Do we really perform physicochemical measurements on polycrystalline substances always with a known crystal structure?

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Despite great advances in single crystal structural analysis, growing a suitable single crystal for a routine experiment can be a difficult task. Often only a few single crystals can be prepared, or it is necessary to select a single crystal from a polycrystalline mixture - usually more phase. After solving the crystal structure, it is common practice to correlate it with the results of other physicochemical methods such as e.g. infrared and UV / VIS spectroscopy, EPR spectroscopy, magnetic measurements, etc. However, one single crystal is not sufficient for these methods, and repeated preparation of a larger amount of predominantly polycrystalline sample requires control for the purity and “identity” of the crystal structure of the powder sample and single crystal. Powder diffraction analysis is a suitable method, but in its practical application we have observed occasional, commonly overlooked discrepancies. Standard powder diffraction analysis is performed at room temperature ($\sim$ 298K) but single crystal structural analysis at 100K. By comparing the experimental diffractogram of the powder sample with the simulated from the structural data of the solved crystal structure, we can eliminate the influence of the thermal expansion of the sample. In many cases, however, this will not help, and even if the diffractograms on the eye are the same, we will not achieve their "identity". It has been shown and other physicochemical measurements (but also single crystal structural analysis) have confirmed that a change in temperature in the experiments can also lead to phase changes, the formation and interconversion of polymorphs or the formation / extinction of a disorder. These transformations can be irreversible as well as reversible and significant as well as subtle.

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