SUPPORTING INFORMATION FOR PUBLICATION RELAXING UNDER PRESSURE WITH RIGID NICCOLITE FORMATE FRAMEWORK



1. Structural investigation

Fig. S1. (a) Structural disorder of DAB^{2+} around 3-fold *c* axis in three neighboring cages in phase **I**, all DAB^{2+} are symmetry equivalent; (b) three symmetry independent DAB^{2+} in **II** at 200 K; hydrogen bond interactions are marked as dashed lines, pink and sky-blue colors denote carbon and nitrogen atoms, respectively, from the second positon occupied in every C cavity.

2. Dielectric measurements under high pressure

The frequency-dependent dielectric loss spectra $\varepsilon''(f)$ registered at 306 K during compression from 155 MPa up to 1055 MPa exhibit a single relaxation process, which can be described with the Havriliak-Negami function in the vicinity of the relaxation peak. The obtained fits overlap well with the measured data (see Fig. S2a). As shown in Fig. S2b, despite a significant drop in the amplitude during compression, the shape of the relaxation process remains unchanged.



Fig. S2. (a) Frequency dependence of the imaginary part of the complex dielectric permittivity $\varepsilon''(f)$ obtained along the *a*-axis of the DABZn crystal under the isothermal conditions at 306 K. (b) Frequency dependence of the normalized imaginary part of complex dielectric permittivity $\varepsilon''/\varepsilon''_{max}$ obtained for the pressure range of 155 – 1055 MPa.

3. Molecular dynamics simulations

All classical non-reactive molecular dynamics simulations of DABZn were performed using the GROMACS 2020.2 software suite¹ on a desktop workstation equipped with 16 core AMD Ryzen 1950 Threadripper central processing unit accelerated by NVIDIA GeForce GTX1070 graphics processor for certain routines. The particle interactions were described by the generic Generalized Amber Force Field (GAFF).² The force field parameters were generated using the standard GAFF protocols as implemented in the Antechamber package.³ Gaussian 09 D.01⁴ was utilized for all quantum chemical calculations necessary to obtain the electrostatic potential derived partial atomic charges via the Merz-Kollman scheme.

A 5x3x3 supercell comprising 45 crystallographic unit cells and containing 180 DABZn formula units with dimensions of ~4 nm in each direction was constructed from the

experimentally available crystallographic data. The GAFF optimized structure is identical to the experimental one with lattice parameters being $\sim 2\%$ smaller than the experimental ones, and the obtained density of 2.100 g/cm³ about $\sim 9\%$ higher than the experimental 1.923 g/cm³. We believe that the generic GAFF force field performs reasonably well in describing the structure of this system and can be used for extracting more complex dynamic properties such as reorientation dynamics and relaxation time constants.

All molecular dynamics trajectories in this study were generated in the constant pressuretemperature (NPT) ensemble using the stochastic velocity re-scaling thermostat⁵ and Berendsen thermostat⁶ both with 1 ps time constant. All bonds involving hydrogen atoms were constrained using the LINCS algorithm⁷ allowing to use 2 fs velocity Verlet integration time step. Longrange electrostatic interactions were treated using 4th-order Particle Mesh Ewald method⁸ with a cutoff distance of 1.2 nm. Lennard-Jones interactions were only treated in the real space using a 1.2 nm cutoff distance.

Two sets of ten 20 ns long independent trajectories were simulated at 1 bar and 2 GPa pressures, respectively. An additional 100 ns long trajectory was generated at 1 bar in order to check the long-time reorientational behavior of the system. The reorientation dynamics of DAB²⁺ cations was analyzed by calculating the orientation self-correlation functions of the form:

$$C_{n}(t) = \left\langle P_{n} \frac{u_{NCN}(0)u_{NCN}(t)}{u_{NCN}^{2}(0)} \right\rangle,$$
(S1)

where P_n is the *n*th order Legendre polynomial, $u_{CNC}(t)$ a normal vector to the plane spanned by N1-C1-N2 atoms in the DAB²⁺ unit and < ... > refers to the ensemble average.

The resulting time dependence of the first order $C_1(t)$ at different pressures and 290 K is depicted in Fig. S3. The solid lines represent the orientation self-correlation functions at different pressures averaged over 10 independent trajectories at each pressure. The dashed line is calculated from a single 100 ns long trajectory showing a longer time behavior of this correlation function. The simulation results show only limited reorientational dynamics of the DAB²⁺ cation at the molecular dynamics scale which is not elevated by the extension of the simulation time scale. The application of external pressure shows a statistically significant, but relatively weak slowing down of cation reorientational dynamics at the time scale accessed by the MD in this work.



Fig. S3. C_1 versus simulation time for DAB²⁺ cations in DABZn at 1 bar and 2 GPa pressure and 290 K. C_1 corresponds to the first order Legendre polynomial P_1 in Eq. S1.

The resulting form of $C_1(t)$ was best fitted using a triexponential decay of the form:

$$C_1(t) = a_0 + a_1 e^{-t/\tau_1} + a_2 e^{-t/\tau_2} + a_3 e^{-t/\tau_3},$$
(S2)

where a_i are arbitrary constants constrained to $a_0 + a_1 + a_2 + a_3 = 1$, and τ_i being 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 relaxation time corresponding to the slowest time scale and related to the reorientational relaxation of DAB²⁺ units. The statistical convergence of τ_3 at two pressures with respect to the number of independent MD trajectories is presented in Fig. S4.



Fig. S4. Convergence of the slow molecular reorientation time constant τ_3 at 1 bar and 2 GPa pressure with respect to the number of independent MD trajectories.

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