

Electron Crystallography – a tool to solve polymorphic structures ?

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A common tool to analyse crystal structures is single crystal x-ray diffraction, nowadays a well developed routine method. Nevertheless, many interesting materials are preferentially micro- or nano- crystalline such that no crystals of a size sufficient for single crystal x-ray diffraction can be obtained. Other methods, like single crystal electron diffraction (ED) or x-ray powder diffraction (XRD) still present a challenge, especially for organic compounds. X-ray powder diffraction delivers one-dimensional data, which suffers often from overlapping reflections, inadequate crystal quality, unknown impurities and preferred orientation [1, 2]. Electrons undergo coulombic interactions with matter which are 10^8 times stronger than electromagnetic interactions. Therefore, it is possible to investigate extremely small volumes. In comparison with powder data ED provides us with three dimensional data but suffers from an incomplete reciprocal space (missing cone problem), elongated reflections (spike function) and is affected by multiple scattering and dynamical scattering for thick samples [3, 4]. Because dynamical scattering is less serious for organic materials, structure determination by electron diffraction can be carried out based on a kinematical diffraction theory in the first step and the resulting model can be refined dynamically in a second step.

Properties of a material in the solid state are strongly governed by its molecular and crystal structure and therefore a big effort is put into structure determination. Dependent on the crystallisation parameters used one may derive even different crystal structures from the same molecule constituting different polymorphs. Since the definition of polymorphism can not be given in an overall manner McCrone's definition as "the possibility of a compound to crystallize at least in two different arrangements of the molecules" is used here [5].

The non-linear optical (NLO) active aromatic chalcone 1-(2-furyl)-3-(4-benzamidophenyl)-2-propene-1-one (FAPPO), shown in Fig.1, was found to give a rather big SHG activity of 1-2 order of magnitude higher than crystalline urea [6]. Due to their conjugated system all discussed NLO active molecules are approximately flat. It crystallizes from ethanol in two modifications which could not be separated from each other. Hence, a structure analysis from x-ray powder diffraction or even the indexing of the peaks turned out to be impossible.

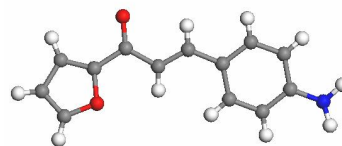


Figure 1: Molecular structure of FAPPO

Structure analysis using electron diffraction provides access to a variety of materials of quite different properties. It has already been proven to work in principle. But like using x-ray powder diffraction it is still a challenge. Due to recent developments and investigations the path of data collection as well as the path of data analysis have been improved and therefore accelerated significantly. This allows studies of polymorphic systems in a reasonable time and opens up new important fields (e.g. polymorphism of drugs and pigments). Some of these compounds especially pigments exist in many phases. Cu-Phthalocyanine, a insoluble nano crystalline material, shows [7] nine polymorphs (α , β , γ , δ , ϵ , π , ρ , ζ , σ and R) and the calcium salt of Pigment Red 53:2, soluble in a variety of solvents, crystallizes in 15 modifications (α , γ , δ , ϵ , ζ , η , θ , π , ι , κ , λ , ν , ξ , \omicron , ρ) [8].

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