Time-resolved streaming crystallography on the study of persistent photoinduced phase transition in RbMnFe prussian blue analogue

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Abstract

Tailor-tuning the physical properties of materials is an important challenge for science and technology. Light, as an ultrafast and selective driver, is interesting as an external stimulus for controlling physical properties. In pursuit of more efficient and robust light-based technologies, materials science aims to develop systems with characteristics such as a wide thermal hysteresis preferably centered at room temperature, and a persistent and ultrafast switching to a photo-induced state, achievable with a single light pulse excitation. Understanding the physical mechanisms of photo-induced phase transitions is crucial for controlling materials' properties.[1]

In this work, we present our time-resolved x-ray diffraction studies on the ultrafast photoswitching structural dynamics of a cyanide-bridged bimetallic molecular material {Rb0.94Mn0.94Co0.06[Fe(CN)6]0.98·0.2H2O}, for which a new streaming crystallography technique was developed.[1] This material undergoes an intermetallic charge-transfer (CT) based phase transition, from a MnIIIFeII tetragonal phase at low temperature to a MnIIFeIII cubic phase at high temperature, exhibiting a wide thermal hysteresis (75 K) centered at room temperature. This transition can also be induced by light, with a single laser pulse excitation within the thermal hysteresis, resulting in a persistent photo-induced cubic (PIC) phase.

Our studies on this light-induced process show that the structural transition is driven by elastic cooperativity. Above a certain laser fluence threshold, the system switches globally to the persistent PIC phase within 100 ps. Below this threshold, a volume expansion occurs, but the system relaxes back to the tetragonal ground state in about 10 µs. These results are also rationalized with a Landau-based model, which accounts for the role of elastic cooperativity in the structural dynamics. Considering the elastic coupling between the CT and symmetry-breaking processes reproduces the simultaneous changes of spin state and symmetry, as well as the widening of the thermal hysteresis.

[1]Hervé, M., Privault, G., et.al. (2024). Nature Comm., 15(1), 1–10