Crystallography at HT: a new device and the case study of jumping crystals

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Abstract. We present here a new HT device and crystal mounting methods that make single-crystal diffraction techniques flexible and fully versatile for studies under different heating (up to ca. 1100°C) and atmospheric conditions, with no limitations to the rotation of goniometer circles. Crystal mounting in quartz vials (in air; in closed atmosphere of virtually any conditions; under vacuum) by making use of quartz wool to avoid mechanical stress on crystal surfaces is compatible with this set-up and proved particularly efficient in the study of jumping crystals, as quartz fibres are flexible enough to accommodate crystal movements.

Key words: single crystal XRD, in situ, high temperature, jumping crystals.

Text. The study of crystal behaviour at high temperature using single-crystal X-ray diffraction and in situ techniques has long tradition, starting with pioneering work of Megaw in the early ’60s [1]. Our 15+ years of experience in studying crystal behaviour and phase transitions at HT by single-crystal X-ray diffraction has brought to two fundamental issues about the use of in situ techniques, namely: (1) the limitations imposed by the furnace itself to the excursions of goniometer circles, which impede to collect data to high resolution; and (2) the difficulties in controlling the physico-chemical and atmospheric conditions of the experiment.

Our new HT device makes use of a vertical air or gas flow to heat the sample. It is mounted externally, just above the crystal at a fixed angle, and therefore it allows full liberty to the rotation of all goniometer circles. A thermocouple is placed at the exit of the gas flow. The blower can make use of air, N2 or other gases to heat the sample, thus allowing studying the high-temperature behaviour of crystals under different atmospheric conditions. Standard mounting in quartz vials is also compatible with this set-up and methods will be described for mounting by making use of quartz wool to keep the crystal in position and avoid the use of glues or cements and for sealing the vial under vacuum or other conditions.

In this talk, examples will be shown of both inorganic and organic crystals, which exhibit the thermostalient effect, despite showing different structural behaviours with temperature causing them to jump. Examples will include the jumping effect associated with the first-order tetragonal-to-cubic phase transition in Mg2Cu1.5Cr2O4 spinel solid solution. In this structure, the cooperative Jahn-Teller distortion imposing the tetragonal symmetry can be suppressed either by increasing the temperature or by gradually substituting the d9 Cu(II) cation with the spherical and closed-shell Mg(II) cation. It will be shown how the temperature variations of spinel crystal structures can be analysed by mode decomposition techniques and the structural evolutions inferred from the temperature dependences of the spontaneous strain and the associated order parameter [2].

Other examples will come from organic crystals (collaboration with Ž. Skoko, G. Ventruti and J. Popović) and include oxitropium bromide (OTB) and hydrated methscopolamine bromide (SMBH), where the jumping effects seems to be associated, respectively, with an isosymmetrical phase transition or with a dehydration/re-hydration process. Both transformations are responsible for a fairly large first-order jump, are reversible and show some hysteresis on cooling. In both cases, in situ HT SC-XRD data were collected at regular intervals up to above the transition temperature and down to room temperature. All samples show negative thermal expansion of at least one cell parameter. OTB undergoes a structural transition at 330 K with some hysteresis on cooling. Variation of the unit-cell parameters with T shows a large first-order jump. SMBH clearly shows a sudden jump at ca. 320 K, also in this case reversible and with some hysteresis on cooling. Preliminary structure refinements indicate a single crystal-to-single crystal transformation due to a dehydration/re-hydration process rather than a phase transition.
References
