MS34-O4

Analysis of the dynamics of a jumping crystal with Molecular Dynamics and TLS analysis from powder diffraction data

Jacco van de Streek[1]

1. Avant-garde Materials Simulation, Merzhausen, Germany

email: jacco.vandestreek@avmatsim.eu

Jumping crystals often shatter as a result of the phase transformation causing their jumping, making it difficult to analyse the structure after the phase transition.

For a compound for which the structure of the low-temperature phase was known from single-crystal analysis but where the disintegration of the crystals during the phase transformation prevented the elucidation of the high-temperature phase, we were able to observe a discontinuity in the unit-cell parameters when the temperature of the low-temperature phase was increased with Molecular Dynamics (MD). The new phase had a higher symmetry than the low-temperature phase and the anisotropic displacement parameters calculated from the Molecular Dynamics trajectory identified strong libration of the molecules as the cause of the phase transition.

Temperature-dependent powder diffraction experiments confirmed the structure of the new phase, but because anisotropic displacement parameters cannot be reliably refined against powder diffraction data, it seemed impossible to verify experimentally that molecular libration caused the phase transition.

This was solved by refining the anisotropic displacement parameters using a TLS (Translation-Libration-Skew) model, reducing the number of parameters required to describe the anisotropic motion of the non-hydrogen atoms by a factor of four. Additionally, the TLS approach allowed us to include the description of the anisotropic motion of the hydrogen atoms, even though only laboratory X-ray powder diffraction data were available. The results from the experimental TLS analysis were an excellent match with the results from the Molecular Dynamics calculations.

The combination of Molecular Dynamics simulations and TLS refinement against XRPD data therefore allowed a full characterisation, at the atomic level, of the anisotropy of the dynamics of the individual molecules leading up to, during and after a phase transition despite the destruction of the single-crystals during the phase transition.

Keywords: TLS, Molecular Dynamics, XRPD

MS34-O5

Is single-crystal diffraction a suitable technique to study jumping crystals in situ?

Michele Zema[1], Željko Skoko[2], Gennaro Ventruti[3], Jasminka Popović[4], Serena C. Tarantino[3]

1. Department of Earth and Environmental Sciences, University of Pavia, Pavia, Italy
2. Department of Physics, University of Zagreb, Zagreb, Croatia
3. Department of Earth and Geo-environmental Sciences, University of Bari, Bari, Italy
4. Division of Materials Physics, Ruđer Bošković Institute, Zagreb, Croatia

email: mz@iucr.org

Thermally induced mechanical properties of crystals, including the thermosalient effect manifested by some crystalline materials that jump many times their own size when heated or cooled, are known since the ‘80s. Modern analytical techniques have allowed deeper and deeper insights into the transformations that rule this phenomenon, and renewed the interest in a class of mechanically responsive materials that hold potential for a broad range of applications in electronics, soft robotics, regenerative medicine, and related fields [e.g., 1-2].

However, potential applications of the thermal-to-mechanical energy conversion through thermosalient effect require detailed understanding of the structural changes at the atomic/molecular level. This proves to be quite challenging, because of decreased crystal quality, latent/permanent crystal deformations, or simply because of technical difficulties of performing in situ single-crystal X-ray diffraction (SC-XRD) analyses. As a consequence, very few evidences on the atomic-scale mechanisms driving these transitions are available, mainly on non-molecular compounds [e.g., 3].

We have developed a new device and crystal mounting methods that make this technique 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 at the transition.

We present here the first results on three thermosalient crystals, oxitropium bromide (OTB), scopolamine methyl bromide (SMB) and hydrated SMB (SMBH). In all 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 fairly large first-order jump. No discontinuities have been observed in the unit-cell parameters evolution with T for SMB, whereas 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.

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Keywords: thermosalient effect, negative thermal expansion, in situ XRD

MS35 From 0- to 3-dimensional porous systems

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MS35-O1

Metalorganic frameworks as platforms for biosignaling molecules

Elisa Barea[1], Francisco J. Carmona[1], Carmen R. Maldonado[1], Shuya Ikemura[2], Carlos C. Romão[3], Zhehao Huang[4], Xiaodong Zou[4], Susumu Kitawaga[5], Shuhei Furukawa[5]

1. Department of Inorganic Chemistry, University of Granada, Granada, Spain
2. Institute for Integrated Cell-Material Sciences, Kyoto University, Kyoto, Japan
3. ITQB, Universidade Nova de Lisboa, Oeiras, Portugal
4. Berzelii Centre Exselent, Stockholm University, Stockholm, Sweden
5. Institute for Integrated Cell-Material Sciences, Kyoto University, Kyoto, Japan

email: ebaream@ugr.es

Since pioneering work of Nobel laureates Furchogtt, Ignarro and Murad concerning nitric oxide (NO) as an important biosignaling molecule in the cardiovascular system, significant attention has been paid on the physiological and potential therapeutic role of NO and other endogenously produced small gas molecules, such as carbon monoxide (CO). The easiest administration route for these gas molecules into the body is the inhalation of their air mixtures. However, this strategy lacks of specificity and, in the case of CO, the higher affinity of this gas to haemoglobin/myoglobin compared to oxygen, as well as its poor solubility in water, means that high doses of inhaled CO are required to obtain a beneficial effect with the concomitant associated safety risk. In order to overcome these drawbacks, CO/NO-releasing materials (CORMAs and NORMAs) appear as solid CO/NO storage materials able to deliver the corresponding gas in a triggered manner. In this context, one of the most versatile strategies to design new CORMAs/NORMAs consists in the use of MOFs as biocompatible vehicles of these therapeutic gases.[1]

Taking into account this background, firstly, we have combined an existing CO-releasing molecule with the biocompatible MOF $[Al(OH)(SDC)]_n$ (H_2SDC: 4,4'-stilbenedicarboxylic acid) (CYCU-3) to obtain a new CORMA. In this work, we have shown the feasibility to control particle size and morphology in CYCU-3 by means of the coordination modulation method. With this aim, we have screened different reagent concentrations and modulator/ligand ratios. As a result, CYCU-3 materials with different particle features have been isolated including a new crystalline phase, for which a structural model based on a squeezed and defective structure of pristine CYCU-3 has been proposed. Besides, the air-stable and photoactive CO-releasing molecule ALF794 ($Mo(CNCMe_2CO_2H)_3(CO)_3$), which has demonstrated efficacy against acute liver injury in animal models, has been selected to be encapsulated in three selected CYCU-3 materials. Then, the influence of structure,