# Some Chalcogenides and their Low Thermal Conductivity

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## Abstract

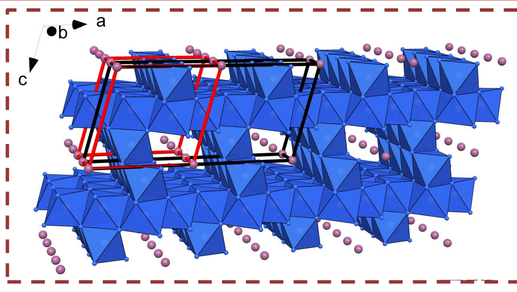
This study presents research on chalcogenides that exhibit or might show low thermal lattice conductivity. The low dimensionality is a main point in our research on finding such candidates. Going from quasi one-dimensional compounds to complex three-dimensional framework, through two-dimensional layered structure, we have found at least 6 compounds presenting low thermal conductivity (below the unity for most of them), two of which being new compounds, i.e. $In_2Ge_2Te_6$ and $Ba_xCr_5Se_8$.

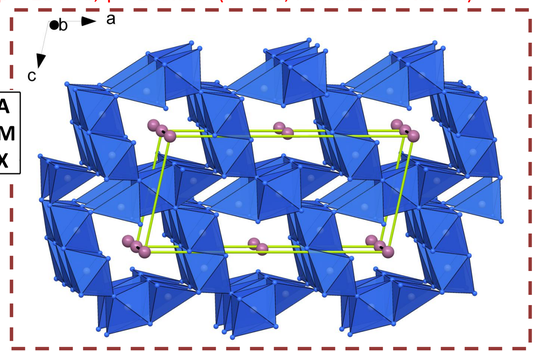
## Introduction

All samples have been prepared by mixing the pure elements in sealed and evacuated silica tubes. Transport and magnetic properties measurements have been performed on sintered materials using a Spark Plasma Sintering device. Neutron diffraction has been performed at the LLB Laboratory with the help of F. Damay.
Thermoelectric figure-of-merit $ZT = ST/\rho(\kappa_{el} + \kappa_{latt})$ is one of the parameters that defines a good thermoelectric (with S the Seebeck coefficient, T the absolute temperature, ρ the resistivity and **κ** the electronic and **lattice (phonons) thermal conductivity**. We associate different techniques: neutron diffraction, transmission electron microscopy and X-ray diffraction to understand the possible reasons of such low thermal conductivities. We also characterize the structural, transport, and magnetic properties of our samples.

## $Ba_xCr_5Se_8$ with $0.5 \leq x \leq 0.55$ (1)

P-1 a = 9.51; b = 7.17; c = 8.93 Å; α = 89.99;
β = 104.40; γ = 100.89 ° (x = 0.5, no variation with x)



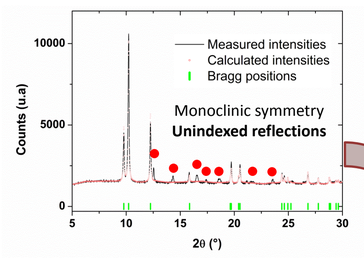

## $A(Cr/Ti/V)_5Se_8$ (2)

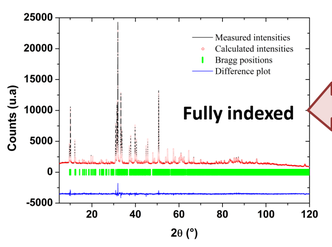
C2/m a = 18.70; b = 3.59; c = 8.94 Å; β = 104.70° ($TlCr_5Se_8$)

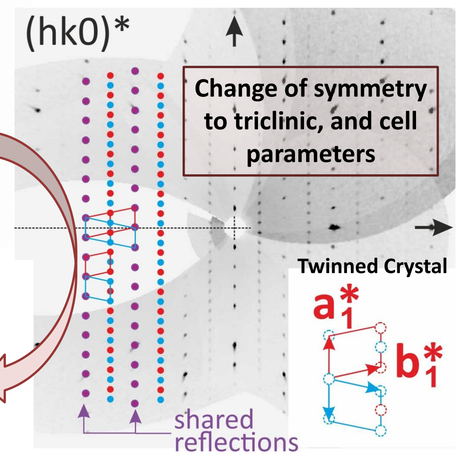
## (3) $TlIn_5Se_8$

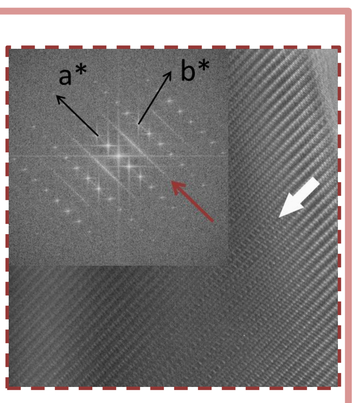
C2/m a = 19.99; b = 3.99; c = 9.62 Å; β = 101.49°

## $Ba_xCr_5Se_8$, x = 0.5



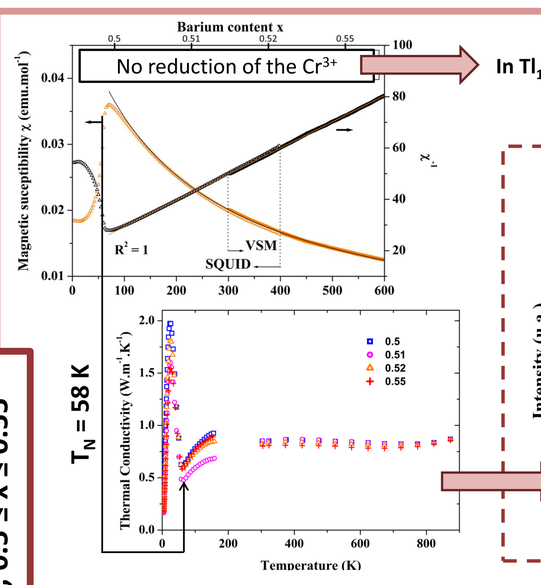




The same twinning effect is observed on TEM/HREM study on powder

**Lowering of symmetry from usual pseudo-hollandite monoclinic to triclinic confirmed with $0.5 \leq x \leq 0.55$. No cell parameter modifications are observed.**

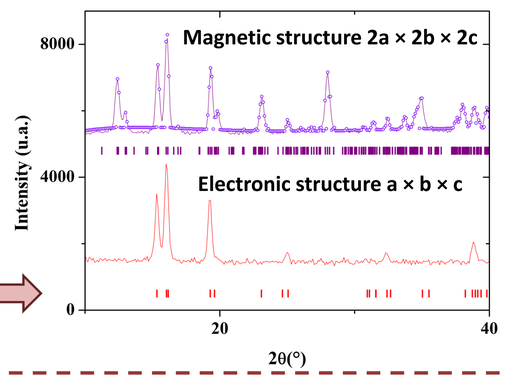
## $Ba_xCr_5Se_8$, 0.5 ≤ x ≤ 0.55

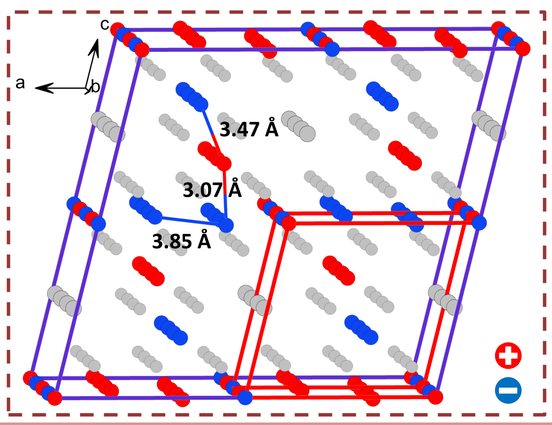



$T_N$ = 58 K

In $Tl_{1-x}Cr_5Se_8$, the Cr was shown to oxidize to $Cr^{4+}$

$RbCr_5Se_8$ shows also a 2a' × 2b' × 2c' (4)



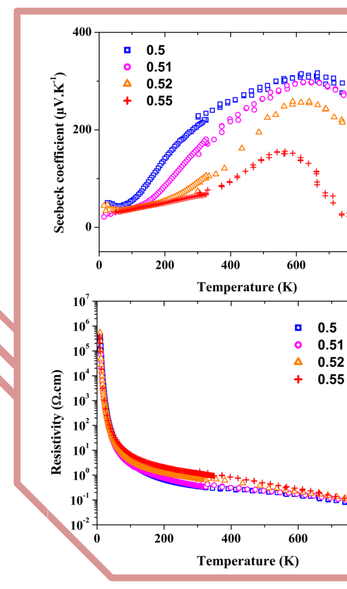

**Model of the magnetic structure of $Ba_{0.5}Cr_5Se_8$ is shown centered on Cr1**

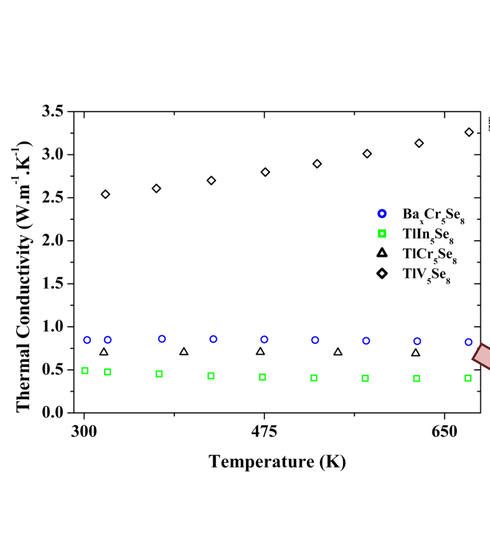
$d_{Cr\text{-}Cr}$ = 3.07 Å: clear **antiferromagnetic** interactions

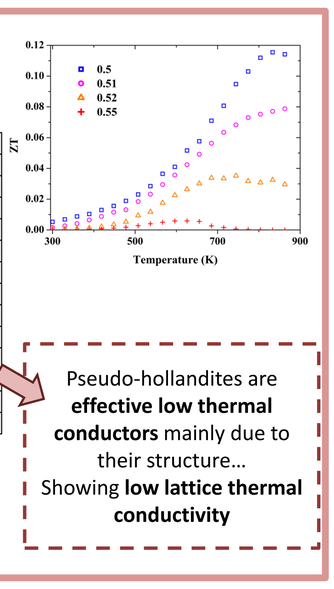
$d_{Cr\text{-}Cr}$ = 3.85 Å: clear **ferromagnetic** interactions

$d_{Cr\text{-}Cr}$ = 3.47 Å: has to be **antiferromagnetic** interactions due to the multiplicity

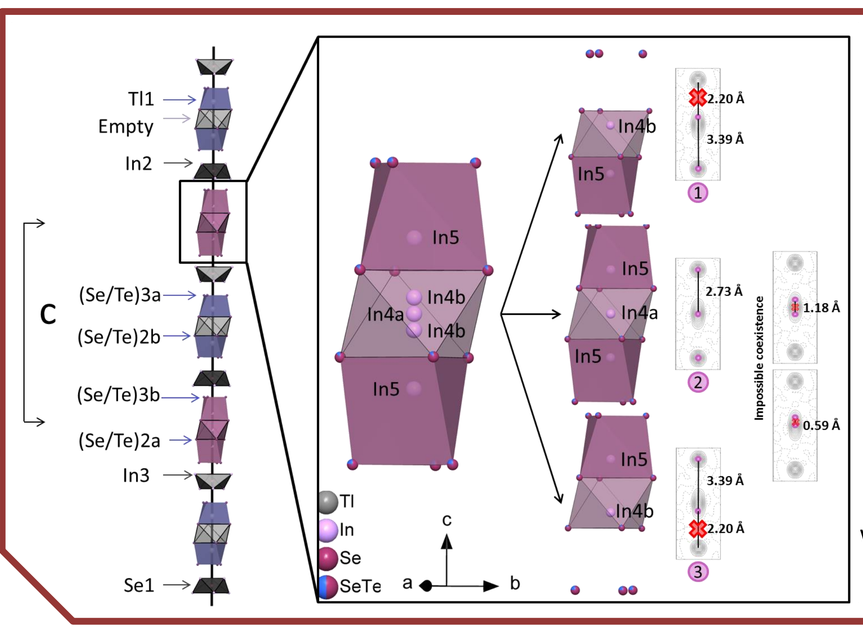
**The inversion center should be taken into account to inverse spins**




Pseudo-hollandites are **effective low thermal conductors** mainly due to their structure…
Showing **low lattice thermal conductivity**

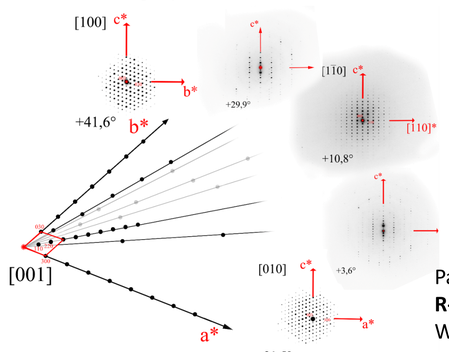


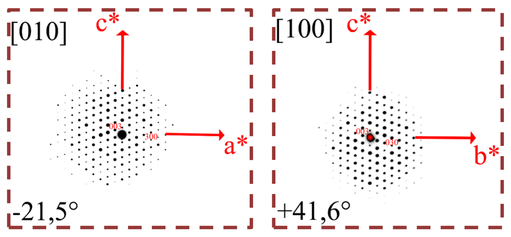

Acquisition made at **150 K**

A disorder is still observed on the In4 site showing a **static disorder**

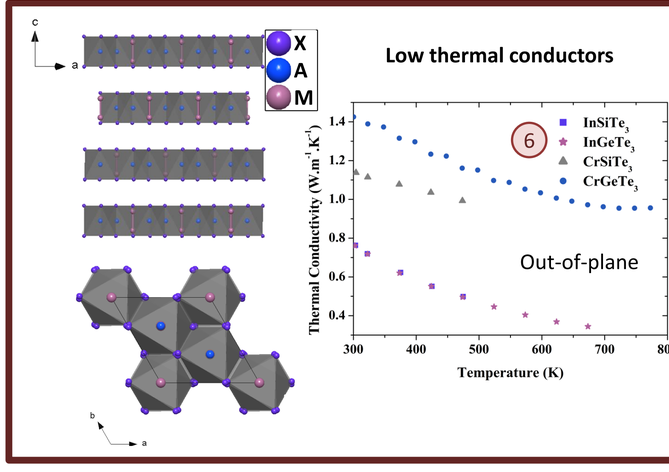
This compound, a reddish powder when ground, is expected to provide a **low thermal conductivity** with such complex structure.

Trying to improve the resistivity of $TlIn_5Se_8$…
We synthesized **$TlIn_5Se_7Te$**: with TEM study we found a phase with cell parameters similar to **$K_2In_{12}(Se_{1-x}/Te_x)_{19}$** (5)



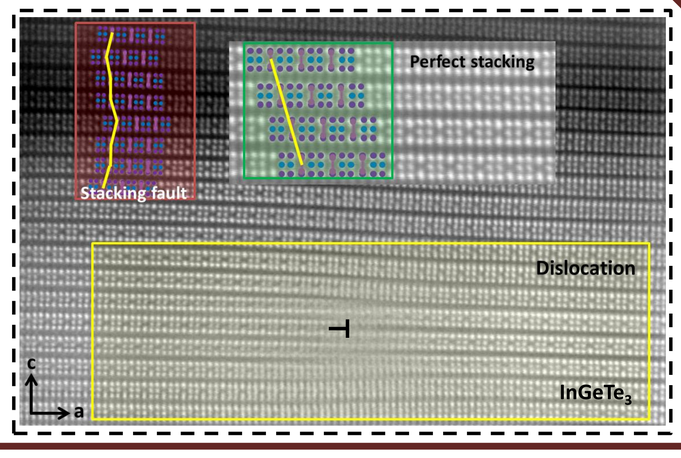



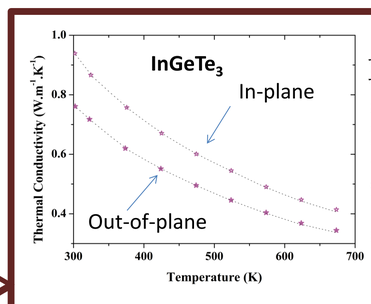

Parameters confirmed after single crystal structure refinement
**R-3 a = 13.839(5), c = 35.18(3) Å**
With final composition being: **$Tl_{0.977}In_{13.118}Se_{19-z}Te_z$, z = 2.328**

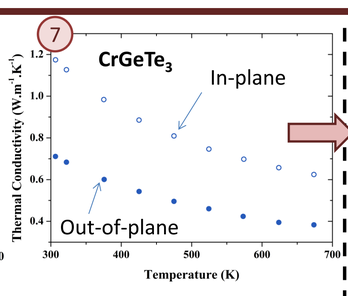


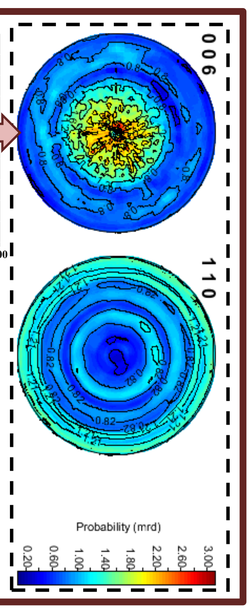

## Low thermal conductors




**A slight texturation of the grain towards 006 (the pressing direction while sintering) of about 3 MRD.**

**This texture strength cannot explain such anisotropy in the structure.**

**However other parameters as the microstructure (grain boundaries, crystallite size anisotropy) could explain the difference between in- and out-of-plane measurements.**

## Conclusion & Perspectives

* **The crystal structure of $Ba_{0.5}Cr_5Se_8$ has a lower symmetry than usual pseudo-hollandites due to the barium arrangement**
* **The solid solution in barium presents radical change in the transport properties**
* **A super-cell has been discovered for the magnetic structure below the antiferromagnetic transition**
* **A new quaternary compounds has been discovered, i.e. $Tl_{0.977}In_{13.118}(Se_{1-z}Te_z)_{19}$**
* **4 phases of the $AMX_3$ system show low thermal conductivity, one of them being a new compound, i.e. $InGeTe_3$**

**Electrochemical extraction of the barium for Li-battery tests**

**Resolve the magnetic structure**

**Studying new ternary and quaternary systems…**

**References:**

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