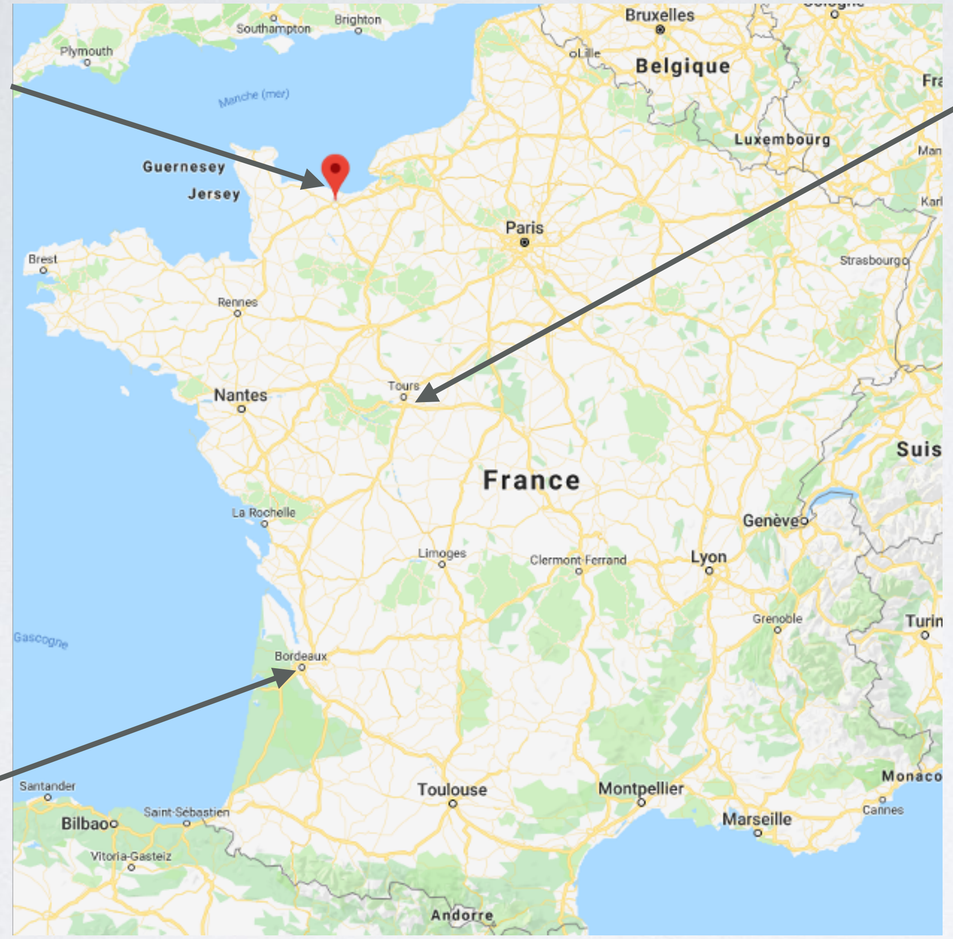
Ruthenium oxide peculiarities probed by the Seebeck effect and prospection of novel thermoelectric chalcogenide materials assisted by machine learning

Florent PAWULA

Tours, February 7th 2023

Overview

Caen - Normandy
(2015-2018)



(2009-2014)

Tsukuba
(2022 - to date)

(2019-2021)

(2014-2015)

PhD thesis work:

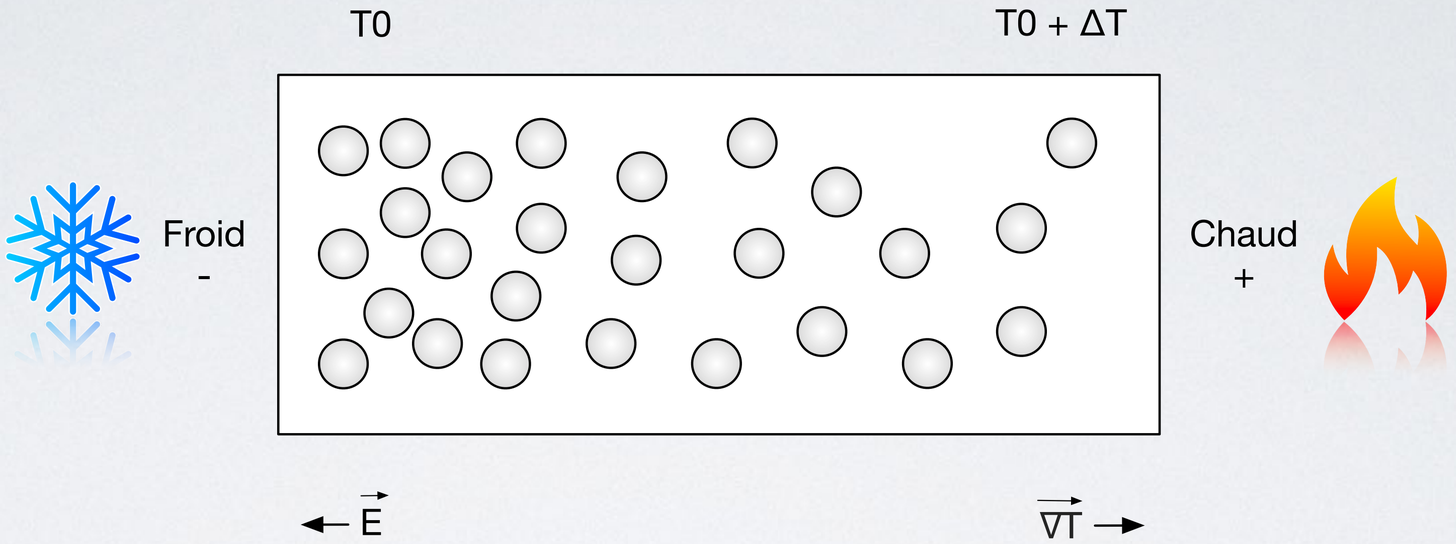
Ruthenium oxide peculiarities probed by the Seebeck effect

With Antoine MAIGNAN and Sylvie HÉBERT

- Solid-state synthesis of oxoruthenates
- Crystallographic characterization (XRD and TEM)
- Thermoelectric and magnetic properties characterization

Introduction

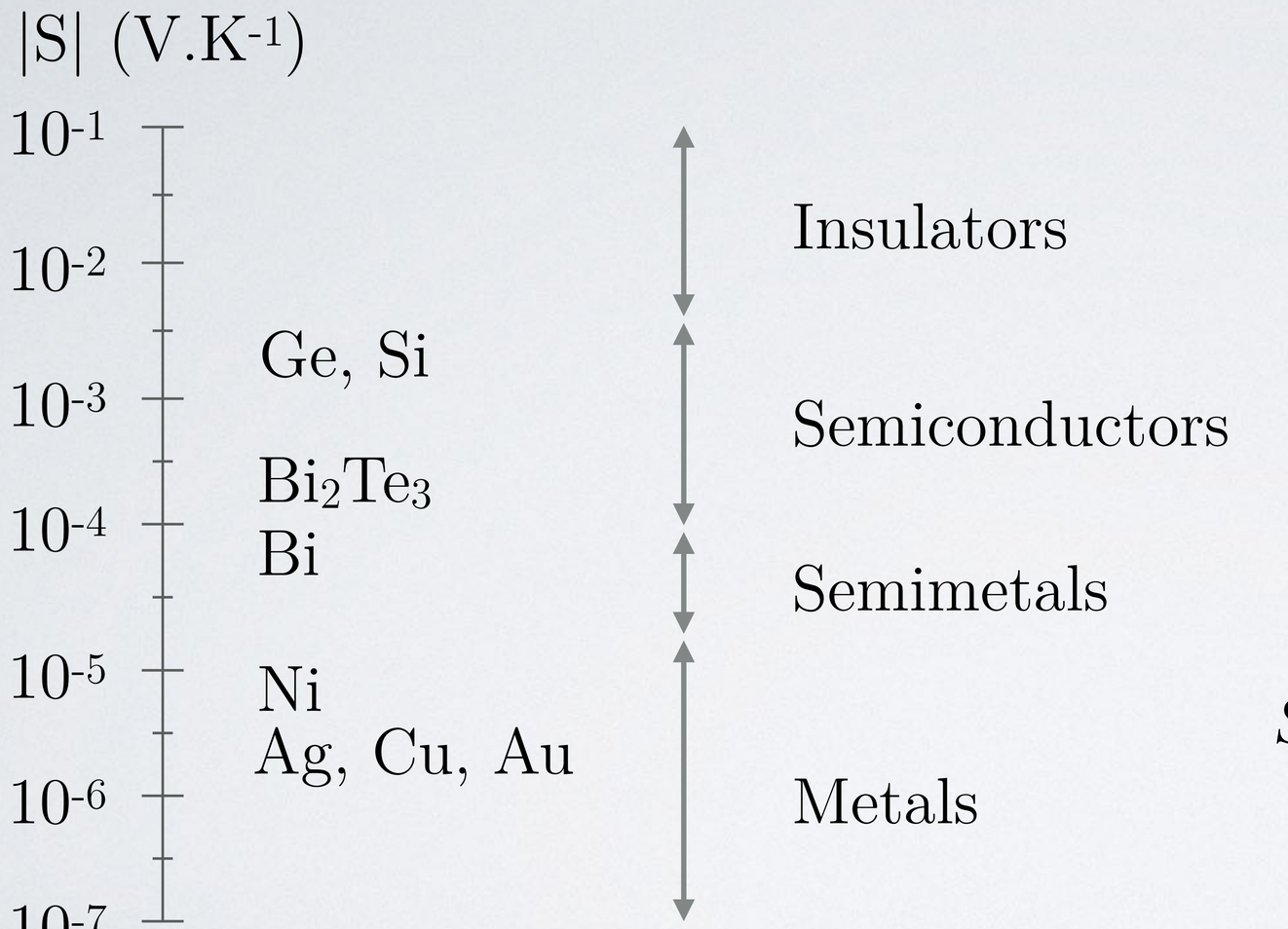
The Seebeck effect:



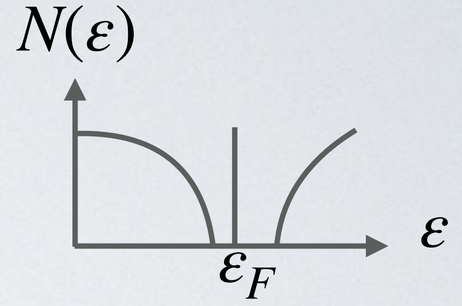
$$S = -\frac{\nabla V}{\nabla T}$$

Chaikin, P. M. *Organic Superconductivity*, Springer (1990)

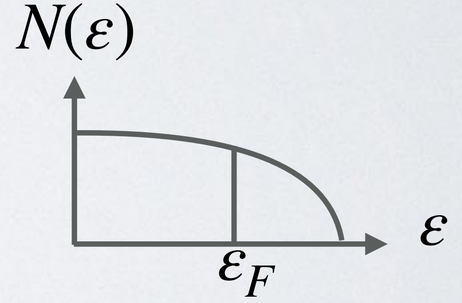
The Seebeck coefficient: magnitude at 300 K



$$S \propto \frac{\varepsilon_F}{k_B T}$$



$$S \propto T \frac{\partial ln(\sigma(\varepsilon))}{\partial \varepsilon}\bigg|_{\varepsilon = \varepsilon_F}$$

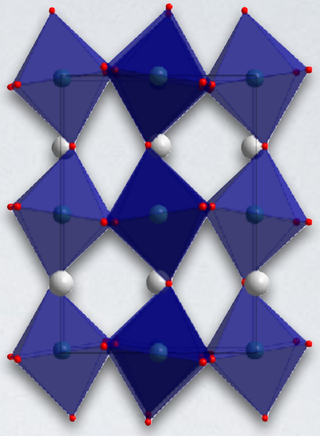


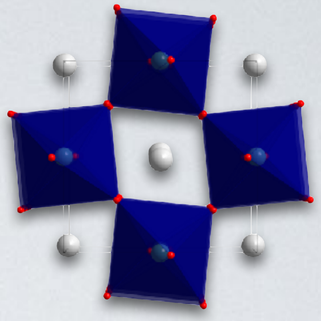
Lenoir, Ecole du GDR thermoélectricité (2004)

Ruthenium oxides:

Intriguing observation on S(T) of perovskites:

- $A\mathrm{RuO_3}$: corner-shared octahedra.





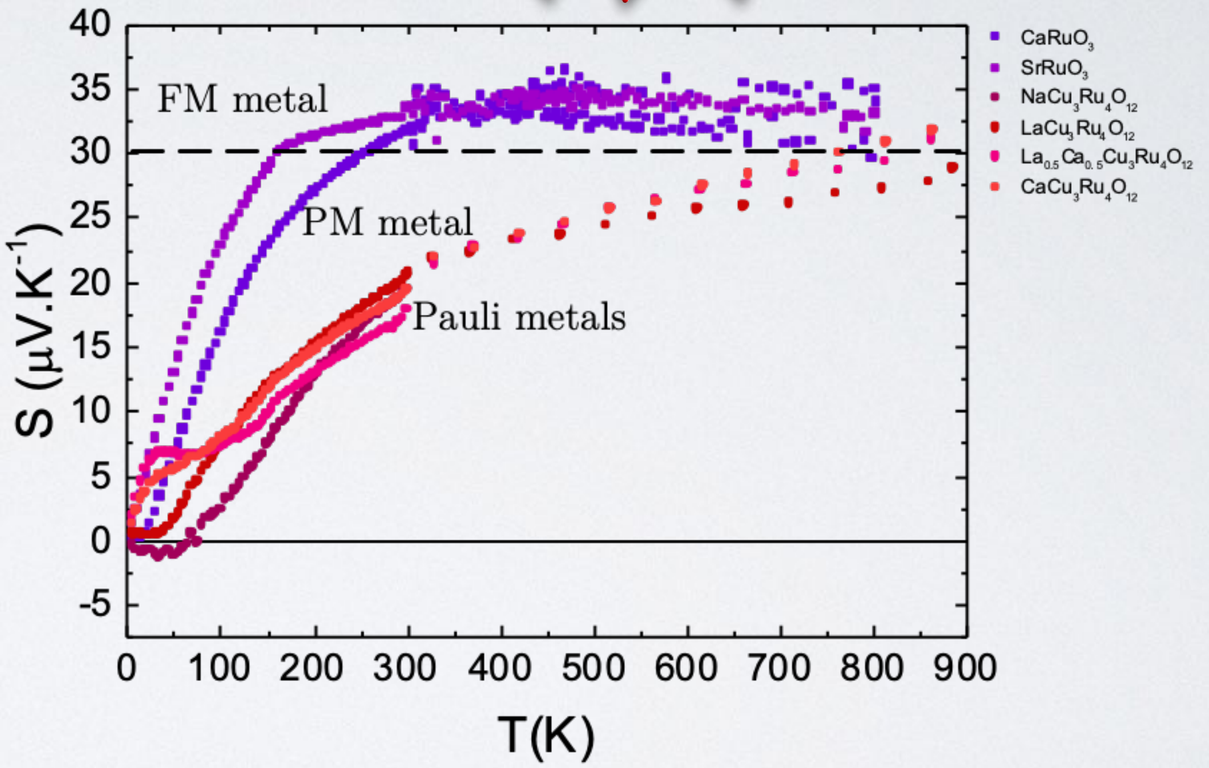
Generalized Heikes formula:

$$S = \frac{k_B}{e} ln\left(\frac{\beta_{n+1}}{\beta_n}\frac{c}{1-c}\right)$$

Ru(IV)

$$S = \frac{k_B}{2e} ln\left(\frac{2S_{n+1}+1}{2S_{n-1}+1}\right) \sim 30\mu V.K^{-1}$$

$$S = S_{transport} + S_{entropy}$$



S of perovskites dominated by Ru(IV) spin entropy at high temperature

Klein et al., Phys. Rev. B 2006, 77 2774
Peterson et al., Phys. Rev. B 2007, 76 125110

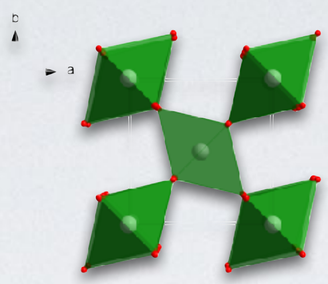
Hébert et al., Phys. Rev. B 2015, 91 045106
Doumerc, J. Solid State Chem. 1994, 110 419

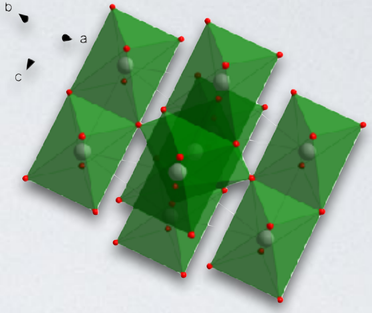
Mravlje et Georges, Phys. Rev. Lett. 2016, 117 036401

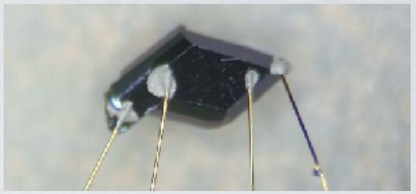
Ruthenium oxides:

My work :

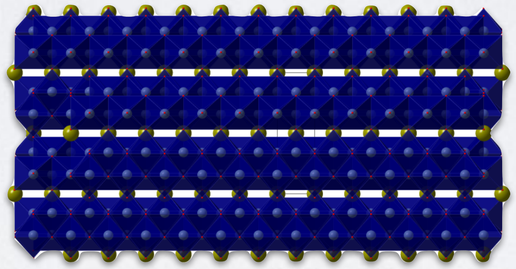
- RuO_2 rutile: edge-shared RuO_6 octahedra **chains** with coner-shared interconnections.

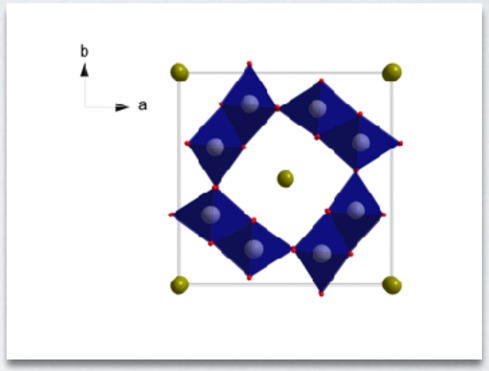




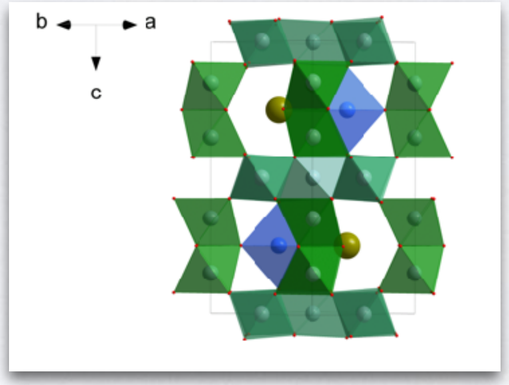


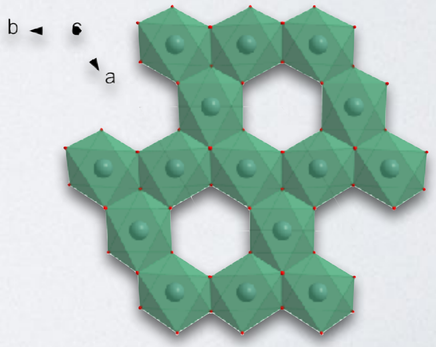
- $A_{1.5}Cr_{1.9}Ru_{6.1}O_{16}$ hollandites: edge-shared MO_6 octahedra **double-chains** with coner-shared interconnections.





- $AM_2Ru_4O_{11}$ R-type hexaferrites: edge-shared MO_6 octahedra **Kagome layer** interconnected by a face-shared octahedra M_2O_9 and a trigonal bipyramid MO_5.





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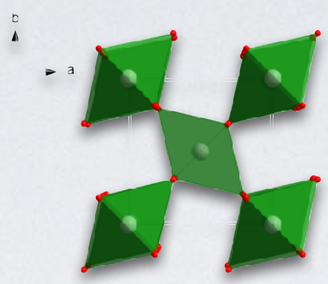

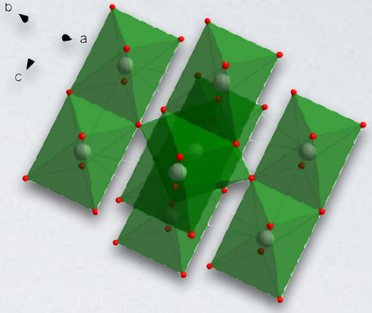

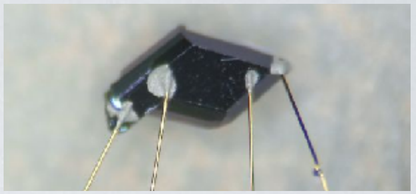

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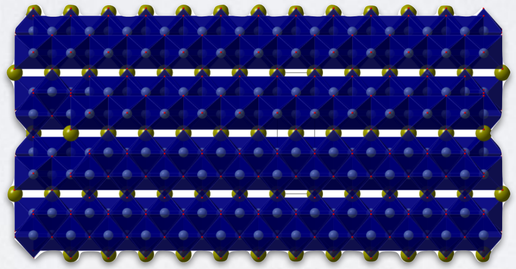

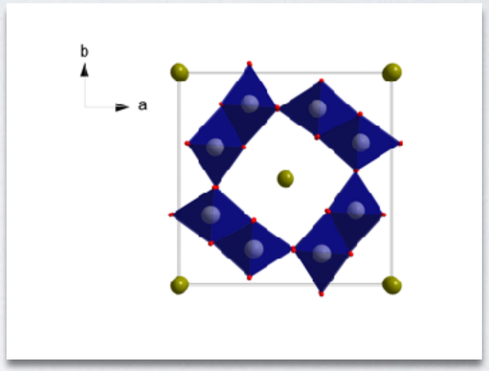

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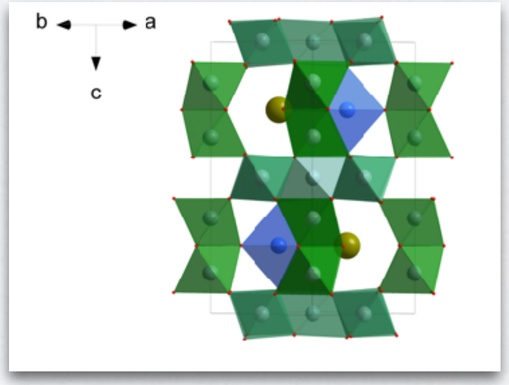
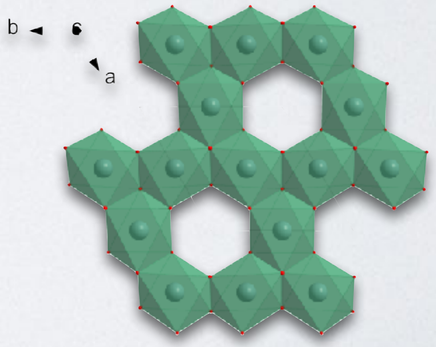
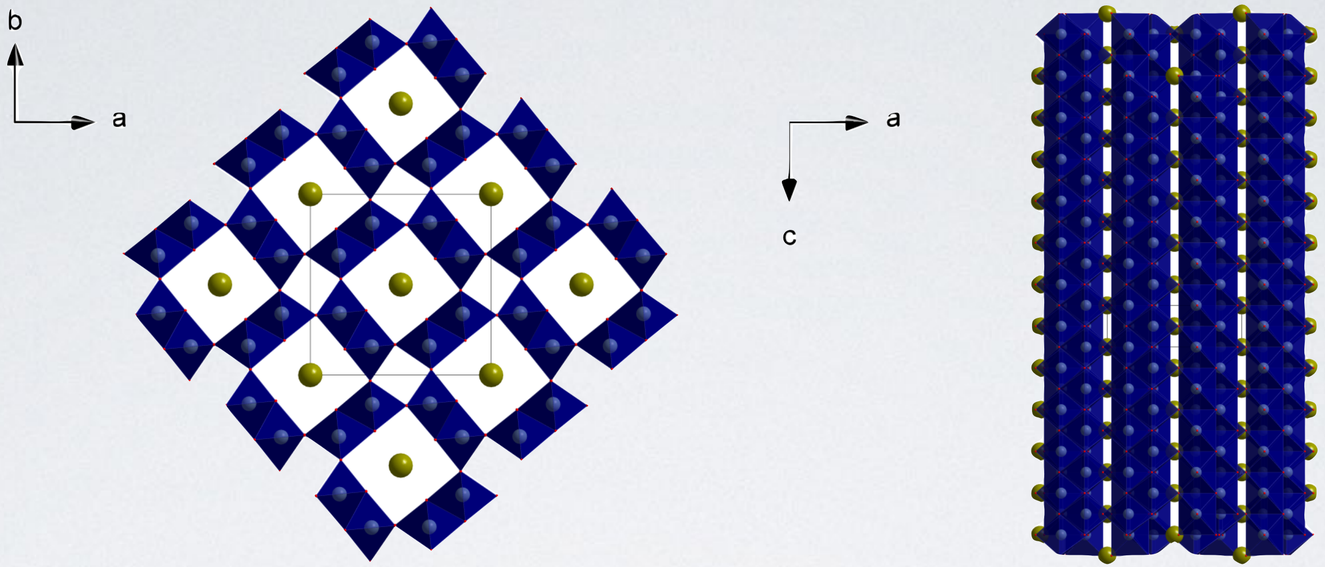




$A_xM_8O_{16}$ hollandites



Reported hollandites: $A_xM_8O_{16}$ with M=Ti, V, Cr, Mn, Mo, Ru, Rh, Ir and A=K^+, Li^+, Rb^+, Cs^+, Sr^{2+}, Ba^{2+}, Bi^{3+} .

Ru hollandites: $BaRu_6O_{12}$, KRu_4O_8, $BaCr_2Ru_6O_{12}$

Zandbergen et coll., Mater. Res. Bull. 22 431 (1987)

Okada et coll., Mater. Res. Bull. 13 1047 (1978)

Klimczuk et coll., Mater. Res. Bull. 39 1671 (2004)

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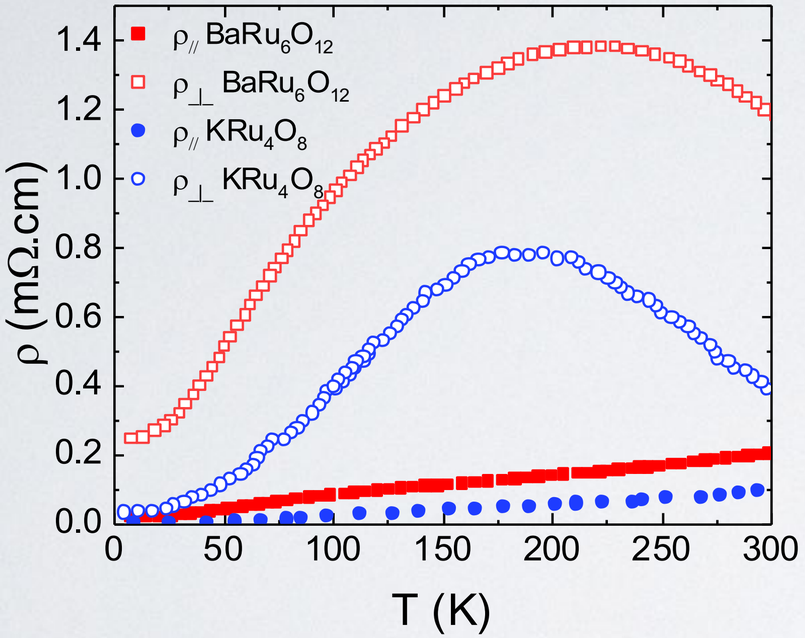

	Space group	Z	Magnetism	Resistivity
$BaRu_6O_{12}$	*P4/nZ*	3	?	Metal
KRu_4O_8	*I4/m*	*2*	Para	Metal
$BaRu_4Cr_2O_{12}$	*P4*	*1*	?	?
$K_2Cr_8O_{16}$	*I4/m*	*1*	Ferro	Insulator

Kobayashi et coll., Phys. Rev. B 79, 155116 (2009)

Mao, Phys. Rev. Lett. 90, 186601 (2003)

Cadée et Prodan, Mater. Res. Bull. 14 613 (1979)

Takeda et coll., Phys. Rev. B 88, 165107 (2013)

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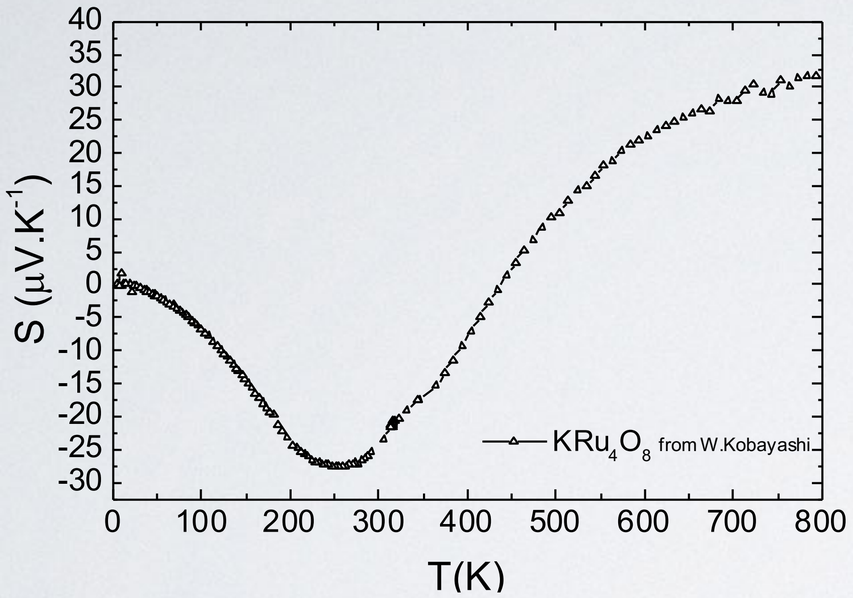

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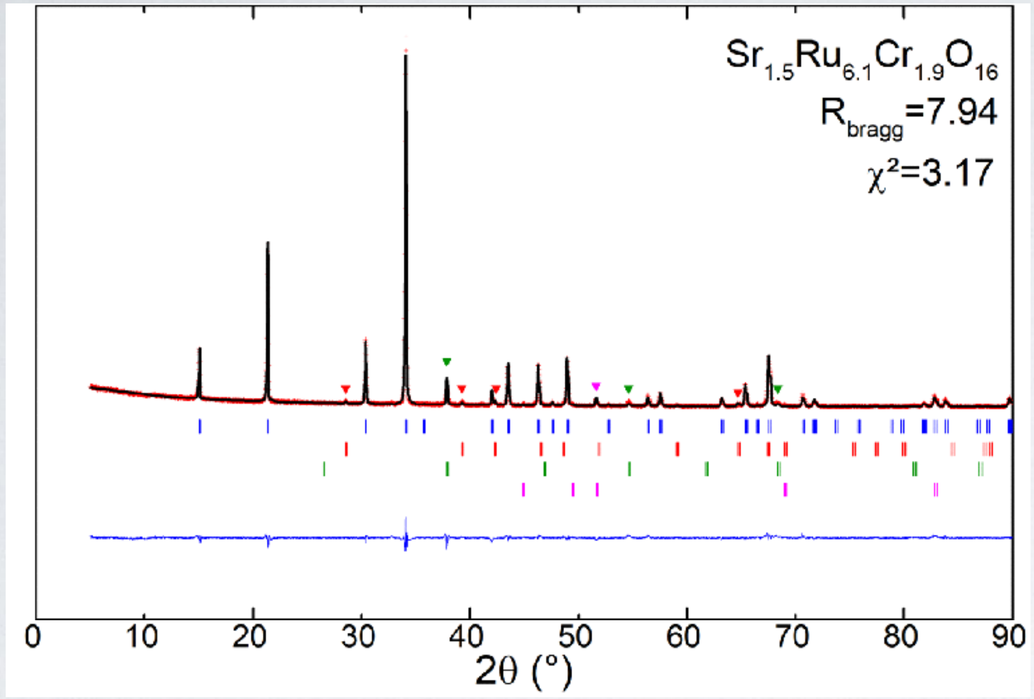
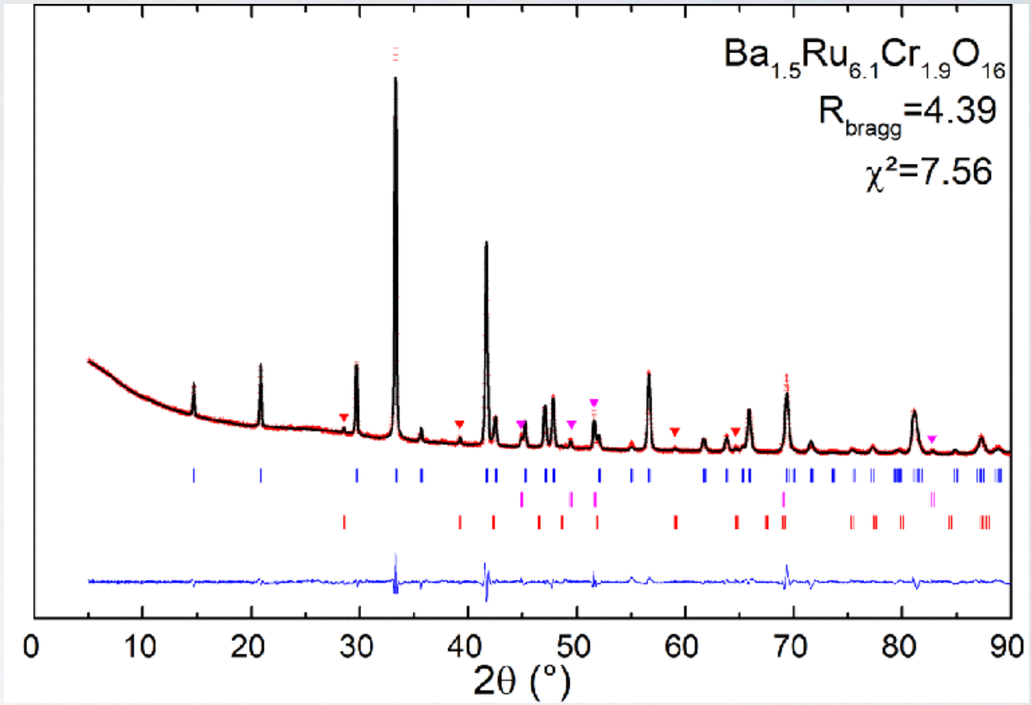
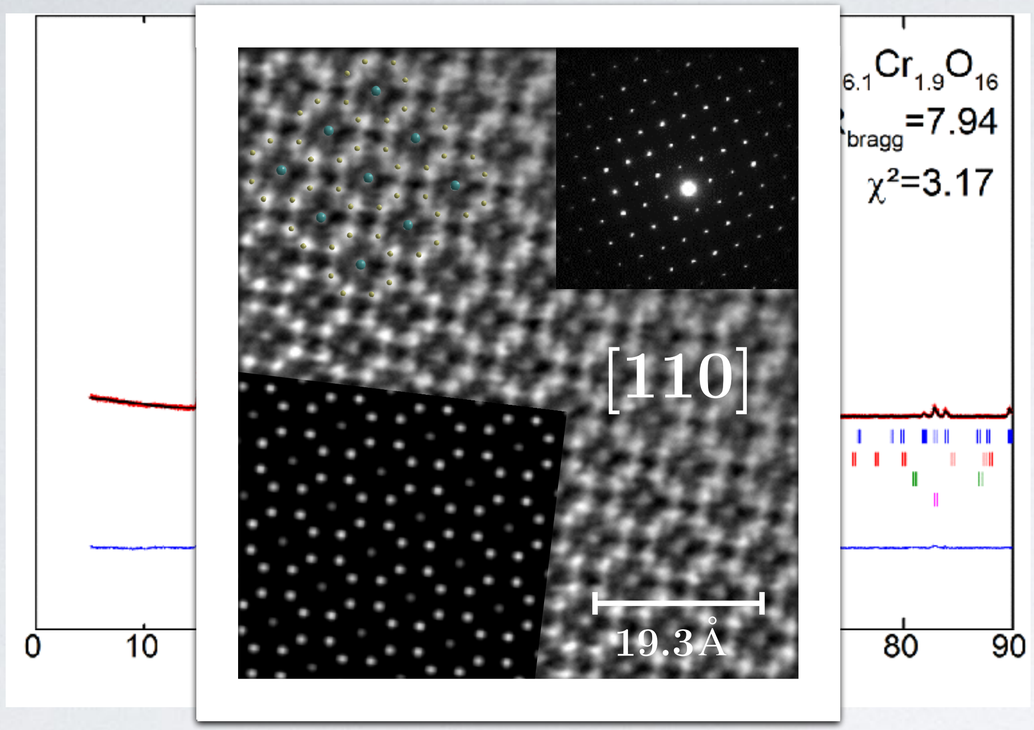
$A_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ hollandites: crystallochemistry

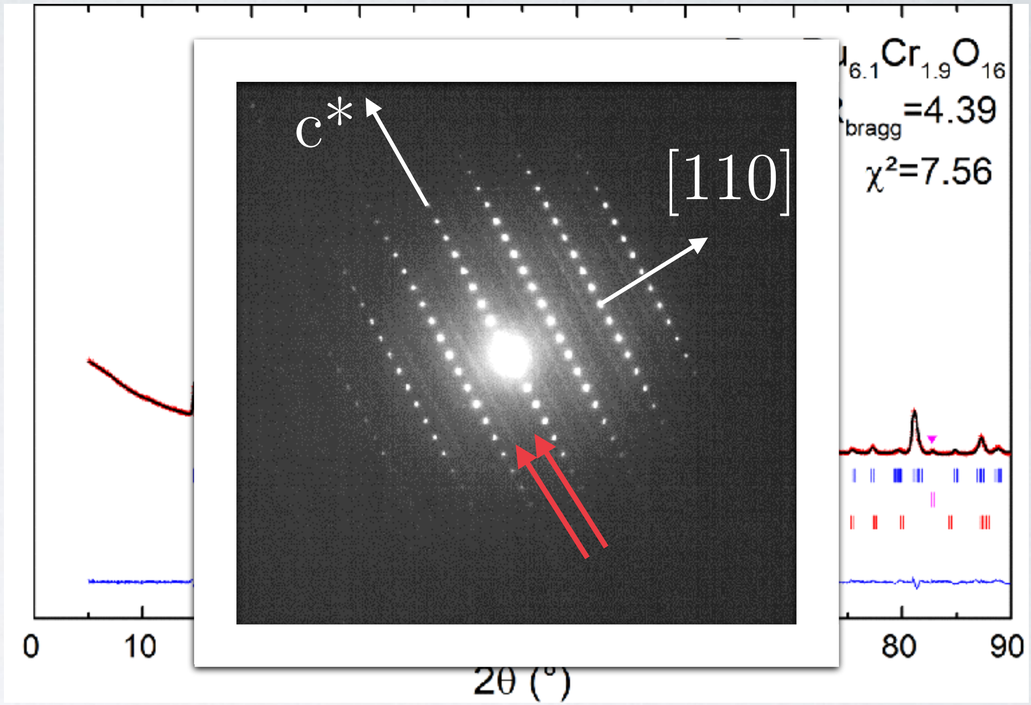




I4/m	$Sr_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$	$Ba_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$	Δ
a (Å)	9.6593(2)	9.87504(5)	0.216
c (Å)	3.0588(2)	3.06085(3)	0.002
V (Å^3)	285.39	298.48	13.1

$A_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ hollandites: crystallochemistry





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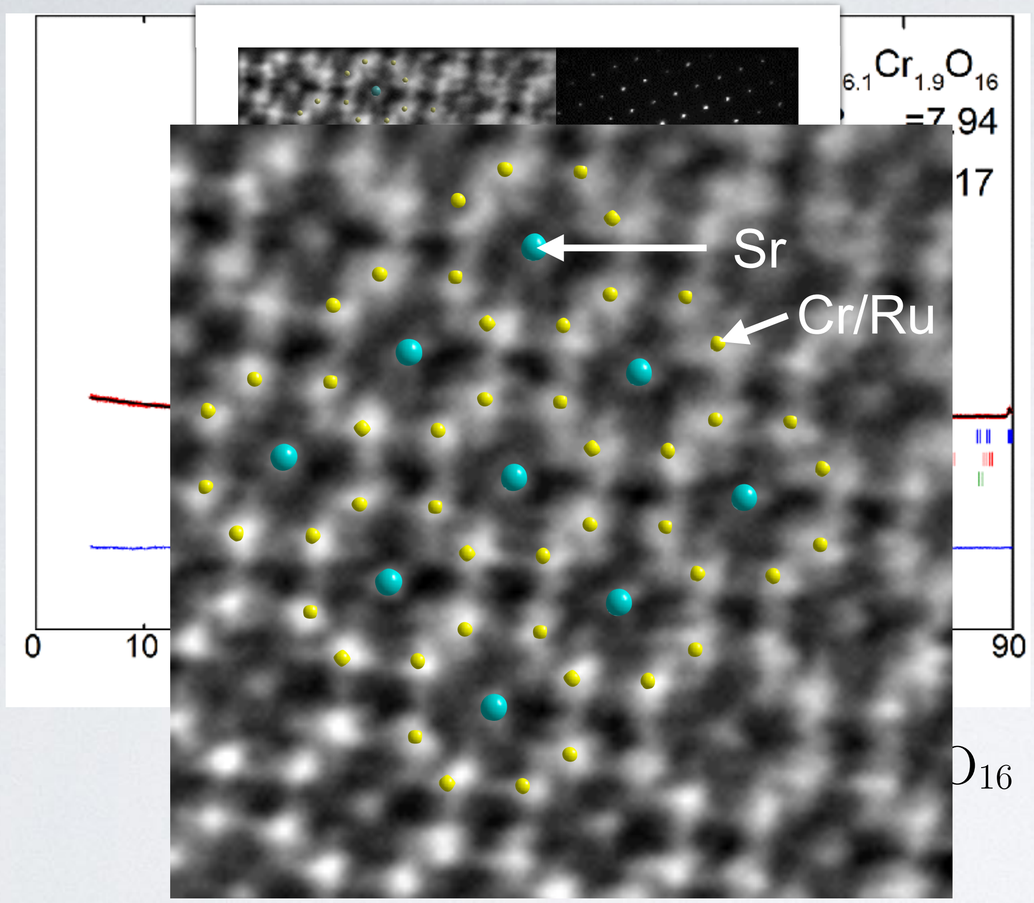

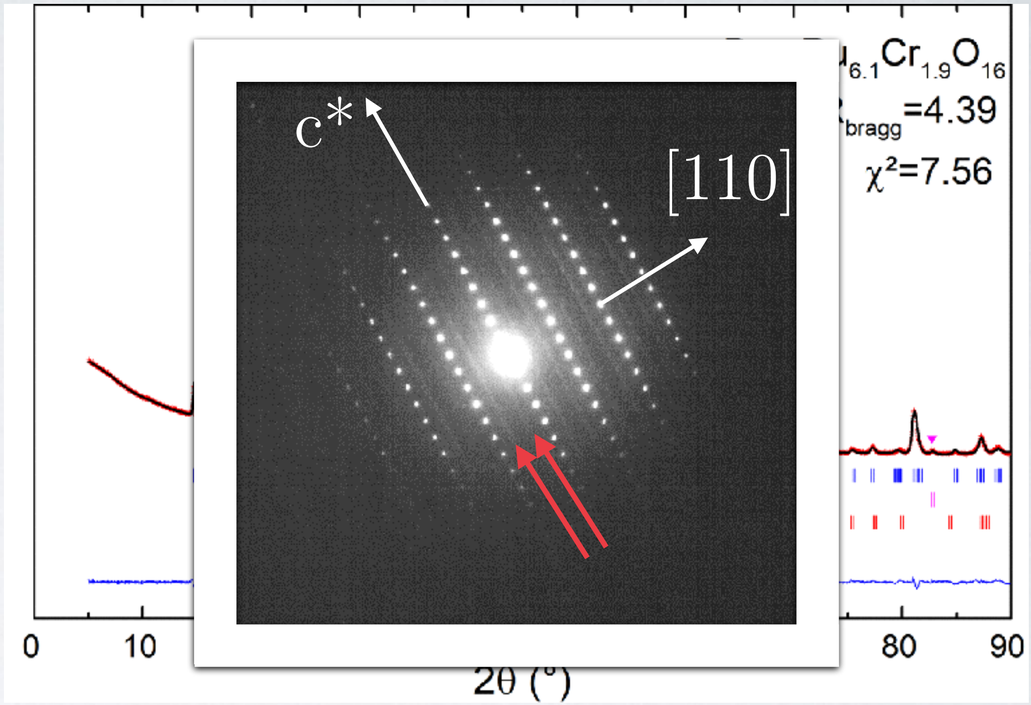

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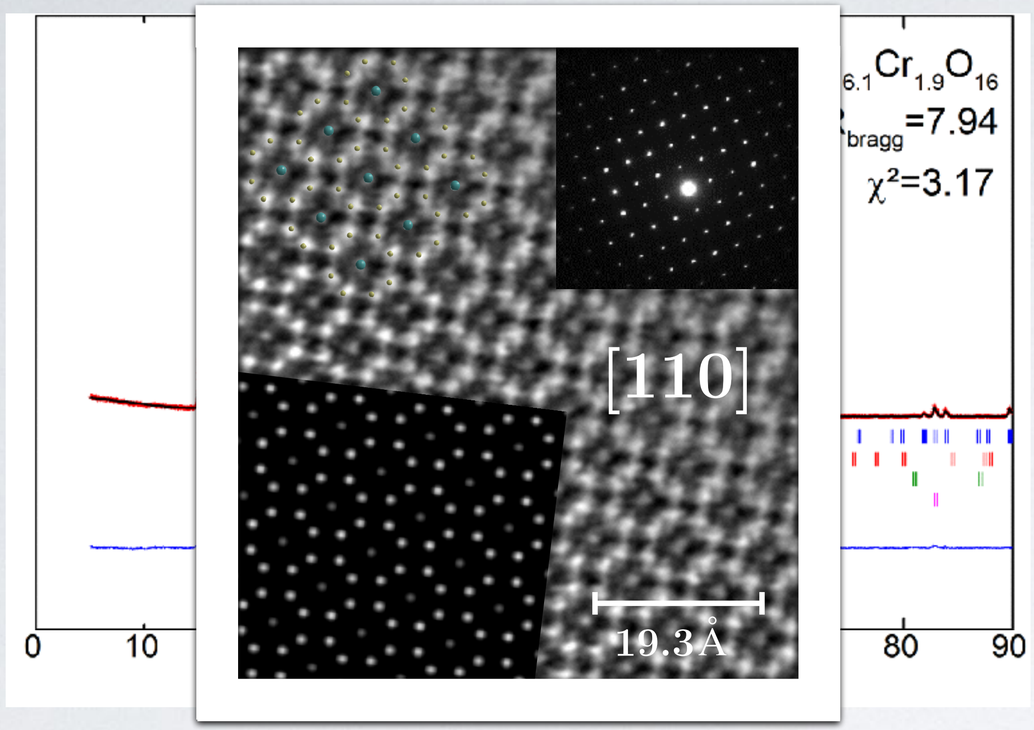

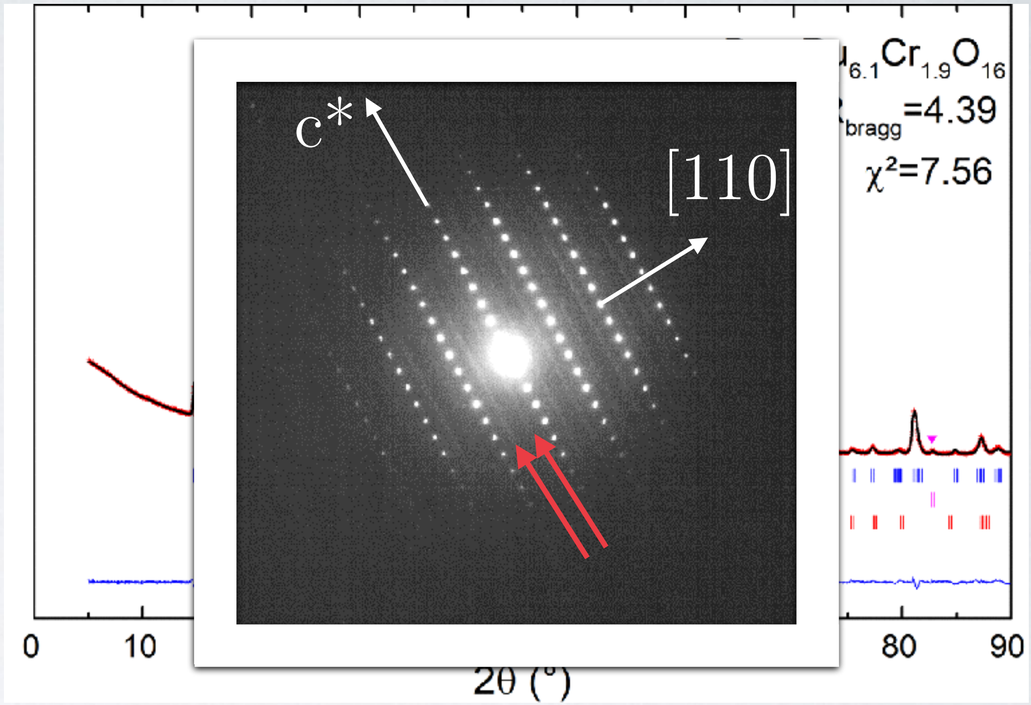

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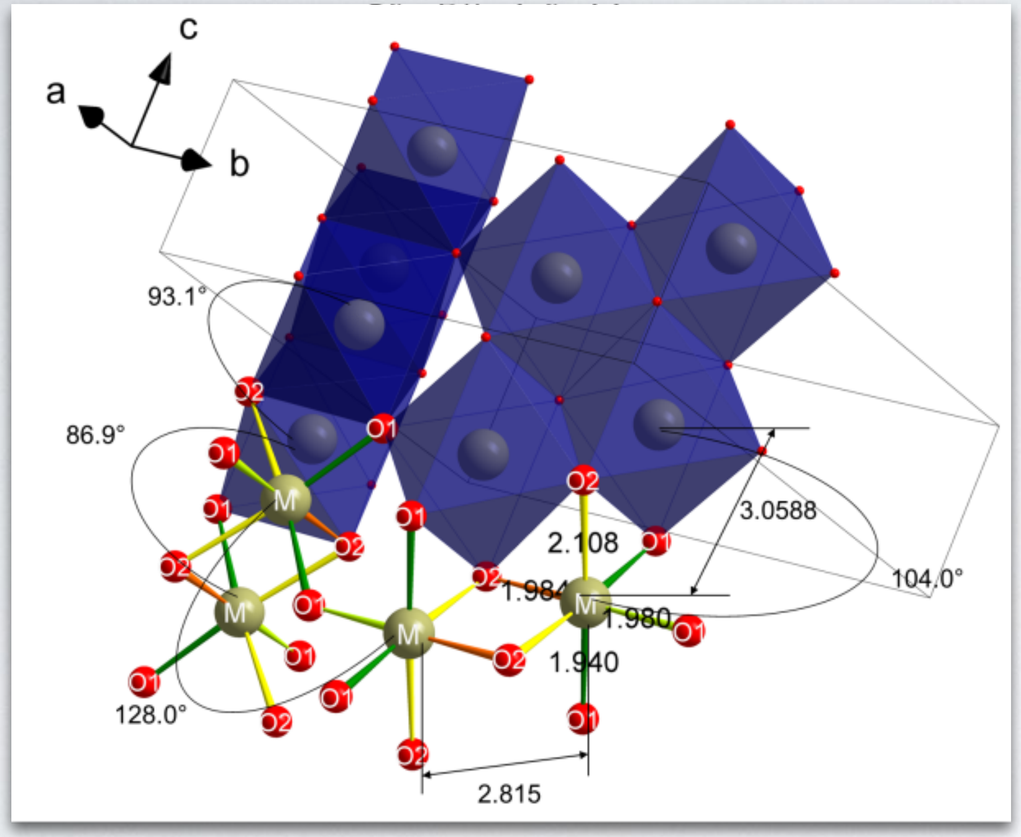

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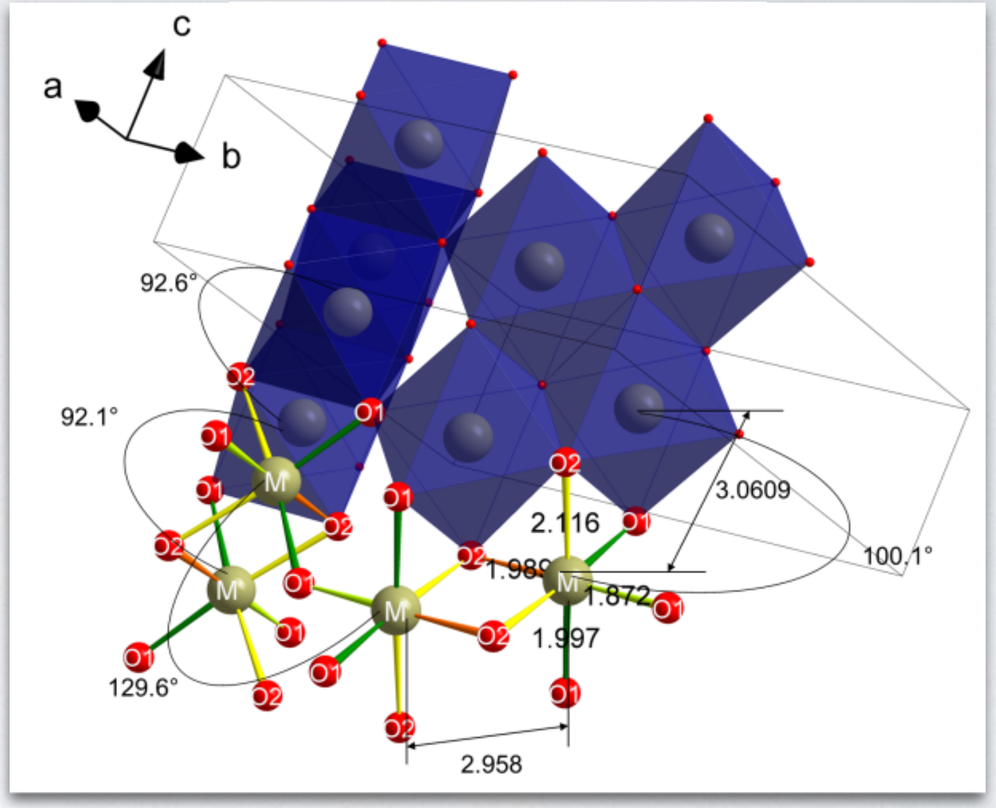

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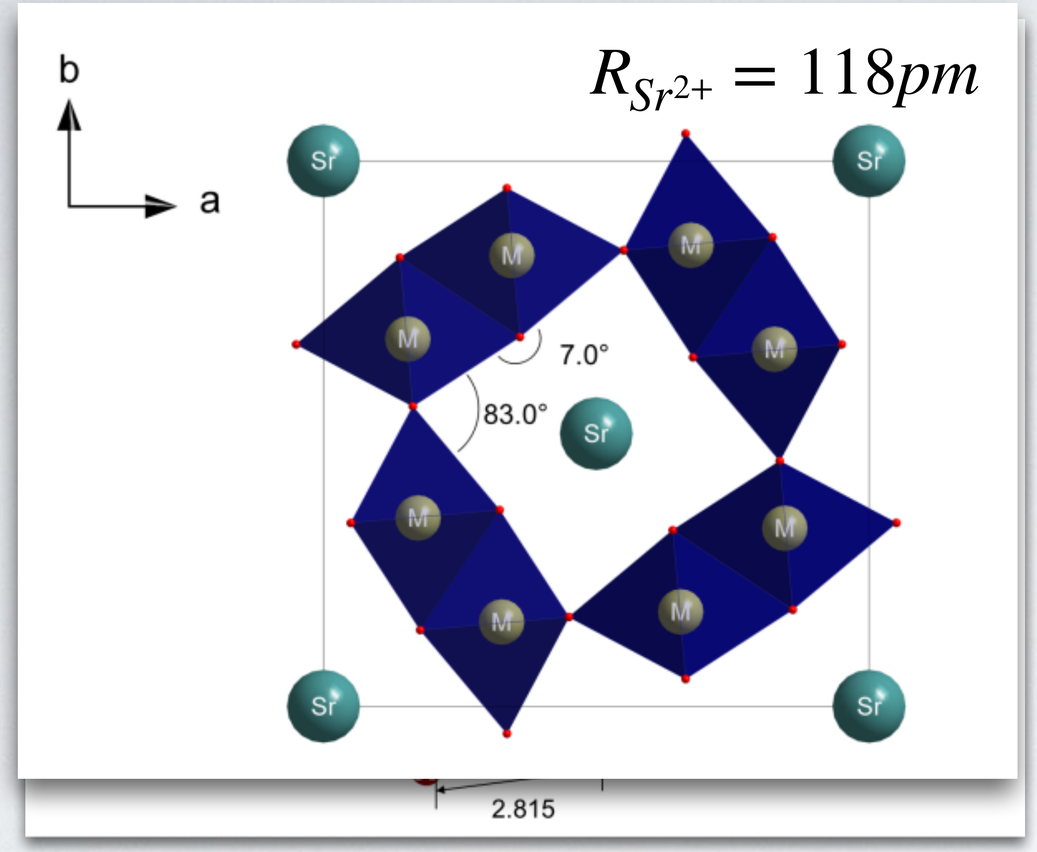

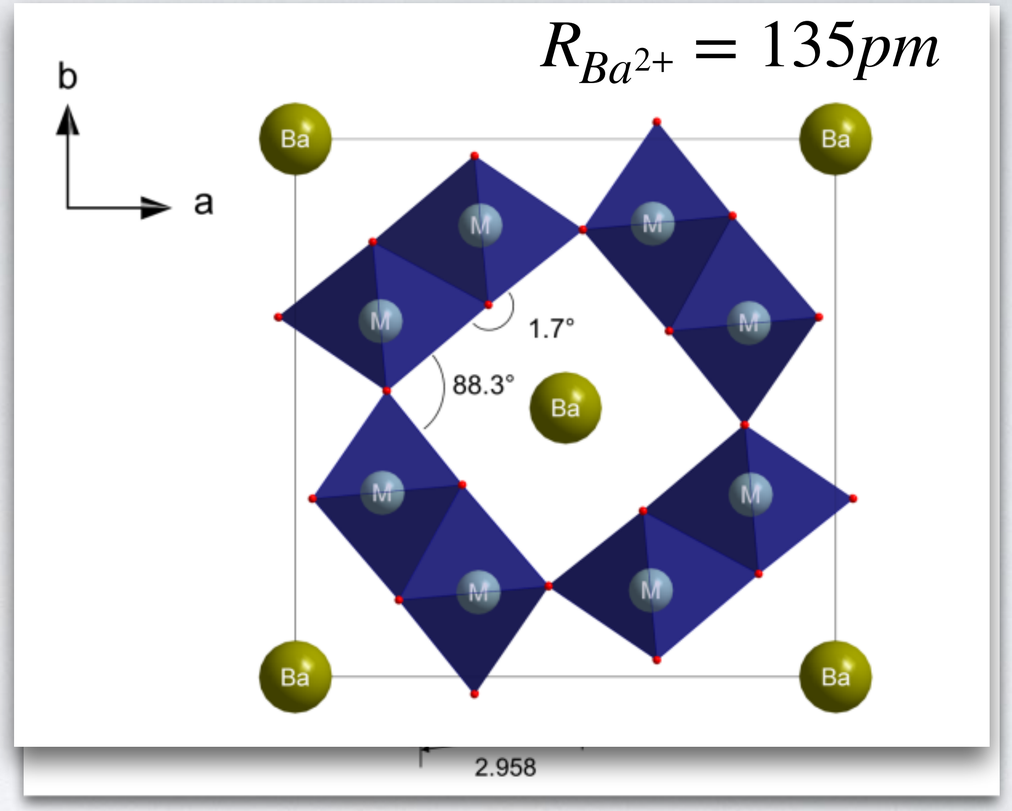

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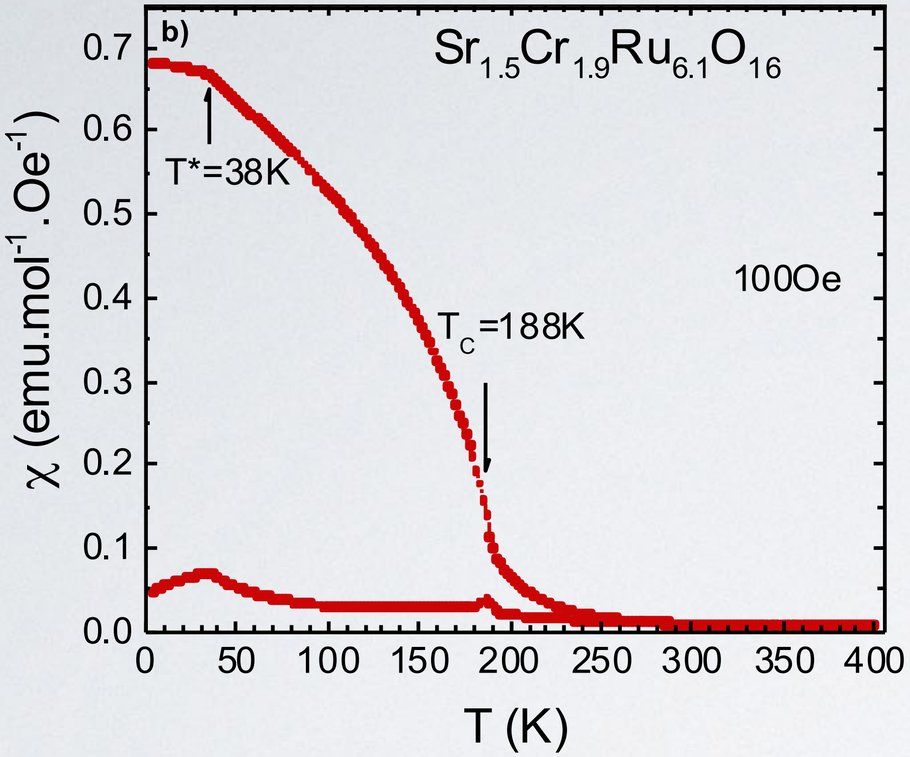
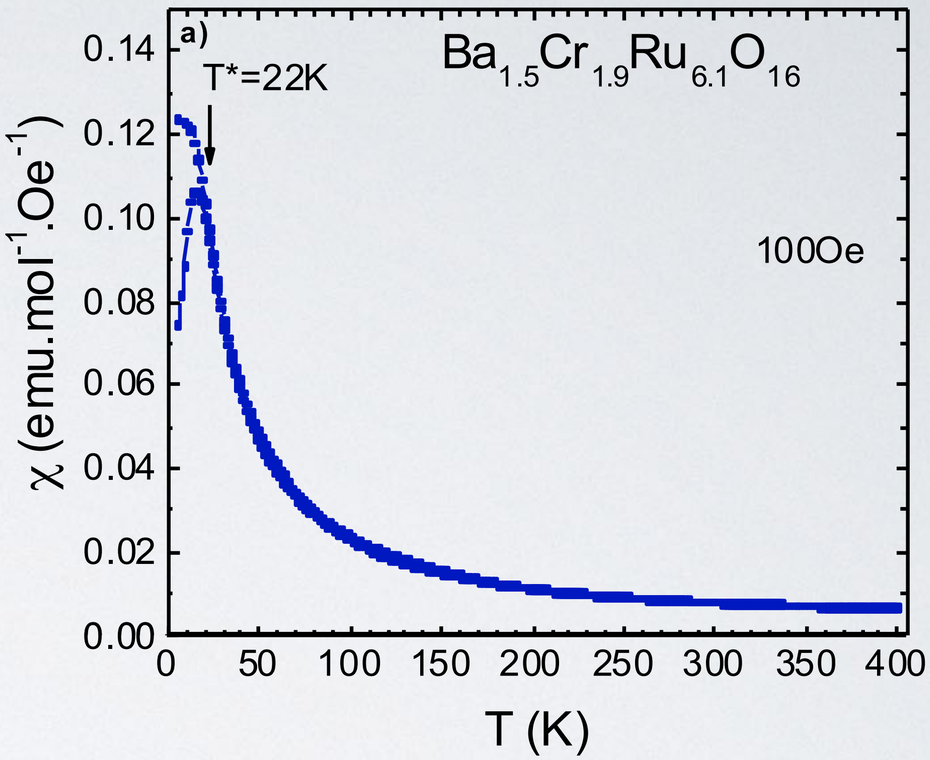
$A_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ hollandites: Magnetic properties

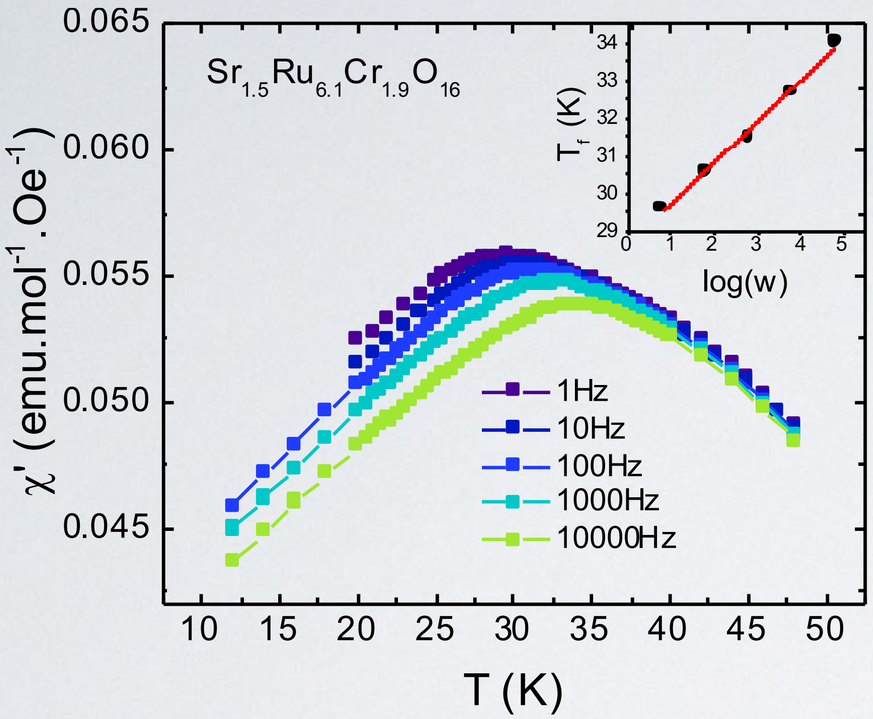


- Glassy behavior
- Transition at 188K

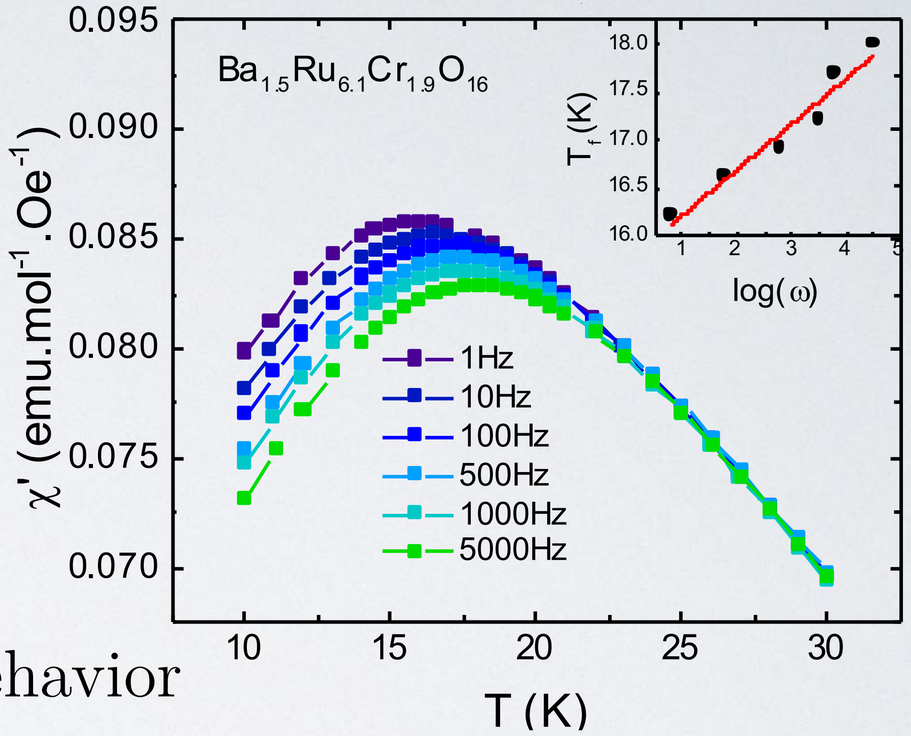


- Glassy behavior

$A_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ hollandites: spin dynamic



$$\delta f = \frac{\Delta T_f}{T_f \Delta ln(\omega)}$$



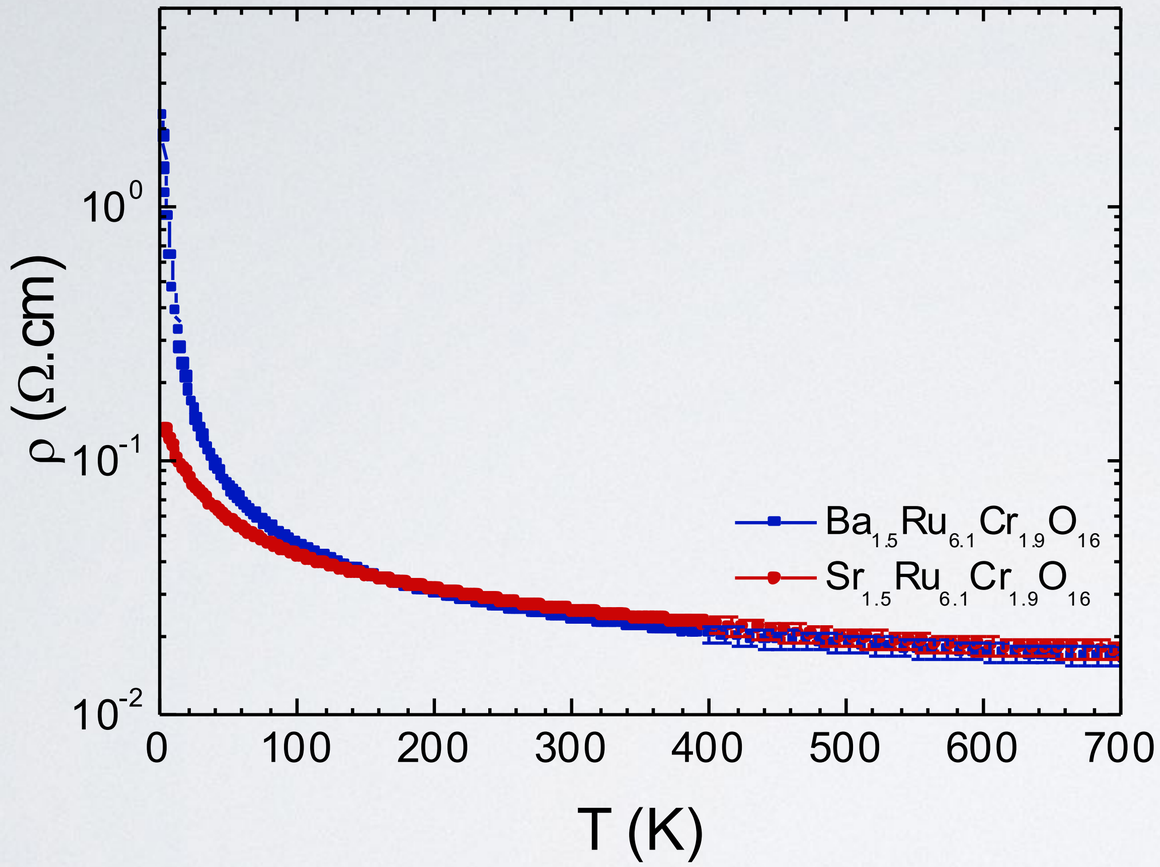
Cluster glass behavior

$\delta f = 0.037(2)$ $\quad 0.03 < \delta f < 0.06$ $\quad \delta f = 0.033(4)$

Aging and relaxation time measurements → Glassy behavior confirmed

Mydosh J. A., *Spin Glasses - An Experimental Introduction*, Taylor & Francis (1993)

$A_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ hollandites: transport properties



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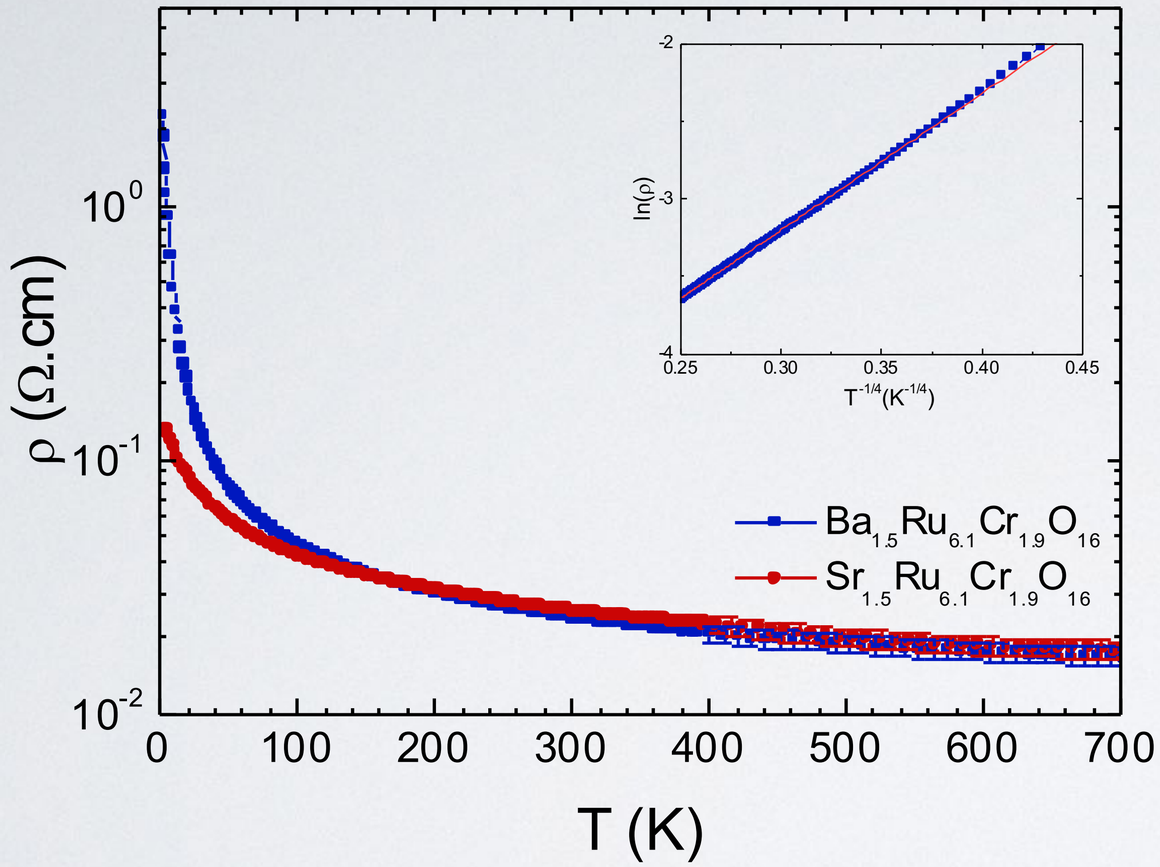
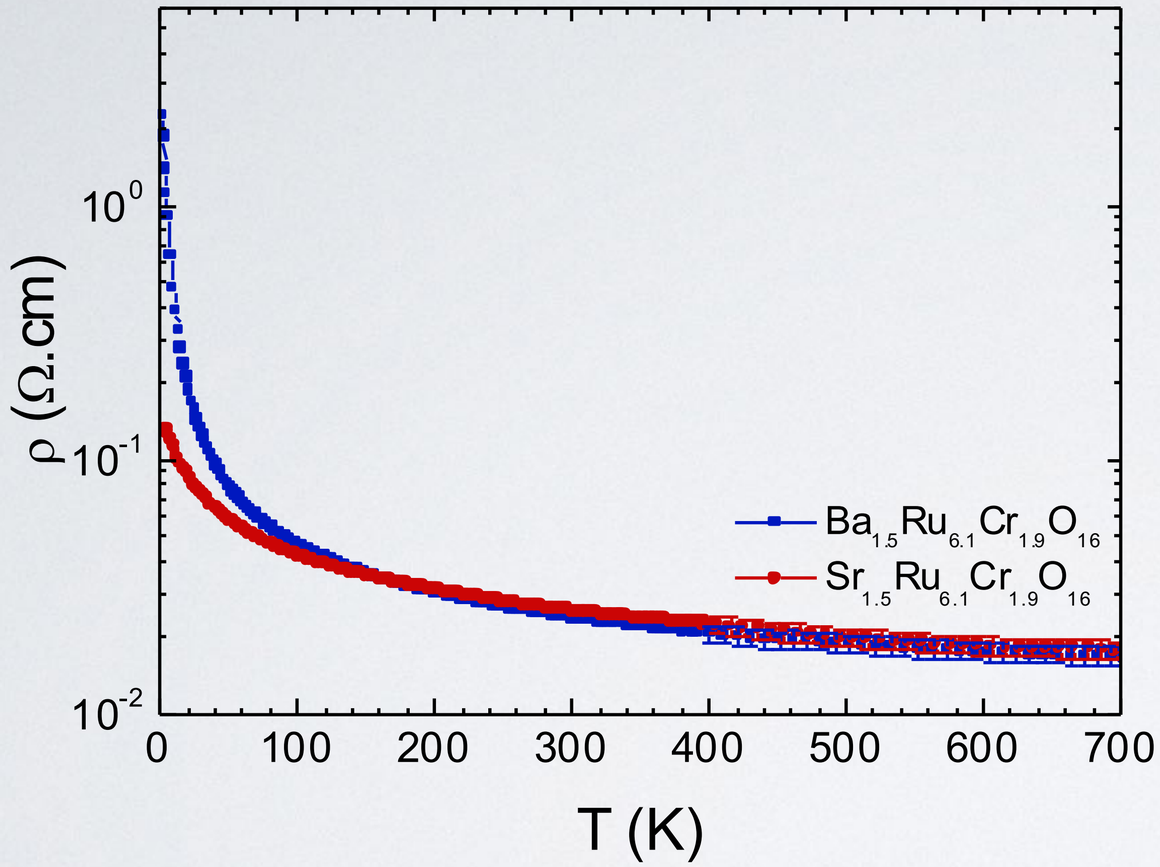
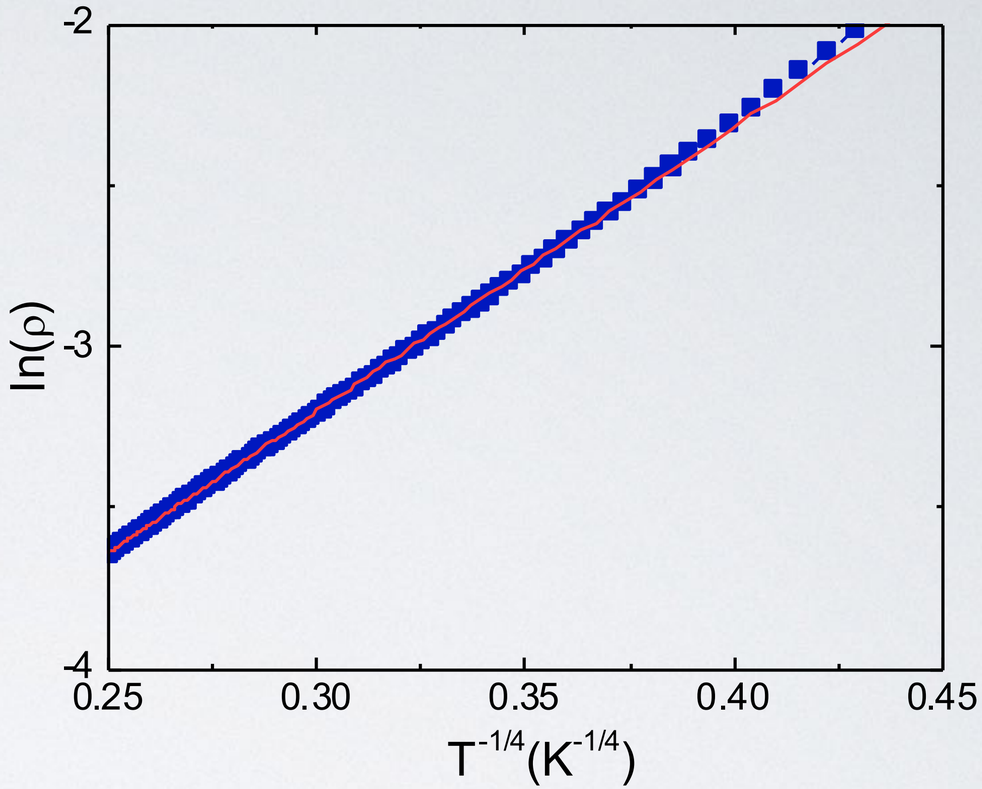


$A_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ hollandites: transport properties





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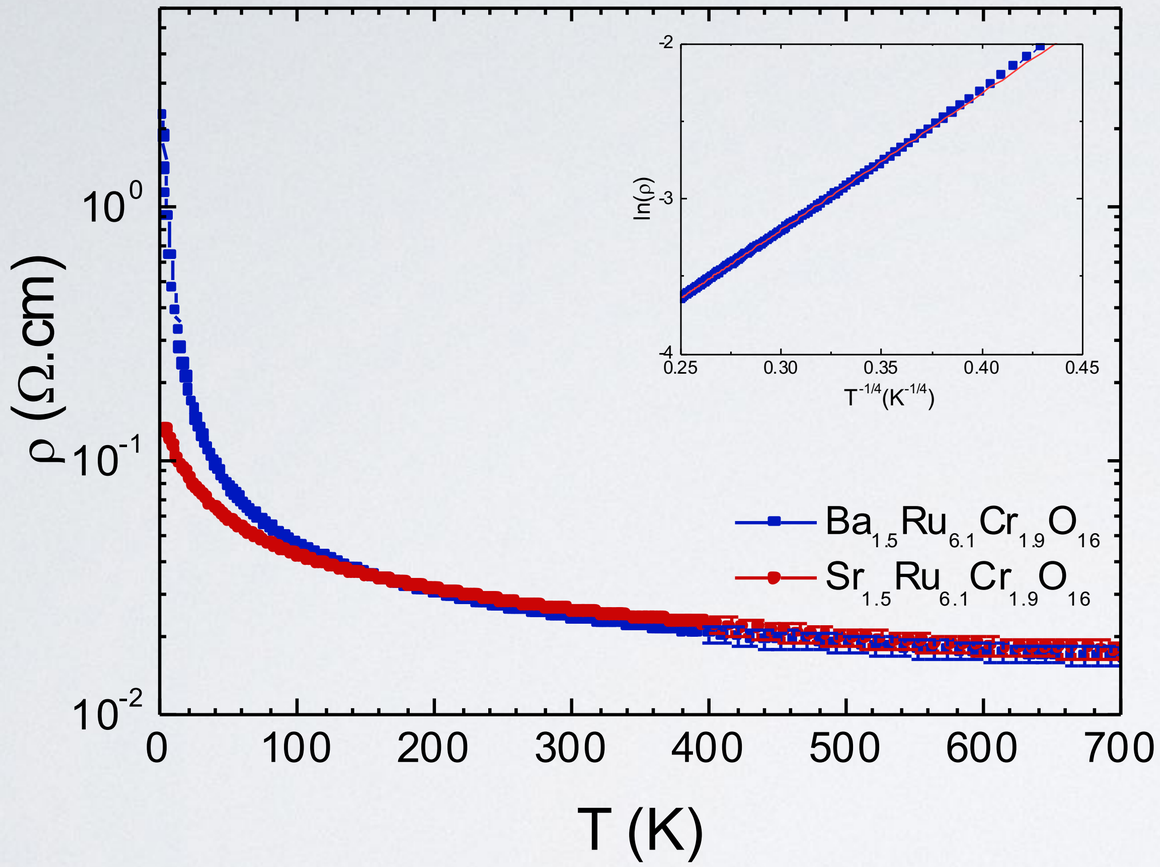

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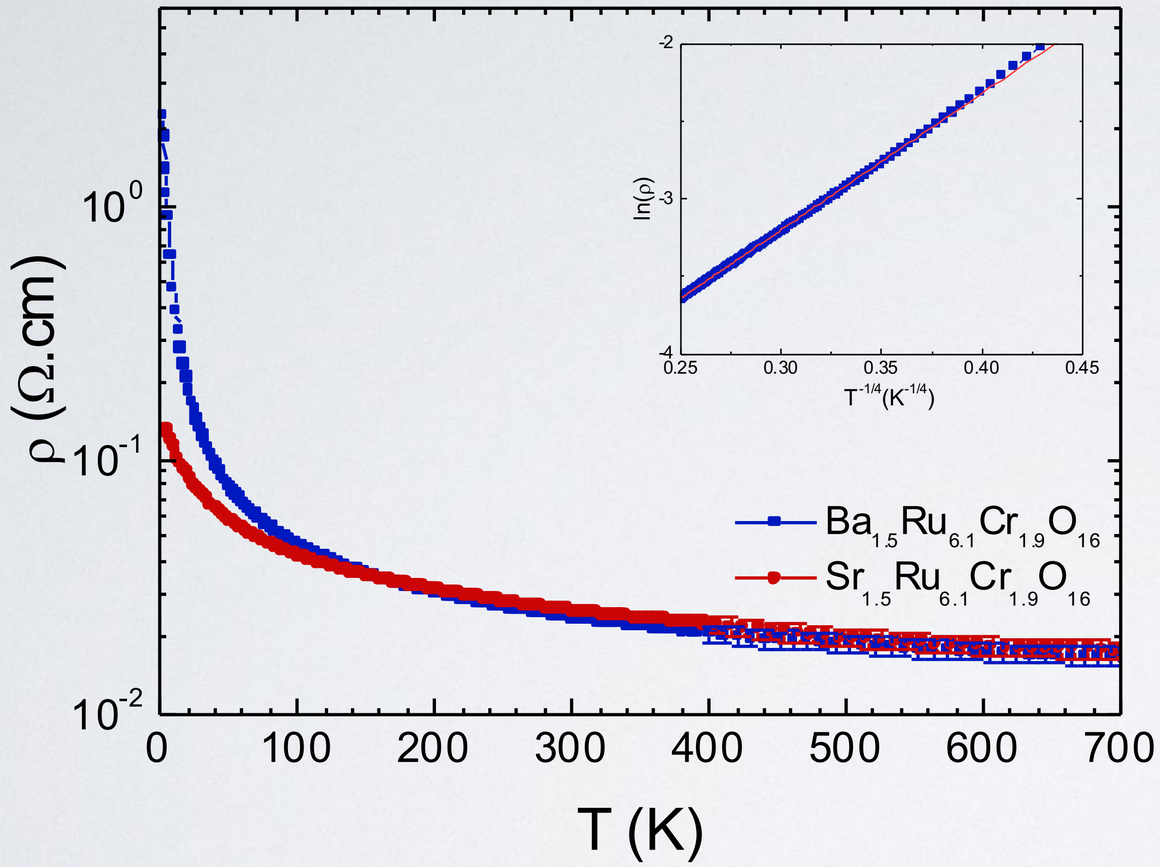


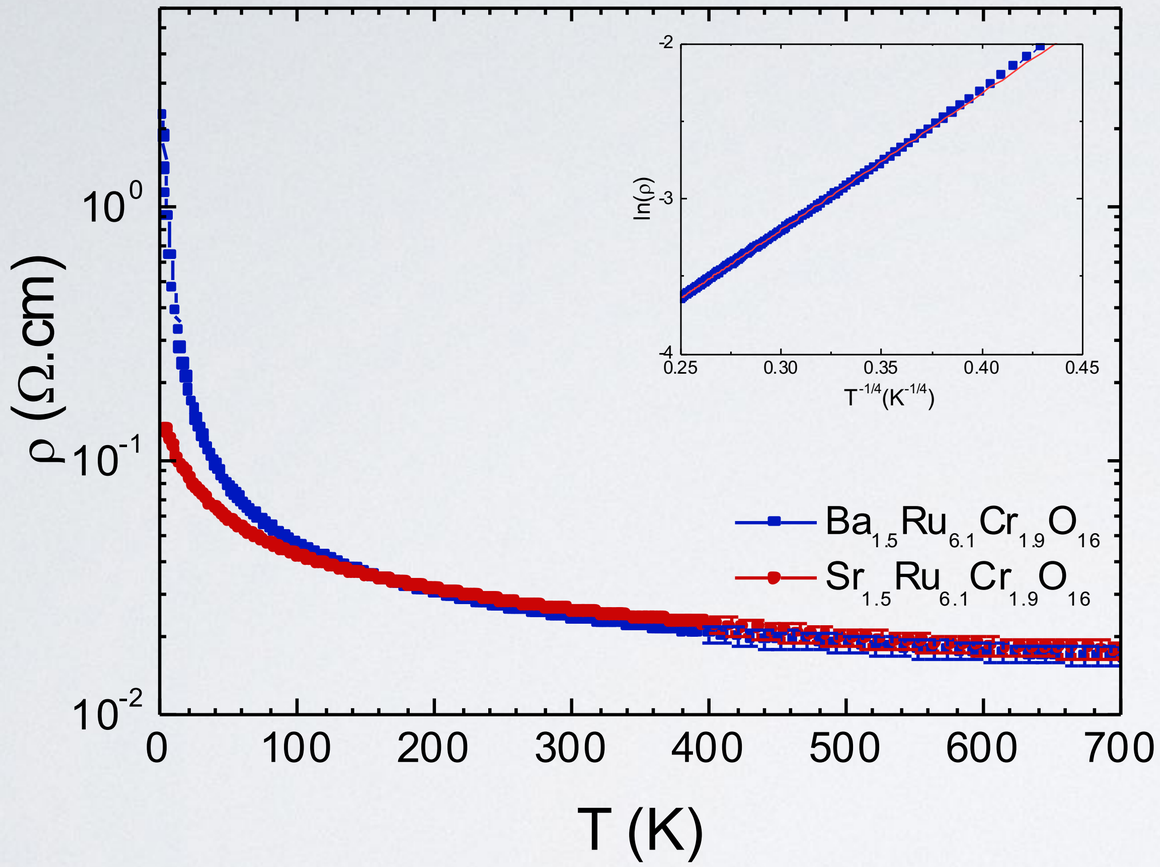
- Localised
- $Ba_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ VRH

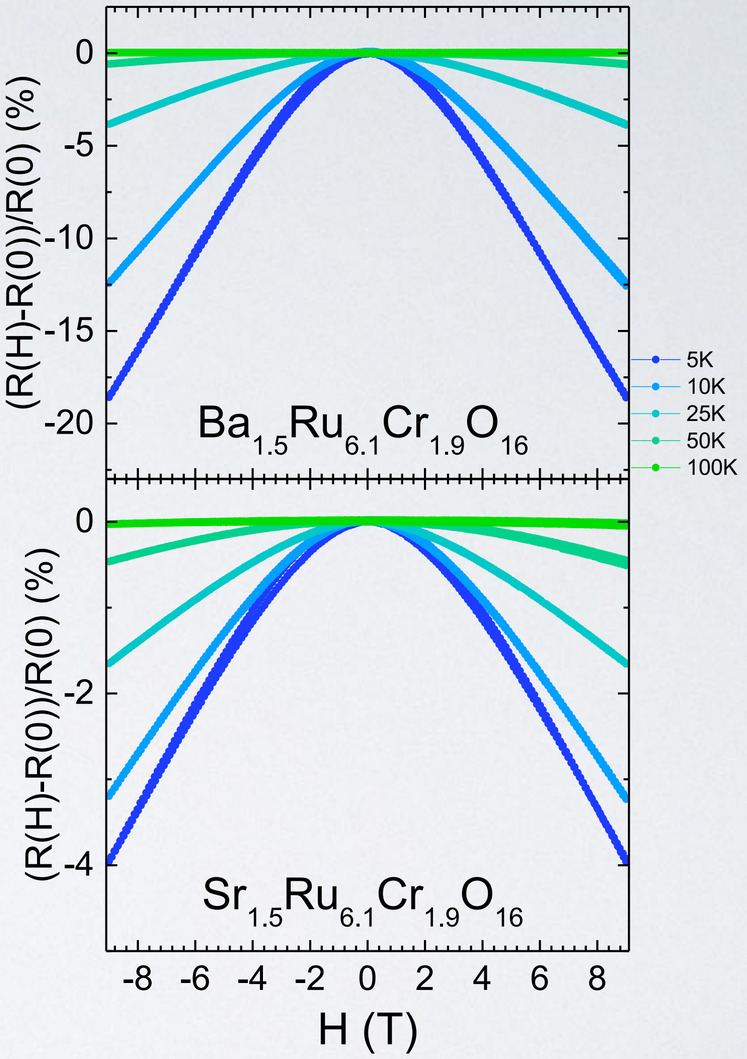
$$\rho(T) = \rho_0 e^{(\frac{T_0}{T})^{1/4}}$$

$$T_0 \sim 6000K$$

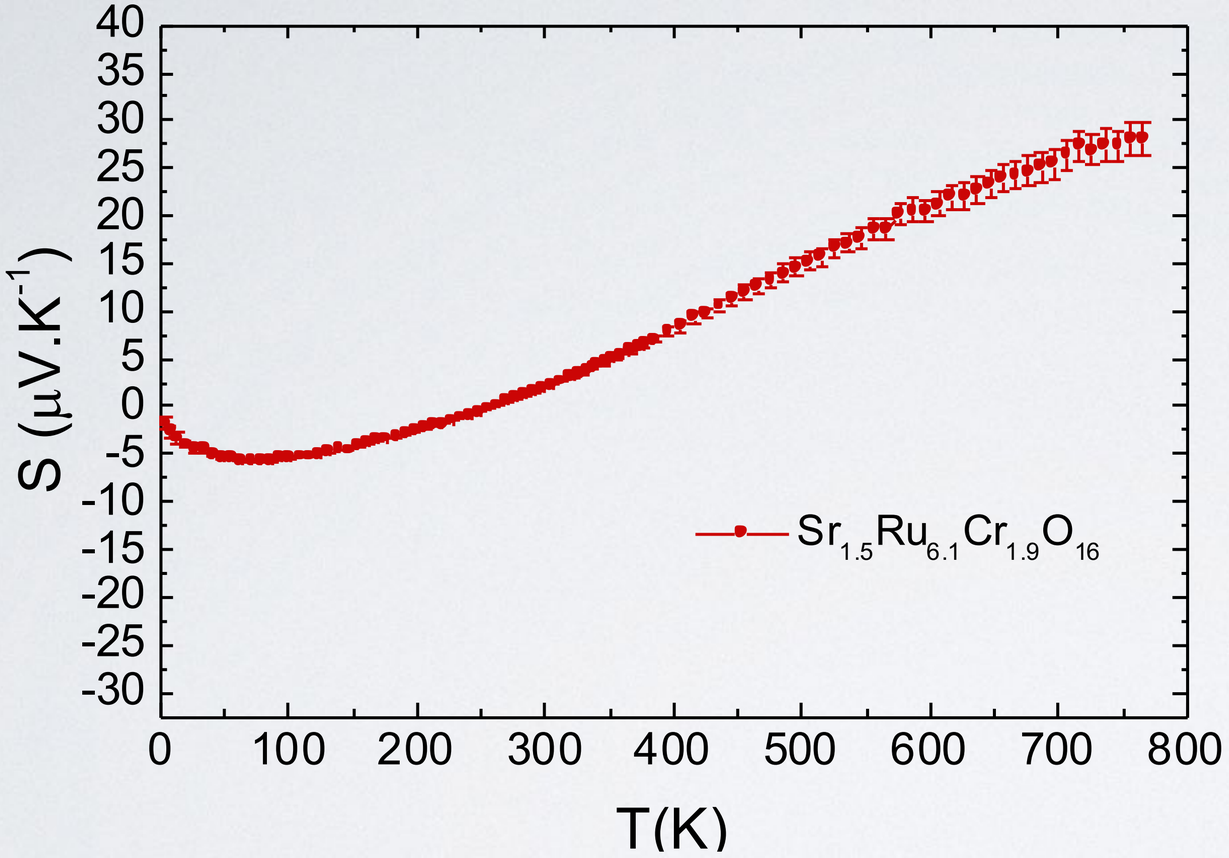
- Disorder dominated
- Magnetotransport coupling (MR)

$A_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ hollandites: transport properties





$A_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ hollandites: Seebeck coefficient



- S<0 then S>0
- Minima
- No linearity at T⟶0 K
- S ~ 30μV.K^{-1} at high T

Kobayashi et coll., Phys. Rev. B 79, 155116 (2009)

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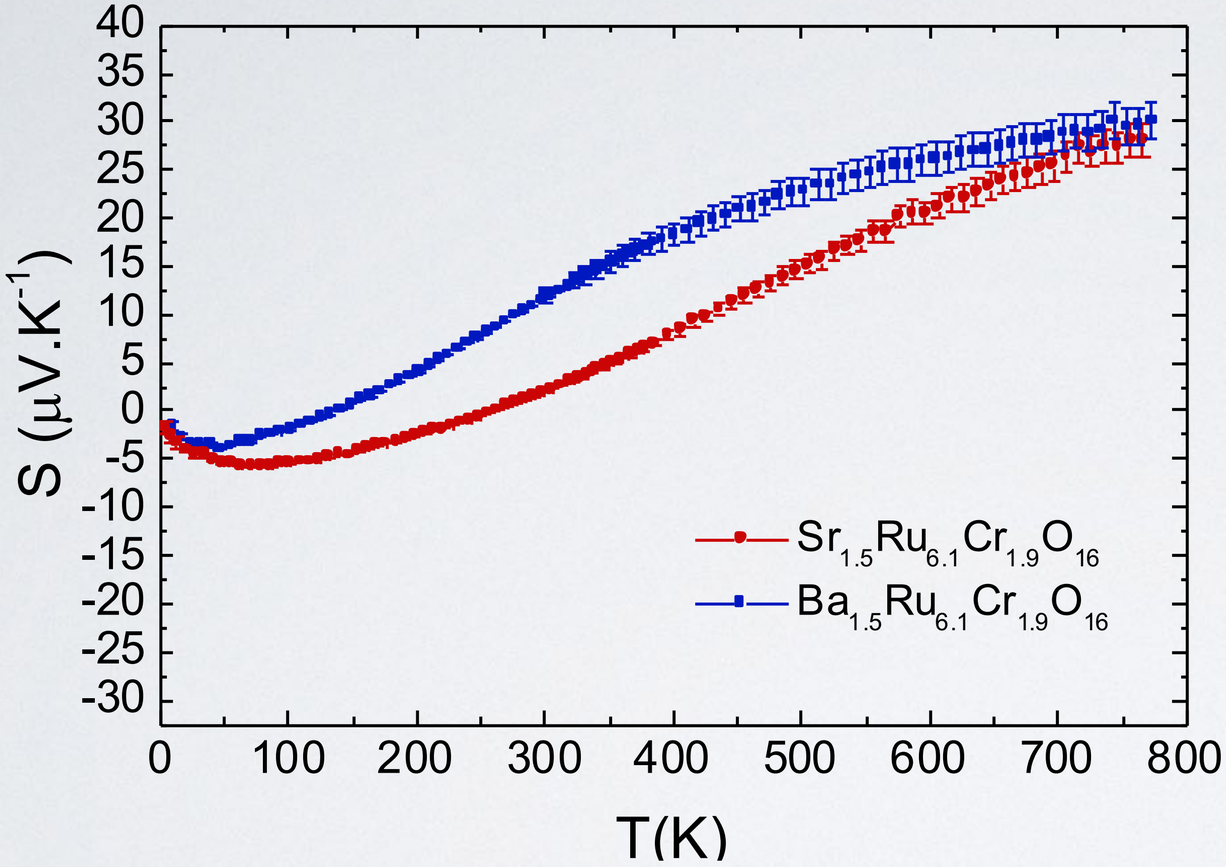

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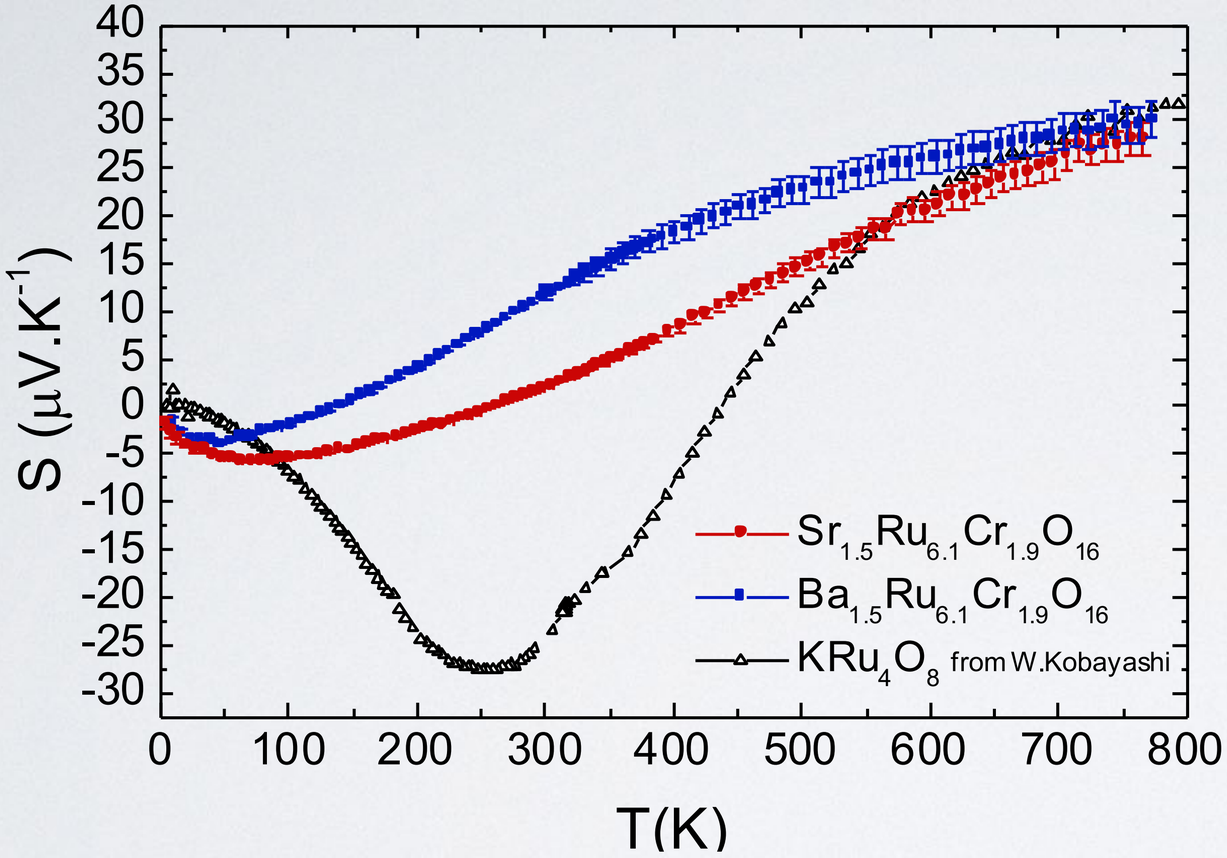

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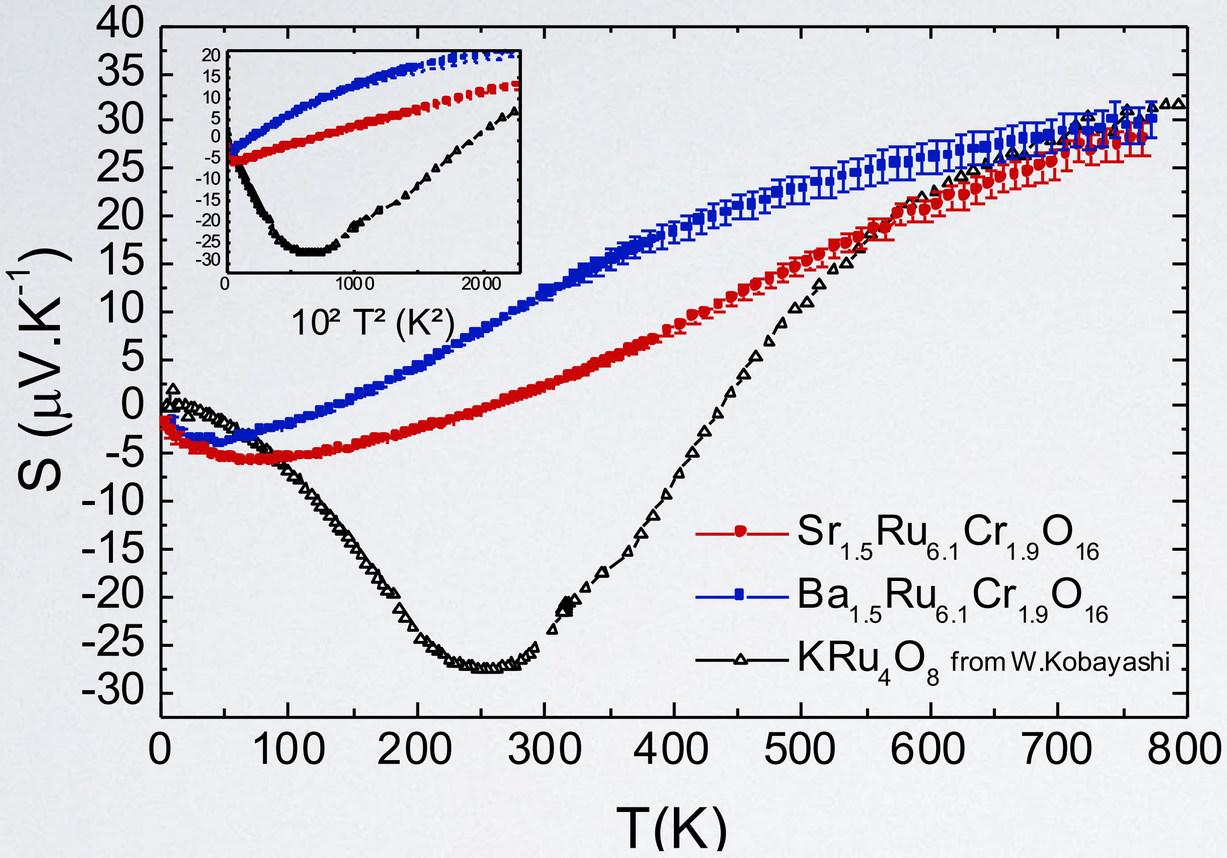

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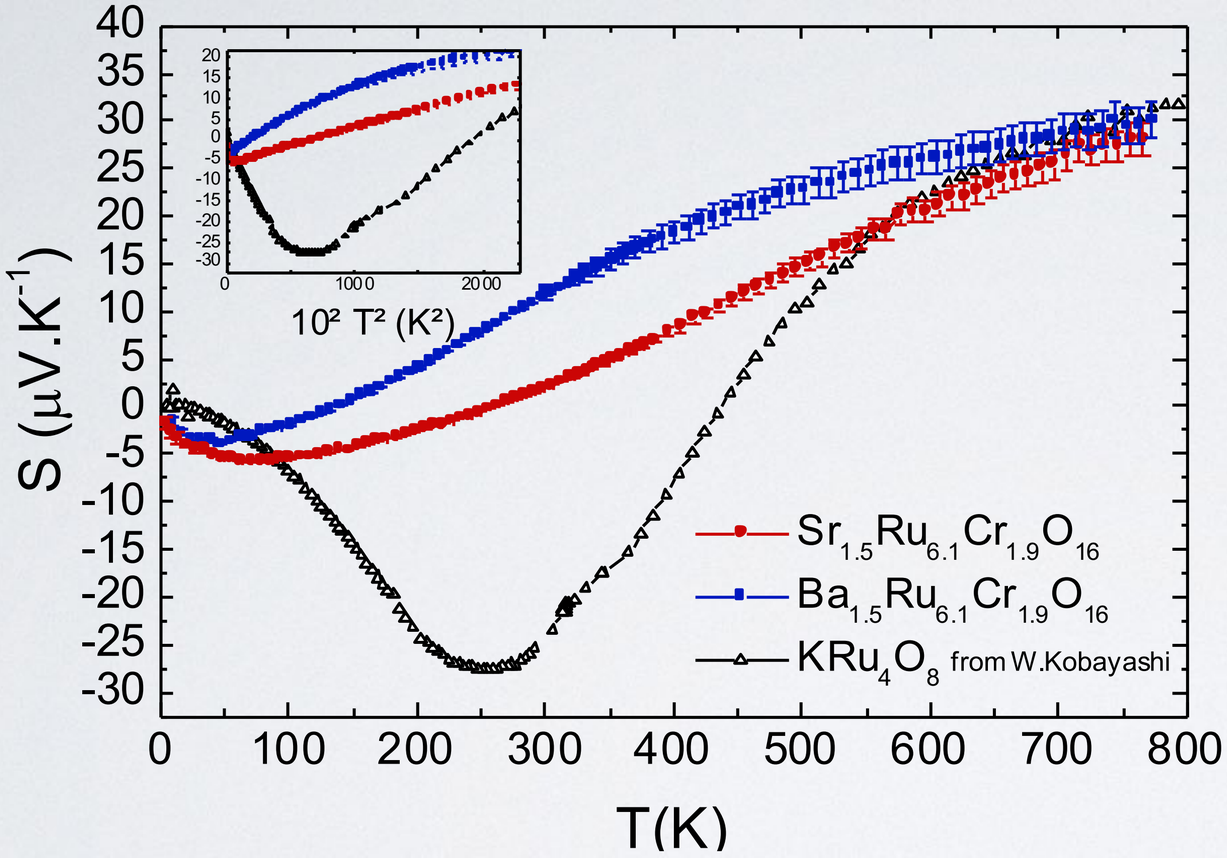

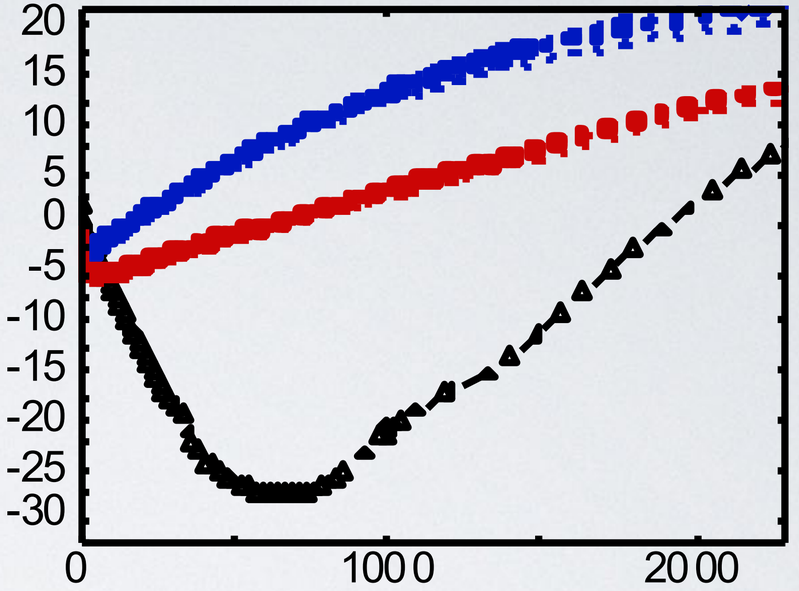

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$A_{1.5}Ru_{6.1}Cr_{1.9}O_{16}$ hollandites : summary

- Substitution 25% Cr :
  - Localized transport.
  - Magnetism: cluster-glass behavior.
- Unprecedented magnetoresistance in Ru-hollandites (MR<0 and strong).
- Seebeck coefficient:
  - Surprisingly weak for localized charge carriers.
  - S at high T dominated by Ru(~IV) spin entropy.

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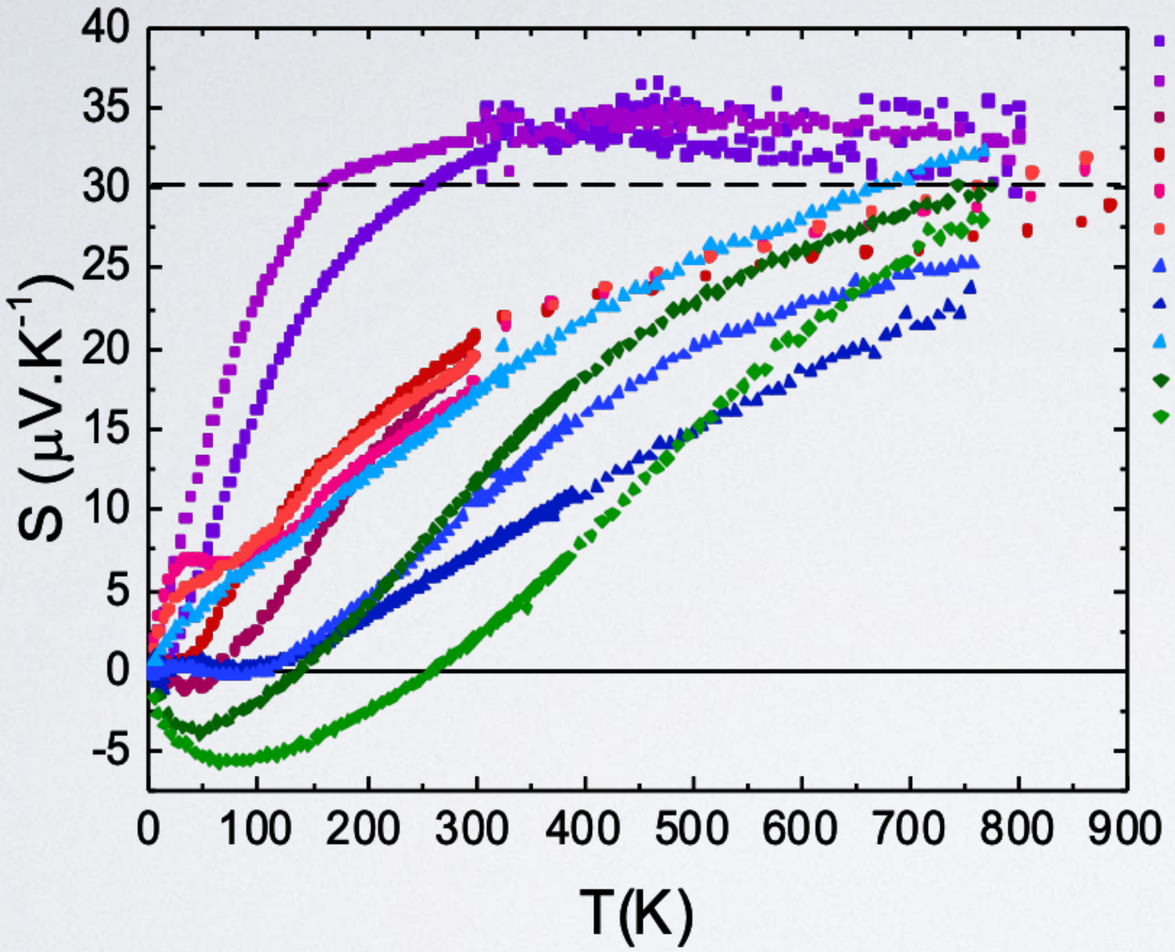
→ Perspectives: sign change and T^2 behavior at low S(T)

Ruthenium oxides:



$CaRuO_3$ — Paramagnetic metal

$SrRuO_3$ — Ferromagnetic metal

$NaCu_3Ru_4O_{12}$, $LaCu_3Ru_4O_{12}$, $La_{0.5}Ca_{0.5}Cu_3Ru_4O_{12}$, $CaCu_3Ru_4O_{12}$ — Pauli metals

$BaCo_2Ru_4O_{11}$, $BaMn_2Ru_4O_{11}$ — Soft ferromagnetic poor metals

$SrFe_2Ru_4O_{11}$ — Ferromagnetic semiconductor

$Ba_{1.5}Cr_2Ru_6O_{16}$, $Sr_{1.5}Cr_2Ru_6O_{16}$ — Cluster-glass semiconductors

∀ RuO_6 octahedra link

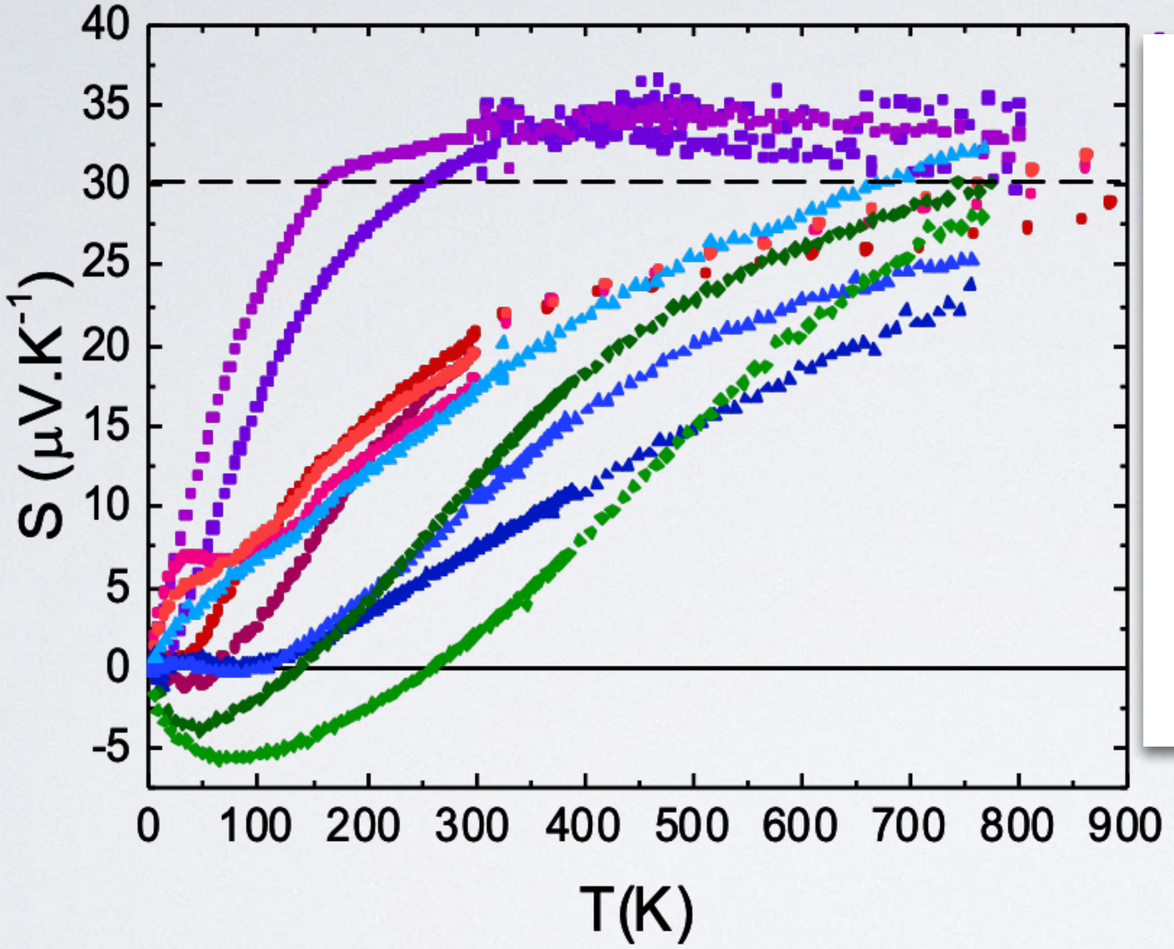
∀ %Ru (at least down to 70%)

∀ electrical transport behavior

∀ magnetism behavior

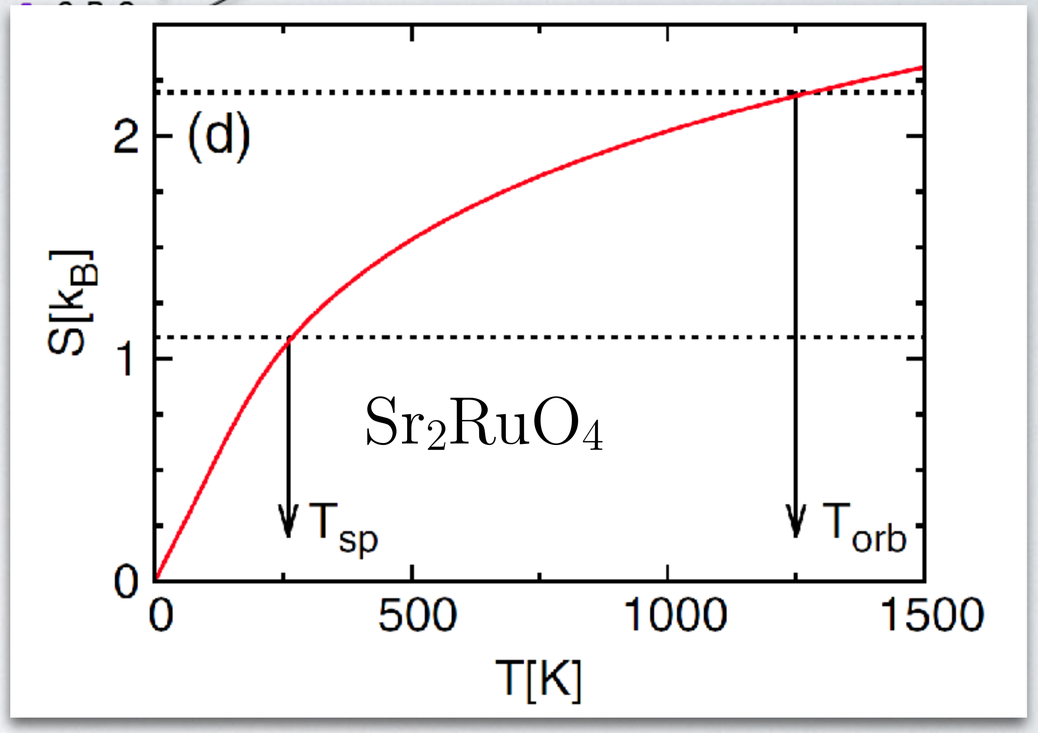
S high T dominated by Ru(~IV) spin entropy only ⟹ Frozen orbital degrees of freedom

Ruthenium oxides:



Paramagnetic metal

Ferromagnetic metal



∀ **electrical transport behavior**

∀ **magnetism behavior**

S high T dominated by Ru(~IV) spin entropy only ⟹ Frozen orbital degrees of freedom

Mravlje and A. Georges, Phys. Rev. Lett. 117, 036401 (2016)

Peterson and Shastry, Phys. Rev. B 82, 195105 (2010)

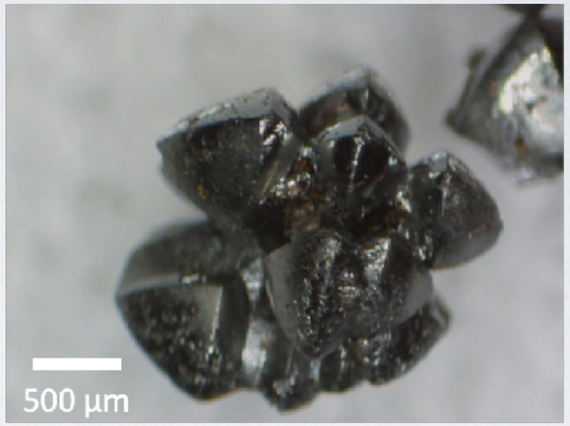
Postdoctoral research:

Semi-metallic Polymers and Hybrid Halide Perovskites for Thermoelectric Application

Prof. Guillaume FLEURY and Prof. Georges HADZIIOANNOU

- Crystallizations:
  Anti-solvent vapor-assisted
  Inverse temperature crystallization
  Acid-way
- Crystallographic characterization:
  SCXRD (Dr. Stan PECHEV - ICMCB)
  TEM (Dr. Oleg LEBEDEV - CRISMAT)
- Impedance and transport properties (myself and Dr. Ali FAKIH CRISMAT)

Hybrid Halide Perovskites:

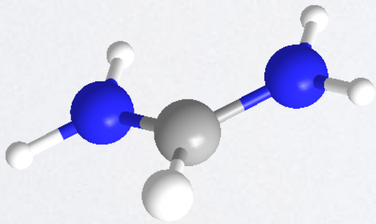


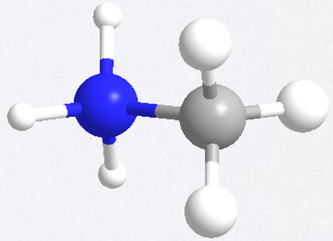
Pb-based

Sn-based

Nominal compositions: $(FA)_{0.85}(MA)_{0.15}PbI_{2.55}Br_{0.45}$

MA_xSnI_3

FA: $(CH_5N_2)^+$ 

MA: $(CH_3NH_3)^+$ 

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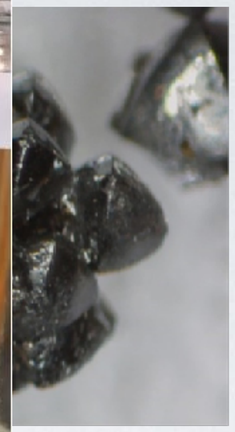
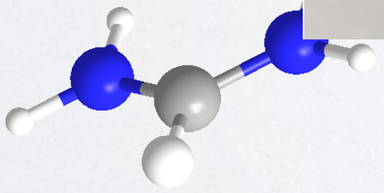
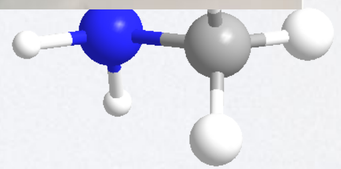


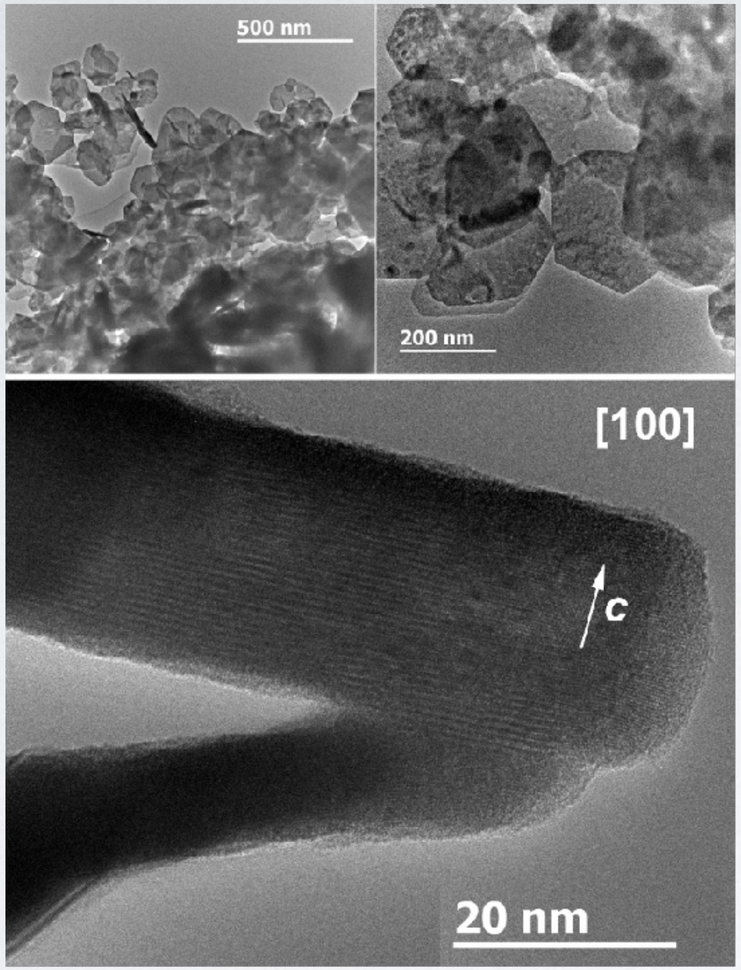
Pb-ba ed

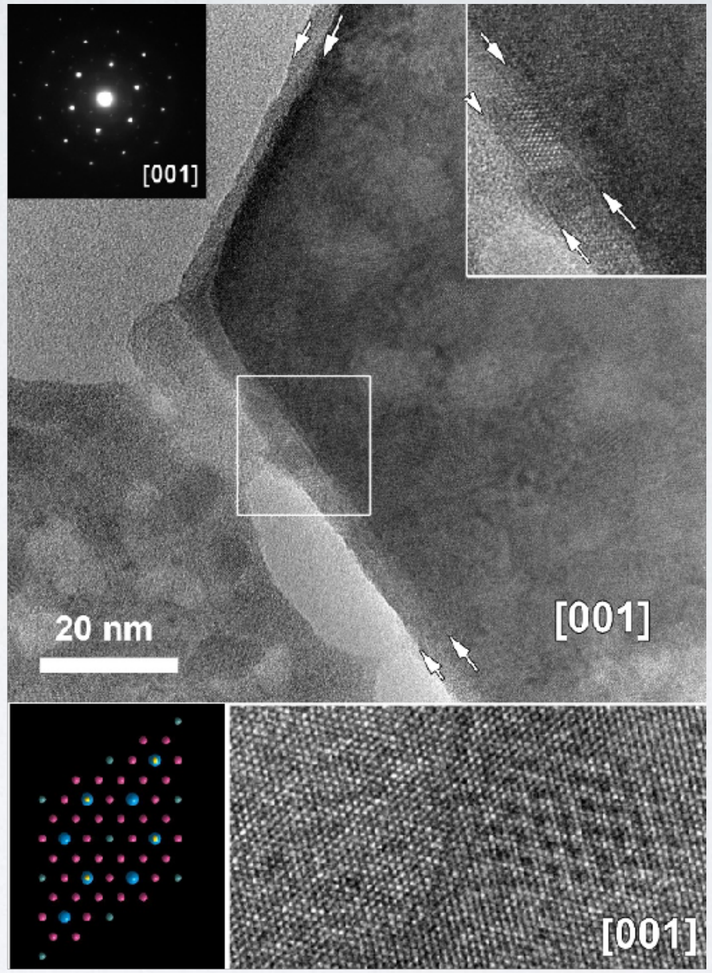
Nominal compositions: $(FA)_{0.85}(MA)_{0.15}Pb$ $_3$

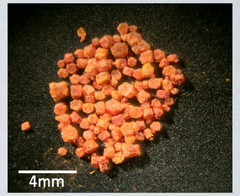
FA: $(CH_5N_2)^+$ 

MA: $(CH_3NH_3)^+$ 

Hybrid Halide Perovskites: Pb-based







Hybrid Halide Perovskites: Pb-based 150 K

4H-perovskite

$P6_3/mmc$

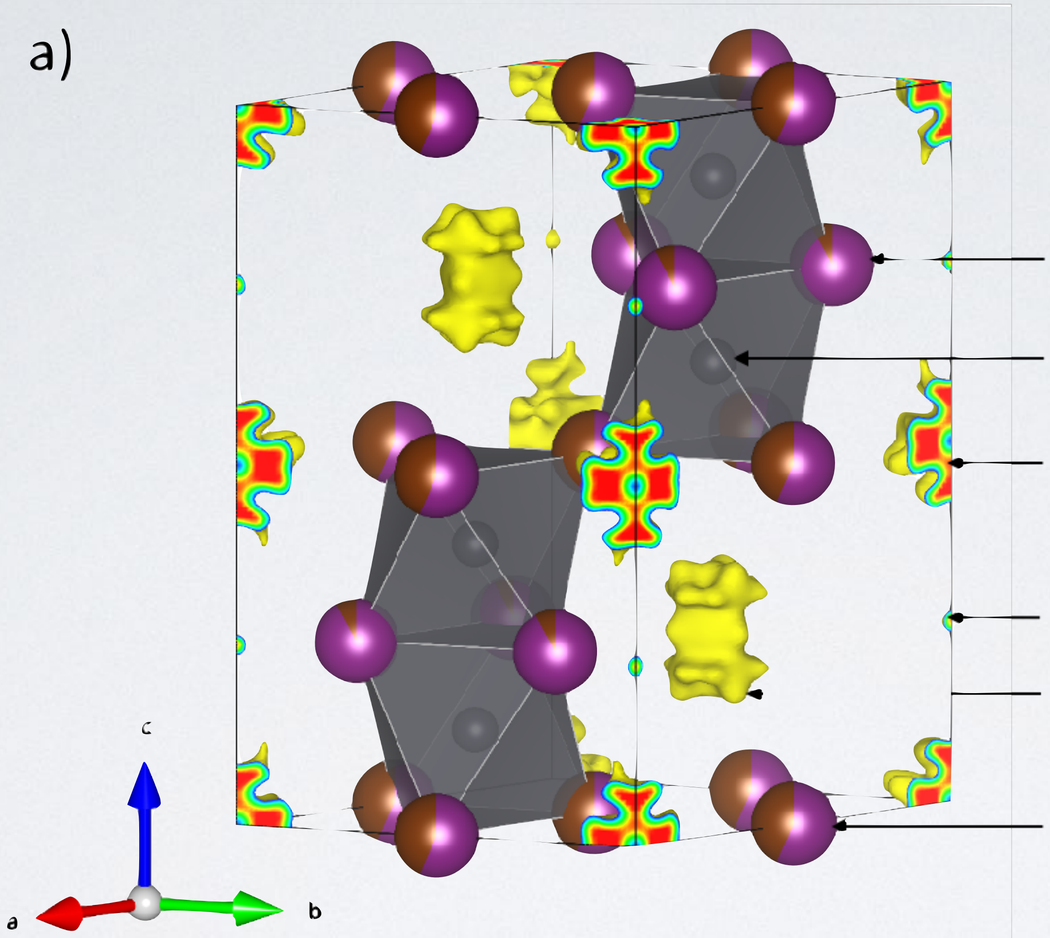
a = 8.6945(4) Å

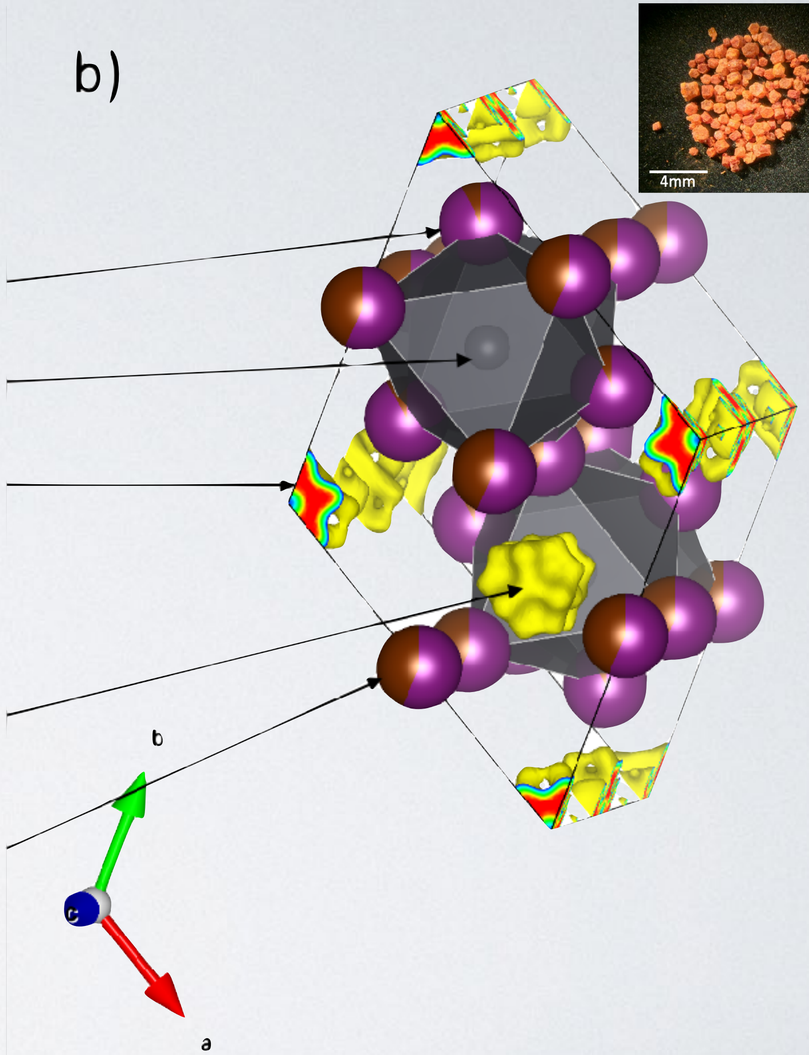
c = 15.1119(7) Å

c/a = 1.7381

V = 989.3(1) Å^3

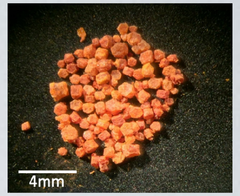
Z = 4



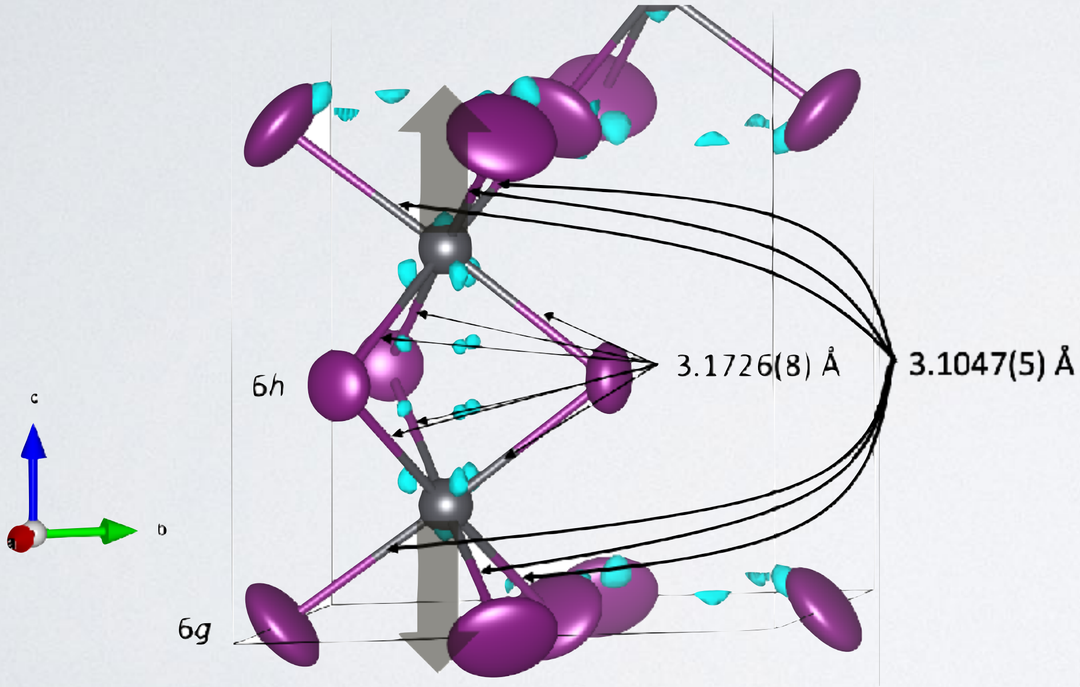


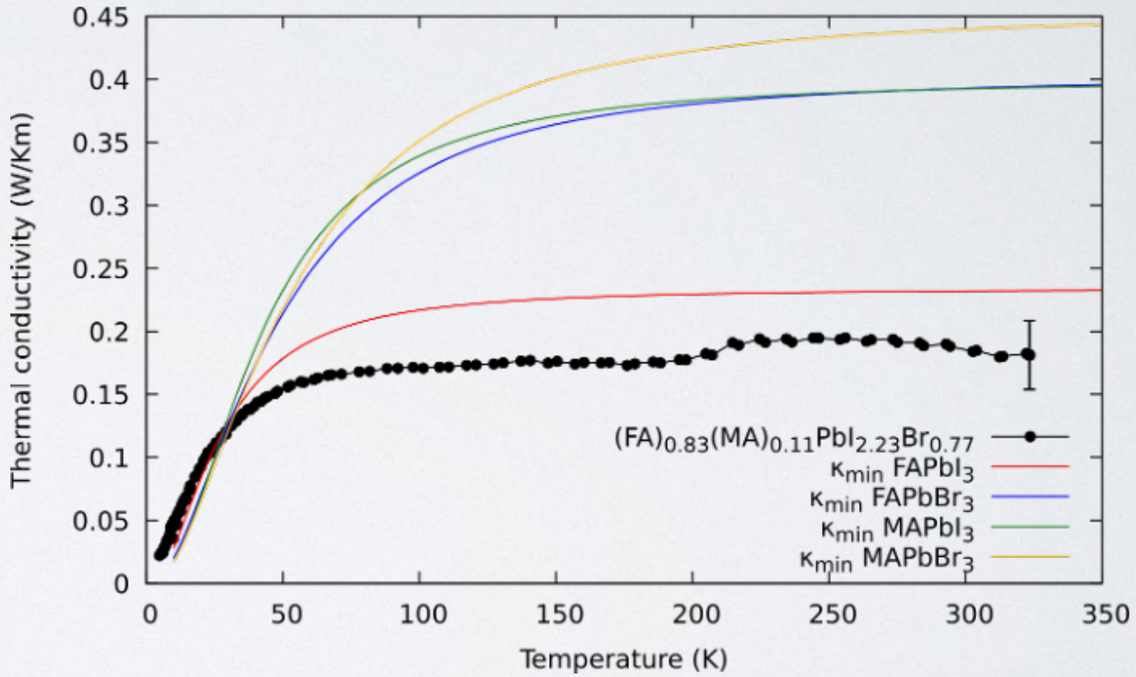
Refined composition : $(FA)_{0.83}(MA)_{0.11}PbI_{2.23}Br_{0.77}$

Hybrid Halide Perovskites: Pb-based



- Anisotropic thermal displacement
- Distorted polyhedra





Fabini, Seshadri and Kanatzidis, MRS Bulletin 45 6 (2020)

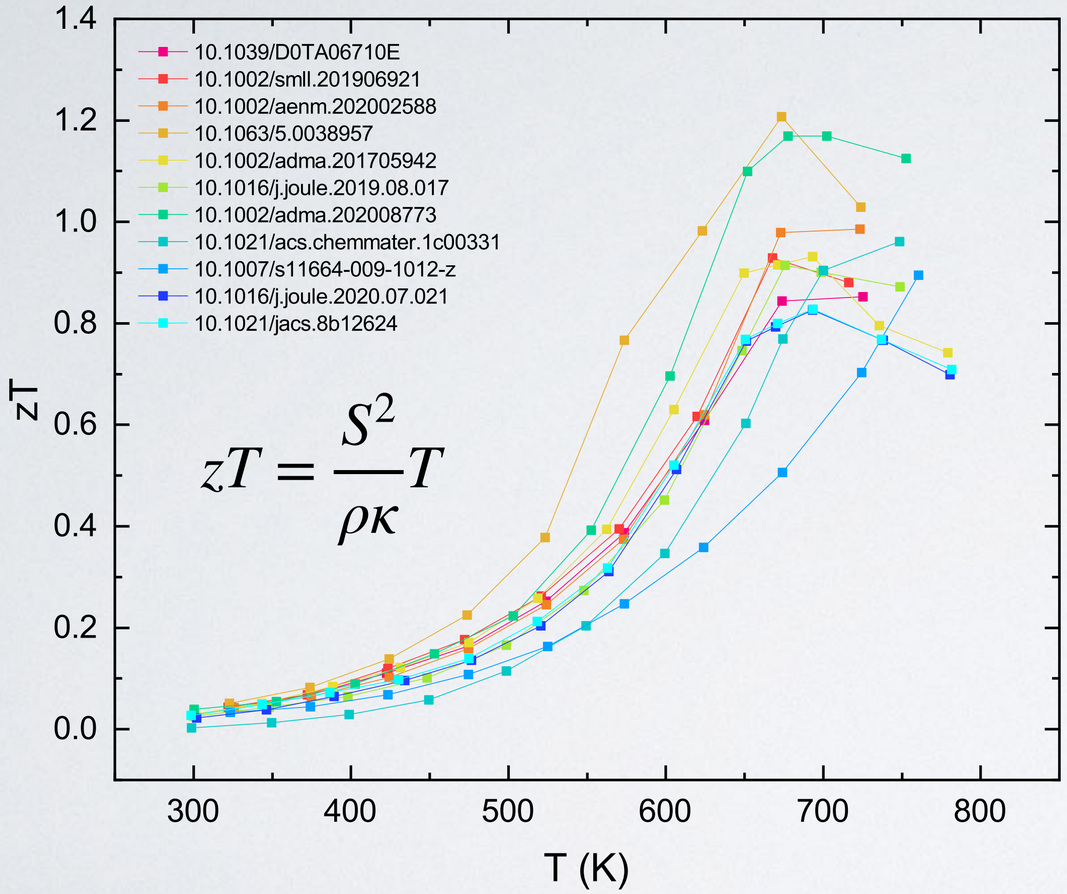
Postdoctoral research:

Prospection of thermoelectric chalcogenide materials assisted by active learning and Bayesian optimization

Dr. David BERTHEBAUD, Dr. Jean-François Halet
and Dr. Guillaume LAMBARD

- Machine learning: From scratch
- Solid-state reaction and Spark Plasma Sintering densification
- PXRD and thermoelectric characterizations at high-T

Why GeTe?



GeTe $R3m$

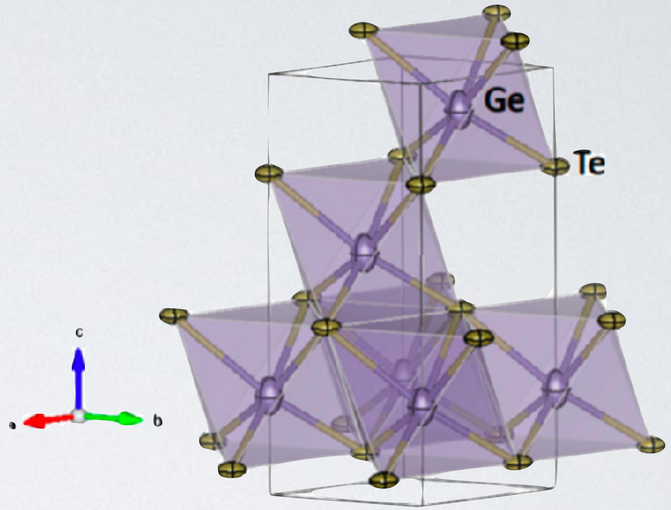
a = 8.38 Å

c = 10.65 Å

$\alpha = 90°$

$\gamma = 120°$

V = 647 Å^3



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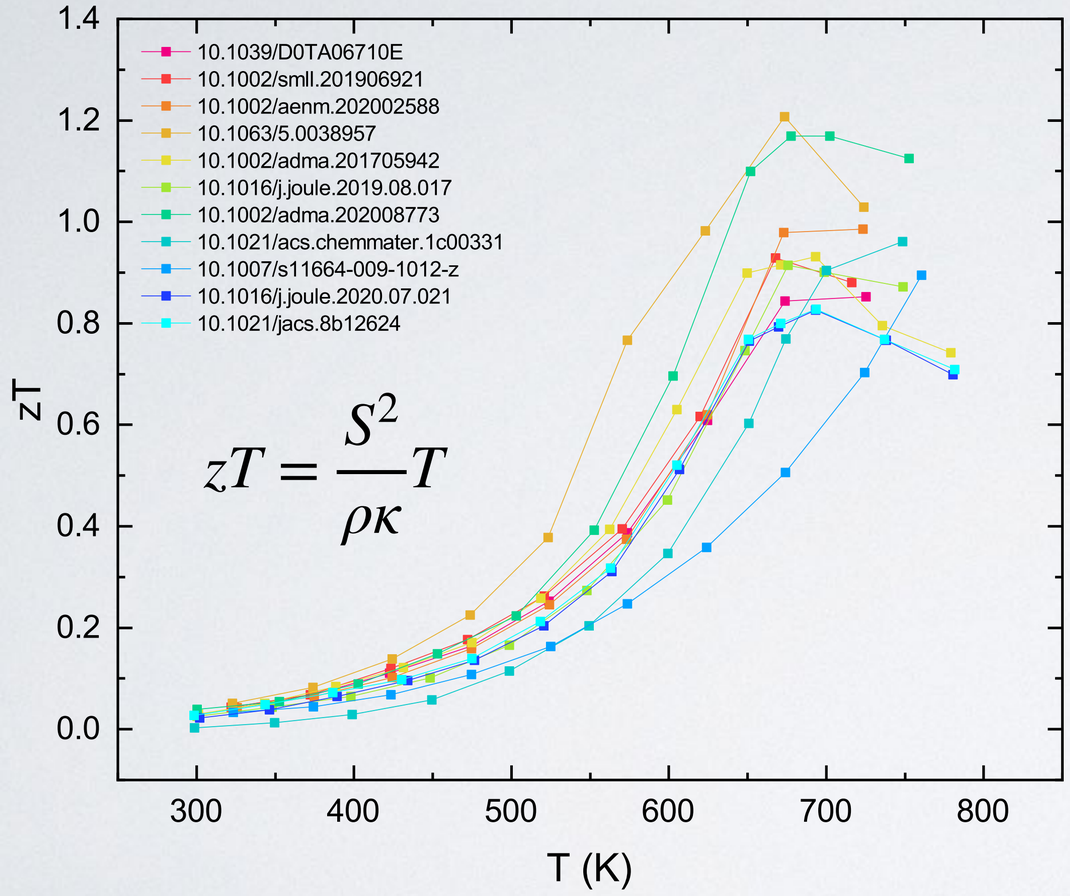

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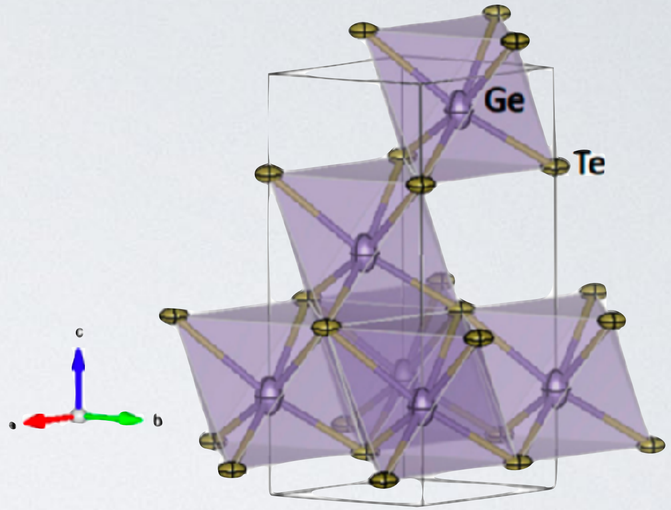

- Cationic substitution: $zT \approx [1;2.3]$ at 673 K
- About 60 samples synthesized in the lab

Why Machine Learning assistance?

- Seems advantageous when coupled to chemistry knowledge
- Saving (time, energy, ressources) —> sustainable
- Unconventional propositions

Main goal: Develop a fast predictive model based on simple descriptors

Nugraha et al., J. Mater. Chem. A 8, 13532 (2020)

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- 2 models tested: ElasticNet and Random Forest
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Nugraha et al., J. Mater. Chem. A 8, 13532 (2020)

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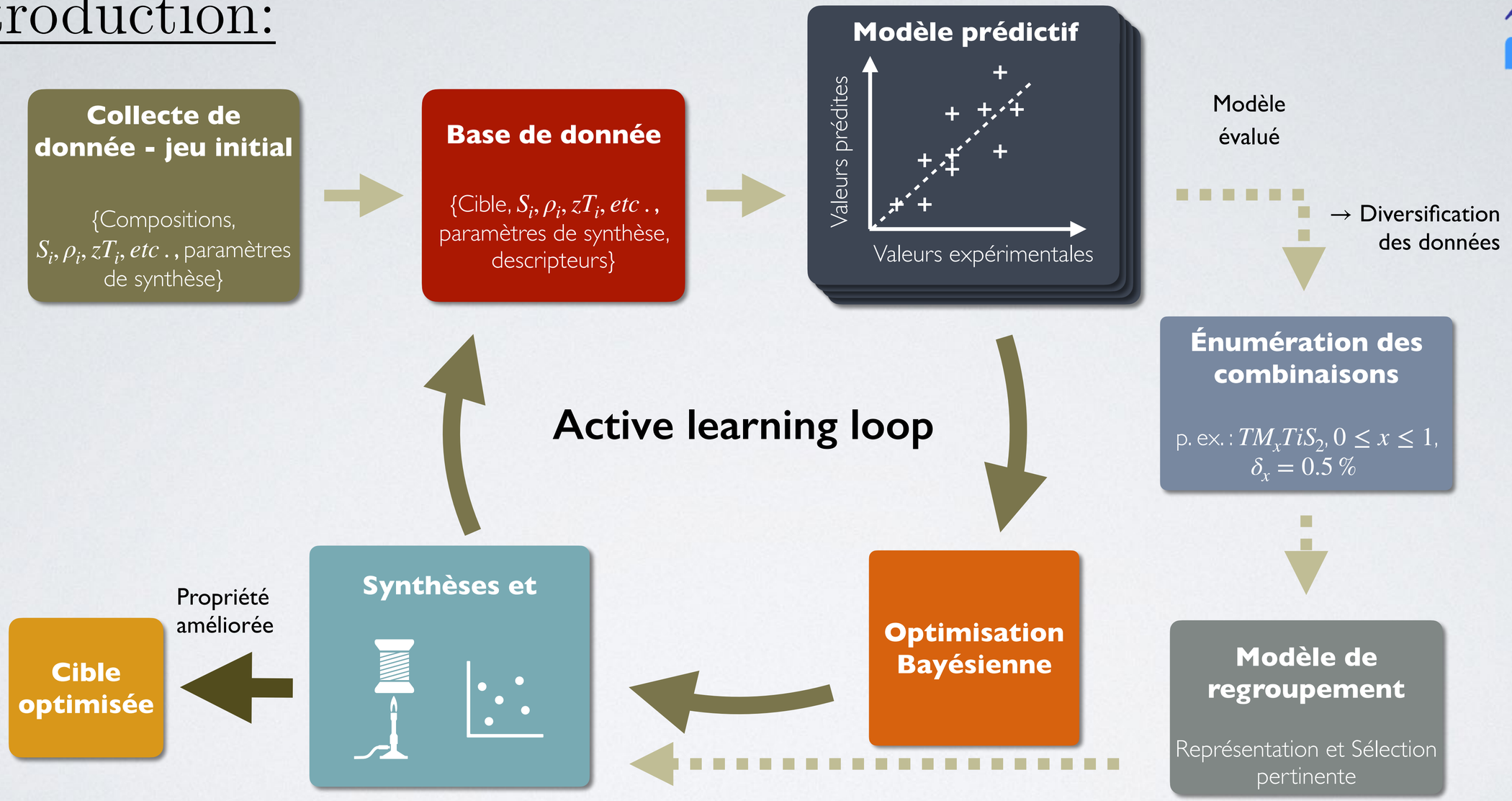
—> Requires a well framed database

Nugraha et al., J. Mater. Chem. A 8, 13532 (2020)

Introduction:



Lambard et al., Scripta Materiala 209, 114341 (2022)
Nugraha et al., J. Mater. Chem. A 8, 13532 (2020)

Database overview:

Highest zTs at 673 K

Composition	% subs.	sigma	S	PF	kappa	zT	B_E mean	
		10^4 S/m	μV/K	10^-3 W/m/K^2	W/m/K		μW/cm/K^2	
		673K	673K	673K	673K	673K		
Ge0.94Bi0.06Te	6	5.96	241.40	3.47	1.50	1.58	9.56	[Shuai2019] SI 10
Ge0.88Ga0.02Sb0.1Te	12	5.40	240.88	3.13	1.30	1.62	8.84	[Srinivasan2019]
Ge0.92Cr0.03Sb0.05Te	8	7.58	229.12	3.95	1.60	1.62	8.71	[Shuai2020] 10.1
Ge0.94Cr0.03Sb0.03Te	6	8.39	218.72	4.00	1.63	1.63	8.49	[Shuai2020] 10.1
Ge0.90Ga0.02Sb0.08Te	10	8.05	216.79	3.78	1.55	1.64	10.00	[Srinivasan2019]
Ge0.92Cr0.03Bi0.05Te	8	5.02	256.12	3.26	1.33	1.64	8.57	[Shuai2020] 10.1
Ge0.93Y0.02Bi0.05Te	7	4.50	261.14	3.07	1.23	1.67	9.61	[Gao2021] 10.106
Ge0.85Sn0.05Sb0.1Te	15	8.05	209.17	3.47	1.36	1.69	9.03	[Hong2021] 10.1
Ge0.895Sb0.1In0.005Te	10.5	4.84	237.02	3.02	1.23	1.74	8.35	[Hong2018] 10.1
Ge0.935In0.005Bi0.06Te	6.5	14.99	184.30	5.12	1.97	1.74	12.00	[Perumal2019] 1
Ge0.94Bi0.06Te	6	7.30	234.66	3.97	1.52	1.78	10.42	[Xing2021] 10.10
Ge0.88Zn0.02Sb0.1Te	12	6.34	236.16	3.63	1.24	1.84	10.13	[Hong2019] 10.1
Ge0.92Mg0.02Bi0.06Te	8	11.55	200.10	4.65	1.68	1.84	12.02	[Xing2021] 10.10
Ge0.888Sb0.1In0.012Te	11.2	4.34	267.96	3.24	1.04	1.88	10.34	[Hong2018] 10.1
Ge0.87Sn0.05Sb0.08Te	13	9.25	201.57	3.76	1.30	1.91	9.61	[Hong2021] 10.1
Ge0.94Cr0.03Bi0.03Te	6	7.01	240.72	4.08	1.43	1.92	9.17	[Shuai2020] 10.1
Ge0.893Sb0.1In0.007Te	10.7	4.96	254.29	3.21	1.11	1.96	8.85	[Hong2018] 10.1
Ge0.86Zn0.04Sb0.1Te	14	5.93	246.50	3.68	1.15	2.02	10.75	[Hong2019] 10.1
Ge0.93In0.01Bi0.06Te	7	12.54	221.74	5.40	1.76	2.07	13.26	[Perumal2019] 1
Ge0.83Zn0.06Sb0.1Te	17	4.95	255.36	3.59	1.15	2.09	10.55	[Hong2019] 10.1
Ge0.89Sb0.1In0.01Te	11	5.48	262.28	3.69	1.12	2.27	10.78	[Hong2018] 10.1
Ge0.9Mg0.04Bi0.06Te	10	9.90	236.12	5.34	1.52	2.34	14.32	[Xing2021] 10.10
Mean	9.95	7.45	233.84	3.86	1.39	1.85	10.18	
Rel. StdDev (%)	32	39	10	19	18	12	16	

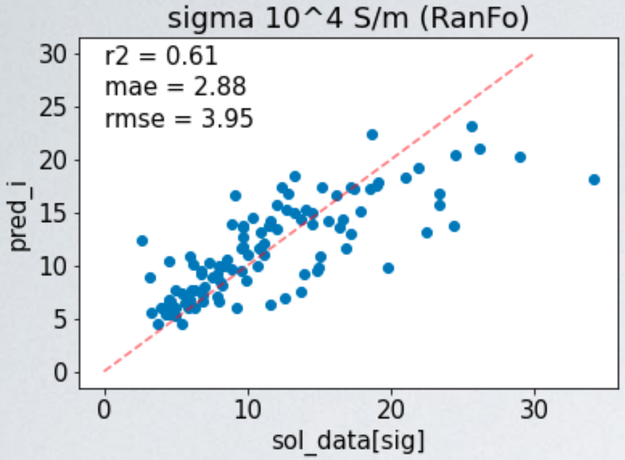
Frame:

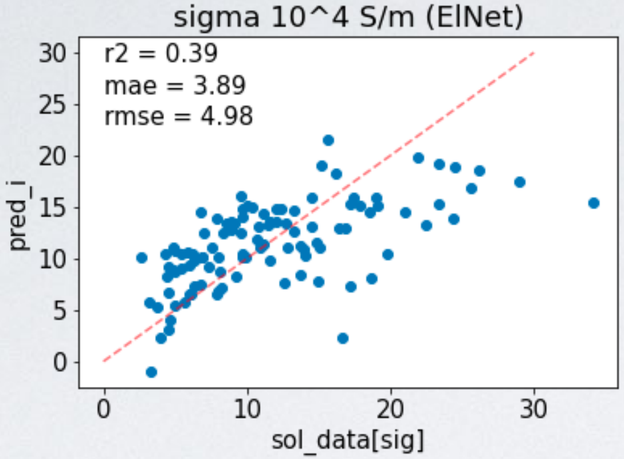
- Only experimental data
- Only densified samples
- Only at 673 K
- Only unique composition

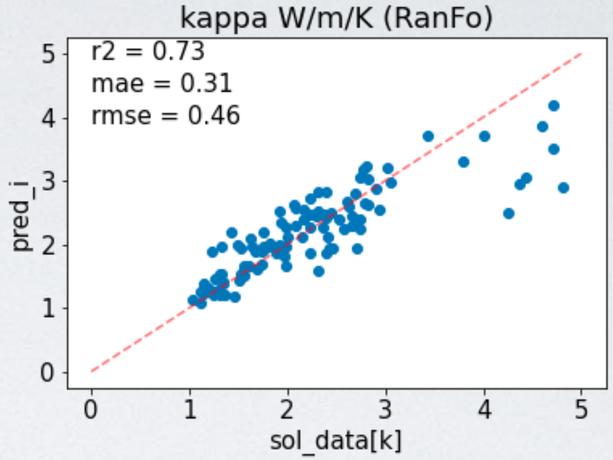
First lesson:

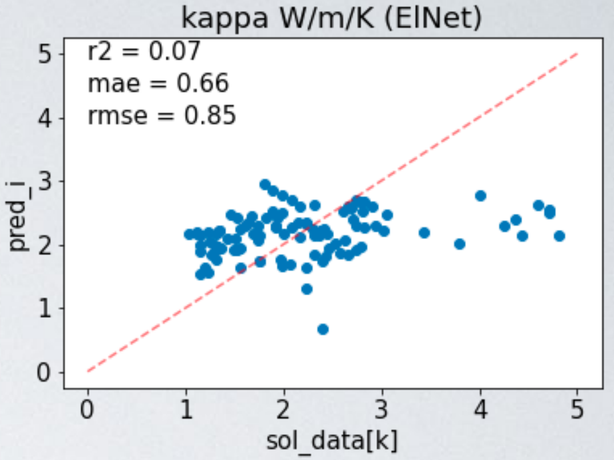
- Mainly codoping
- Relatively heavy doping
- Either Sb or Bi —> bias

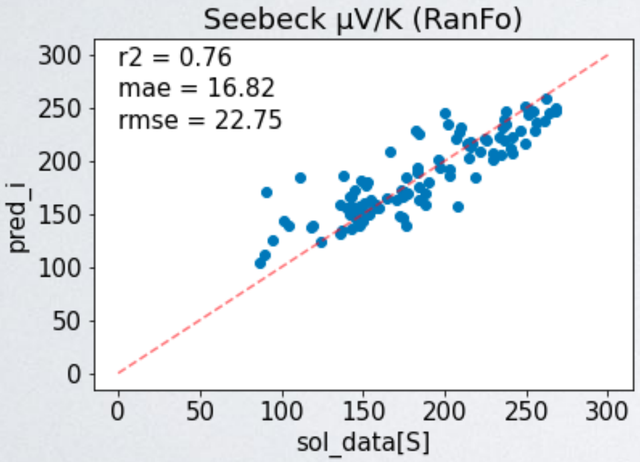
Models comparison:

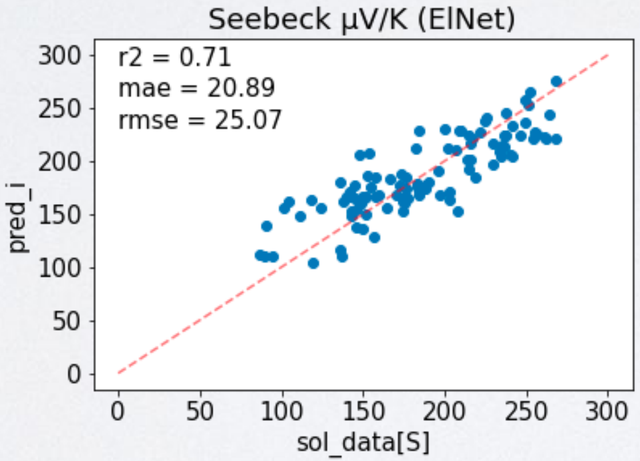


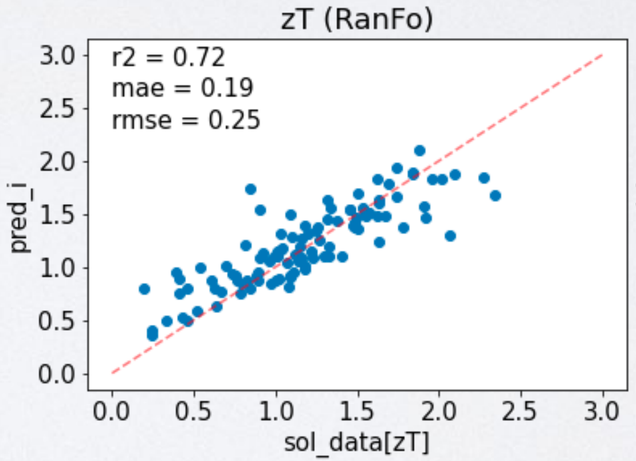


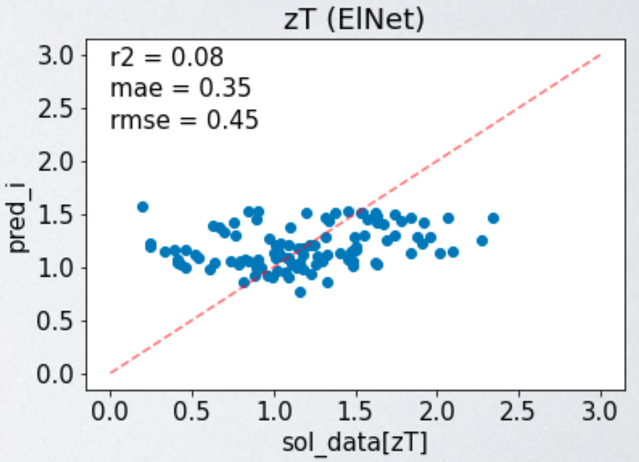




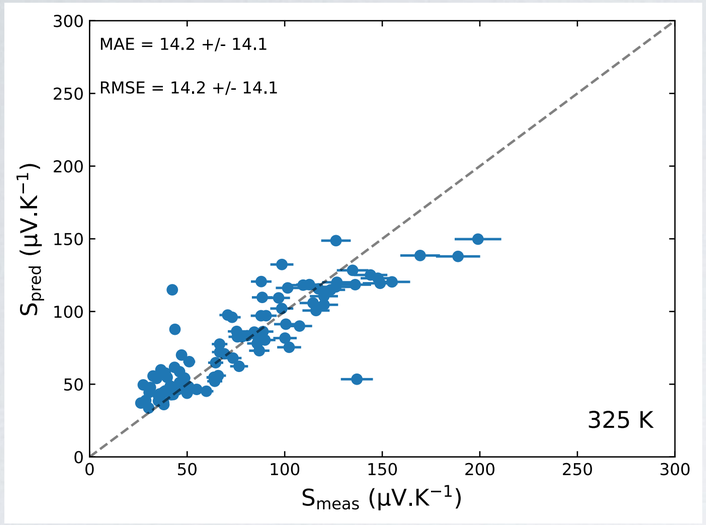


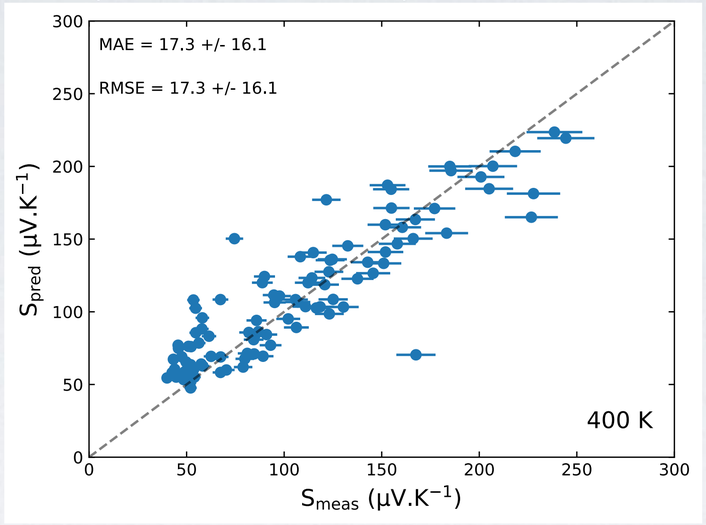


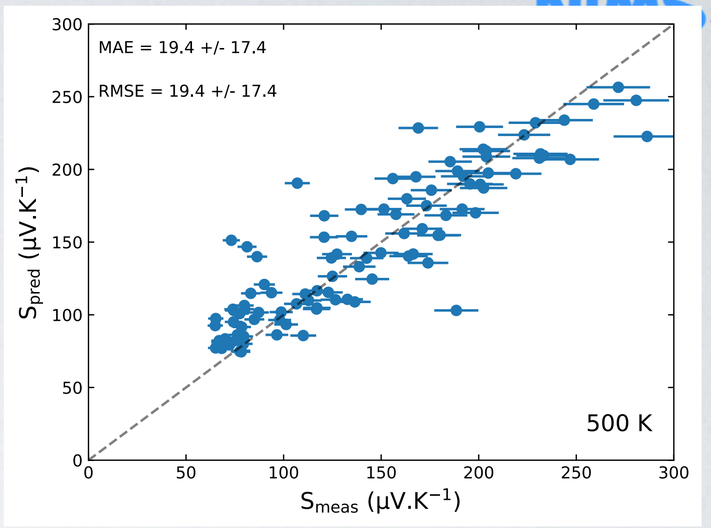


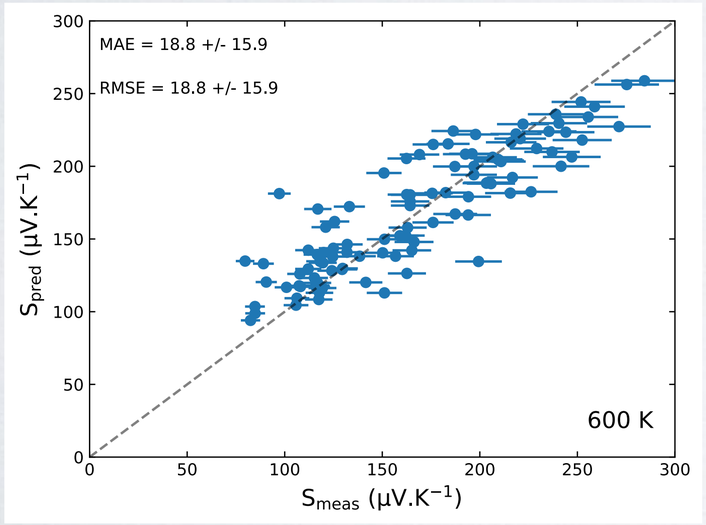


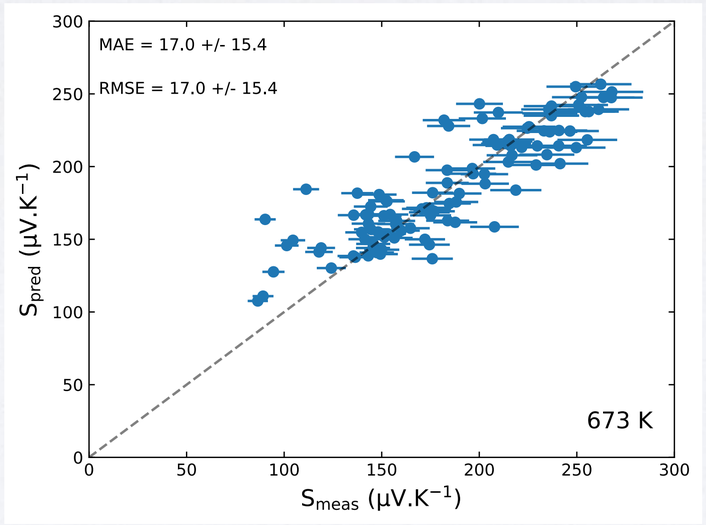
Training Random Forest (n = 100): Cross validation: LeaveOneOut

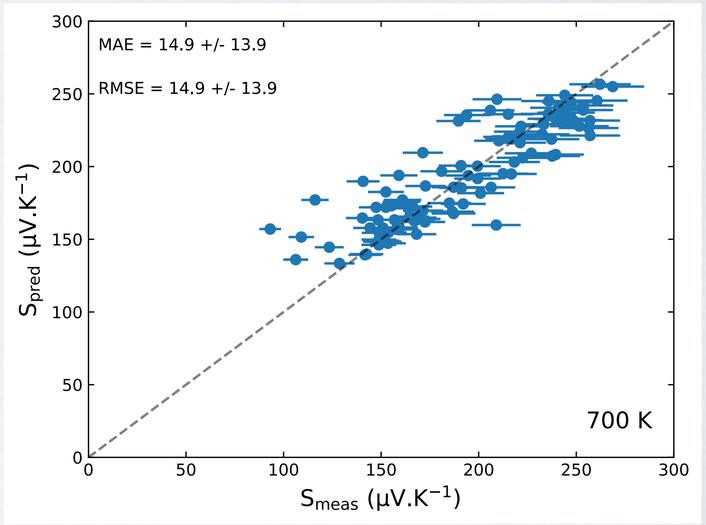








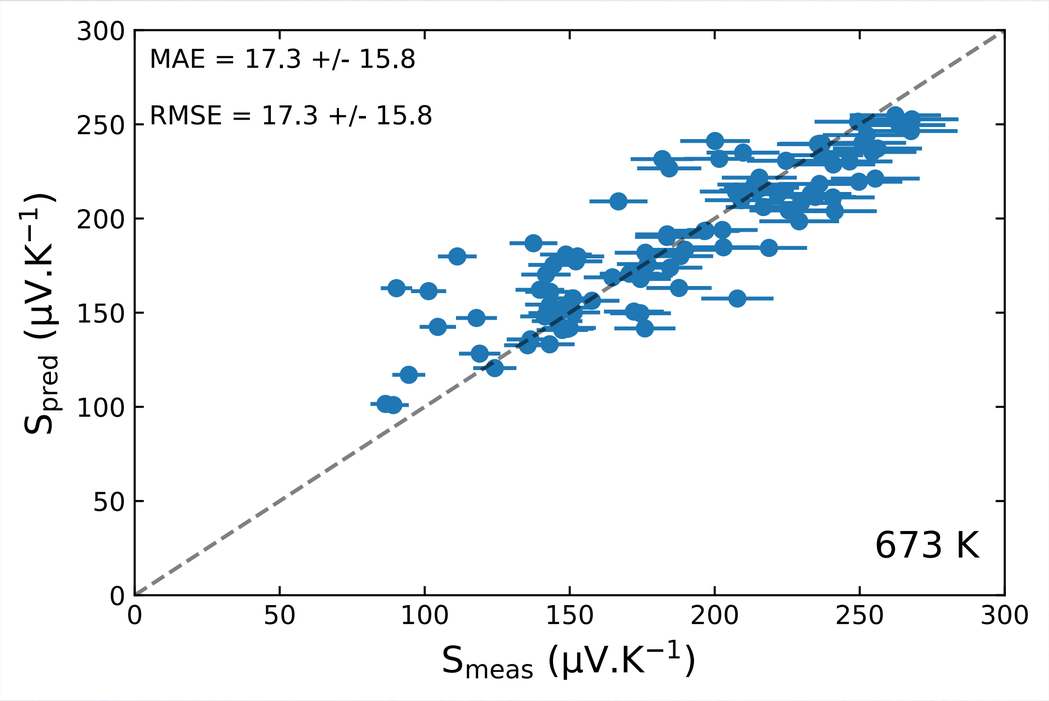




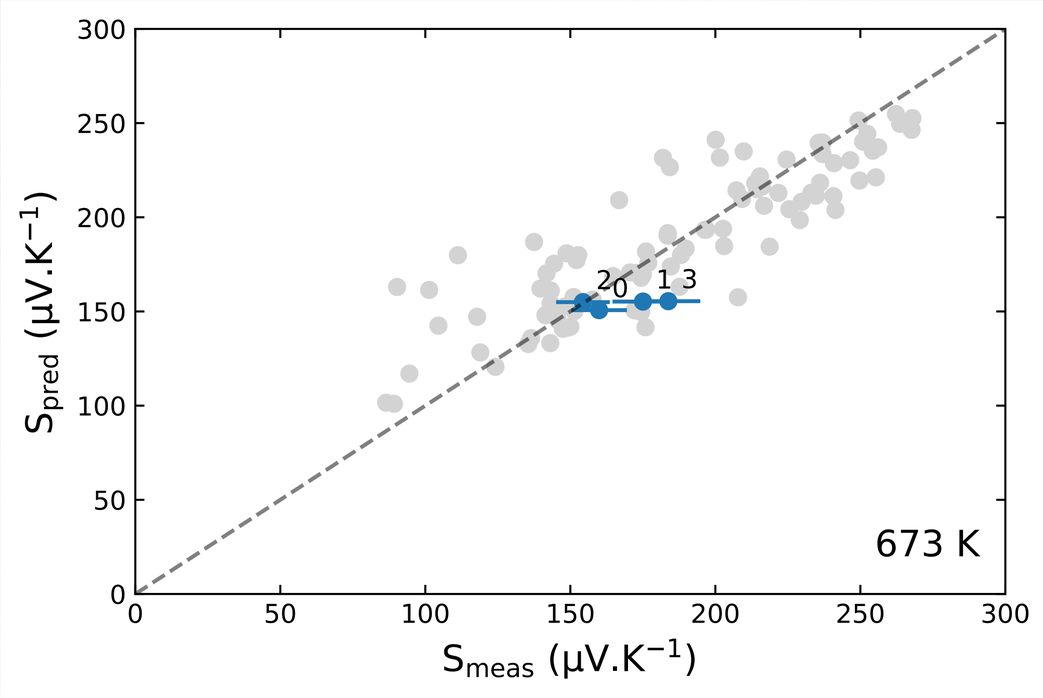
Random Forest (n = 100):

Cross validation: LeaveOneOut

Training



Prediction on $Ge_{1-x-y}In_xSb_yTe$



—> Requires improvement

Broadening of the chemical space:

Elemental combinations: $Ge_{1-x-y}A_xB_yTe$ with $x + y \leq 20\,\%\,;\delta_{x,y} = 1\,\%$

```python
# List of abundant elements with abundance in Earth's crust > 0.01%

the_abun = ['C', 'Na', 'Si', 'Mg', 'Ti', 'Mn', 'Ba', 'Zr', 'Cr', 'V', 'K', 'Ca', 'Fe', 'Sr']
# 'O', 'S', 'H', 'F', 'Cl', 'P' have been removed because of their gas, anionic nature or synthetic issues.
```

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```

About 9380 compositions : —>

Where to start ?

Broadening of the chemical space:

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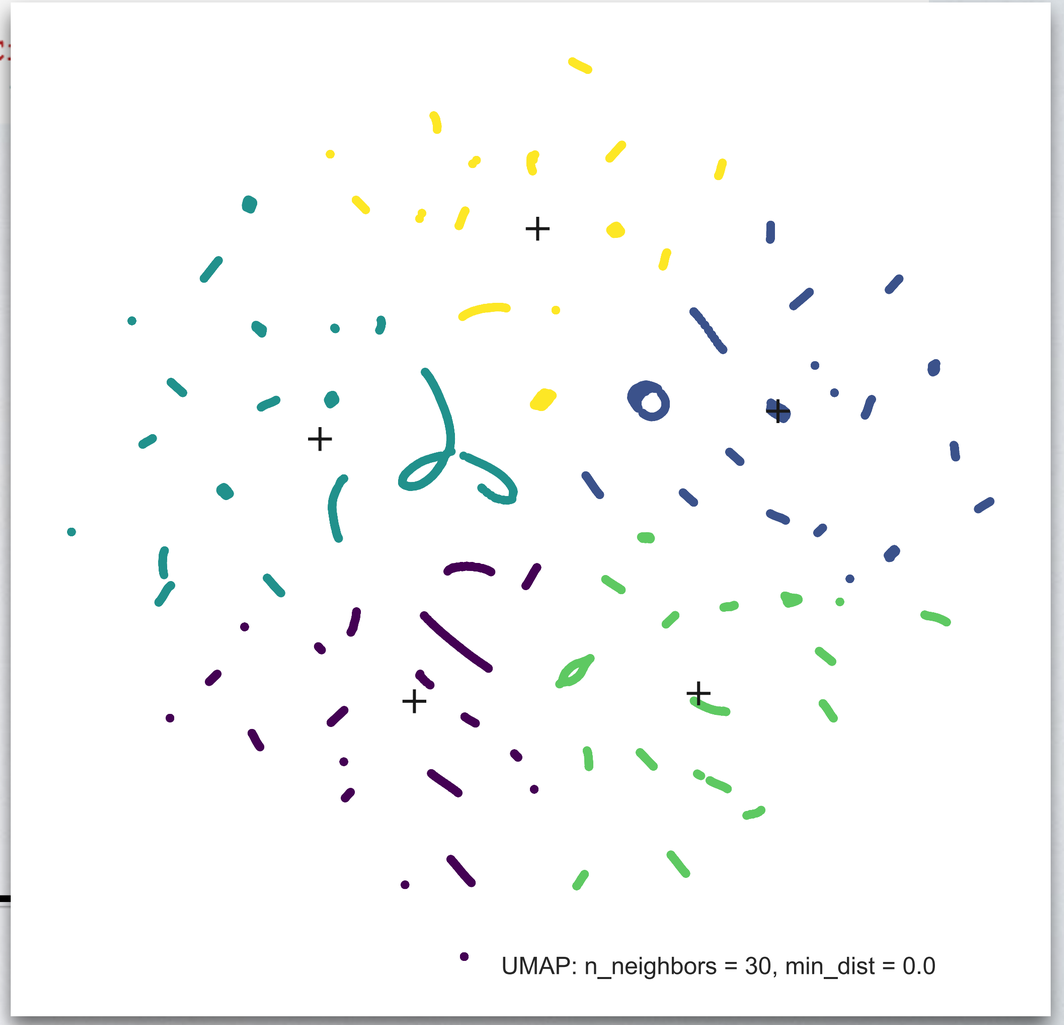
About 9380 compositions : —>

Where to start ?



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# 'O', 'S', 'H', 'F', 'Cl', 'P' have been removed because of
```
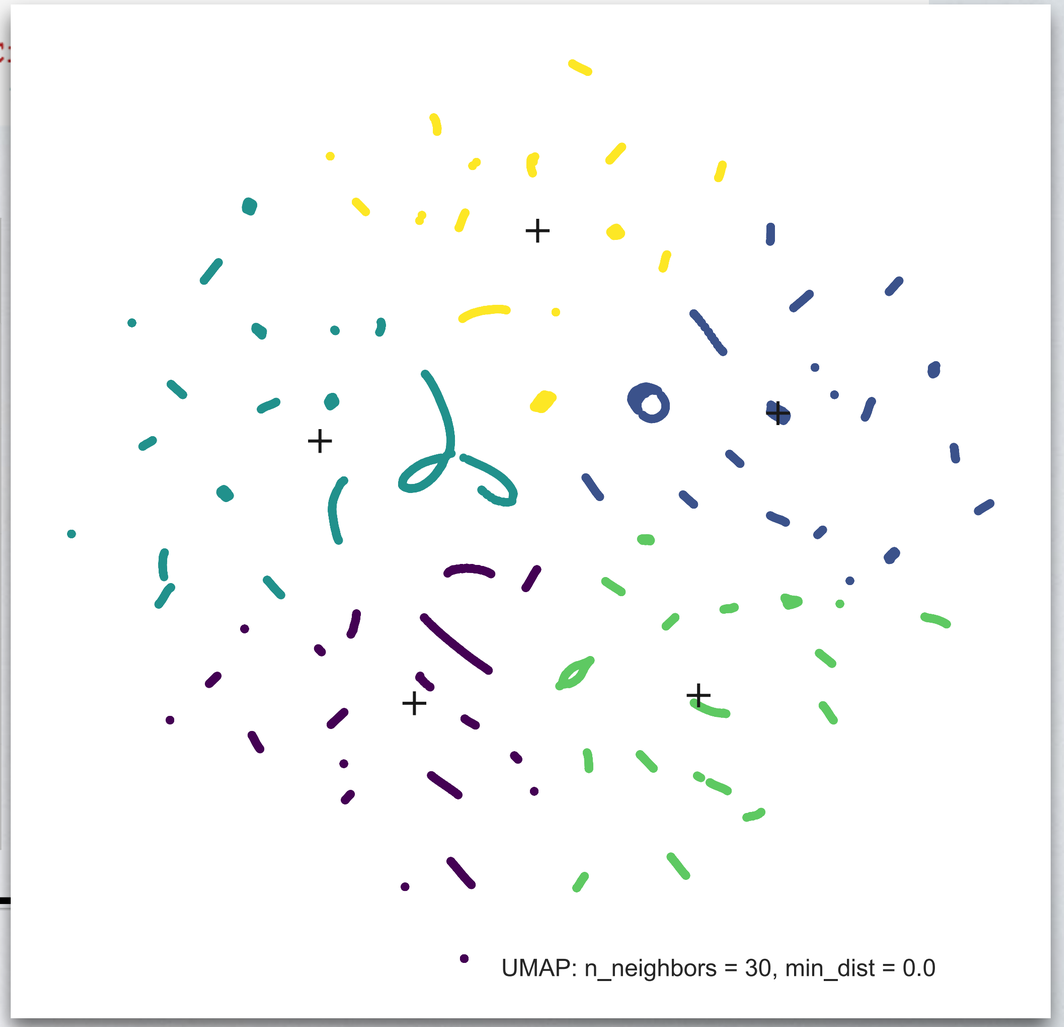
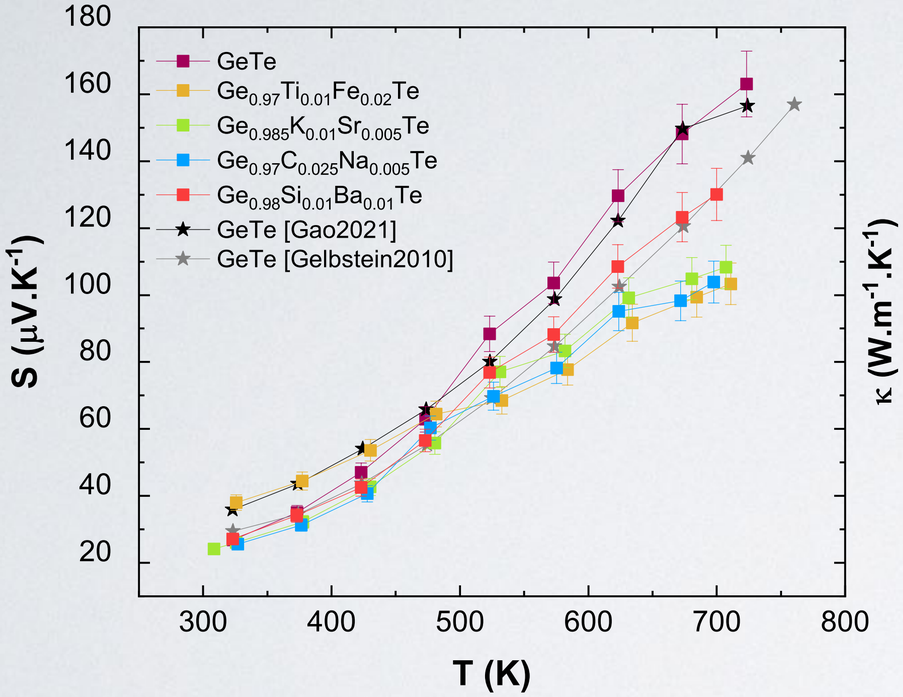

About 9380 compositions : —>

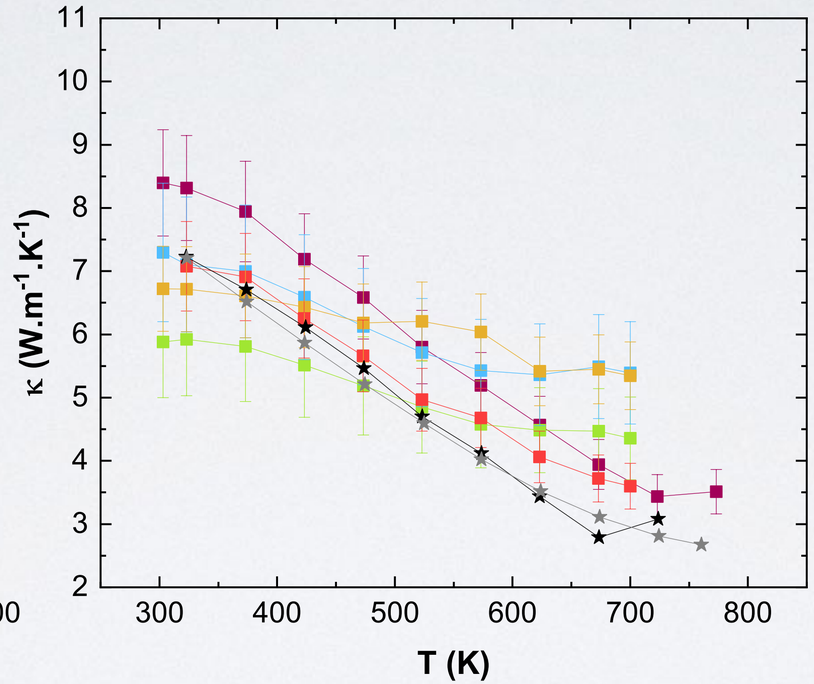
Where to start ?

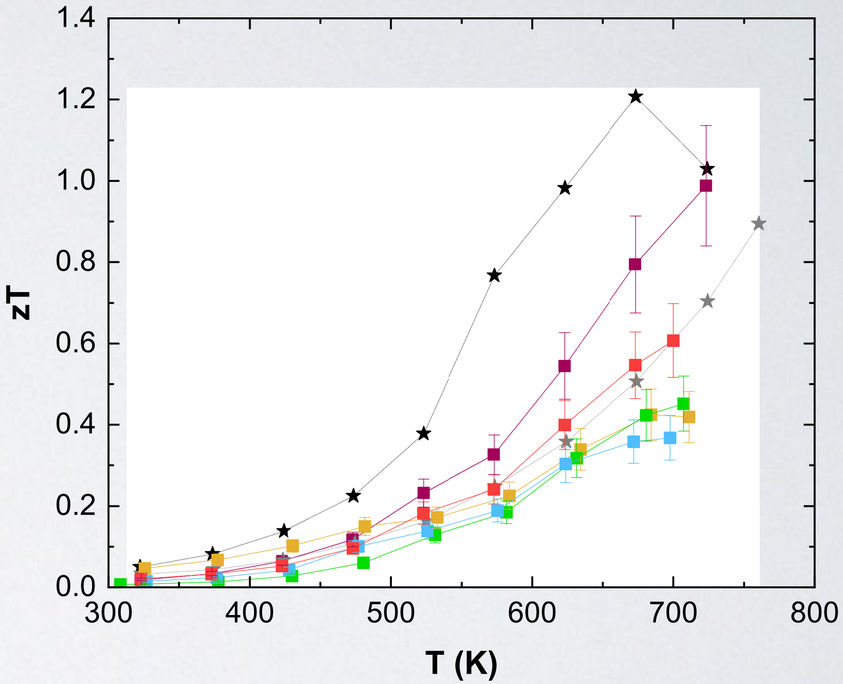
	Centroids
✔	$Ge_{0.97}C_{0.025}Na_{0.005}Te$
✔	$Ge_{0.97}Ti_{0.01}Fe_{0.02}Te$
✔	$Ge_{0.98}Si_{0.01}Ba_{0.01}Te$
	$Ge_{0.985}Ba_{0.005}Mg_{0.01}Te$
✔	$Ge_{0.985}K_{0.01}Sr_{0.005}Te$



First measurements:

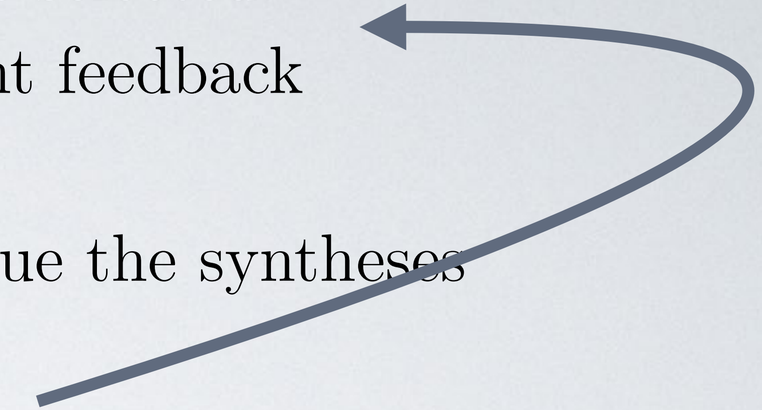






Conclusions and perspective:

- Random Forest with *matminer* descriptors are selected.
  Model seems relatively good —> need relevant feedback
- Datasets at all T —> prediction of S(T)
- Chemical compositions propositions —> pursue the syntheses



- Characterizations in progress —> New data

—> Analyzing the descriptors - property correlations
—> Ending the first loop including Bayesian optimization
—> Application to ρ, κ, PF, zT
—> GeTe pristine, SnTe doped,

Dr. Linda Abassi

Dr. Guillaume Lambard

Dr. David Berthebaud

Prof. Jean-François Halet

Dr. Bhuvanesh Srinivasan

Prof. Takao Mori