

MECHANOCHEMICAL SYNTHESIS OF FLUORINATED PEROVSKITES: A GREEN APPROACH

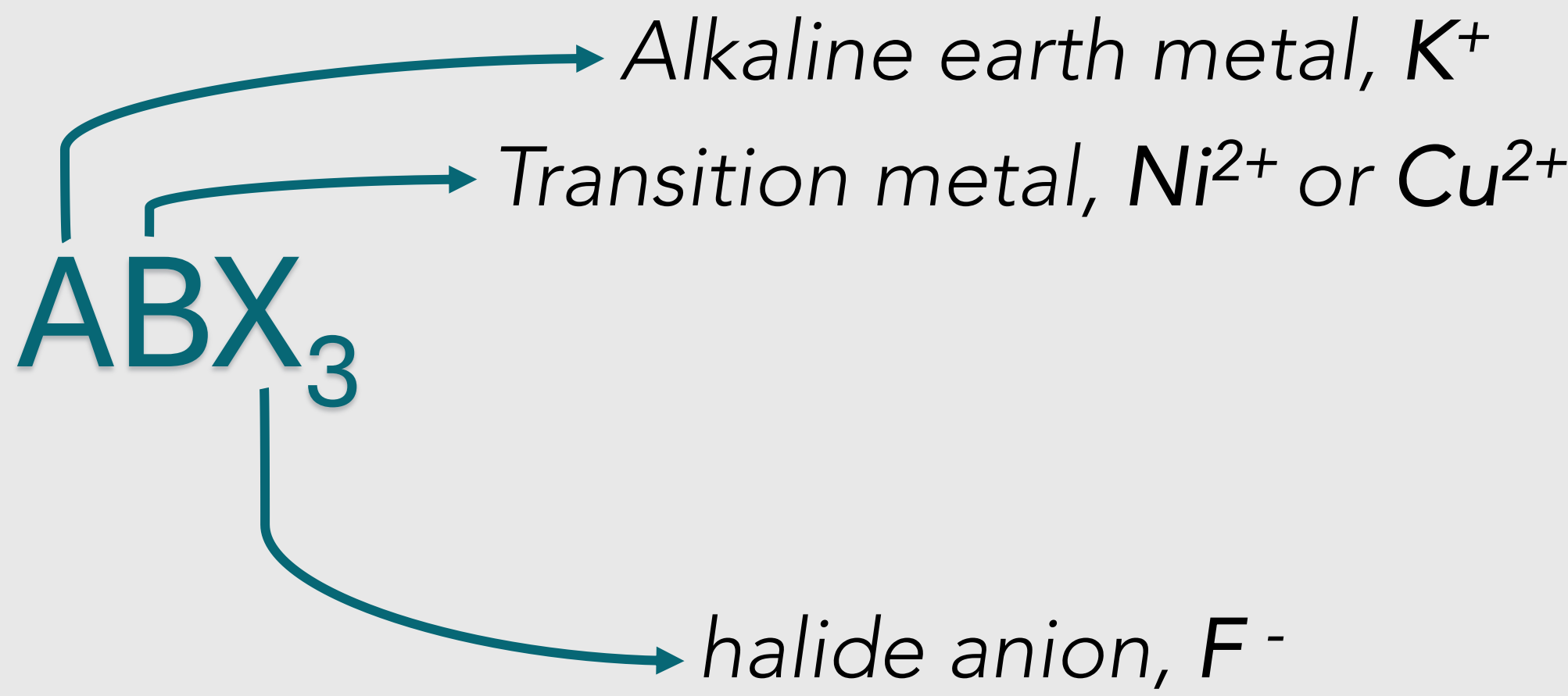
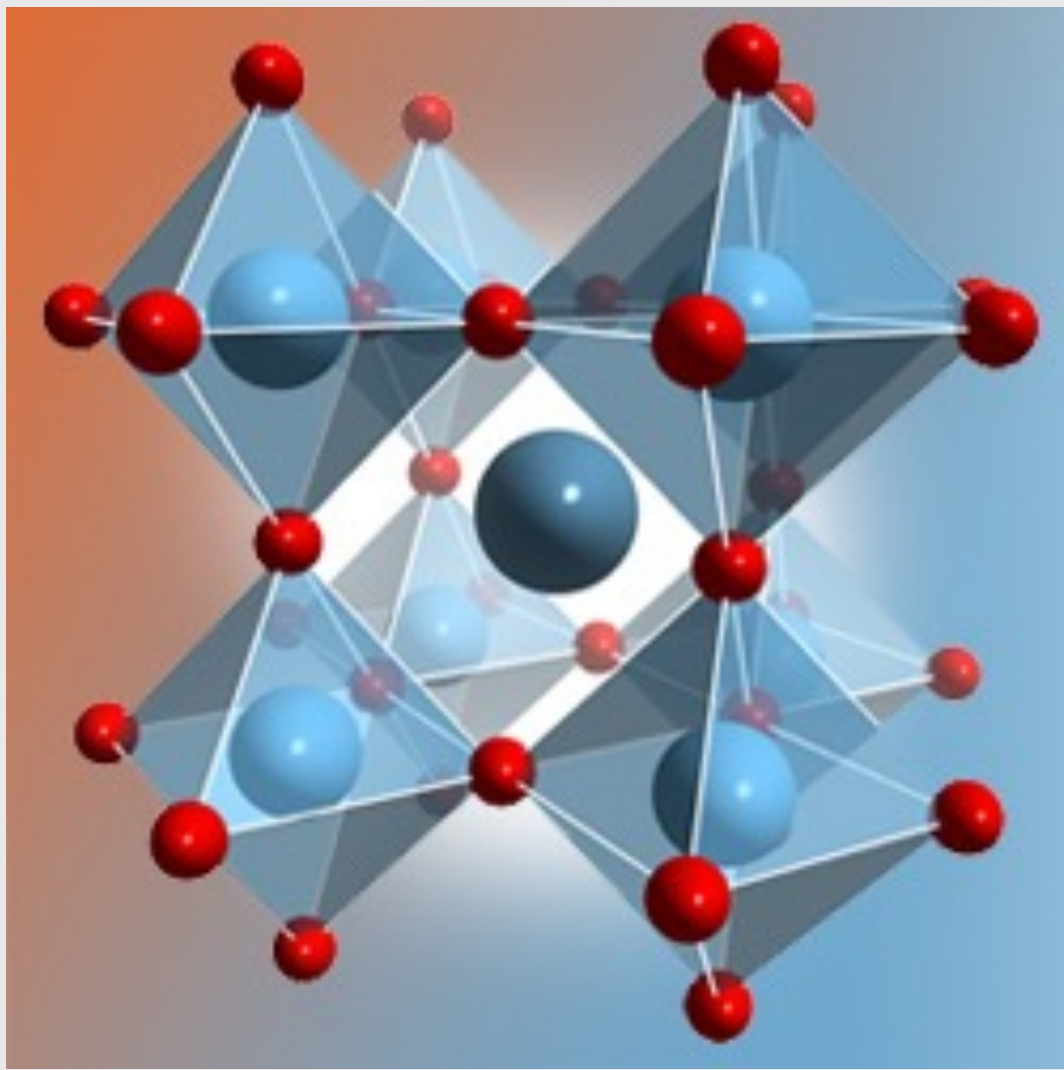
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INTRODUCTION

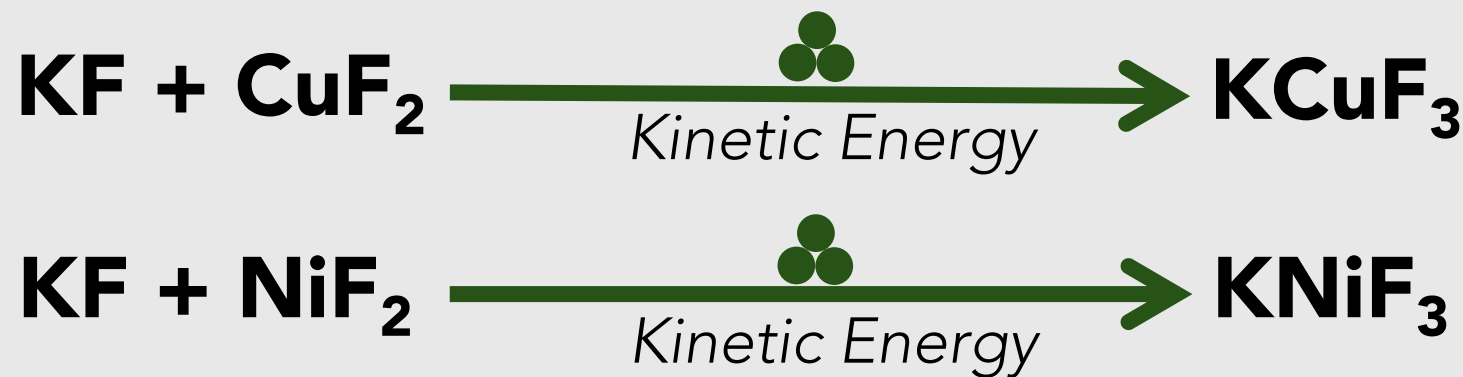
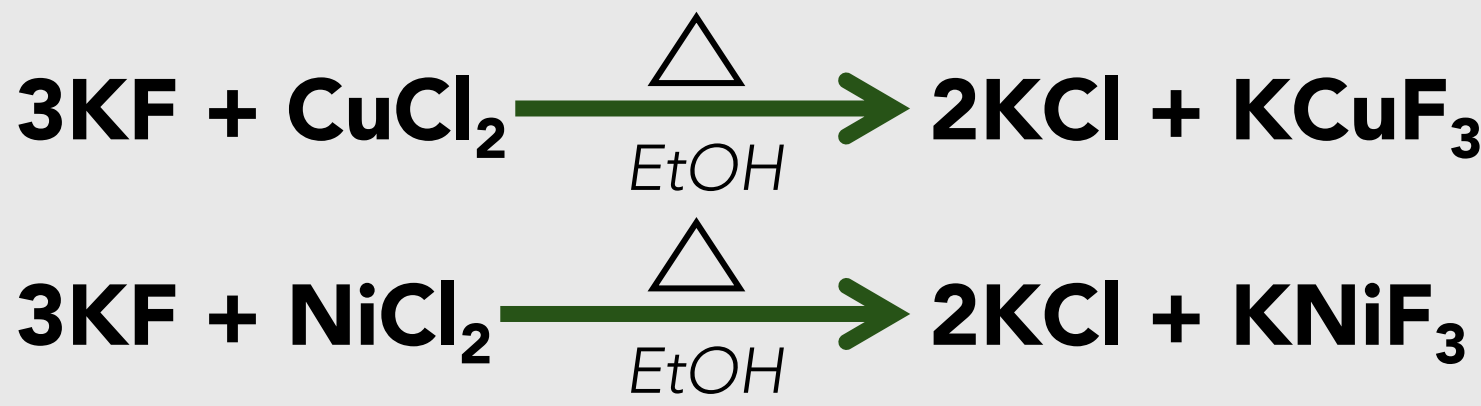
Fluoride-based perovskites are a class of materials with promising properties for applications in energy storage and electronics due to their magnetic, optical, and electrical characteristics. Conventional approaches include high-temperature solid-state reactions, hydrothermal techniques, and microemulsion-based methods. In recent years, mechanochemical synthesis has emerged as a green and solvent-free alternative, enabling rapid formation of perovskites through high-energy ball milling.



SYNTHESIS PROCEDURE



Solvochemical method
Solvent: water + ethanol
Temperature: 185°C
Time: 16 h



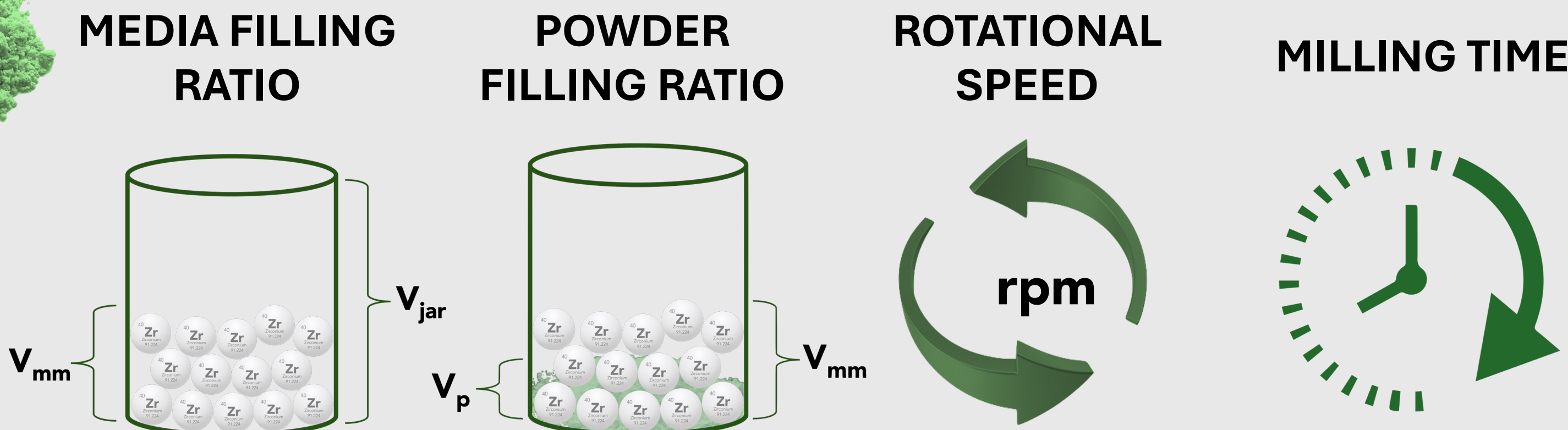
Mechanochemical method
Solvent: *no solvent*
Temperature: T_{amb}
Time: 3 h - 6 h - 12 h



The two perovskites were synthesized via a solvent-free mechanochemical approach, forming directly crystalline fluorinated perovskites at room temperature through a ball milling procedure.

Mechanochemistry efficiency is strictly influenced by the milling energy, which depends on the milling parameters.

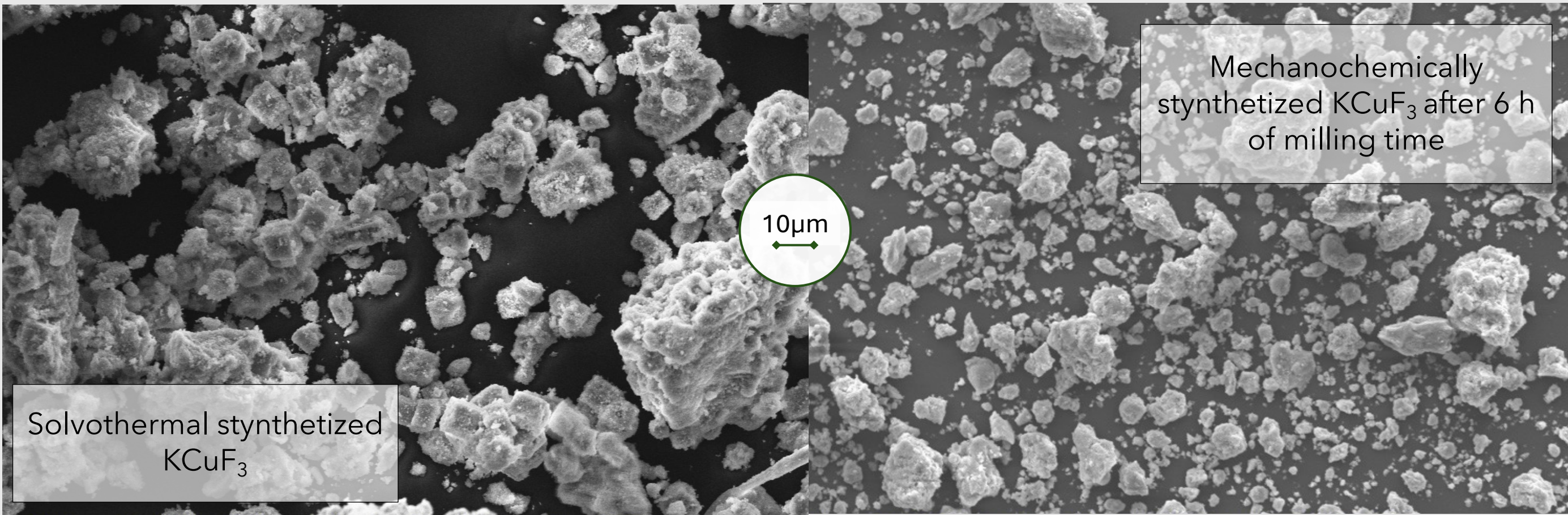
Optimal media and powder filling ratios were selected, with a fixed rotational speed of 350 rpm. Three different milling times were tested to determine the duration required for complete precursor conversion and target phase formation.



POWDERS CHARACTERIZATION

XRD, XPS, and SEM analyses

SEM images revealed particle size decreasing from ~28–50 μm (after 3 h) to ~17 μm after 12 h of milling. Solvochemical products showed ~11 μm cubic crystals, while mechanochemically synthesized perovskites exhibited similar sizes but with less-defined shapes due to particle collisions.

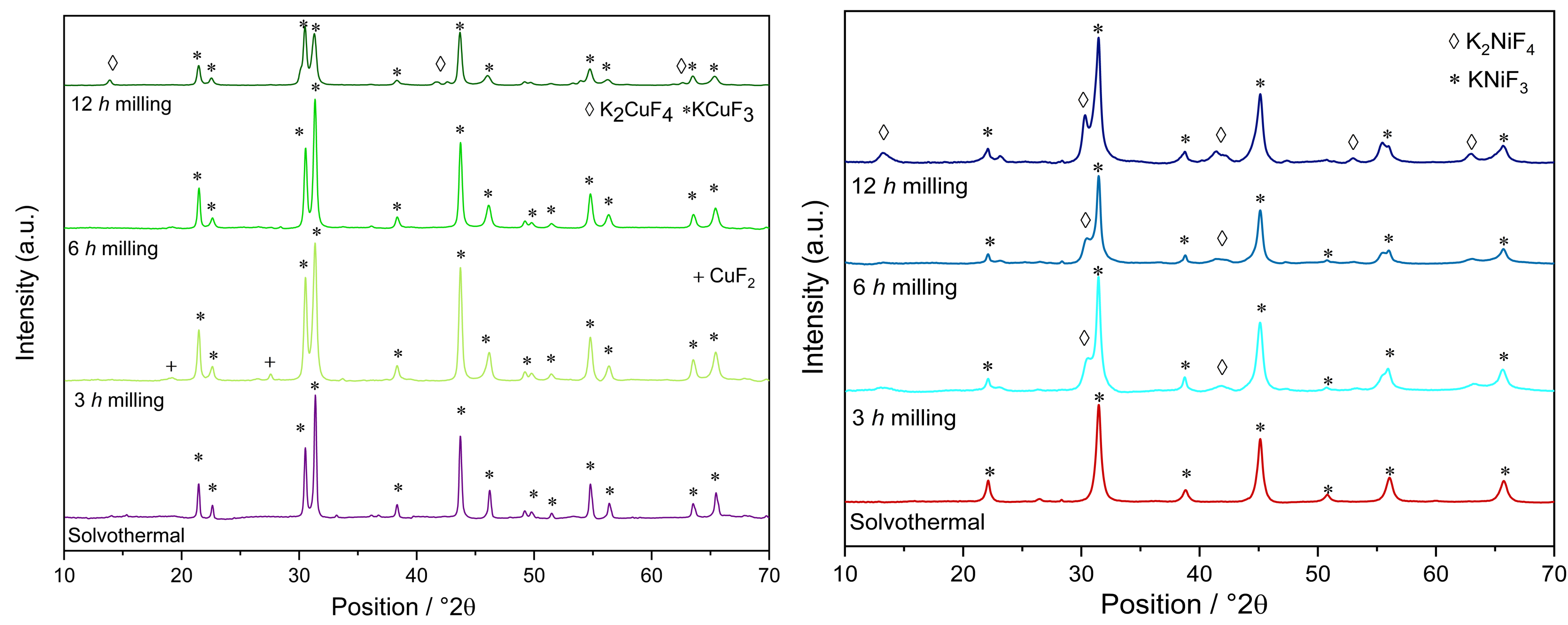


XRD confirmed the formation of the desired KCuF₃ and KNiF₃ phases, with optimal crystallinity achieved after 6 h of mechanochemical milling. Prolonged milling (12 h) led to the appearance of K₂CuF₄ and K₂NiF₄ as secondary phases.

KCuF₃ exhibits a tetragonal distortion due to Jahn-Teller effects from Cu²⁺, resulting in anisotropic magnetic interactions and one-dimensional antiferromagnetism. In contrast, KNiF₃ adopts a nearly ideal cubic perovskite structure and displays three-dimensional antiferromagnetism.

XPS analyses confirmed the elemental composition and oxidation states of the ABF₃ structure. Deviations from theoretical stoichiometry after extended milling were attributed to the formation of side phases, such as K₂CuF₄ and K₂NiF₄. Spectra showed also the presence of residual parts of the starting materials, KF, CuF₂, NiF₂, and KCl.

Sample	K at%	Cu at%	F at%	Sample	K at%	Ni at%	F at%	Cl at%
6 h milling	22.0 (±0.3)	22.0 (±1.1)	56.0 (±0.6)	6 h milling	25.5 (±0.3)	18.3 (±0.7)	56.2 (±0.6)	—
12 h milling	23.8 (±0.3)	15.6 (±0.7)	60.6 (±0.6)	12 h milling	28.8 (±0.4)	14.1 (±0.5)	57.1 (±0.6)	—
Solvochemical	20.7 (±0.3)	13.0 (±0.6)	64.3 (±0.7)	Solvochemical	19.8 (±0.3)	18.4 (±0.7)	59.6 (±0.6)	2.2 (±0.02)



XRD pattern of KCuF₃

XRD pattern of KNiF₃

CONCLUSIONS

KCuF₃ and KNiF₃ were successfully synthesized via a mechanochemical approach and this synthesis was compared to a mild solvochemical process. The mechanochemical method proved to be fast, solvent-free, and efficient, with optimized yield and selectivity achieved after 6 h of milling. XRD, XPS, and SEM analyses confirmed the formation of the target perovskites with comparable particle sizes across both methods. The mechanochemical route showed significant environmental advantages in terms of atom economy and lower energy consumption, highlighting it as a sustainable and promising alternative for the synthesis of fluorinated perovskites.