Phase Transitions in Ferroelectric, Layered CPA_2PbCl_4: A Multifunctional Hybrid Perovskite

Mirosław Mączka,[1] Jan K. Zaręba[2], Anna Gągor[1], Katarzyna Fedoruk-Piskorska[3], Dagmara Stefańska[1], Dawid Drozdowski[1], Maciej Ptak[1], and Adam Sieradzki[3]

[1]W. Trzebiatowski Institute of Low Temperature and Structural Research of the Polish Academy of Sciences, Okólna 2, 50-422 Wroclaw, Poland, [2]Advanced Materials Engineering and Modeling Group, Faculty of Chemistry, Wroclaw University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370, Wrocław, Poland, [3]Department of Experimental Physics, Wrocław University of Science and Technology, Wybrzeże Wyspiańskiego 27, 50-370 Wrocław, Poland

a.gagor@intibs.pl

Two-dimensional Ruddlesden–Popper hybrid perovskites are emerging as multifunctional materials for optoelectronic and nonlinear optical applications. Here, we present the phase situation and characterization of CPA_2PbCl_4, a layered lead chloride perovskite incorporating 3-chloropropylammonium (CPA^+) cations.

Structural, dielectric, SHG, and DSC analyses revealed a sequence of four temperature-dependent phases, with transitions at 353.1 K, 211.7 K, and 182.0 K. Single-crystal X-ray diffraction confirmed that phases II–IV are non-centrosymmetric (*Cmc*2_1, *Pna*2_1, *Pca*2_1), whereas the high-temperature parent phase I is (*Cmce*). Importantly, the I to II phase transition is related to the *mmmFmm*2 symmetry reduction and is purely ferroelectric, i.e. without the formation of ferroelastic strain. The ferroelectric nature of phase II is verified by pyroelectric measurements, which exhibit a reversible current response upon reversal of the poling field. Spontaneous in-plane polarization develops along the crystallographic c-axis in all phases stable below T_1, primarily originating from the intrinsic dipole moments of the CPA^+ molecular cations. Notably, the structural phase transitions induce linear negative thermal expansion (NTE) along the b-axis, with a further increase in the b lattice parameter observed upon transition to phases III and IV. Second-harmonic generation (SHG) studies demonstrate robust on–off thermal bistability with a high contrast ratio of 300:1 CPA_2PbCl_4 also shows broadband photoluminescence, transitioning to white-light emission above 180 K. This unique combination of ferroelectricity, SHG switching, white-light emission, and NTE makes CPA_2PbCl_4 a rare and versatile hybrid material for next-generation multifunctional devices [1].

[1] M .Mączka et al. *ACS Applied Materials and Interfaces (2024)* **16**, 44, 60564 - 605756