Liquid additive directed mechanosynthesis of copper (II) based Ruddlesden-Popper perovskites

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Ruddlesden-Popper perovskites have, in recent years, garnered significant attention due to their distinct optoelectronic and thermal properties. While mechanochemistry was successfully employed to prepare these materials, such endeavours were often done without the aim of understanding the underlying mechanisms. [1, 2] Liquid-assisted grinding (LAG) is a mechanochemical technique in which a small amount of liquid is added, typically a solvent in microliter quantities. This often influences reaction kinetics, either by altering the reaction rate or its mechanistic pathway. While numerous studies have explored the effects of LAG in organic and metal-organic systems, purely inorganic reactions have been largely overlooked.[3-5] In this study, we report a series of inorganic mechanochemical reactions involving stoichiometric mixtures of caesium halides (CsX, X= Cl, Br) and anhydrous copper(II) chloride ($CuCl_2$), conducted with and without the addition of liquid. The detailed evolution of crystalline species during the mechanochemical processing was monitored using synchrotron in situ powder X-ray diffraction. Results suggest that the formation of intermediates and Cu (II) solvates can significantly influence the reaction mechanism. Depending on the solvates' stability, they can either act as a solvent reservoir, accelerating $Cs_2CuCl_2X_2$ perovskite formation, or as a barrier, halting it.

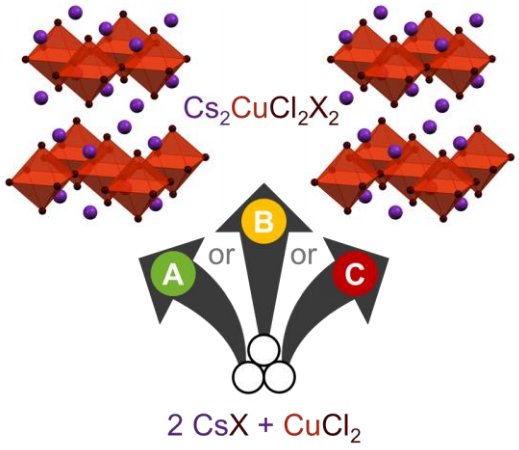


Figure 1. *Mechanochemical synthesis pathways of $Cs_2CuCl_2X_2$ (X= Cl, Br) perovskites, influenced by different types of liquid additives (A, B, C)*

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