

## A one-dimensional perovskite with ferroelectric and switchable nonlinear optical properties: [azetidinium]CdCl<sub>3</sub>

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Organic–inorganic perovskite hybrids (OIPHs) have been a topical area of interest in recent years. This stems from their key features such as facile and inexpensive solution based synthesis, high mechanical flexibility, structural tuneability, and chemical diversity, to name a few. Additionally, the frequently observed emergence of ferroelectric or piezoelectric properties along with optical properties renders them promising for photovoltaic energy conversion or mechanical energy harvesting applications. Herein, we report the synthesis of a novel ABX<sub>3</sub>-type ferroelectric crystal **AZECdCl<sub>3</sub>** of formula [C<sub>3</sub>H<sub>8</sub>N]CdCl<sub>3</sub>, forming an infinite one-dimensional [CdCl<sub>3</sub>]<sup>-</sup><sub>n</sub> chain along the *c* direction, with azetidinium (AZE) cations C<sub>3</sub>H<sub>8</sub>N<sup>+</sup> fitted in-between the inorganic chains. Calorimetric (DSC) measurements revealed that the crystal undergoes a complex sequence of phase transitions, at 495 K (discontinuous **I** → **II**), 202 K (continuous **II** → **III**) and 167K (discontinuous **III** → **IV**). **AZECdCl<sub>3</sub>** is characterised by a strongly enhanced electric permittivity around the paraelectric–ferroelectric transition at 202 K, exhibiting excellent ferroelectric hysteresis loops with a spontaneous polarization (*P*<sub>s</sub>) of 4 μC cm<sup>-2</sup> (168 K) and with a relatively small coercive electric field (*E*<sub>c</sub>) of 1.02 kV cm<sup>-1</sup>. The crystal exhibits also ferroelastic properties over all low temperature phases. The experimental value of *P*<sub>s</sub> agrees with theoretical predictions based on density functional theory-based calculations. The temperature-resolved second-harmonic generation (SHG) measurements attest to the polar order of this phase. First-order phase transition **IV** ↔ **III** was demonstrated to feature robust, high contrast SHG-off–SHG-on switching functionality. The broadband luminescence reveals thermal quenching when going from cryogenic temperatures to room temperature. The emission was assigned to the synergistic emissions of excitons due to the structural deformation of the lattice.

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