DOPAGE ET PROPRIETES THERMOELECTRIQUES DE L'OXYDE D'INDIUM $In_{2-x}M_xO_3$

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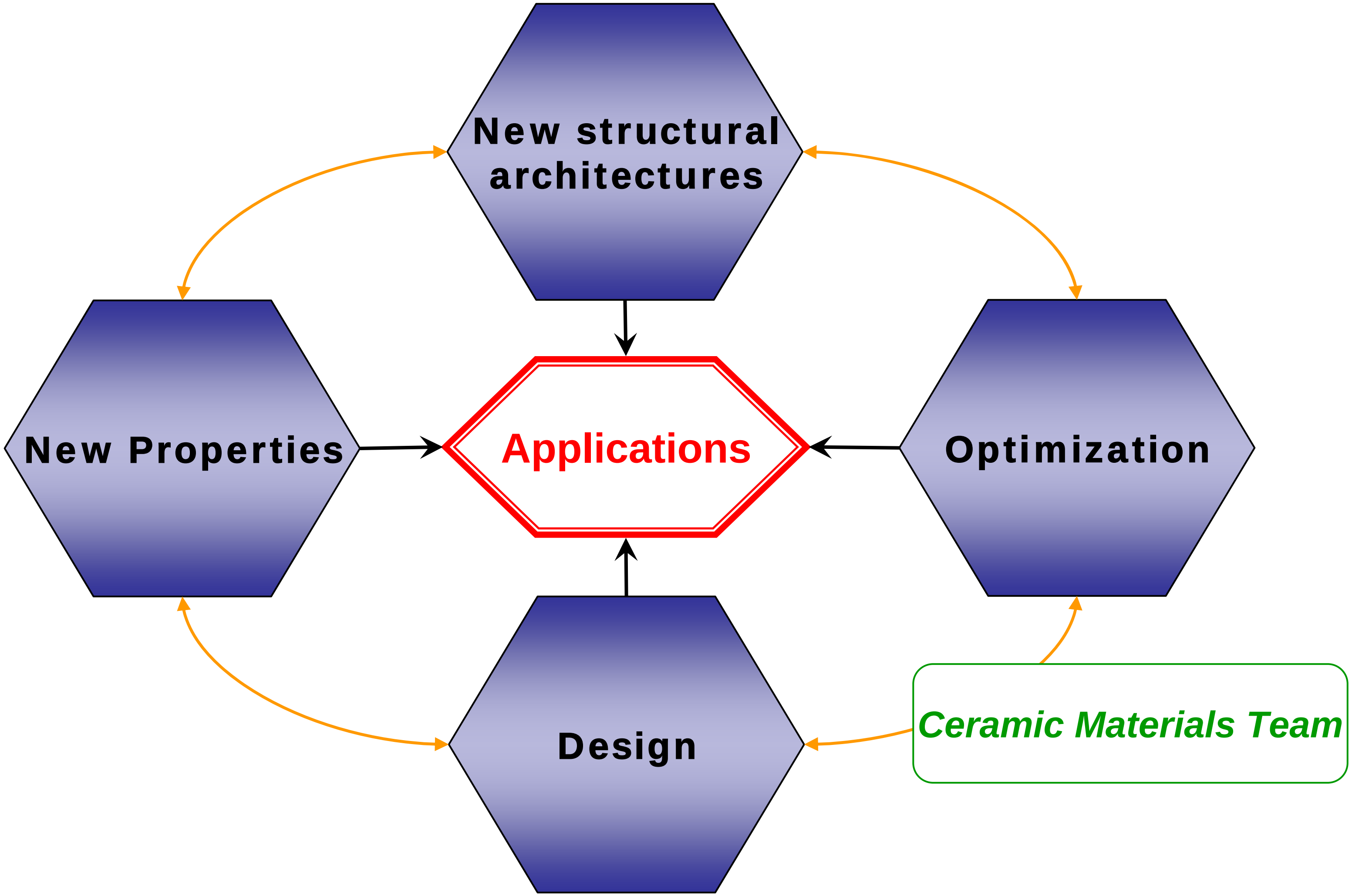
GDR Thermoélectricité, Nancy, 8 Juillet 2009

Outline

- **Introduction:** Context of the Study
- **$In_{2-x}M_xO_3$:** *Dopant, Hall effect and TE properties*
- **Nanostructuration :** Prediction
- **Nanostructuration :** Preliminary results

CRISMAT Lab.



New structural architectures

New Properties

Applications

Optimization

Design

Ceramic Materials Team

CRISMAT & Thermoelectrics (1999-2009)

- **A.C. Masset *et al., PR B 62 (2000) 166***

  "Misfit layered cobaltite with an anisotropic giant magnetoresistance: $Ca_3Co_4O_9$"

- **H. Leligny *et al., Acta Cryst. B 56 (2000) 173***

  "A five-dimensional structural investigation of the misfit layer compound $[Bi_{0.87}SrO_2]_2[CoO_2]_{1.82}$"

- **J. Hejtmanek *et al., PR B 60 (1999) 14057***

  "Interplay between transport, magnetic, and ordering phenomena in $Sm_{1-x}Ca_xMnO_3$"

- **M. Prevel *et al., Solid State Sci. 9 (2007) 231***

  "Bulk textured $Ca_{2.5}RE_{0.5}Co_4O_9$ (RE: Pr, Nd, Eu, Dy and Yb) thermoelectric oxides by sinter-forging"

- **S. Lemonnier *et al., J. Appl. Phys. 104 (2008) 014505***

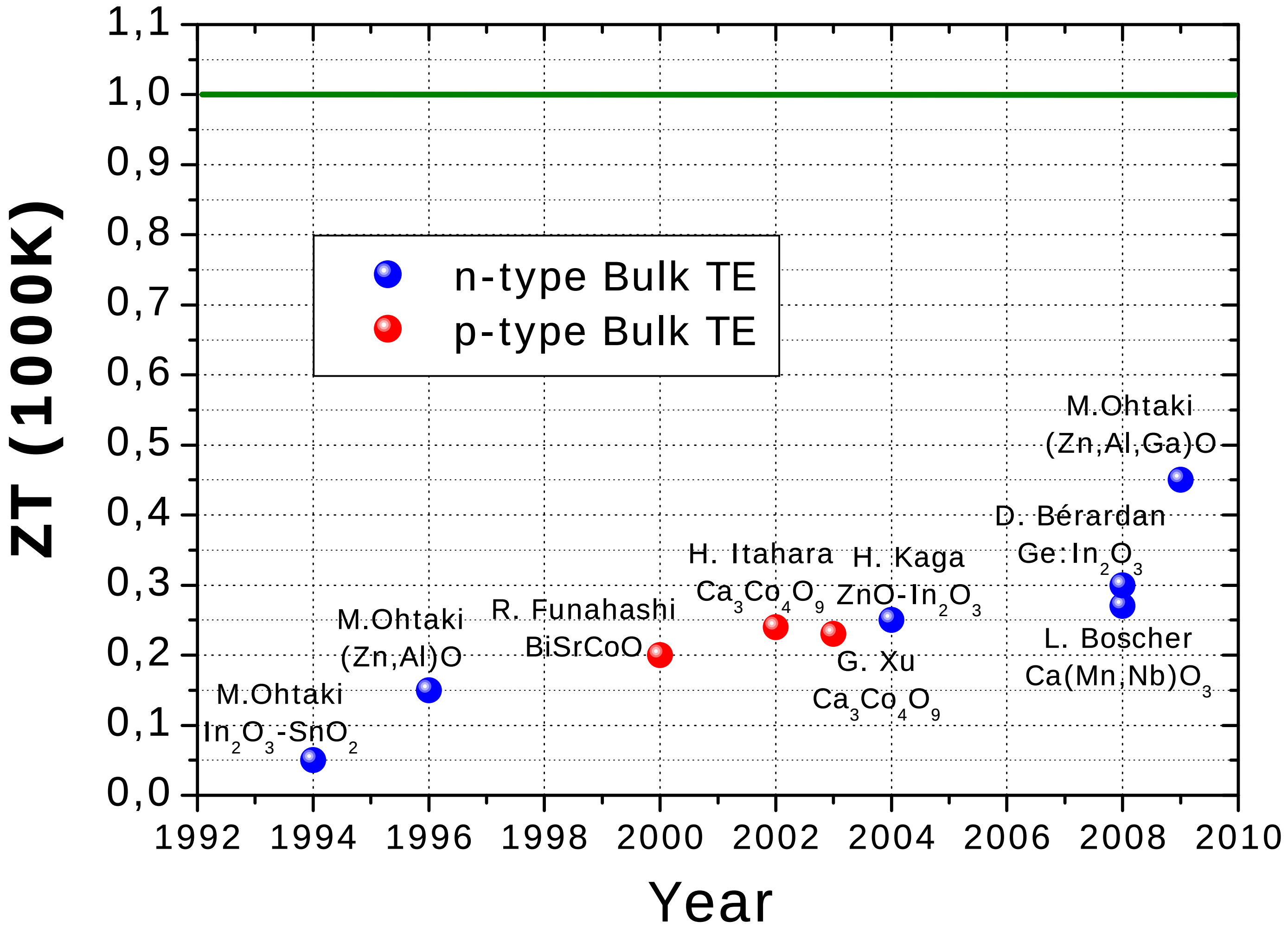
  "Four-leg $Ca_{0.95}Sm_{0.05}MnO_3$ unileg thermoelectric device"

- **D. Bérardan *et al., Solid State Comm. 146 (2008) 97***

  "In_2O_3:Ge, a promising n-type thermoelectric oxide composite"

Bulk Oxides

Bulk oxide Thermoelectrics



Ceramic Process

Nominal composition: $In_{2-x}M_xO_3$

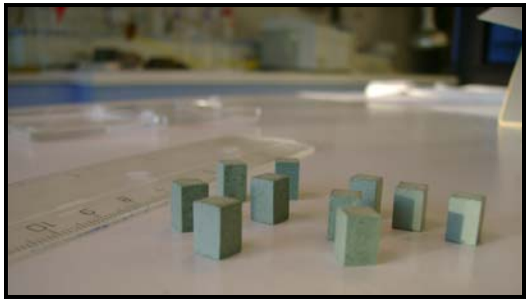
Precursor Powders
Oxides or
carbonates

Ball-milling

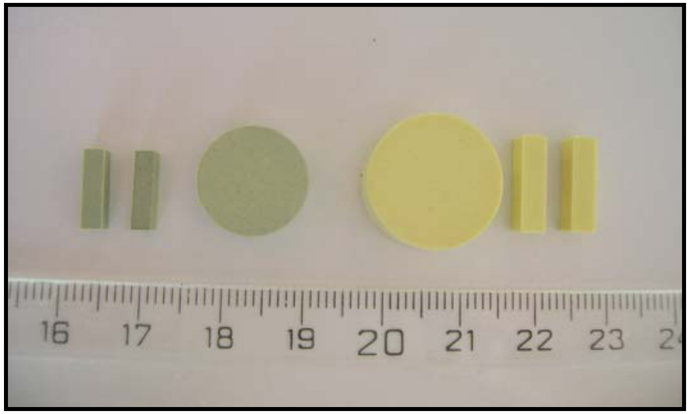
Bars/pellets shaping

Green density=60%

Sintering
1300°C/48h



Shrinkage=15%, Density~90%



Highly dense and pure samples

Facilities

Structure & Microstructure

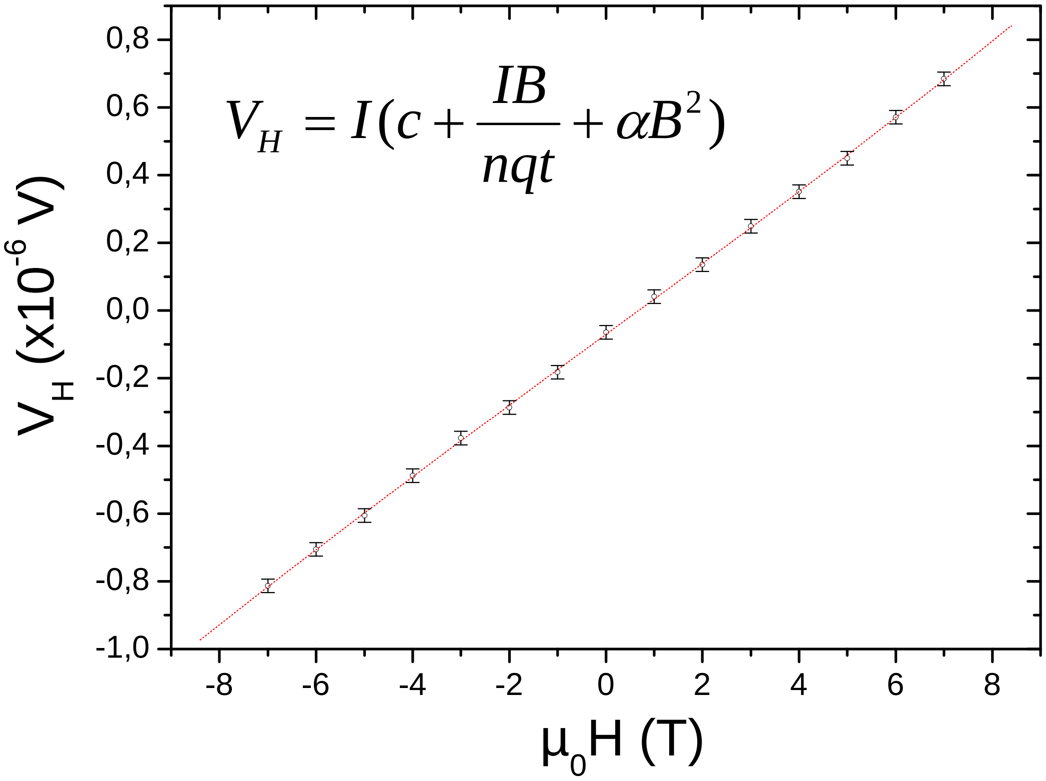
-X-ray & neutron diffraction, SEM, TEM, Grain size analyzer, dilatometer, TG/DTA, DSC…

HT Transport Properties

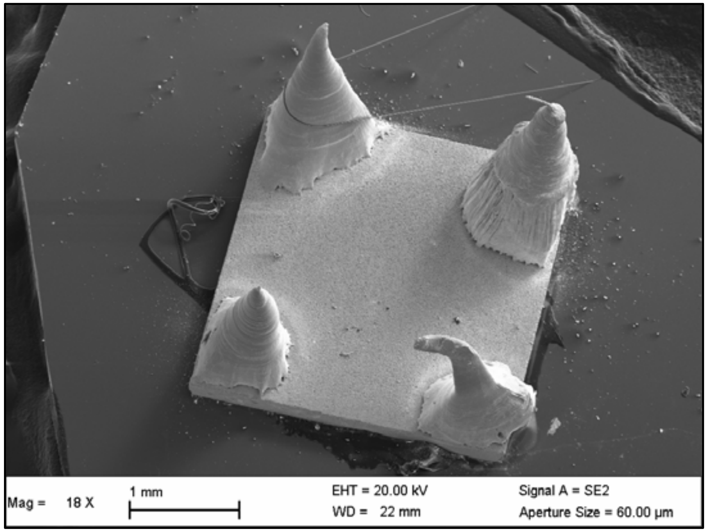
-ULVAC-RIKO, ZEM3 (Seebeck, resistivity → 800°C)
-Netzsch, LFA 457 (thermal diffusivity→1000°C)
-Netzsch, DSC 404C (heat capacity→1000°C)
- PPMS (low T, ρ, λ, TEP, n)

Facilities

Hall Effect



$$V_H = I\left(c + \frac{IB}{nqt} + \alpha B^2\right)$$



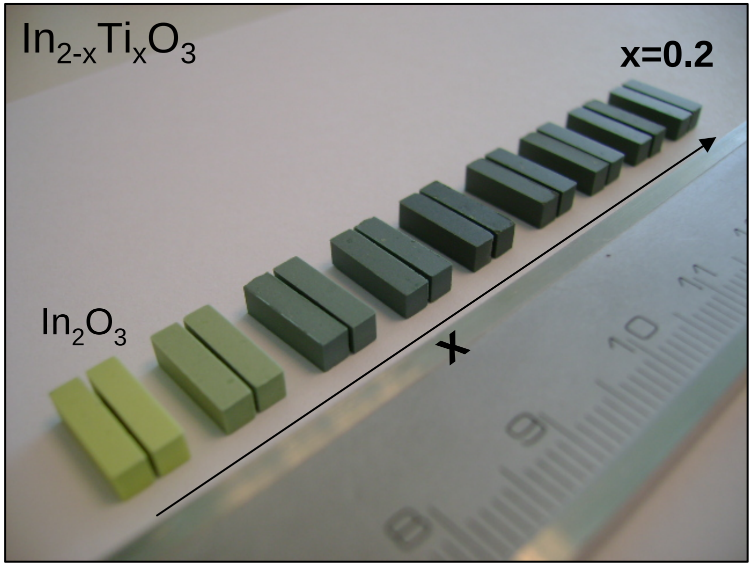
- Good ohmic contact
- Contact alignment, Thickness uniformity

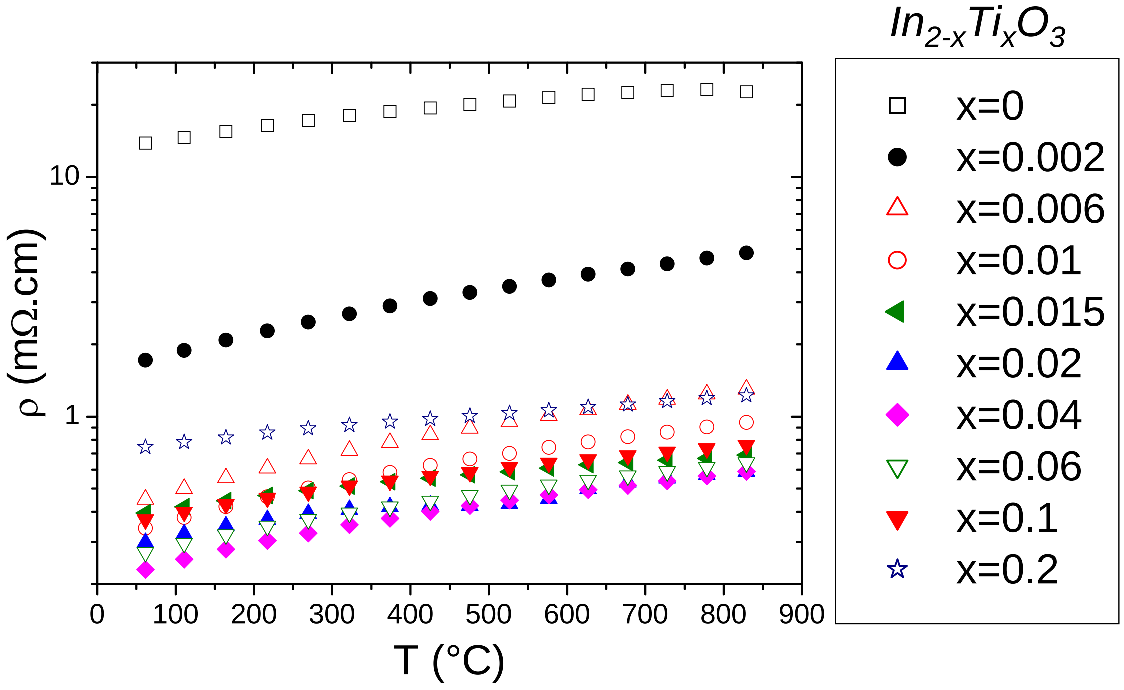
Recent results: $In_{2-x}M^{4+}_{x}O_3$ and $In_{2-x}M^{5+}_{x}O_3$

« To clarify dopant and concentration effects is a key to understand and optimize the TE properties »*

$In_{2-x}M_{x}O_3$

- Tetravalent cations (M≡Sn^{4+}, Ti^{4+}, Zr^{4+})
- Pentavalent cations (M ≡Nb^{5+} and Ta^{5+})





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* *E. Guilmeau et al., J. Appl. Phys. (Accepted)*

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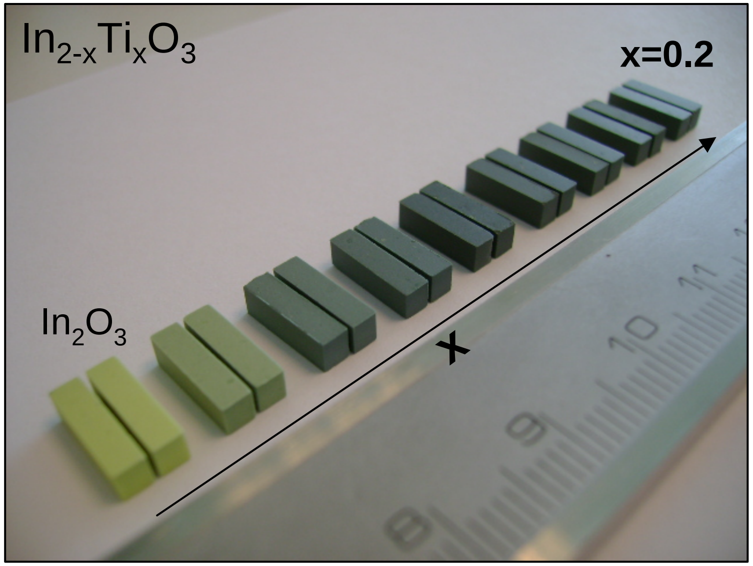

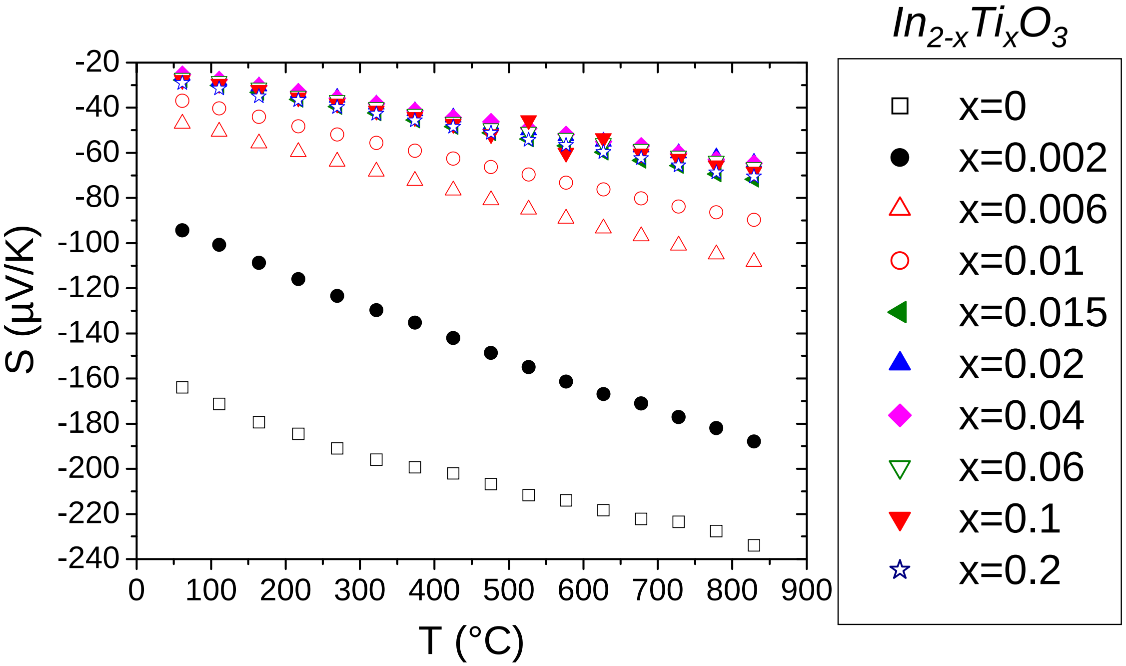

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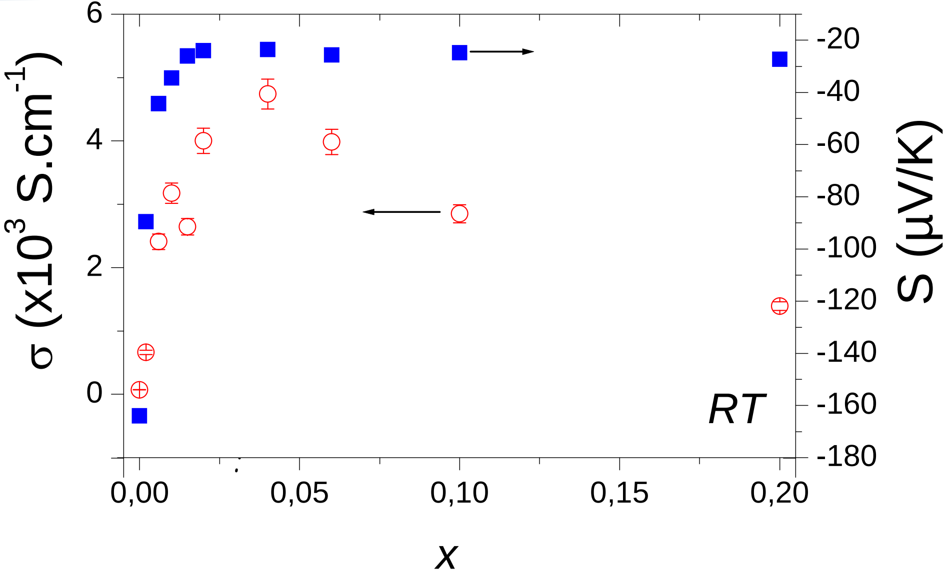

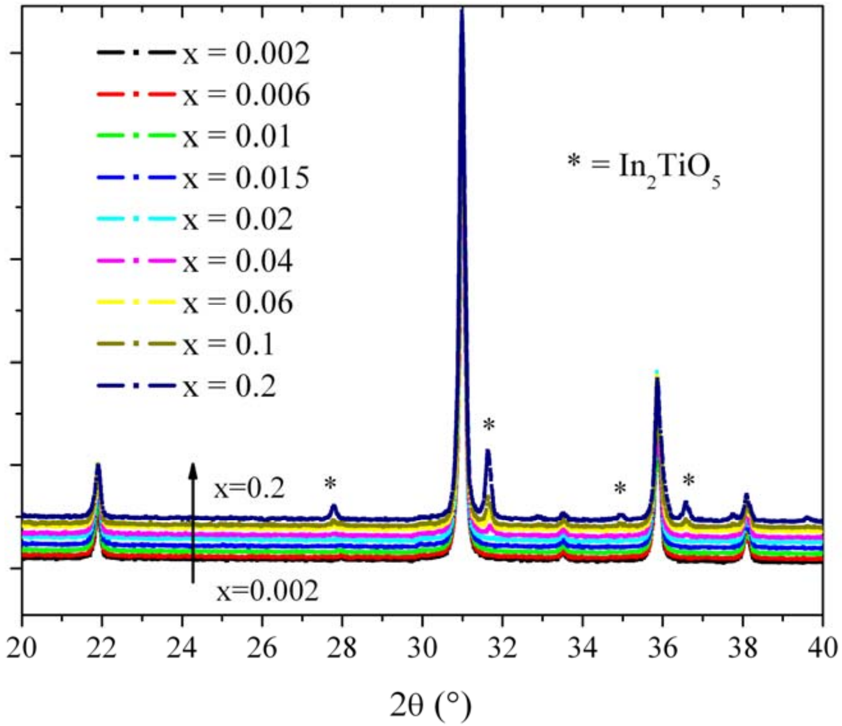

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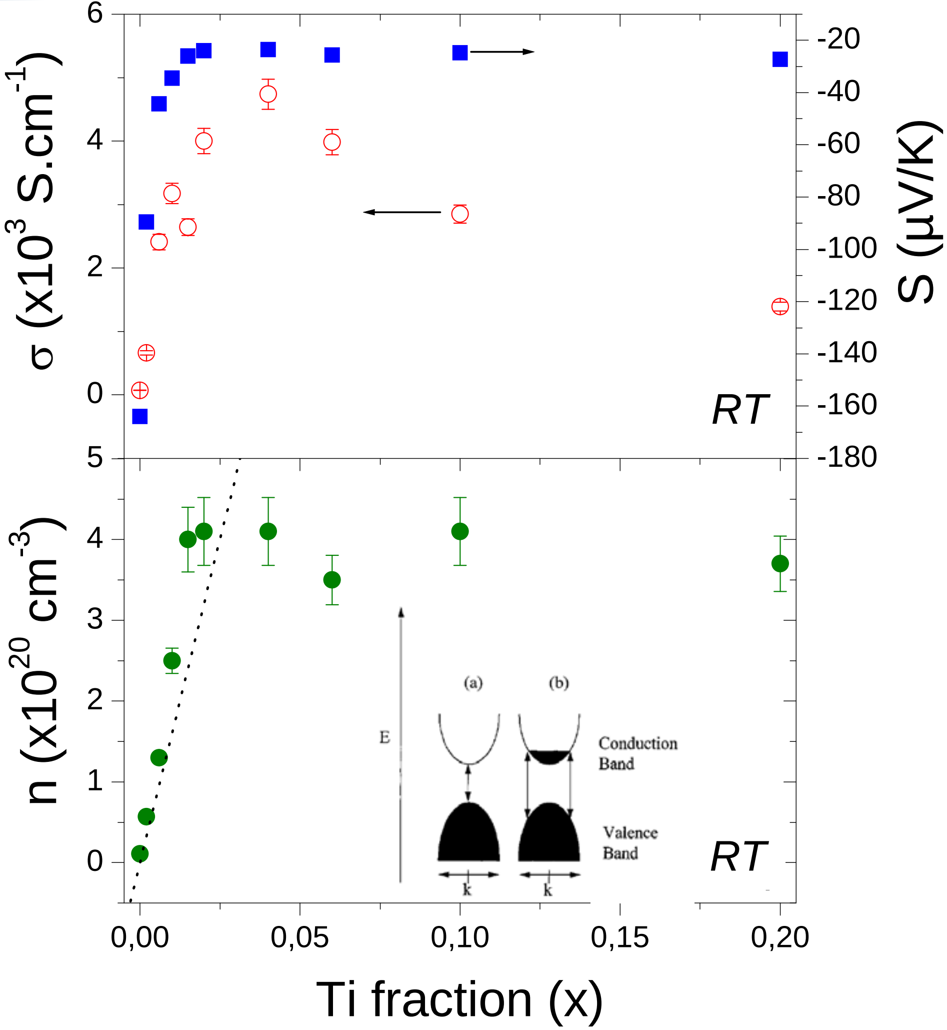
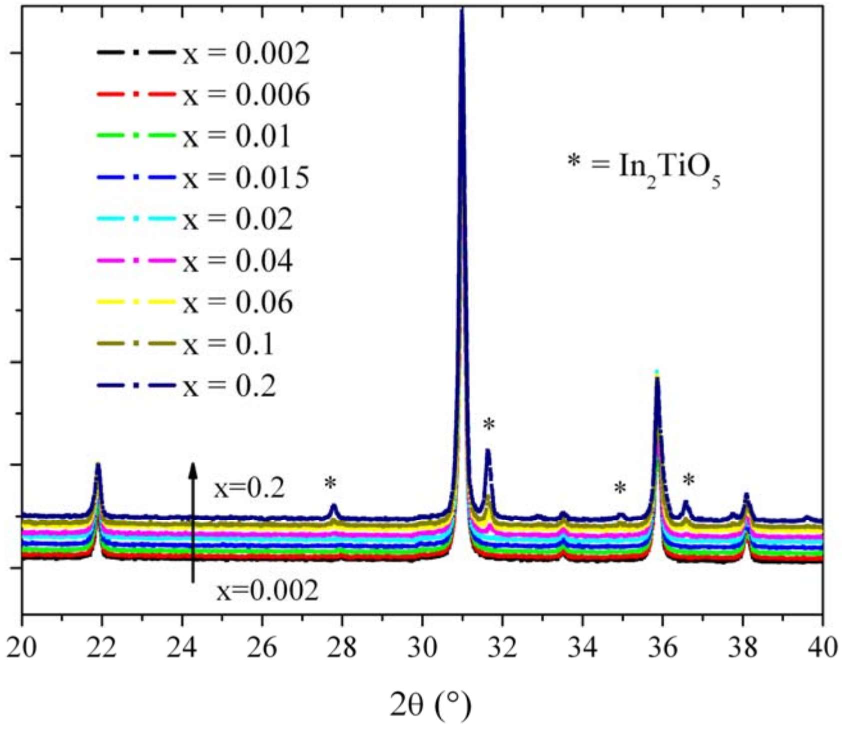




- **Ti^{4+} substitution generates 1 e- per dopant cation**
- **Additional donors**

$$In_2O_3 \rightarrow In_2O_{3-x} + x/2\ O_2(g) + xV_O^{\circ\circ} + 2x.e'$$

Recent results: $In_{2-x}M^{4+}_xO_3$ and $In_{2-x}M^{5+}_xO_3$

x ($In_{2-x}M_xO_3$)	S ($\mu V.K^{-1}$)					σ ($\times 10^3$ $S.cm^{-1}$)				
	Sn^{4+}	Ti^{4+}	Zr^{4+}	Ta^{5+}	Nb^{5+}	Sn^{4+}	Ti^{4+}	Zr^{4+}	Ta^{5+}	Nb^{5+}
0.000	-163	-163	-163	-163	-163	0.08	0.08	0.08	0.08	0.08
0.002	-91	-90	-94	-75	-82	0.6	0.7	0.7	0.6	0.5
0.006	-53	-44	-55	-43	-43	1.4	2.4	1.8	1.9	1.7
0.01	-42	-35	-42	-42	-38	1.9	3.2	3.4	2.1	2.1
0.015	-35	-26	**-28**	**-38**	**-36**	1.8	2.6	**3.6**	**1.9**	**2.3**
0.02	-23	**-24**	-27	-41	-38	2.8	4.0	2.6	1.7	2.1
0.04	-22	-24	-26	-54	-39	4.5	**4.7**	2.6	0.9	1.8
0.06	**-21**	-26	-27	-52	-52	**4.9**	4.0	2.5	0.9	0.8
0.1	**-20**	-25	-28	-67	-64	4.5	2.8	1.5	0.4	0.7
0.2	-22	-27	-30	-60	-70	3.6	1.4	1.4	0.2	0.2

	$n \times 10^{20}$ (cm^{-3})					μ ($cm^2.v^{-1}.s^{-1}$)				
	Sn^{4+}	Ti^{4+}	Zr^{4+}	Ta^{5+}	Nb^{5+}	Sn^{4+}	Ti^{4+}	Zr^{4+}	Ta^{5+}	Nb^{5+}
0.000	0.11	0.11	0.11	0.11	0.11	41.8	41.8	41.8	41.8	41.8
0.002	0.58	0.57	0.51	1.36	1.16	58.2	72.6	85.9	27.2	26.1
0.006	1.8	1.26	1.45	3.2	2.03	50.1	119.5	76.1	36.1	52.2
0.01	2.56	2.6	**2.77**	**4.5**	3.54	47.5	76.3	77.3	29.1	37.6
0.015	3.4	3.98	2.55	2.78	**4.32**	33.3	41.5	40.2	43.7	33.6
0.02	6.77	**4.1**	2.93	2.9	2.87	25.6	36.2	56.3	37.7	44.8
0.04	6.9	4.15	2.88	1.58	3.36	40.9	71.4	56.2	35.3	32.6
0.06	**9.43**	3.56	1.93	1.54	1.92	32.4	69.9	73.6	39.02	28.1
0.1	**10.8**	4.09	2.61	1.1	1.66	25.9	43.5	7.6	22.1	27.1
0.2	8.55	3.68	1.66	1.4	1.54	26.0	23.6	9.6	10.9	9.0

- $|S|$ reaches minima for different x_ℓ
- σ reaches maxima for the similar x_ℓ
- *n* reaches maxima for the similar x_ℓ

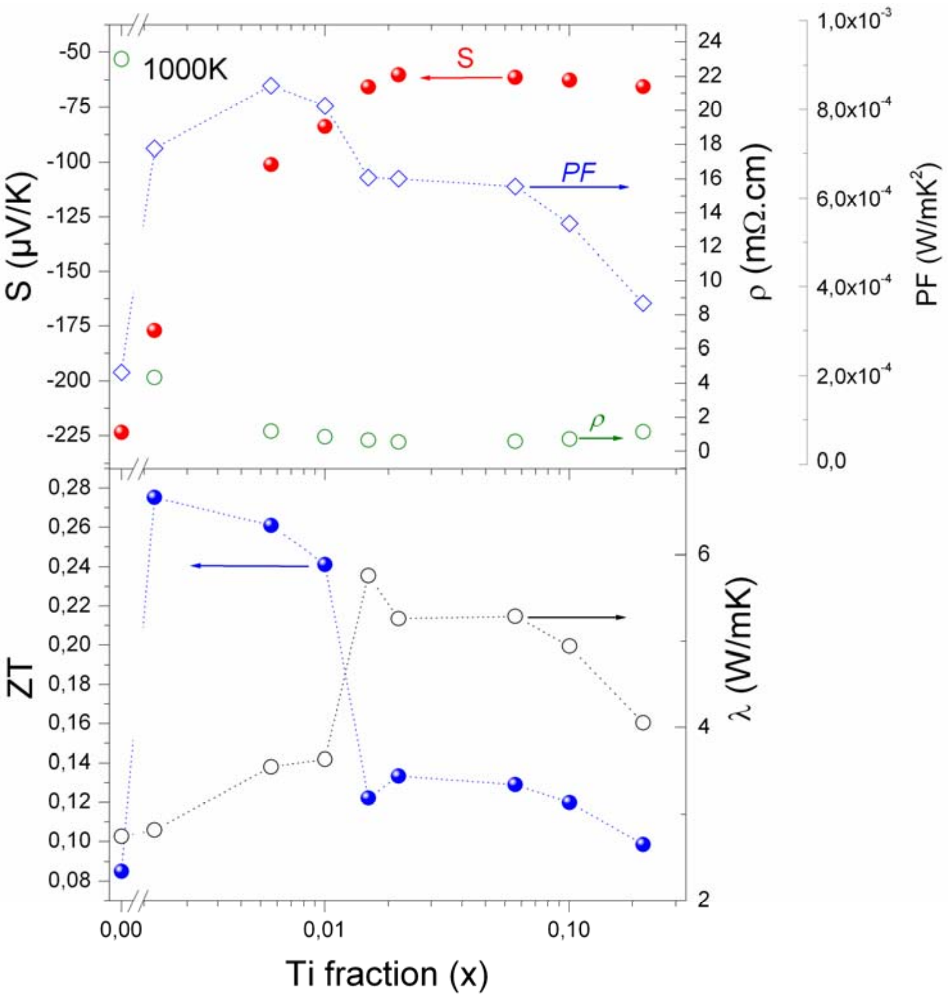
Recent results: $In_{2-x}M^{4+}_{x}O_3$ and $In_{2-x}M^{5+}_{x}O_3$

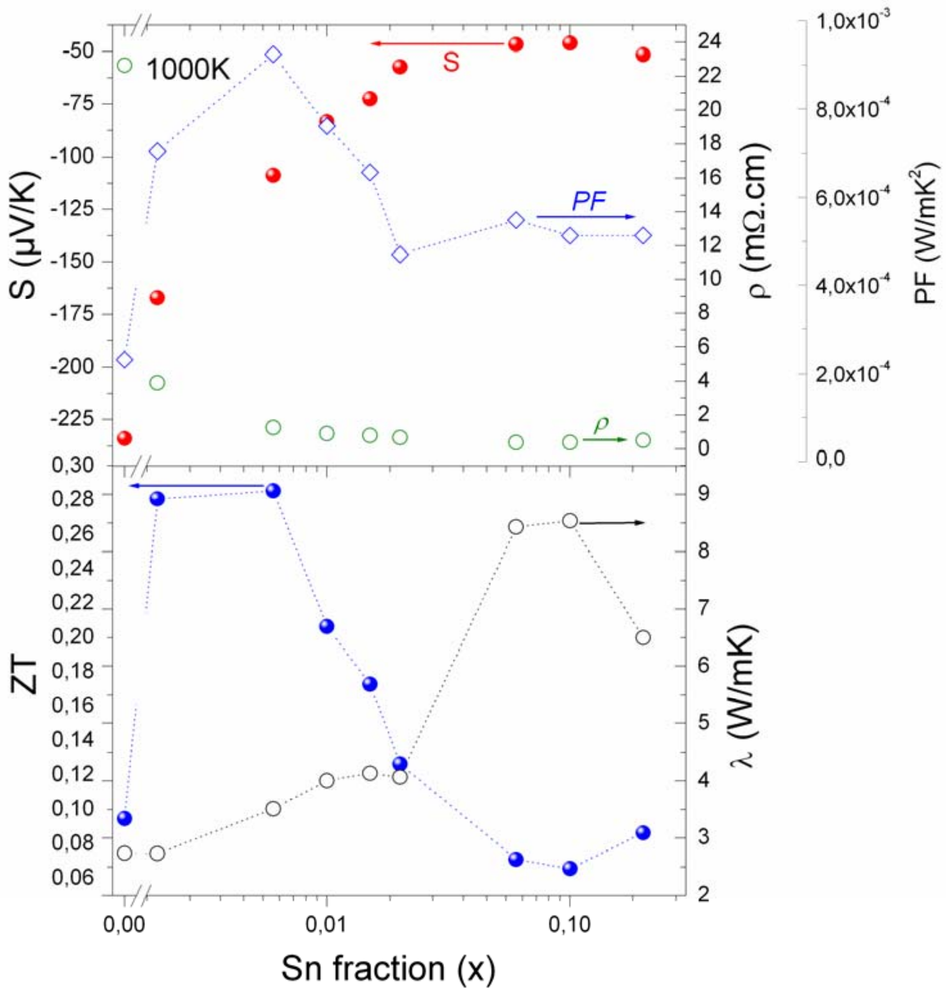
x ($In_{2-x}M_xO_3$)	μ ($cm^2.v^{-1}.s^{-1}$)				
	Sn^{4+}	Ti^{4+}	Zr^{4+}	Ta^{5+}	Nb^{5+}
0.000	41.8	41.8	41.8	41.8	41.8
0.002	58.2	72.6	85.9	27.2	26.1
0.006	50.1	119.5	76.1	36.1	52.2
0.01	47.5	76.3	77.3	29.1	37.6
0.015	33.3	41.5	40.2	43.7	33.6
0.02	25.6	36.2	56.3	37.7	44.8
0.04	40.9	71.4	56.2	35.3	32.6
0.06	32.4	69.9	73.6	39.02	28.1
0.1	25.9	43.5	7.6	22.1	27.1
0.2	26.0	23.6	9.6	10.9	9.0

- $\left|S\right|$ reaches minima for different x_ℓ
- σ reaches maxima for the similar x_ℓ
- *n* reaches maxima for the similar x_ℓ

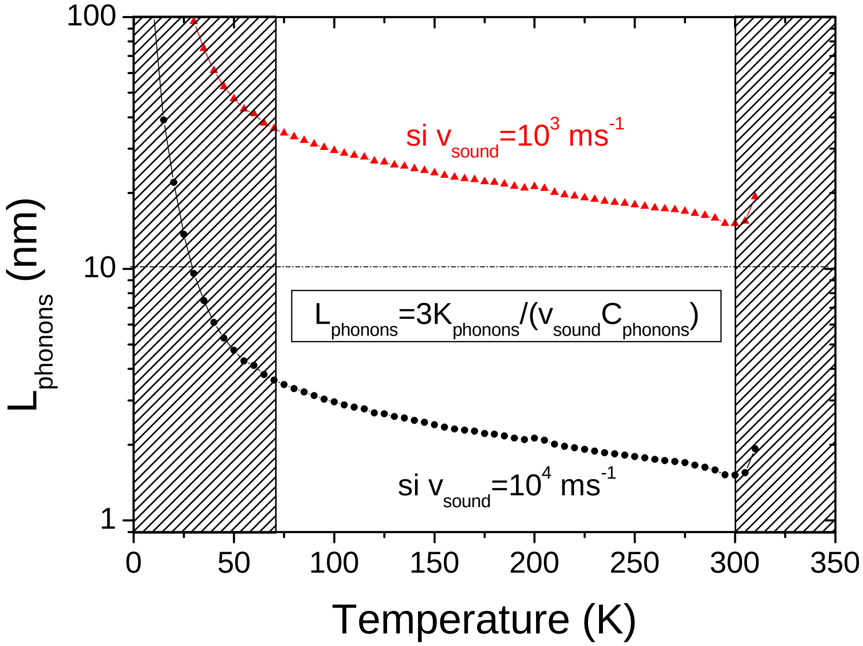
- Higher mobilities for Sn, Ti and Zr at x=0.006
- Lower mobilities for Nb and Ta (e^--e^- scattering)

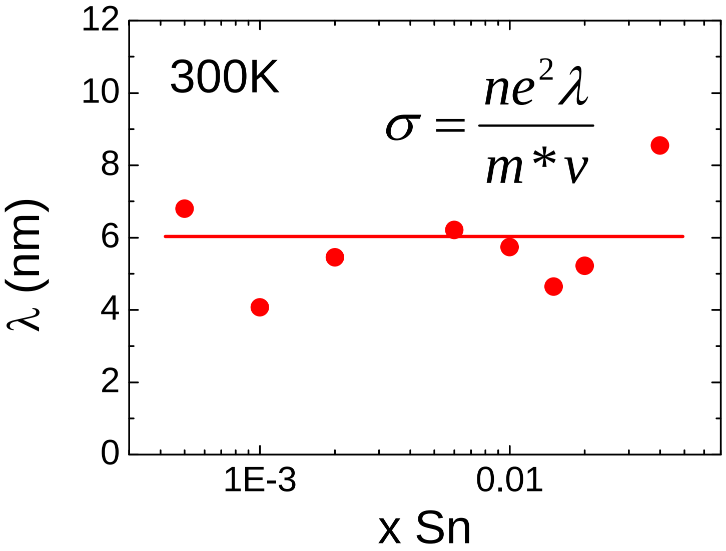
Recent results: $In_{2-x}M^{4+}_{x}O_3$ and $In_{2-x}M^{5+}_{x}O_3$





3D Nanostructuration: prediction





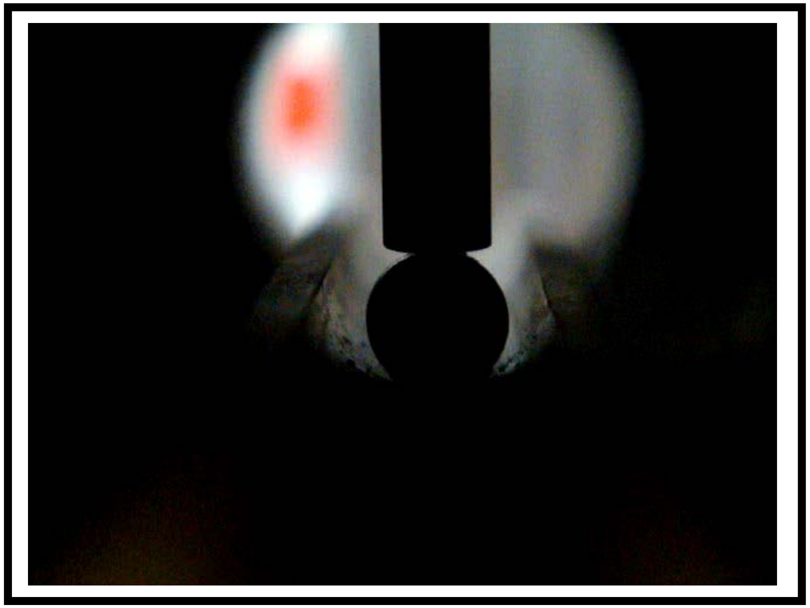
**Good agreement with J.R. Bellingham et al. J.P. Cond. Matter 2 (1990) 6207*

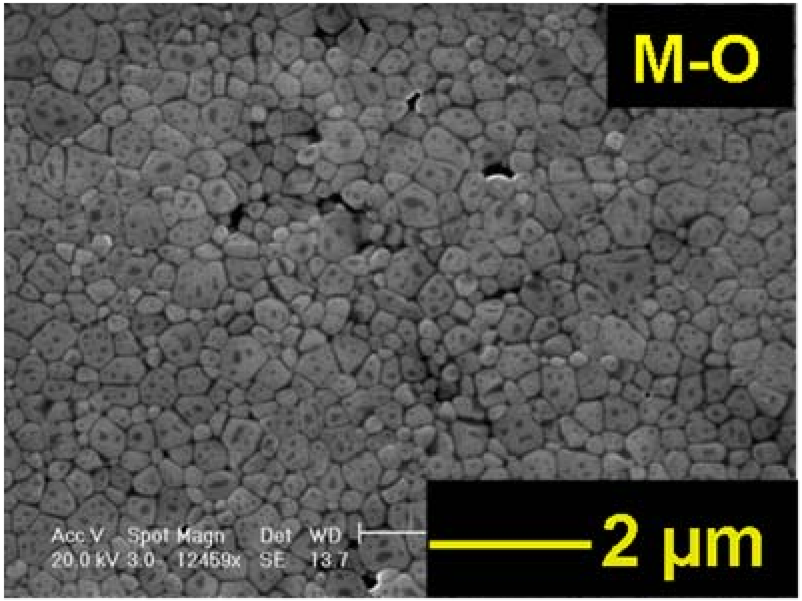
mfp ph ~ 2-10 nm

mfp e$^-$ ~ 6 nm

3D Nanostructuration: experimental

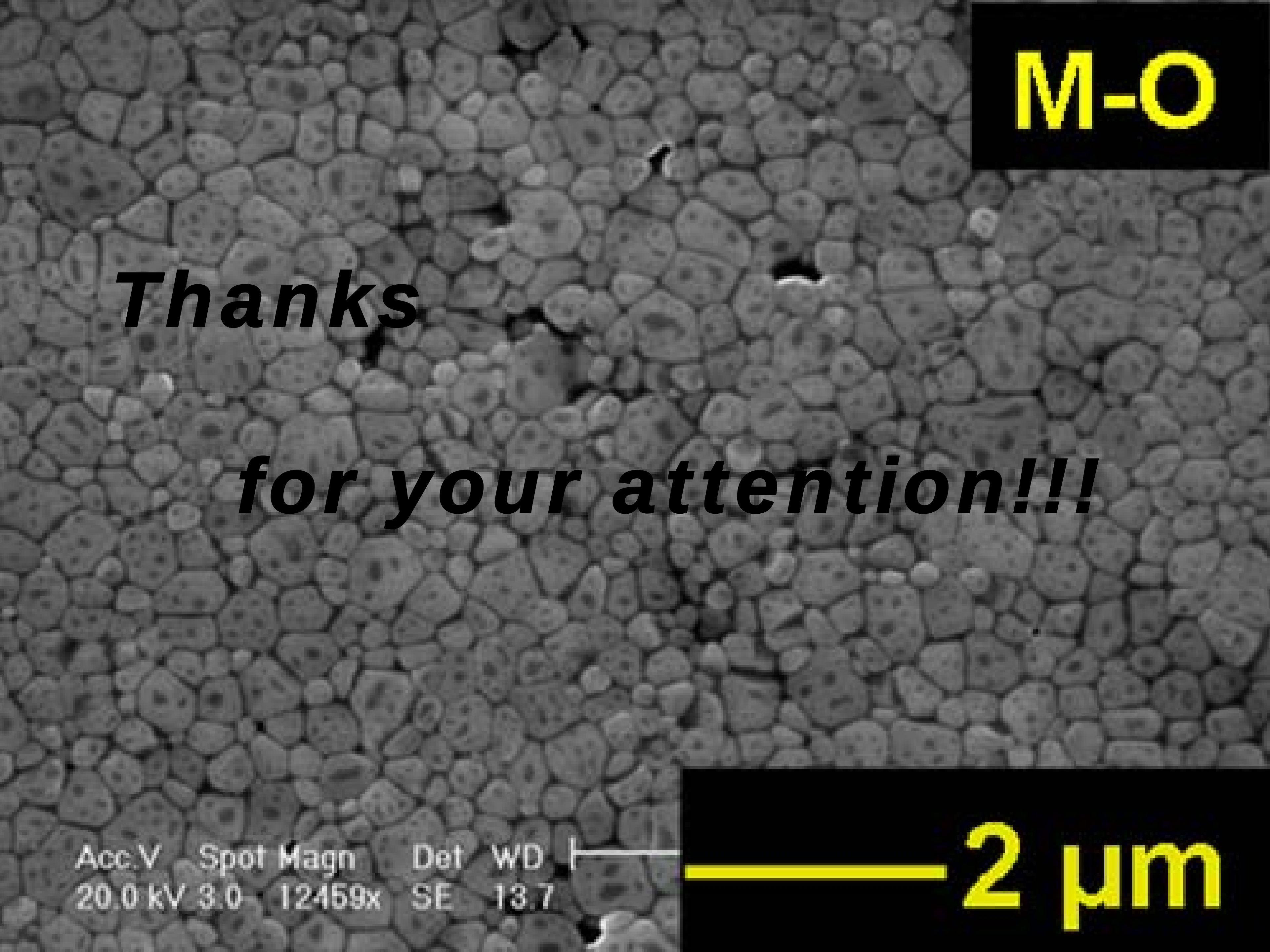
Nanoceramics processing





Thanks

for your attention!!!



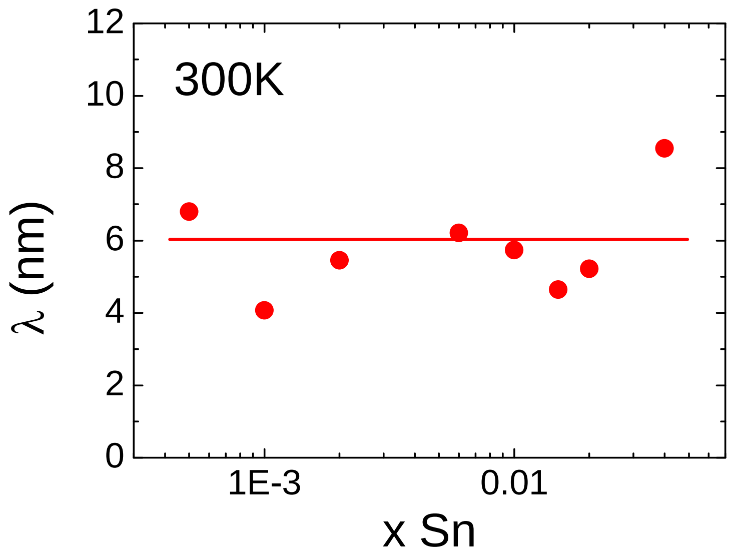
Conductivité (modèle de Drude): $\sigma = \frac{ne^2 \lambda}{m^* v}$

Libre parcours moyen

Vitesse des électrons : $v = \sqrt{v_{Fermi}{}^2 + v_{Thermique}{}^2}$

Vitesse thermique : $k_B T = \frac{1}{2} m^* v_{Thermique}{}^2$

Vitesse de Fermi (approximation parabolique): $v_{Fermi} = \frac{\hbar^2}{2m^*}\left(2\pi^2 n\right)^{2/3}$



- λ indépendant de x
- λ est faible (6 nm)

→Nano-structuration fine possible pour optimiser le ZT