Frontiers between crystal structure prediction and determination by powder diffractometry

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Prediction is not the estimation of atomic coordinates of atoms or molecules inside of a cell previously obtained by indexing the diffraction pattern : such a job is a structure solution. Prediction is supposed to anticipate accurately the possible crystal structures (chemical content, cell, atomic positions) before synthesis or discovery in nature. Efforts in organic chemistry to predict the packing of previously known molecules, thus providing the cell, are progressing slowly through blind tests organized by the CCDC. However, if the use of a previously established molecular formula is invaluable for the search of the structures of possible polymorphs, this approach is obviously unable to predict any new molecule.

Why researchs about structure prediction appear so closely related to powder diffraction ? The fact is that structure determination from single crystal data is currently almost totally efficient at solving any problem, provided one suitable single crystal is available. The consequence is that most efforts are now concentrated on cases still unsolved, due to the absence of this essential, large- and well organized-enough, single crystal. A too large structure complexity can preclude the structure determination by powder diffractometry (SDPD) in spite of a successful indexing. Moreover, there are cases where indexing is not realized at all. However even if showing strong iso or anisotropic line broadening, precluding indexing, the powder diffraction pattern remains a fingerprint which can be used for the selection of the best model, if any, among the generally too numerous predictions.

In summary, we feel that structure prediction is useless when structure determination is possible, and useful otherwise. This is a short-term vision due to the current inefficiency of systematic total predictions, consequence of a poor theory of materials, or at least a poor use of quantum mechanics and chemistry (first-principle calculations, DFT, ab initio, etc).

Massive inorganic crystal structure predictions were done recently. For millions of virtual zeolites [1] or related materials the composition is imposed : SiO_2 or $AlPO_4$ etc, and this is finally also a search for polymorphs. For some other predicted inorganic compounds the exact composition was not imposed, but at least elements were selected and some geometrical rules for organizing them were applied (exclusive corner sharing of polyhedra within the GRINSP software [2-3]). This is the very beginning of a promising field, justifying the creation of a database, the PCOD [4], containing the crystal data of predicted titanosilicates, phosphates, vanadates, niobates, fluoroaluminates (etc). Prediction looks thus as a marginal way to solve crystal structures unsolved by the classical crystallography. But of course, the whole potential of the prediction approach is much broader than crystal structure solution alone : predicting any possible crystal structure in any physical conditions in the universe would allow for the prediction of the physical properties as well. This, added to progress in prediction of synthesis conditions, would allow for a new era of research, overcoming serendipity. That way will obviously be long, made of small steps. As one of these steps, It is expected that identification of inorganic compounds by using a search-match software including powder data calculated from the 10.000 PCOD entries will be demonstrated for the first time in Brazil, 2007.

[1] Hypothetical Zeolites Database: http://www.hypotheticalzeolites.net/
[2] A. Le Bail, *J. Appl. Cryst*. **38** (2005) 389-395.
[3] A. Le Bail and F. Calvayrac, *J. Solid State Chem.* **179** (2006) 3159-3166.
[4] Predicted Crystallography Open Database – http://www.crystallography.net/pcod/