Methods

Sample preparation

The $Rb_{0.94}Co_{0.06}Mn_{0.94}[Fe(CN)_6]_{0.98}\bullet 0.2H_2O$ material, referred to $RbMn_{0.94}Co_{0.06}Fe$ in the present work, was synthesized according to the procedure reported in previous works[1], where extensive characterization data can be found. Briefly, it consists of cubic-shaped crystals, with good crystallinity and an average size of 0.9 ± 0.3 µm. Fig. S1 shows the thermal magnetic susceptibility measurements ($\chi_m T$ vs T) of the material, which indicates a broad bistability regime around room temperature, between the low temperature (LT) and high temperature (HT) phases. Conventional X-ray diffraction (XRD) powder pattern of the LT phase corresponds to a tetragonal lattice, with a_{LT} = b_{LT} = 10.0051(11) Å and c_{LT} = 10.4744(16) Å in the $F\bar{4}2m$ space group, while the XRD pattern of the HT phase corresponds to a cubic lattice ($F\bar{4}3m$), with a_{HT} = 10.5495(6) Å. In this work, we studied the out-of-equilibrium dynamics of photoexcited $RbMn_{0.94}Co_{0.06}Fe$ crystals in the LT phase and at room temperature (293 K), where both phases are stable.

Powder of $RbMn_{0.94}Co_{0.06}Fe$ was dispersed in ethanol, with a crystal-solvent weight ratio of 1:90. The solution was cycled 4 times between a liquid nitrogen bath (77 K, below the hysteresis) and a heating bath (set at 350 K, above the hysteresis), and then let in the ultrasonic bath for 4 h, in order to avoid possible aggregates of crystals. The solution was finally kept at 193 K overnight, to ensure that the crystals are fully in the LT phase.

Setup for combined time-resolved XAS/XRD

Time-resolved X-ray measurements were performed at the X-ray pump-probe (XPP) beamline of the LCLS X-ray Free-Electron Laser (X-FEL)[2]. As schematically shown in Fig. 1b of the Main Text, the prepared solution was used in the streaming powder configuration, which makes it possible to study ultrafast and persistent photoinduced phase transitions[1, 3]. Using an HPLC pump, the solution of dispersed crystals was streamed at room temperature through a 75-µm free-flowing jet to interact the laser and X-ray pulses[4]. The flow rate was set to 2 $mL.min^{-1}$, which corresponds to a jet velocity of 7.5 $\mu m.\mu s^{-1}$. This ensures a complete refreshment of the sample between two consecutive X-ray shots (intervals of 8.3 ms at the LCLS repetition rate of 120 Hz).

X-ray pulses from the X-FEL were monochromatized using a silicon (111) double crystal monochromator ($\Delta E/E \approx 10^{-4}$), and the X-ray photon energy was varied from 6.53 keV to 6.59 keV, to scan the Mn K-edge. The X-ray beam was focused to a spot size of 5×5 μm^2 at the sample position. It was synchronized with 560 nm laser pulses produced by an optical parametric amplifier, whose spot size was 220×385 μm^2 at the interaction region. For delay scans in the femto- to picosecond range, the relative arrival time between the X-ray and optical pulses was recorded using the timing tool diagnostic[5]. The optical laser fluence was tuned up to 80 $mJ.cm^{-2}$.

In the present work, we simultaneously recorded the X-ray absorption signal and the X-ray diffraction pattern, based on a shot-to-shot collection on two distinct detectors, at the repetition rate of the X-FEL (120 Hz). X-ray absorption was measured through total fluorescence using an epix100 detector at 90°, and the obtained fluorescence yield was normalized on the X-ray shot intensity. Diffraction signal was collected using an epix10k2M detector[6] in the transmission geometry. Each 2D image was azimuthally integrated using pyFAI[7] and normalized on the X-ray intensity as well. After normalization, a typical number of 2000 shots are averaged for each delay. Reference shots without laser irradiation were also measured during data collection, with a laser on:laser off ratio of 2.5.

Analysis of time-resolved XAS data

The X-ray absorption spectra (XAS) were obtained by scanning the incident photon energy over the Mn K-edge. They display a small pedestal below 6.537 keV, that was subsequently removed to all the (time-resolved) XAS signals. For the measurements of XAS spectra at specific delays, the spectra were normalized over the high-photon range ([6.58 keV; 6.59 keV]) of the reference spectrum without laser irradiation.

For the time-resolved XAS (TR-XAS) measurements and fluence-dependent measurements at specific X-ray photon energies, we extracted the normalized difference of XAS intensity as:

$$\Delta XAS(t) = \frac{S(t) - S_{off}}{S_{off} - S_{pedestal}}$$

where $S(t)$ is the measured XAS intensity at the delay t, S_{off} the XAS intensity measured without laser irradiation, and $S_{pedestal}$ is the pedestal signal, previously determined in the energy-resolved measurements. In the specific case of measurements done at a photon energy corresponding to the maximum absorption of Mn^{3+} or Mn^{2+} species (6.5577 keV and 6.5520 keV respectively), $\Delta XAS(t)$ was further rescaled to the corresponding difference between the static HT and LT spectra. The obtained variation, e.g., $\Delta XAS(\%\, Mn^{2+})$ at 6.5520 keV, was thus:

$$\Delta XAS(\%\, Mn^{2+}) = \frac{\Delta XAS^{6.552}(t)}{\Delta XAS^{6.552}_{HT-LT}} \times 100$$

with:

$$\Delta XAS^{6.552}_{HT-LT} = \frac{S^{6.552}_{HT} - S^{6.552}_{LT}}{S^{6.552}_{LT} - S_{pedestal}}$$

As such, this relative change provides an estimate of the percentage of Mn^{3+} or Mn^{2+} species in the crystals, as shown in Figs. 2 and 3 of the Main Text.

To extract the timescales of the different processes from time-resolved XAS measurements, the obtained $\Delta XAS(t)$ signal was then fitted using a series of exponential dynamics. Each time-resolved XAS measurement (at a single X-ray photon energy and laser fluence) was fitted with a sum of exponential population functions convoluted with the experimental instrument response function (IRF):

$$\Delta XAS_{fit}(t) = S_{IRF}(t) \otimes P(t)$$

with $S_{IRF}(t) = \frac{1}{\sigma_{IRF}\sqrt{2\pi}} \exp\left(-\frac{t^2}{2\,\sigma_{IRF}{}^2}\right)$, characterized by the gaussian standard deviation σ_{IRF}, and:

$$P(t) = \left[A_s + \sum_{i=1}^{N} A_i.\left(1 - \exp\left(-\frac{t - t_0}{\tau_i}\right)\right)\right].H(t - t_0)$$

where N is the number of decay constants chosen for the fit ($N \in [1; 3]$), τ_i are the exponential decay times, A_i are the amplitudes of the population function associated to each τ_i, A_s is the step amplitude (instantaneous change of signal), t_0 is the laser – X-ray overlap time and $H(t - t_0)$ is the Heaviside function. Global fits of datasets including several TR-XAS scans (taken at different photon energies and laser fluences) were performed using a least-square procedure, with common timescales and IRF value σ_{IRF}. t_0 and the amplitudes A_s and A_i were fitted independently for each scan of a dataset, while the timescales τ_i and the IRF σ_{IRF} were fitted as common values for all the scans. The reported uncertainties correspond to the standard deviation of the global fit.

Analysis of time-resolved XRD data

After azimuthal integration, the resulting pattern extends in the [0.5 Å^{-1}; 3.1 Å^{-1}] Q-range. It contains a broad scattering contribution associated with the solvent, which is dominant due to the low crystal concentration (Fig. S2a). We first remove this contribution by subtracting the scattering pattern of pure ethanol measured in the same conditions. The resulting pattern is shown in Fig. S2b, and displays the Bragg peaks of $RbMn_{0.94}Co_{0.06}Fe$. It also contains a remaining background, due to the temporal evolution of the X-ray fluorescence from the sample and scattering from the surrounding gas and X-ray optics. Given the complex time evolution of the full patterns, we subsequently analyzed the time-resolved XRD patterns (TR-XRD) by looking at individual peaks or groups of peaks.

For each group of peaks, a systematic error is observed along the Q vector, that is visible as high-frequency oscillations in Q. We corrected it by applying a Fast Fourier Transform (FFT) filter to the data, where the high-frequency part of the XRD patterns is removed without impact on the peak shape (Fig. S3).

We then analyzed the diffraction patterns of each group of peaks as follows. We first fitted the Bragg peak(s) of the reference pattern without laser irradiation, using the same approach as in[8]. The individual Bragg peaks are fitted using split pseudo-Voigt peak profiles to account for their high anisotropy (see Fig. S8a for an example with the peak (111), and Fig. S10a for (002)/(200) peaks):

$$S_{fit}(Q) = S_{bkg}(Q) + \sum_{i=1}^{N_{SPV}} SPV_i(Q)$$

where $S_{bkg}(Q)$ is a second-order polynomial to model the background, and N_{SPV} is the number of fitted peaks ($N_{SPV} \in [1; 2]$). $S_{bkg}(Q)$ was fitted outside of the Bragg peaks, and then fixed during the fit of the peaks. The split pseudo-Voigt profile $SPV(Q)$ is defined as an asymmetric peak shape, where the left (L) and right (R) sides around the peak center Q_O are described as two distinct pseudo-Voigt functions:

$$SPV(Q) = \begin{cases} A_L.PV_L(Q), & for\ Q < Q_0 \\ A_R.PV_R(Q), & for\ Q \geq Q_0 \end{cases}$$

where $PV_X(Q)$ $(X = L, R)$ is the usual combination of a Lorentzian and a Gaussian profile with a common half width at half maximum σ_X and a mixing fraction $\alpha_X \in [0; 1]$:

$$PV_X(Q) = \alpha_X \frac{1}{\pi} \frac{\sigma_X}{(Q - Q_0)^2 + \sigma_X^2} + (1 - \alpha_X) \frac{\sqrt{\ln 2}}{\sigma_X \sqrt{\pi}} \exp\left(- \ln 2 \frac{(Q - Q_0)^2}{{\sigma_X}^2} \right)$$

Finally, ensuring continuity at the peak center Q_0 imposes:

$$A_R = \frac{PV_L(Q_0)}{PV_R(Q_0)} \cdot A_L$$

where A_L and A_R represent the peak integral of the left and right side of the Bragg peak, respectively.

When the crystals are irradiated by the laser, a new contribution appears in the diffraction patterns, in addition to the initial Bragg peaks. We thus fitted the TR-XRD patterns by including an additional Gaussian peak profile to $S_{fit}(Q)$, that describes the appearing contribution (see for instance Fig. S8b-c):

$$S_{fit}(Q, t) = S_{bkg}(Q, t) + \sum_{i=1}^{N_{SPV}} SPV_i(Q, t) + S_{HT}(Q, t)$$

The fit was done at each delay, where $S_{bkg}(Q, t)$ depends on the delay (variations of the X-ray fluorescence and solvent scattering), and $SPV_i(Q, t)$ describes the time evolution of the initial Bragg peak(s), through the evolution of $Q_0(t)$, $A_X(t)$, $\sigma_X(t)$ and/or $\alpha_X(t)$. The additional Gaussian profile is described as:

$$S_{HT}(Q, t) = A_{HT}(t) \times \frac{2\sqrt{\ln 2}}{\sigma_{HT}(t).\sqrt{\pi}} \exp\left(-4 \ln 2 \frac{[Q - Q_{HT}(t)]^2}{\sigma_{HT}(t)^2} \right) \times H(t - t_{HT})$$

where $A_{HT}(t)$ is the peak integral, $\sigma_{HT}(t)$ is the full width at half maximum of the Gaussian peak, $Q_{HT}(t)$ is the peak center, and t_{HT} is the delay after which the contribution appears. In the fit of the TR-XRD patterns, the parameters of the Gaussian contribution were set free, and the appearance delay t_{HT} was set by visual inspection of the patterns. The fit of all the patterns was conducted in a sequential way, meaning that for each delay the initial conditions of the fit consisted in the fit result of the preceding delay. The reported uncertainties correspond to the standard deviation of the least-square fit.