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Multivariate innovative methods for the analysis of in situ X-ray powder diffraction data collected in the presence of chemical, spatial, temperature or time gradients

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X-ray powder diffraction (XRPD) is a key technique for the characterization of phases in solid samples, with applications spanning from materials and earth science to chemistry, pharmaceutics and engineering. The obtained information can be either qualitative or quantitative, related to phase composition, crystallite size, stress, texture. In the last decades in situ experiment allowed to evaluate such properties while the samples evolve by internal (e.g. chemical) and/or external (e.g. temperature, pressure…) stimuli. Such experiments allow exploring the structural properties in presence of gradients of several types. Chemical (when composition is changing, or a gas pressure is applied) and energetic (when temperature and/or pressure are being modified during the experiment) are the most investigated gradients within in situ XRPD experiments. When a static sample is studied by microdiffraction, a spatial gradient can be studied by collecting XRPD pattern scanning the surface of the sample itself: in other words, the structural features are studied depending on the xy coordinates of the sample surface. In all these cases, large dataset can be collected both by lab instruments and synchrotron facilities. Facing such datasets requires new approaches, complementary to traditional XRPD analysis methods, which are very powerful but time and resource consuming.

The amount of useful information that can be extracted from a XRPD dataset can be maximized exploiting multivariate analysis techniques such as principal component analysis (PCA), while reducing the experimental noise. Within the presentation, the application of multivariate approaches to X-ray diffraction will be described presenting both assessed and under development approaches. Particular attention will be given to pre-processing selection in relation to specific data features. Then, case studies are presented to show potentialities and limitations of each approach. At first, regression and PCA methods are applied to chemical gradient, to carry out a quantitative of some ad hoc designed mixtures showing preferred orientation and microabsorption, illustrating how they can overperform traditional Rietveld-based approaches. The PCA is then used to analyze the temperature gradient, studying the crystallization and melting of eutectic mixtures by an XRPD experiment run at variable temperature conditions. By combining multivariate analysis and in situ XRPD, a new approach called differential scanning diffraction (DSD) can be defined and implemented. A phase transition can be now analyzed like a traditional differential scanning calorimetry (DSC) but probing structural effect instead of energy ones. Finally, spatial gradients are analyzed, applying PCA analysis to microdiffraction data collected on the surface of metal object and mineralogic samples.