

Towards a Polar Phase in Organic–Inorganic Metal Halide Thin Films for Ferroelectric Applications

Mia Mesić^a, Lidija Androš Dubraja^a

^aRuder Bošković Institute, Bijenička cesta 54, 10 000 Zagreb, Croatia

mmesic@irb.hr

Metal halide perovskite semiconductors have attracted significant interest for their ability to facilitate the fabrication of devices with excellent optoelectronic and electrical properties through affordable and efficient chemical solution methods.[1] As electrical properties such as polarisation and charge transport are intrinsically dependent on crystal structure, the occurrence of polymorphism presents challenges in the solution processing of thin films.[2] Here, we report the synthesis and thin-film fabrication of novel cobalt halide complexes with *N*-methyl-1,4-diazabicyclo[2.2.2]octanium cations (CH₃-DABCO), aiming to prepare new ferroelectric molecule-based materials. The initial reaction between (CH₃-DABCO) iodide and cobalt(II) chloride yields the non-polar compound [(CH₃-DABCO)CoCl₃], which cannot exhibit ferroelectric behaviour. Chemical solution-based composition engineering produced a new mixed halide compound, [(CH₃-DABCO)CoCl₂I], which crystallises in two polymorphic forms at room temperature: one with a ferroelectric polar structure and one with a non-polar structure. This research focuses on the preparation and characterization of thin films to selectively obtain and stabilise the ferroelectric polar polymorph. Thin films are fabricated using spin coating, drop casting, and dip coating techniques, while systematically varying deposition parameters and environmental conditions to investigate their influence on phase formation.[3] Capturing the polar phase in thin films is a crucial step towards enabling ferroelectric characterisation and understanding the structure–property relationships in these hybrid organic–inorganic systems.[3] This research highlights the importance of combining chemical synthesis with thin-film processing strategies to control polymorphism and material polarity, offering a pathway towards molecular thin films with tuneable ferroelectric properties and potential applications in functional devices.

Keywords:

ferroelectrics, thin films, hybrid organic–inorganic systems

References:

- [1] W. Zhang et. al., *J. Am. Chem. Soc.* **139** (2017) 10897-10902.
- [2] J. Y. Li et. al., *Adv. Funct. Mater.* **31** (2021) 2102848.
- [3] Mesić et. al., *J. Mater. Chem. C* **12** (2024) 12397-12404.

Acknowledgements:

Financial support from the Croatian Science Foundation (UIP-2019-04-7433) is gratefully acknowledged.