

Supporting Information

From ambient- to high-pressure dielectric response of perovskite formamidinium manganese formate

1. Microstructure analysis of the FAMn pellet

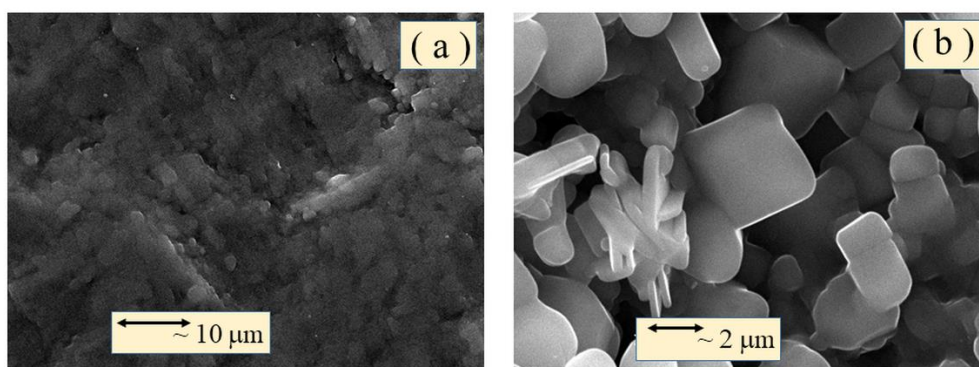


Fig. S1. SEM images of the FAMn pellet sample under magnification of (a) $\times 2000$ and (b) $\times 7000$.

2. MD simulation details and results

A $6 \times 6 \times 6$ supercell comprising 216 crystallographic unit cells and containing 432 FAMn formula units with dimensions of ~ 5 nm in each direction was constructed from the experimentally available crystallographic data of the HT phase. The GAFF optimized structure is identical to the experimental with the obtained density of $1.80913 \text{ g cm}^{-3}$, about 2.5% higher than the experimental $1.76632 \text{ g cm}^{-3}$.

All molecular dynamics trajectories in this study were generated in the constant pressure-temperature (NPT) ensemble using the stochastic velocity re-scaling thermostat¹ and stochastic isotropic barostat², both with a 1 ps time constant. All bonds involving hydrogen atoms were constrained using the LINCS algorithm³, allowing for the use of 2 fs velocity Verlet integration time step. Long-range electrostatic interactions were treated using the 4th-order Particle Mesh Ewald method⁴ with a cutoff distance of 0.9 nm. Lennard-Jones interactions were only treated in

the real space using a 0.9 nm cutoff radial distance. 20 ns long independent trajectories were simulated at 0.1, 100, and 600 MPa pressures and 250, 275, 300, 325, and 350 K temperatures.

The reorientation dynamics of FA cations was analyzed by calculating the orientational (rotational) auto-correlation functions of the form:

$$C_n(t) = \langle P_n \frac{\mathbf{u}_{NCN}(0) \cdot \mathbf{u}_{NCN}(t)}{u_{NCN}^2(0)} \rangle, \quad (1)$$

where P_n is the n -th order Legendre polynomial, $\mathbf{u}_{NCN}(t)$ is a normal vector to the plane spanned by N1-C1-N2 atoms in a FA cation, and $\langle \dots \rangle$ refers to the ensemble average. The resulting form of $C_2(t)$ was fitted using a triexponential decay of the form:

$$C_2(t) = a_0 + a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} + a_3 e^{-t/\tau_3}, \quad (2)$$

where a_i are arbitrary constants constrained to $a_0 + a_1 + a_2 + a_3 = 1$, and τ_i denote characteristic relaxation times for various molecular processes. The first two time constants τ_1 and τ_2 are respectively in the sub-picosecond and picosecond scale and correspond to various local processes such as molecular vibrations and librations. Our further analysis concentrates on the τ_3 corresponding to the slowest time scale τ_{slow} which can be related to reorientational relaxation of FA cations.

The simulation results of a second-order $C_2(t)$ at different pressures and temperatures investigated in this work show only limited reorientational dynamics of the FA cations at the molecular dynamics accessible time scale, with no $C_2(t)$ decaying to zero as $t \rightarrow 20$ ns. The temperature variation showed little effect on the dynamics between 275 K and 350 K. The application of external pressure such as 100 and 600 MPa as compared to ambient pressure showed little effect on the rotational dynamics as well with stronger slowing down at low temperature and higher pressure.

In order to analyze the rotational dynamics of individual FA cations and the distributions of their relaxation times, the rotational auto-correlation functions for each unit were calculated. However, due to very strong statistical noise in some cases, it was impossible to fit the resulting function with a triexponential decay function. Therefore, the rotational relaxation time of individual FA cations was instead estimated as an integral of the following form:

$$\tau_{\text{relax}} = \int_0^T C_2(t) dt, \quad (3)$$

where T is the total MD simulation time.

The results presented in Fig. S1 show a slightly skewed normal distribution of relaxation times obtained at 350 K and 0.1 and 600 MPa pressures. No clear effect of pressure on the FA cation dynamics can be identified. Moreover, the distribution is relatively wide, with a fraction of ions having very fast rotation and a few almost not moving, supporting partial ordering of the FA cations observed experimentally. The mean value of the relaxation time is about 4-5 ns in both cases, which corresponds to a dielectric loss maximum at tens of MHz frequency in agreement with the dielectric experiments. This indicates that the MD simulations and dielectric experiments probe the same process of the FA cation dynamics. Similar results are obtained at other simulation temperatures.

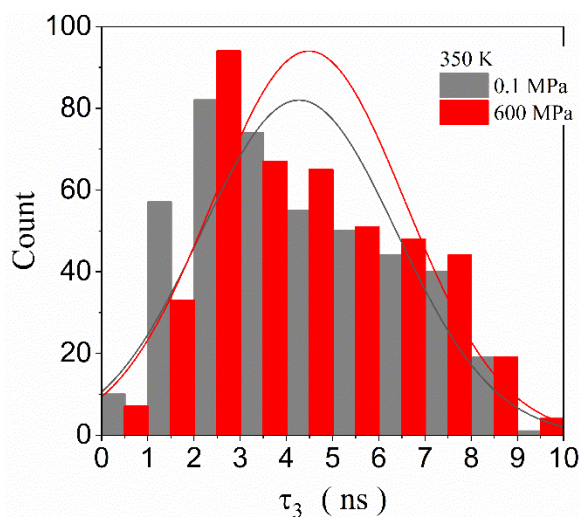


Fig. S2. Distribution of rotational relaxation times of separate FA cations obtained from the MD simulations at 350 K and different pressure.

References

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