,25,30,34]. Possibly higher crystallographic symmetry of a structure model, which was optimized without any symmetry, can be detected by a suitable algorithm, like the ADDSYM routine in the program Platon [35].

A DFT optimization of the Rietveld-refined structure easily gets away from the local minimum of the experiment cost-function. Since Rietveld refinement and the DFT method are based on two very different cost functions, their combination greatly helps to reach a global minimum. We can therefore highly recommend post-experimental DFT optimization of crystal structures for the systems containing light elements such as hydrogen. One must however keep in mind that if used to validate powder structures, one is employing a far more precise method to “validate” a less precise one. Both may be inaccurate though. Thus, optimizing a structure may not necessarily equate to making it more accurate. Well-founded crystallographic and chemical analysis will always remain indispensable [33].

One inconvenient side-effect of the crystals with a disordered nature like complex hydrides for example is that even experimentally-measured room-temperature structures rarely or never represent the ground state itself. DFT calculations are commonly performed at 0 K where dynamics largely freeze. This obviously severely biases structural predictions by *ab initio* calculations. For structural corrections/optimizations, the choice needs to be made to either fix the unit cell to experimentally obtained lattice constants (preferably on powder samples) or optimize the cell geometry along with atomic positions. It is up to the user and his/her experience to decide which is more efficient, depending on the specific problem to be addressed.

5. Perspectives

5.1. Electron Crystallography

Electron diffraction has developed rapidly in recent times as a complementary technique with powder diffraction: first, in collaboration with X-ray powder diffraction providing additional information in the phasing process [36] and, nowadays, as a stand-alone technique for *ab initio* crystal structure solution [37]. The interaction of electrons with the electron density of the crystal being much stronger than that of X-rays means that a single grain (very small single crystal) is enough to produce an exploitable diffraction signal. Having been eliminated from the *ab initio* structure solution due to dynamic scattering effects for a long time (the dark side of the strong electron-matter interaction), this is nowadays solved by precession electron diffraction, decreasing the dynamic contribution to the kinematic scattering [38]. However, its inherent local sampling on a nanometer scale and substantially complex experimental setup inhibiting *in situ* coupling to other methods pose serious problems for some experiments. Additionally, the sensitivity of soft matter to the electron beam will limit the method.

5.2. Nuclear Magnetic Resonance Crystallography

Three-dimensional structures of powdered solids can be determined also by combining solid-state NMR spectroscopy, X-ray powder diffraction and DFT calculations. NMR spectroscopy has from its earliest days provided structural information on both periodic and amorphous compounds, ranging from specific internuclear distances to complete structural models of complex materials and biomolecules. The technique “NMR crystallography” is now recognized by the International Union of Crystallography (IUCr) and expected to be an integral element of modern powder crystallography. For more details, see the recent review [39].

5.3. Serial Snapshot X-ray Crystallography

As one of the possible alternatives to powder diffraction, we may notice the serial femtosecond X-crystallography [40]. Similar to electron crystallography, the serial snapshot X-ray crystallography transforms powder diffraction into single crystal diffraction. Contrary to the former, which works with one sub-micrometric single crystal, the latter method accumulates partial single crystal data obtained very quickly on a series of sub-micrometric crystals, thus avoiding any radiation damage. The partial single crystal data are then merged into a complete single crystal dataset. The method is coupled with the pulse nature of novel sources of synchrotron radiation, free electron lasers and is intensively tested on protein crystals [41].

An interesting variant of the serial snapshot crystallography is Laue microdiffraction [42]. A revival of the Laue method for the *ab initio* structure solution has been observed in the last few years, especially using neutron diffraction. The Laue method allows collecting simultaneously many reflections in one shot and uses the whole spectrum of wavelength available in the primary beam. The serial snapshot version of the Laue method, Laue microdiffraction, works also with a series of sub-microscopic crystals, like serial snapshot crystallography, but thanks to the broad-bandpass mode of some new sources of synchrotron radiation, like the free electron laser constructed at the Paul Scherrer Institute Villigen, Switzerland, with an energy bandwidth of about 4%, the collected data correspond to a series of Laue patterns.

5.4. Pattern Modelling Methods Assisted by *Ab Initio* Calculations

In spite of great effort invested to the structure prediction from first-principles, the *ab initio* calculations are far from being a routine tool for predicting the correct crystal structure only from known chemical composition [43]. The prediction of new systems may, however, be a common ground for both crystallography and computational chemistry. Not only can experimentalists provide theoreticians with information for calculations, but predictions on whole systems can also be confirmed by experiment, as was recently illustrated on potassium silanides [44]. Learning from structure predictions is one of the guides that helps the experimentalist to build a model that is then optimized by a global optimizer in a PM method. Such an approach started with close-packed compounds [45]; the greatest progress may be registered among molecular crystals [46]. Learning from crystal structure prediction done, not by *ab initio* calculations, but by exploiting known topologies and known building units of related crystals, led to the greatest success among framework materials [47–50].

The ideal situation would be naturally the combined use of *ab initio* calculations with the analysis of diffraction data. Should we speak about the prediction-guided solution or about the solution-guided prediction? It is of no importance who guided whom, only the result, i.e., the correct crystal structure counts. The theoretical and experimental information is easily combined in a global optimizer that searches for the best structural model. Several global optimizers were proposed for structural predictions at the DFT level of the *ab initio* calculations, i.e., without active use of diffraction information: the evolutionary algorithm [51], simulated annealing [52] and the molecular dynamics-based algorithm (minima hopping) [53]. The greatest problem of the *ab initio* calculation part is, however, the time needed for the solid state calculations. Without new ideas for how to accelerate the DFT calculations, the global optimization of the structural model using jointly the theory (crystal energy) and experiment (diffraction pattern) will stay limited to structures not going far beyond 100 atoms in the unit cell. One way for improving the situation is distributed computing, i.e., joint use of many computing units: processors in parallel available already nowadays for PM programs like DASH [54] and Fox [12].

5.5. Accumulated Knowledge-Guided Structure Solution

The knowledge accumulated by generations of crystallographers on compounds from a given class of materials must be actively used within the SDPD process. There is no need to reinvent the

wheel. Known topologies, crystal chemistry rules, atomic coordination, interatomic distances and angles, molecular fragments, polyhedral connectivity and other information are valuably concentrated in various databases specialized for organic, inorganic compounds, frameworks and many others. It is of high importance that the database allows for a combined search using various parameters: if during the SDPD process, the reliable indexing provides the unit cell volume and crystal system, chemical analysis provides a reliable chemical composition and the coordination of one or more cations is expected from spectroscopic methods, then the cross search in a database may provide a unique structural prototype, which may immediately lead to the correct structure model for the studied crystal. Such acceleration of the SDPD process cannot be omitted. The utmost care must, however, be paid that the structure solution is the correct one, i.e., not biased and misled to a local minimum in the parameter space of the global optimizer. The wrong conclusions are made easily, and powder diffraction is always limited in its resolving power by the projection of the 3D diffraction pattern on the 1D powder pattern.

6. Conclusions

It is certain that in the future, potentially useful systems in different applications like electroceramics, will involve highly complex and dynamic systems, which are subject to metastability and changing thermodynamic equilibria, particle sizes and crystallinity. The setups at synchrotron beamlines are evolving quickly, and it will become increasingly feasible to study systems under working conditions. The structure solution and complete structural characterization will always be at the forefront of characterizing these systems. Powder diffraction is and will surely remain the most amenable method due to the broad spectrum of information obtainable and the simplicity of in situ experiments coupled to complementary methods, such as X-ray absorption spectroscopy (XAS), vibrational spectroscopy or thermogravimetric analysis (TGA), differential thermal analysis (DTA) and mass spectroscopy (MS), just to name the most useful ones.

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