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Nanocrystal deposition of 2D-transition metal trihalide solid solutions by chemical vapor transport

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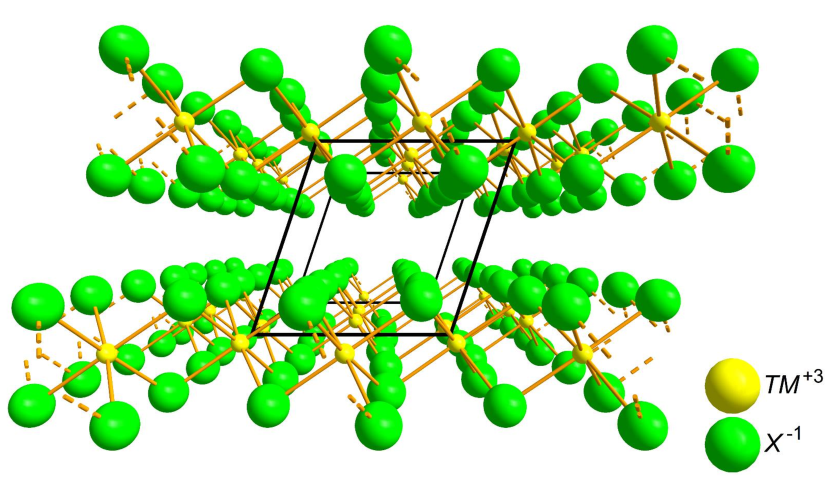
Motivation



Transition metal trihalides with 2D crystal structure offer numerous possible combinations for solid solution formation. Since many of the individual compounds already have interesting properties (e.g. exotic magnetism, catalysis), combining them in solid solutions offers great potential for property tuning or even completely new properties, especially when incorporating downscaling effects to few layer dimensions.

MCl_3

Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

MBr_3

Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

MI_3

Ti	V	Cr	Mn	Fe	Co	Ni
Zr	Nb	Mo	Tc	Ru	Rh	Pd
Hf	Ta	W	Re	Os	Ir	Pt

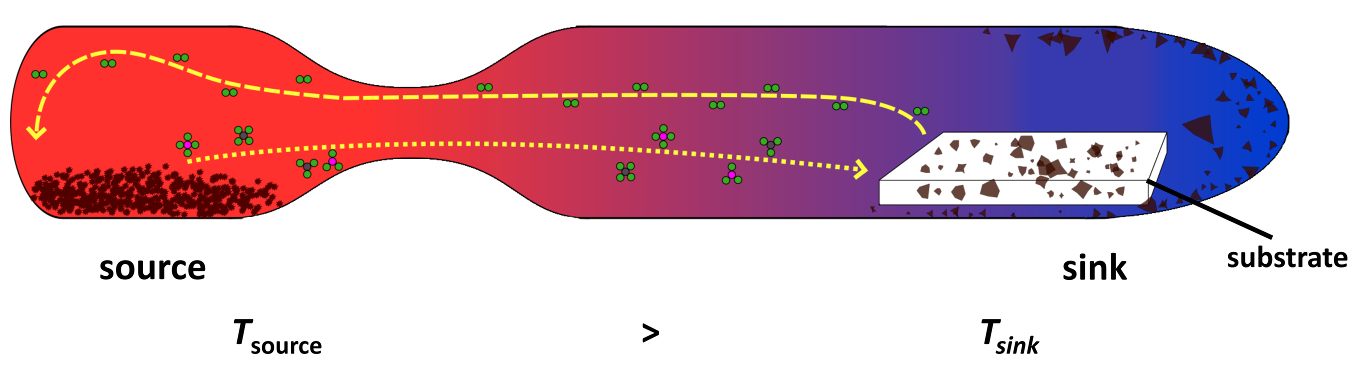
BiI_3 - type | $AlCl_3$ - type

Known *TM*-Trihalides with 2D crystal structure. [1]

Method – Chemical Vapor Transport

High quality crystals of transition metal trihalides can be grown by chemical vapor transport (CVT). This method is frequently used to grow large singe crystals but can also be adjusted to grow nanocrystals directly on a substrate. By optimizing the growth conditions it is possible to obtain high quality as-grown crystals with heights of only few nm and lateral sizes of several µm, which can be used for further characterization of downscaling effects of the material.

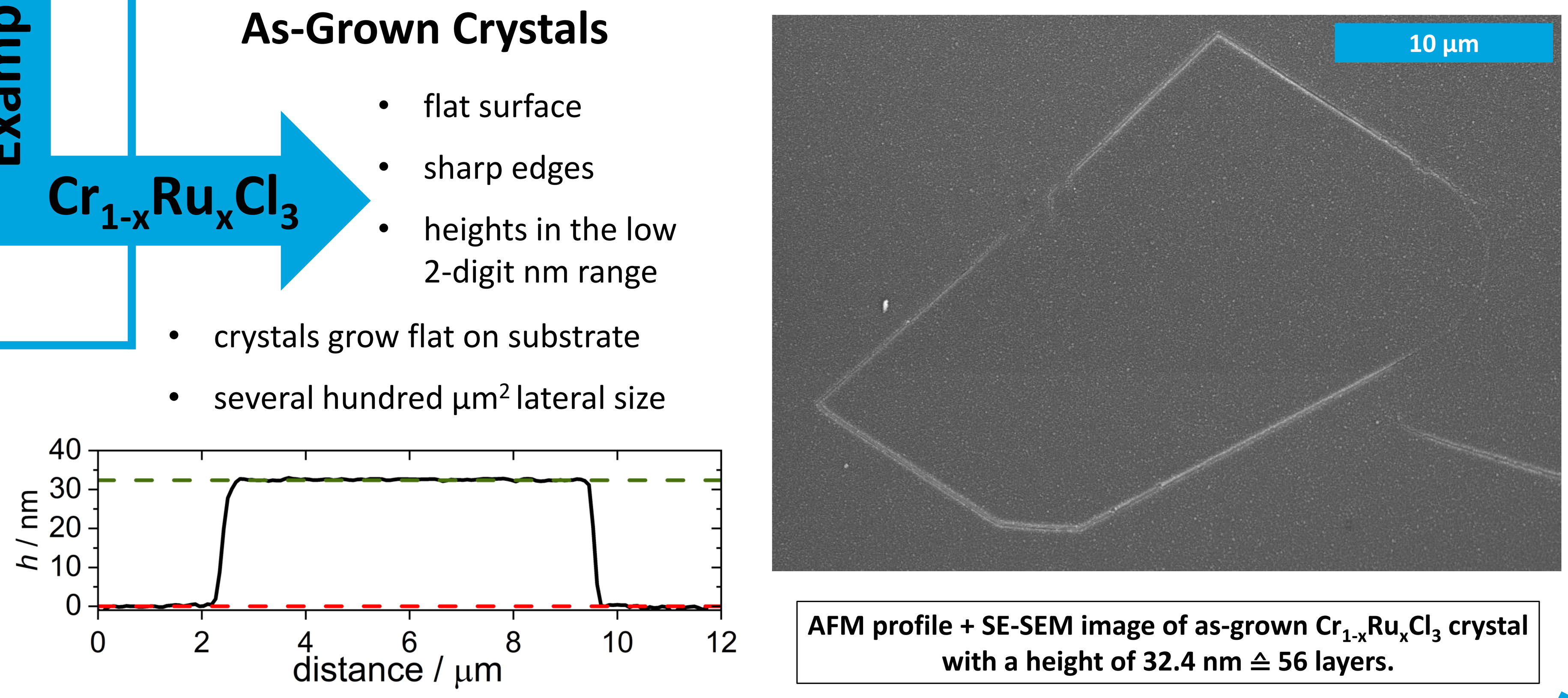
For the transport of solid solutions, enrichment of a specific component might occur due to differences in the vapor chemistry for the mixing components.



Example: $Cr_{1-x}Ru_xCl_3$

As-Grown Crystals

- flat surface
- sharp edges
- heights in the low 2-digit nm range
- crystals grow flat on substrate
- several hundred µm² lateral size



AFM profile + SE-SEM image of as-grown $Cr_{1-x}Ru_xCl_3$ crystal with a height of 32.4 nm ≙ 56 layers.

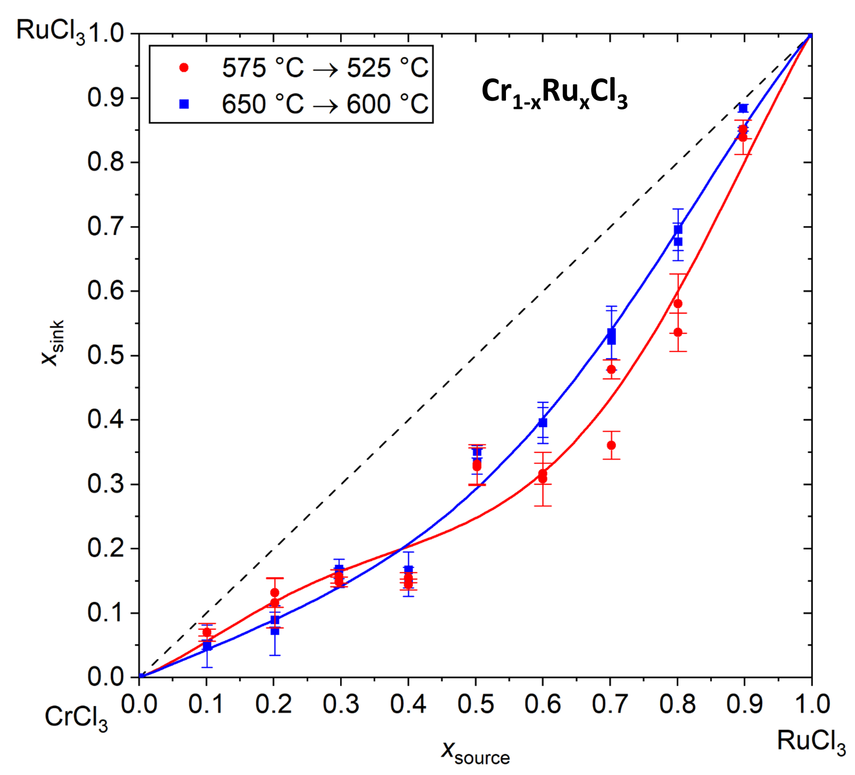
Composition of Deposited Crystals

- deposited crystals show different composition then starting material

→ enrichment of chromium during transport

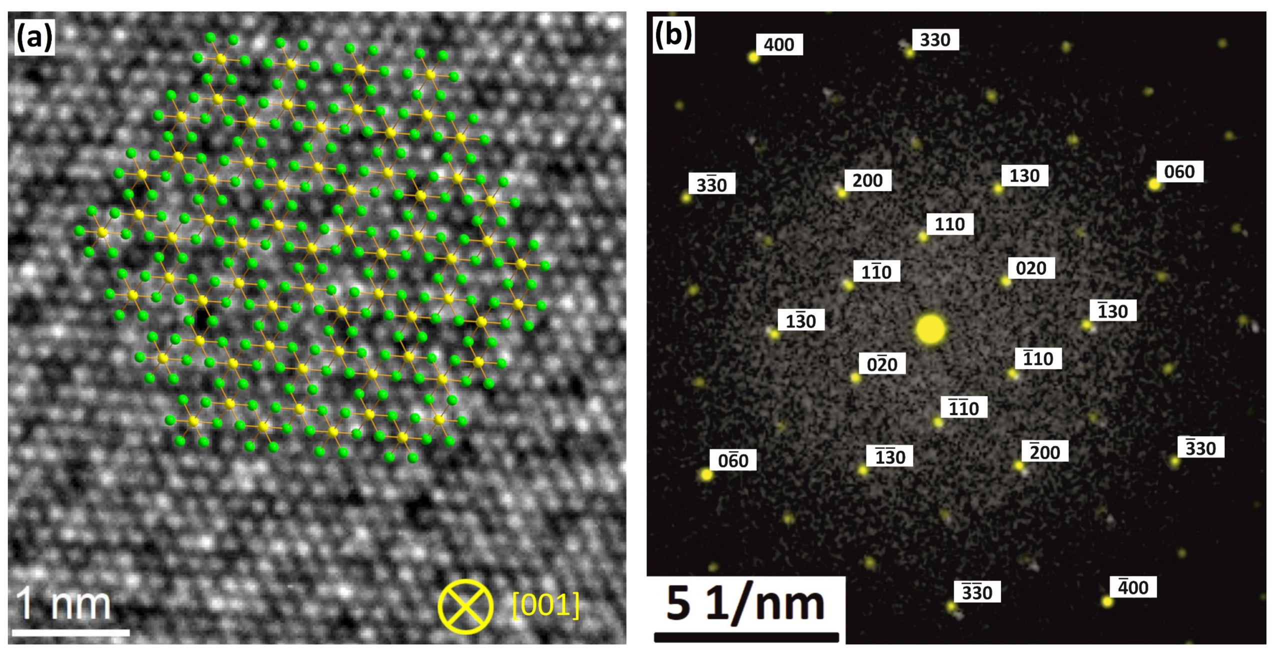
- enrichment sleightly temperature dependent
- stable composition of deposited crystals for each experiment

→ composition of grown crystals controallable!



Composition of grown crystals (sink) compared to composition of starting material (source) for different mean temperatures.

Transmission Electron Microscopy



(a) HR-TEM image with structure inset, (b) fast Fourier transform of (a) (white spots) compared with simulated structure model (overlapping yellow spots).

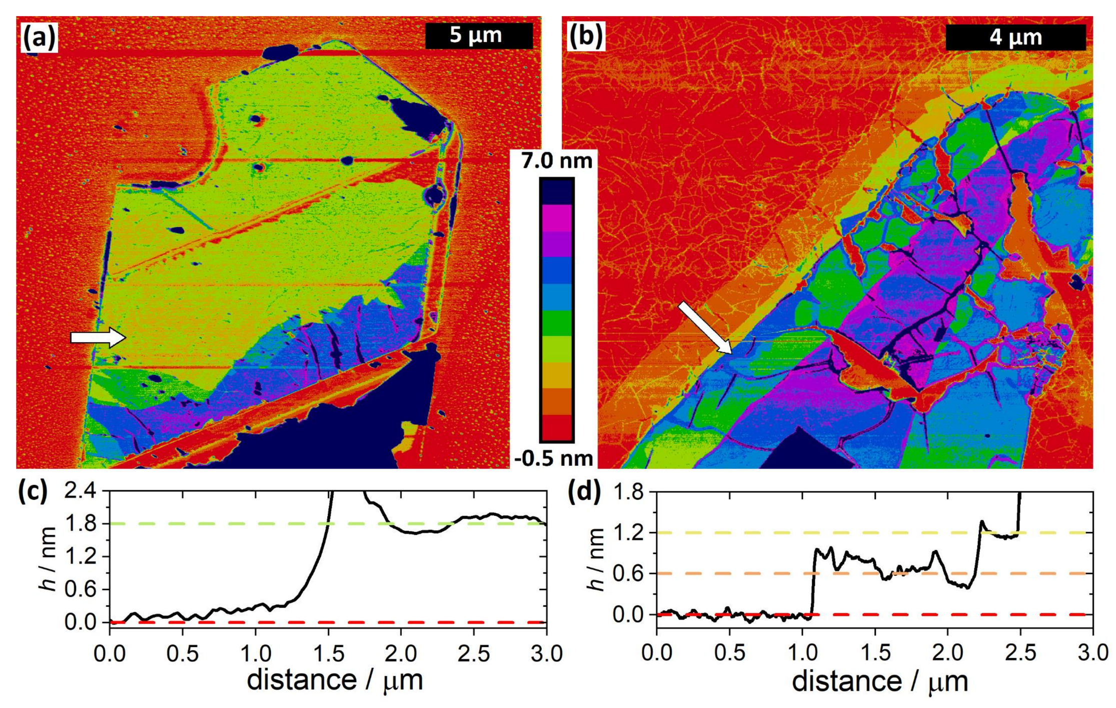
- high quality confirmed by (HR)TEM images
- highly periodic arrangement of atoms
- high crystallinity confirmed by fast Fourier transform of HRTEM images
- great match between measured spots and structure model

Delamination

- thin as-grown crystals can be thinned down even more by top-down approach
- delamination by short ultrasonication in NMP
- mono- + fewlayer structures obtainable on substrate

→ no need for exfoliation!

- crystals suitable for downscaling analysis, e.g. Raman, MFM



AFM measurements of (a+c) large trilayer crystal, (b+d) fewlayer crystal with monolayer stripe at the edge.

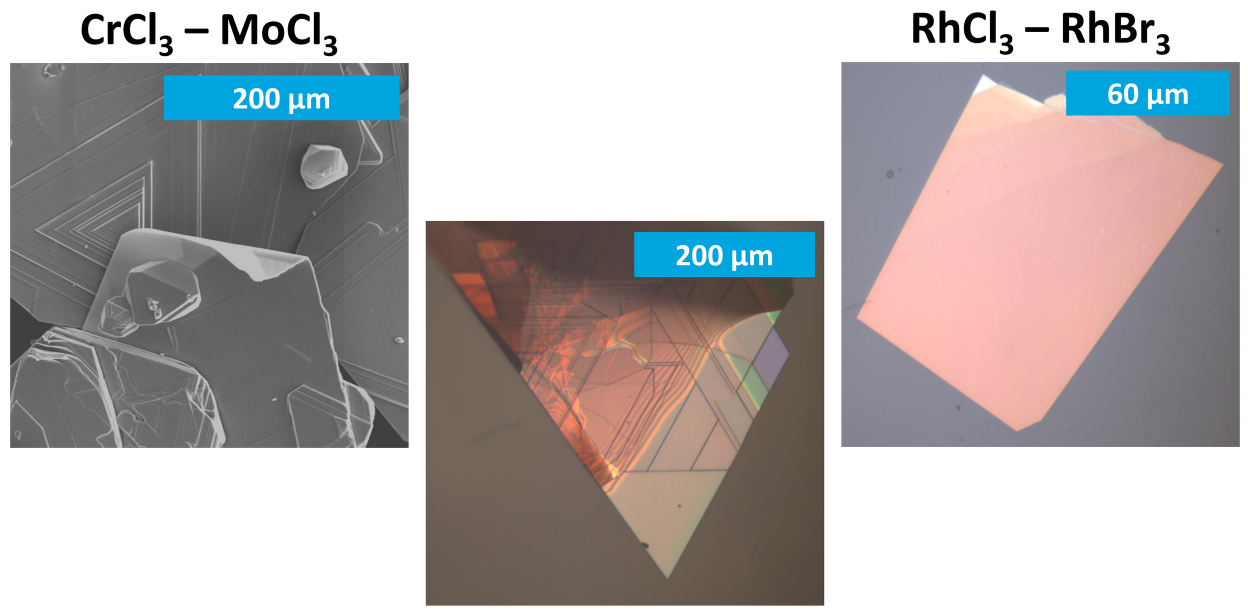
Additional Examples

- method transferable to various other transition metal trihalide solid solutions
- cation and anion solid solutions possible
- growth parameters need to be individually adjusted

→ versatile synthesis method

$CrCl_3 – MoCl_3$

$RhCl_3 – RhBr_3$



$CrCl_3 – CrBr_3 – CrI_3$

Summary / Outlook

With the presented method, high-quality nanocrystals can be obtained from a wide range of different transition metal trihalide solid solutions. Their composition can be controlled by the choice of experimental parameters, even if enrichment effects occur during the vapor transport. Consecutive but straightforward delamination by means of short ultrasonication treatment can thin the as-grown crystals even further, down to few- and even monolayer dimensions. Both the as-grown nanocrystals and those obtained by delamination are suitable samples for researching the downscaling effects on the properties of these solid solutions. These investigations shall be done in the near future to determine the possibilities of transition metal trihalide solid solutions for potential applications or more detailed studies about emerging properties.

Thank you for your interest!
Sincerely - the author

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REFERENCES

[1] M. A. McGuire, Crystals, 7 (2017) 121

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