Luminescent Materials at High-Pressure: Why Crystal Orientation Matters

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Solid state luminophores make inviting targets for high-pressure structural studies owing to their sensitivity to molecular and crystalline environment. Application of quasi-hydrostatic pressure can serve as a means to modify crystalline environment in a controllable manner or induce phase transitions. As a result, applied pressure can modify and regulate chemical bonding, intermolecular interactions and derived physicochemical properties, such colour [1], luminescence emission wavelength and quantum efficiency [2]. Modern quantum crystallography tools, such as TAAM or HAR approaches, allow studying such properties and their evolution with pressure in more detail [3].

Unfortunately, experiments performed at high pressure in a diamond anvil cells (DAC) yield inherently biased intensities and incomplete datasets. The lack of completeness alone may impede space group determination, render solution of a crystal structure or determination of absolute configuration impossible, and conceal or misrepresent fine details such as disorder or unusual charge density distribution (Fig. 1). While data completeness is less of an issue in a regular crystal system, where abundance of symmetry elements allows for the retrieval of almost all unique reflections, the majority of interesting organic and metalorganic materials tend to crystallize in lower-symmetry systems (like monoclinic) or transform to low-symmetry phases as the pressure is increased. The fact that sample orientation in a DAC can improve reciprocal space coverage is generally acknowledged throughout the high-pressure crystallographic community [4, 5]. However, the extent to which data completeness can be improved by proper sample placement and how much can actually be gained by it has not been systematically investigated until recently.

In this presentation, I will present examples where carefully planned in-house experiments and controlled sample orientation allowed to study pressure-induced, symmetry-lowering phase transitions in luminescent organic [6] and organometallic materials. Effective sample orientation and careful data processing has ensured over 90% coverage even for the monoclinic system and enabled unrestrained structure refinements in TAAM formalism and access to complete systematic extinction patterns. I will also shortly comment on what artefacts would have arisen had the datasets been less complete.

Figure 1. The crystal orientation in a DAC affects attainable data completeness and features in the residual density map.