Thermoelectric oxides: challenges and selected approaches for materials design

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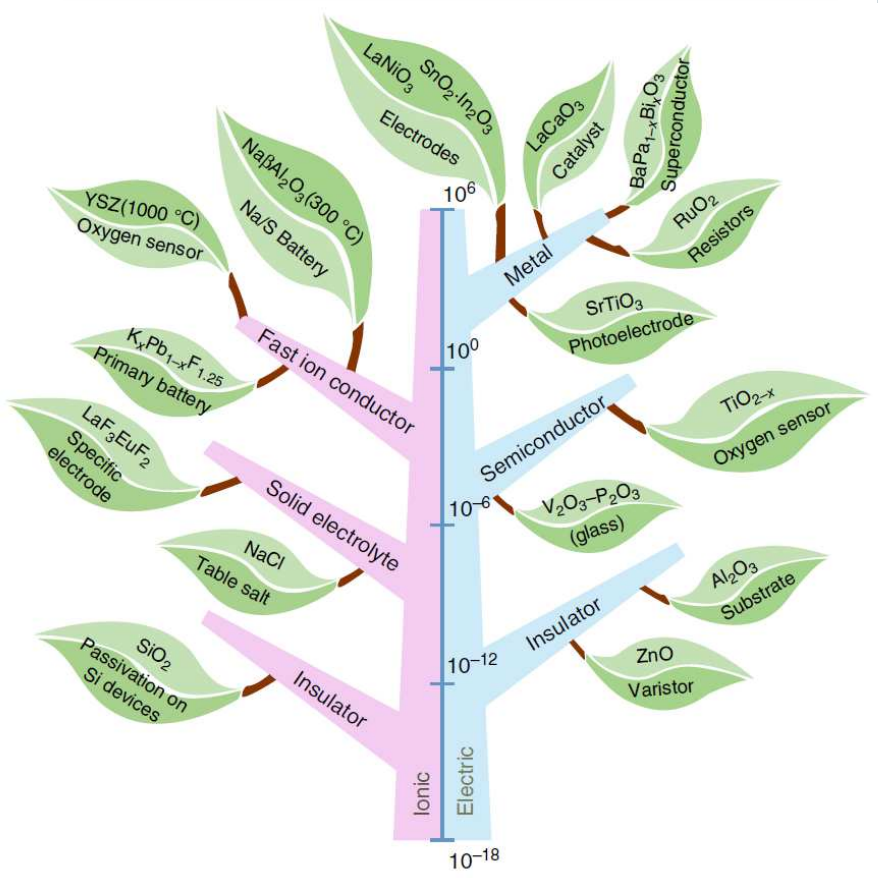
INSTITUTE FOR NANOSTRUCTURES, NANOMODELLING AND NANOFABRICATION
RESEARCH, INNOVATION AND ENGINEERING APPLICATIONS

29.06.2020 - 1st Online Workshop on Sustainable Thermoelectrics

Greetings from Aveiro, Portugal

Introduction - oxides

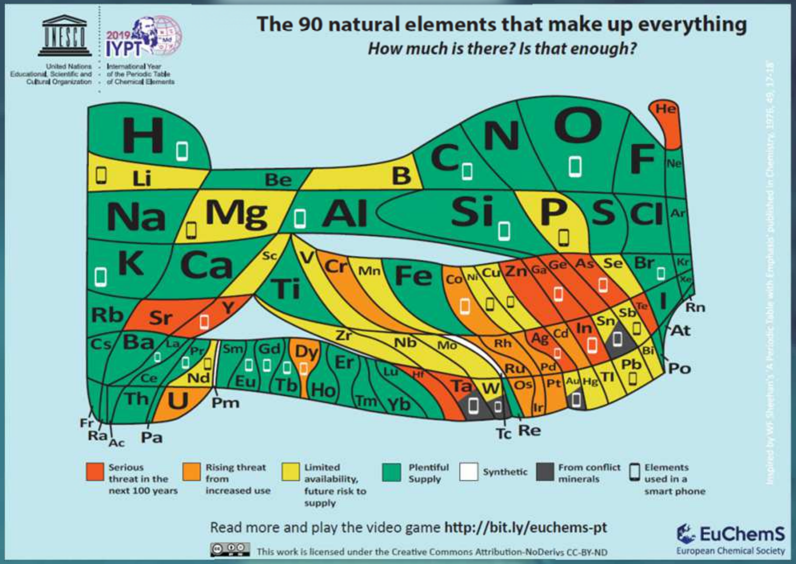
Rich family, rich/unique properties



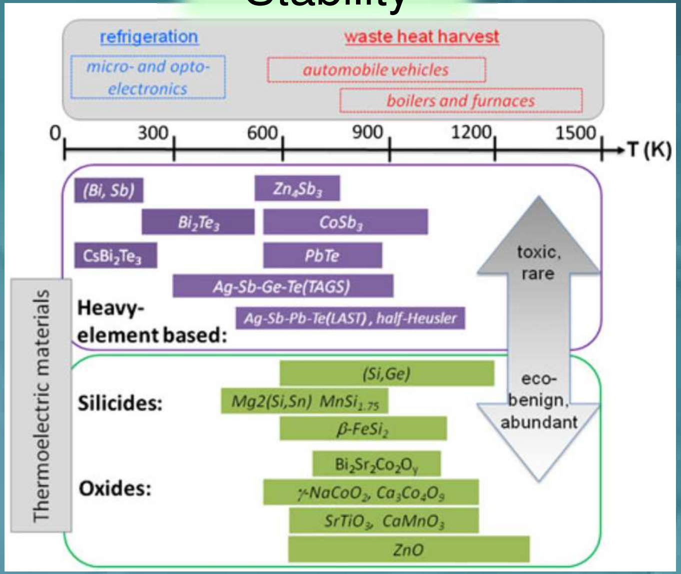
Carter, C.B. and Norton, M.G. (2013). Ceramic Materials: Science and Engineering, 546. Springer.

Yuan-Hua Lin, Jinle Lan, Cewen Nan, Oxide Thermoelectric Materials. From basic principles to applications, Wiley, 2019.

Abundance

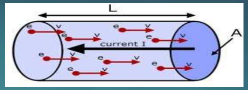


Stability

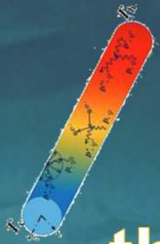


He, J., Liu, Y., & Funahashi, R. (2011). Journal of Materials Research, 26(15), 1762-1772.

TE oxides – challenges

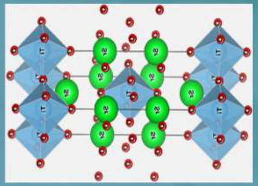


Low mobility of the charge carriers due to ionic bonding



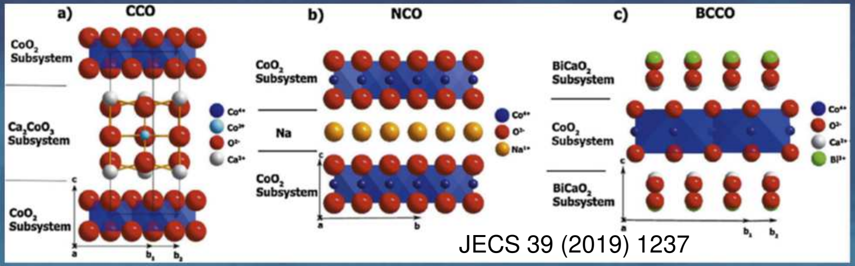
Relatively high thermal conductivity (light oxygen atoms)

Challenges



Complex doping/substitution behaviour

Main thermoelectric oxide families

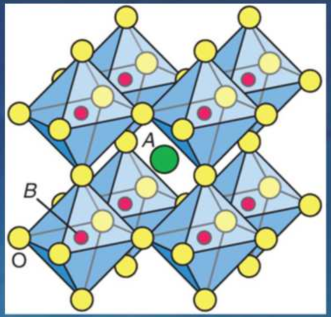


JECS 39 (2019) 1237

Layered cobaltites $Ca_3Co_4O_9$, Na_xCoO_2 and $Bi_2Ca_2Co_2O_9$, ZT reaching 0.3-0.7 at 1000 K.

Butt, S.; Xu,W.; He,W.Q.; Tan, Q.; Ren, G.K.; Lin, Y.; Nan, C.W. Enhancement of Thermoelectric Performance in Cd-Doped $Ca_3Co_4O_9$ via Spin Entropy, Defect Chemistry and Phonon Scattering. **J. Mater. Chem. A**, 2014,2, 19479.

Saini, S.; Yaddanapudi, H.S.; Tian, K.; Yin, Y.; Magginetti, D.; Tiwari, A. Terbium Ion Doping in $Ca_3Co_4O_9$: A Step Towards High-Performance Thermoelectric Materials, **Sci. Rep.** 2017, 7, 1.

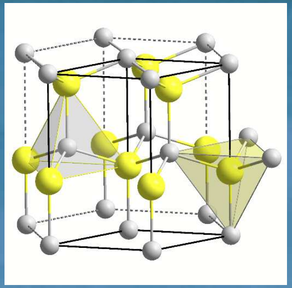


Perovskite-type ($SrTiO_3$- and $CaMnO_3$-based) materials, ZT reaching 0.3-0.5 at 1200 K.

A.V. Kovalevsky, A.A. Yaremchenko, S. Populoh, P. Thiel, D.P. Fagg, A. Weidenkaff, J.R. Frade, **Phys. Chem. Chem. Phys.** 16 (2014) 26946-26954.

J. Wang et al., Record high thermoelectric performance in bulk $SrTiO_3$ via nano-scale modulation doping, **Nano Energy** 35 (2017) 387.

Bocher, L.; Aguirre, M.H.; Logvinovich, D.; Shkabko, A.; Robert, R.; Trottmann, M.; Weidenkaff, A. $CaMn_{1-x}Nb_xO_3$ ($x < 0.08$) Perovskite-Type Phases As Promising New High-Temperature n-Type Thermoelectric Materials. **Inorg. Chem.** 2008, 47, 8077–8085.

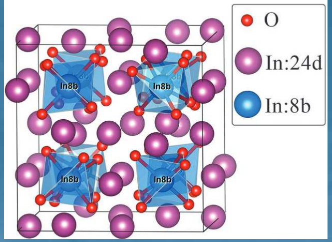


ZnO-based materials, ZT reaching 0.1-0.6 at 1100-1300 K.

M. Ohtaki, T. Tsubota, K. Eguchi, and H. Arai,J., High-temperature thermoelectric properties of $(Zn_{1-x}Al_x)O$, **Appl.Phys.** 79, 1816 (1996).

M. Ohtaki, K.Araki, and K. Yamamoto, High thermoelectric performance of dually doped ZnO ceramics, **Journal of Electronic Materials**, vol. 38, no. 7, pp. 1234 (2009).

Jood, P.; Mehta, R.J.; Zhang, Y.; Peleckis, G.;Wang, X.; Siegel, R.W.; Borca-Tasciuc, T.; Dou, S.X.; Ramanath, G. Al-Doped Zinc Oxide Nanocomposites with Enhanced Thermoelectric Properties. **Nano Lett.** 2011, 11, 4337–4342.



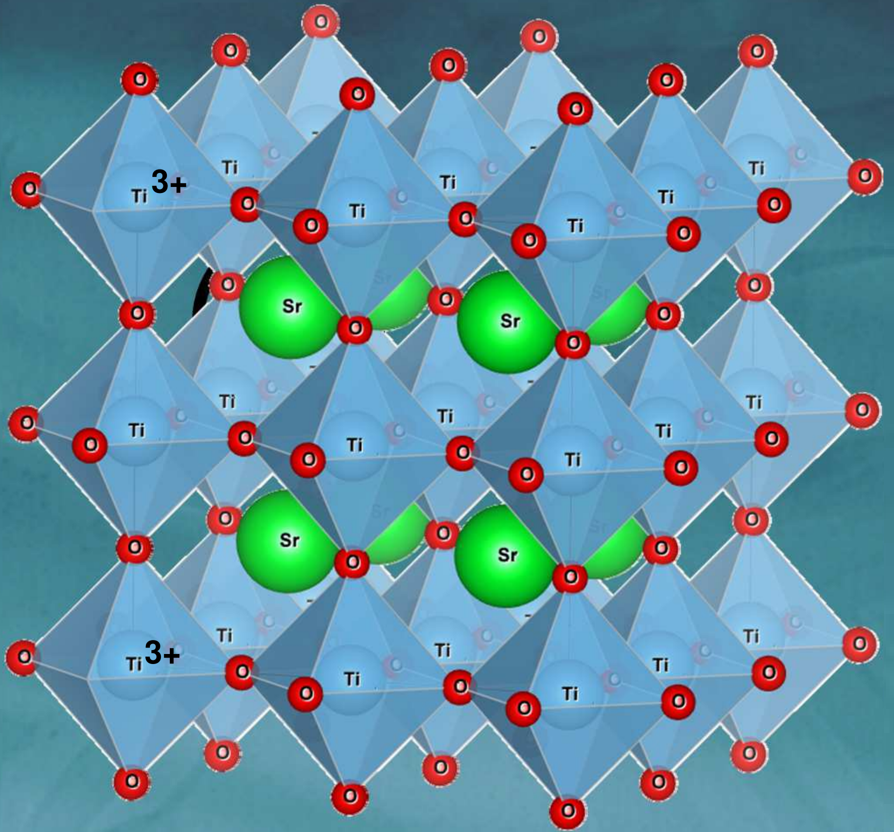
In_2O_3-based materials, ZT reaching 0.2-0.4 at 1000 K.

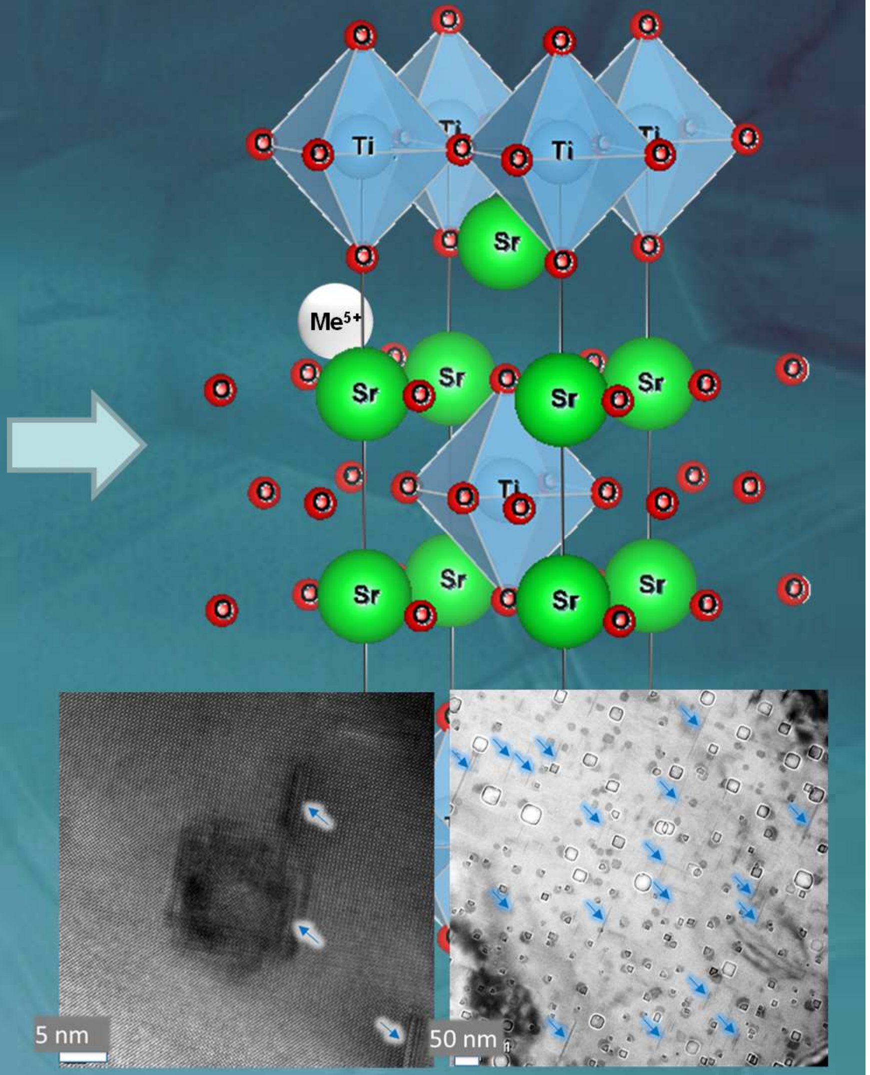
Guilmeau, E.; Bérardan, D.; Simon, Ch.; Maignan, A.; Raveau, B.; Ovono Ovono, D.; Delorme, F. Tuning the transport and thermoelectric properties of In2O3 bulk ceramics through doping at in-site. J. Appl. Phys. 2009, 106, 053715.

Yong Liu, Wei Xu, Da-Bo Liu, Meijuan Yu, Yuan-Hua Lin and Ce-Wen Nan, Enhanced thermoelectric properties of Ga-dopedIn2O3ceramicsviasynergistic band gapengineering and phonon suppression, **Phys.Chem.Chem.Phys.**,2015,17, 11229.

Liu, Y.; Lin, Y.-H.; Xu, W.; Cheng, B.; Lan, J.; Chen, D.; Zhu, H.; Nan, C.-W. High-temperature transport property of $In_{2-x}Ce_xO_3$ ($0 \leq x \leq 0.10$) fine grained ceramics. J. Am. Ceram. Soc. 2012, 95, 2568–2572.

Strontium titanate as a TE platform





A.V. Kovalevsky, M.H. Aguirre, S. Populoh, S.G. Patrício, N.M. Ferreira, S.M. Mikhalev, D.P. Fagg, A. Weidenkaff, J.R. Frade, *Designing strontium titanate-based thermoelectrics: insight into defect chemistry mechanisms*, ***J. Mater. Chem. A***, *2017, vol. 5, pp. 3909-3922.*

Strontium titanate is a semiconductor with 3.2 eV band gap

Donor substitution both in A- and B-site sublattices

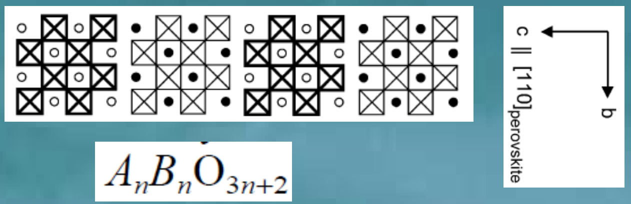
Strontium titanate as a TE platform

How the defect types can be controlled?

Example: $SrTi_{1-x}Ta_xO_{3\pm\delta}$ and $Sr_{1-x/2}Ti_{1-x}Ta_xO_{3\pm\delta}$ series

$$(x/2)Ta_2O_5 + SrO + (1-x)TiO_2 \rightarrow (1-\beta x/2)Sr_{Sr}^{\times} + (1-x)Ti_{Ti}^{\times} +$$
$$+ xTa_{Ti}^{\bullet} + (\beta x/2)V_{Sr}'' + (\beta x/2)SrO^{RP} + ((1-\beta)x/2)O_{layer}'' + 3O_O^{\times}$$

(more oxygen-rich planar defects)



F. Lichtenberg et al. Prog. Solid State Chem. 29 (2001) 1-70.

$$(x/2)Ta_2O_5 + (1-x/2)SrO + (1-x)TiO_2 \rightarrow (1-x/2)Sr_{Sr}^{\times} + (x/2)V_{Sr}'' +$$
$$+ xTa_{Ti}^{\bullet} + (2\delta)Ti_{Ti}' + (1-x-2\delta)Ti_{Ti}^{\times} + (3-\delta)O_O^{\times} + \delta V_O^{\bullet\bullet} + (\delta/2)O_2(g)$$

(more A-site and oxygen vacancies)

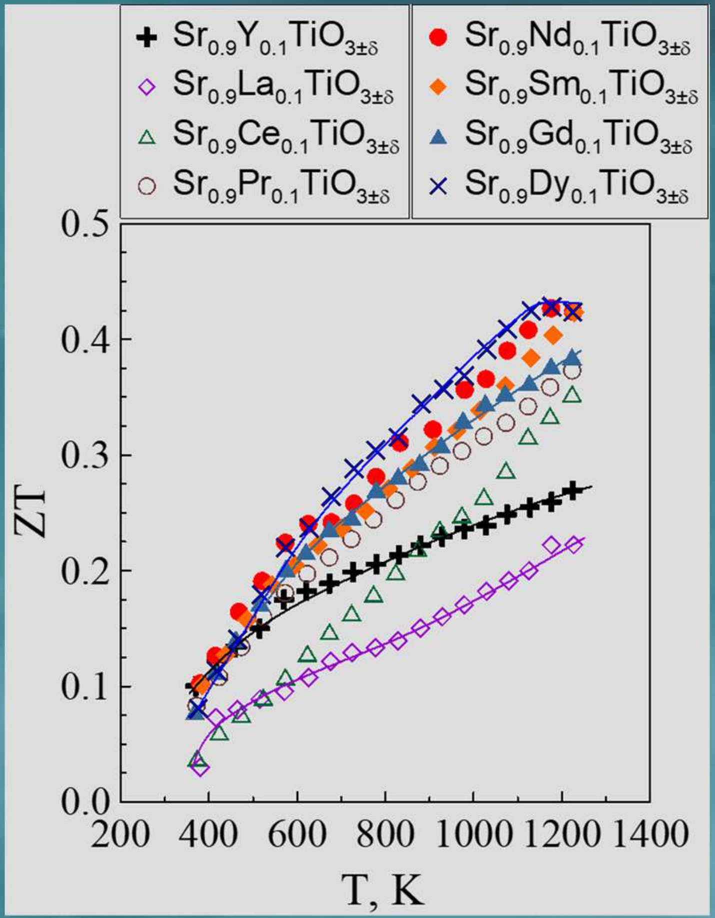
For both: $2Ti_{Ti}^{\times} + O_O^{x} \rightarrow 2Ti_{Ti}' + V_O^{\bullet\bullet} + (\delta/2)O_2$

A.A. Yaremchenko, S. Populoh, S.G. Patrício, J. Macías, P. Thiel, D.P. Fagg, A. Weidenkaff, J.R. Frade, A.V. Kovalevsky, Boosting thermoelectric performance by controlled defect chemistry engineering in Ta-substituted strontium titanate, ***Chem. Mater.****, 2015, vol. 27, p. 4995.*

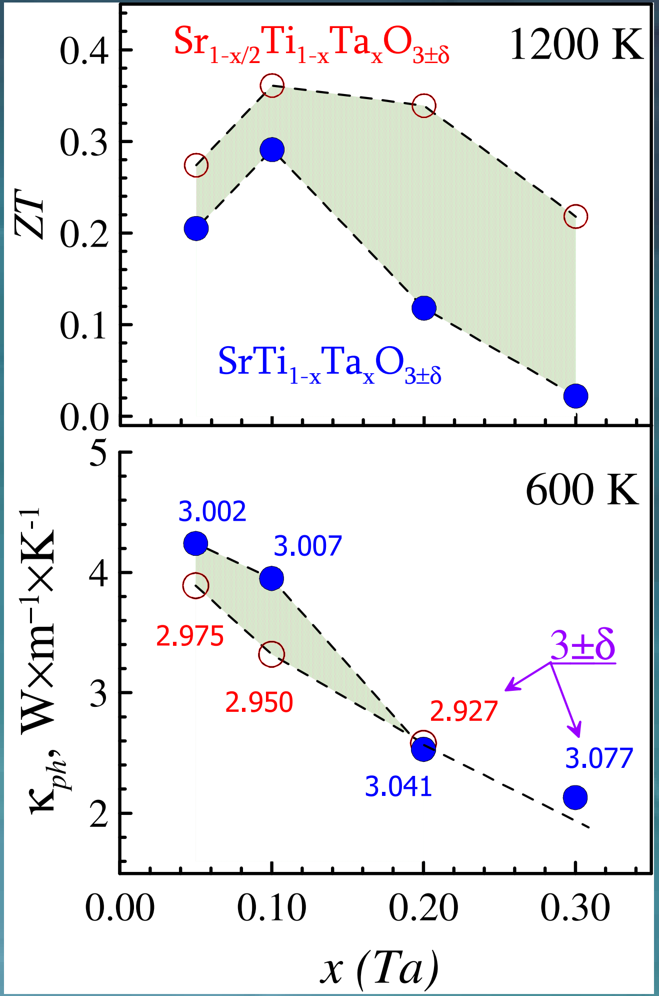
$SrTiO_3$ – effects of oxygen deficiency

Highly reducing conditions are essential: $2Ti_{Ti}^{\times} + O_O^{x} \rightarrow 2Ti_{Ti}' + V_O^{\bullet\bullet} + (\delta/2)O_2$

1500ºC (10h) in 10%H_2-N_2

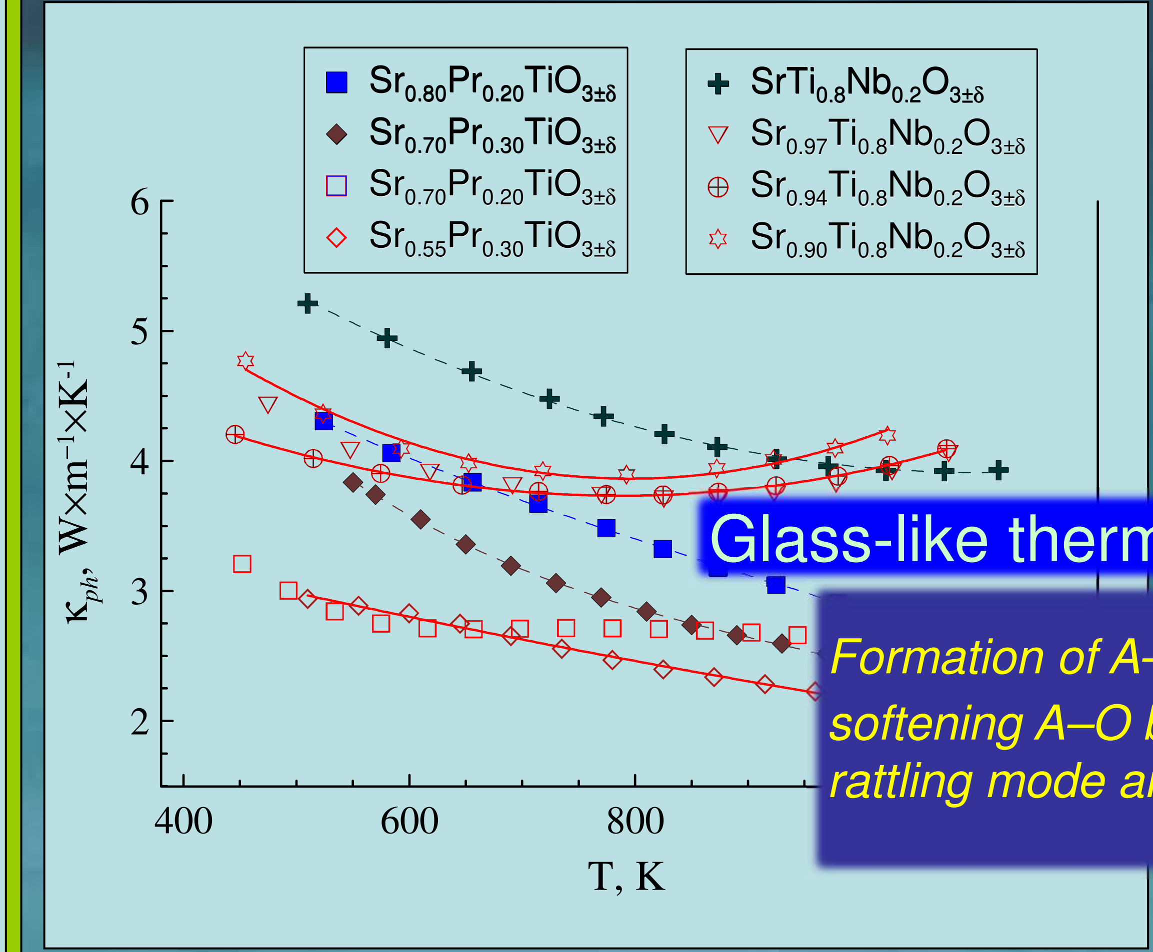


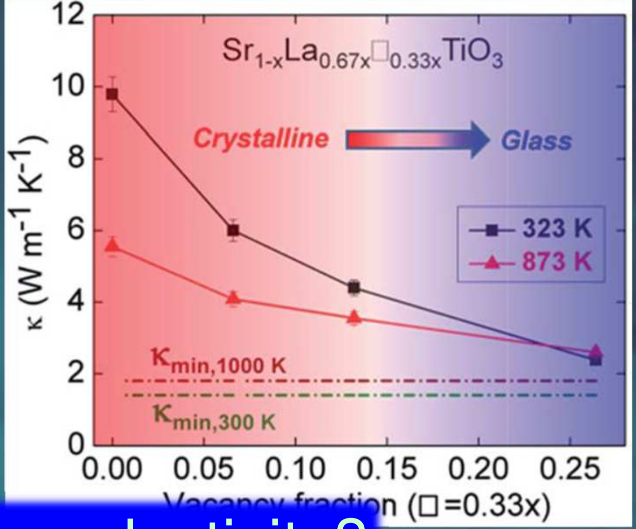
A.V. Kovalevsky, A.A. Yaremchenko, S. Populoh, P. Thiel, D.P. Fagg, A. Weidenkaff, J.R. Frade, Towards a high thermoelectric performance in rare-earth substituted SrTiO3: Effects provided by strongly-reducing conditions, **Phys. Chem. Chem. Phys.**, 2014, vol. 16, pp. 26946-26954.

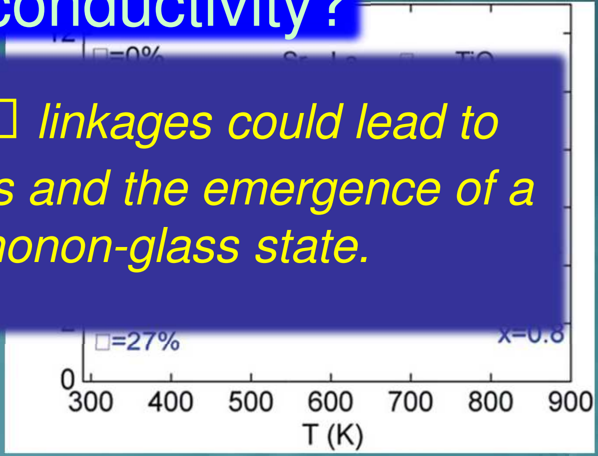


A.A. Yaremchenko, S. Populoh, S.G. Patrício, J. Macías, P. Thiel, D.P. Fagg, A. Weidenkaff, J.R. Frade, A.V. Kovalevsky, Boosting thermoelectric performance by controlled defect chemistry engineering in Ta-substituted strontium titanate, **Chem. Mater.**, 2015, vol. 27, p. 4995.

$SrTiO_3$ – effects of cation deficiency







Glass-like thermal conductivity?

Formation of A–O–□ linkages could lead to softening A–O bonds and the emergence of a rattling mode and phonon-glass state.

A.V. Kovalevsky, A. A. Yaremchenko, S. Populoh, A. Weidenkaff and J. R. Frade, J. Phys.Chem. C 2014, vol. 118, pp. 4596-4606.

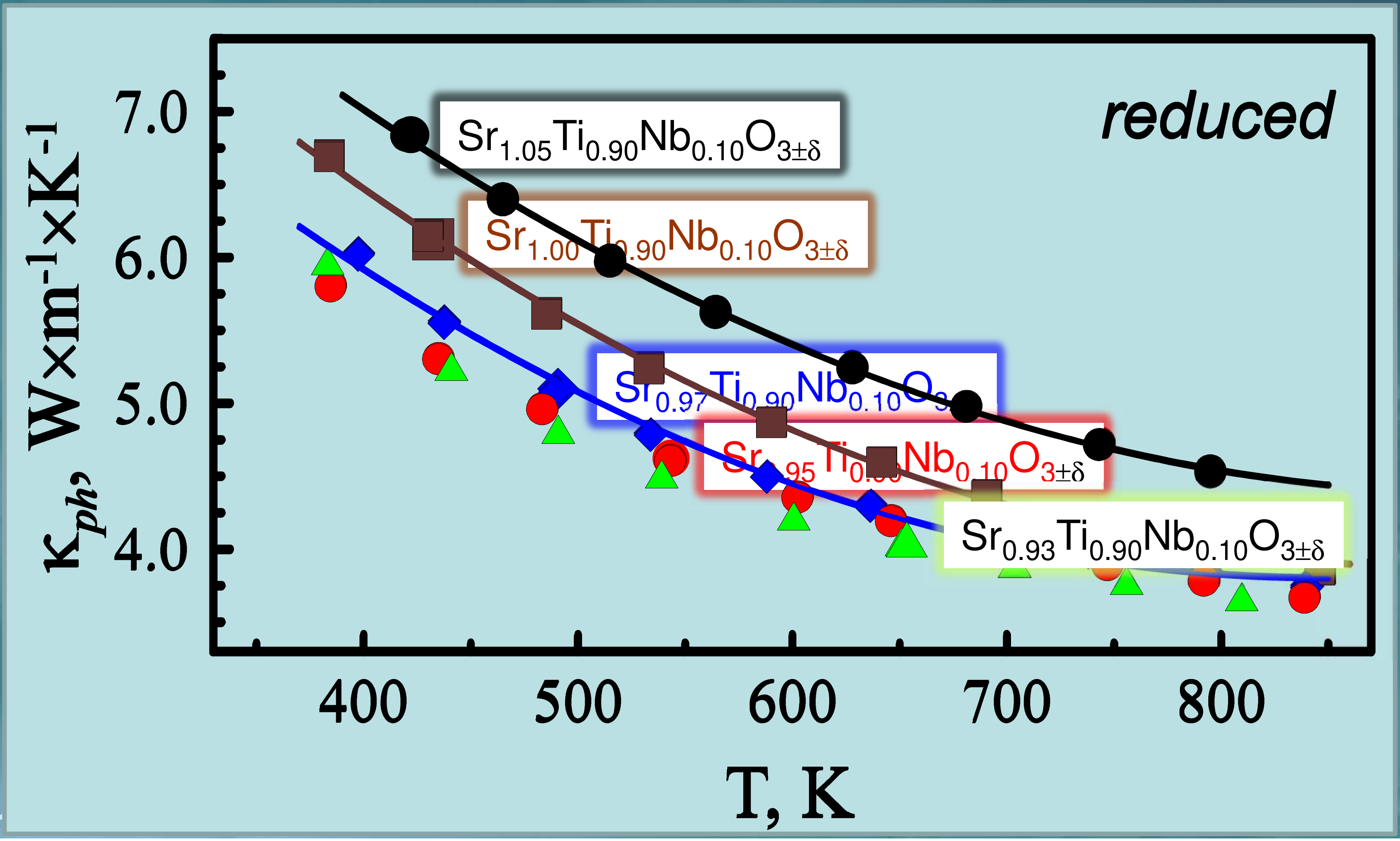
Popuri, S.R.; Scott, A.J.M.; Downie, R.A.; Hall, M.A.; Suard, E.; Decourt, R.; Pollet, M.; Bos, J.-W.G. RSC Adv. ***2014****, 4, 33720-33723.*

$SrTiO_3$ – effects of cation deficiency

$Sr_yTi_{0.90}Nb_{0.10}O_{3\pm\delta}$

A.V. Kovalevsky, M.H. Aguirre, S. Populoh, S.G. Patrício, N.M. Ferreira, S.M. Mikhalev, D.P. Fagg, A.Weidenkaff, J.R. Frade, Designing strontium titanate-based thermoelectrics: insight into defect chemistry mechanisms, ***J. Mater. Chem. A****, 2017, vol. 5, pp. 3909.*

"stoichiometric"



more

$(SrO)^{RP}$

↑

↓

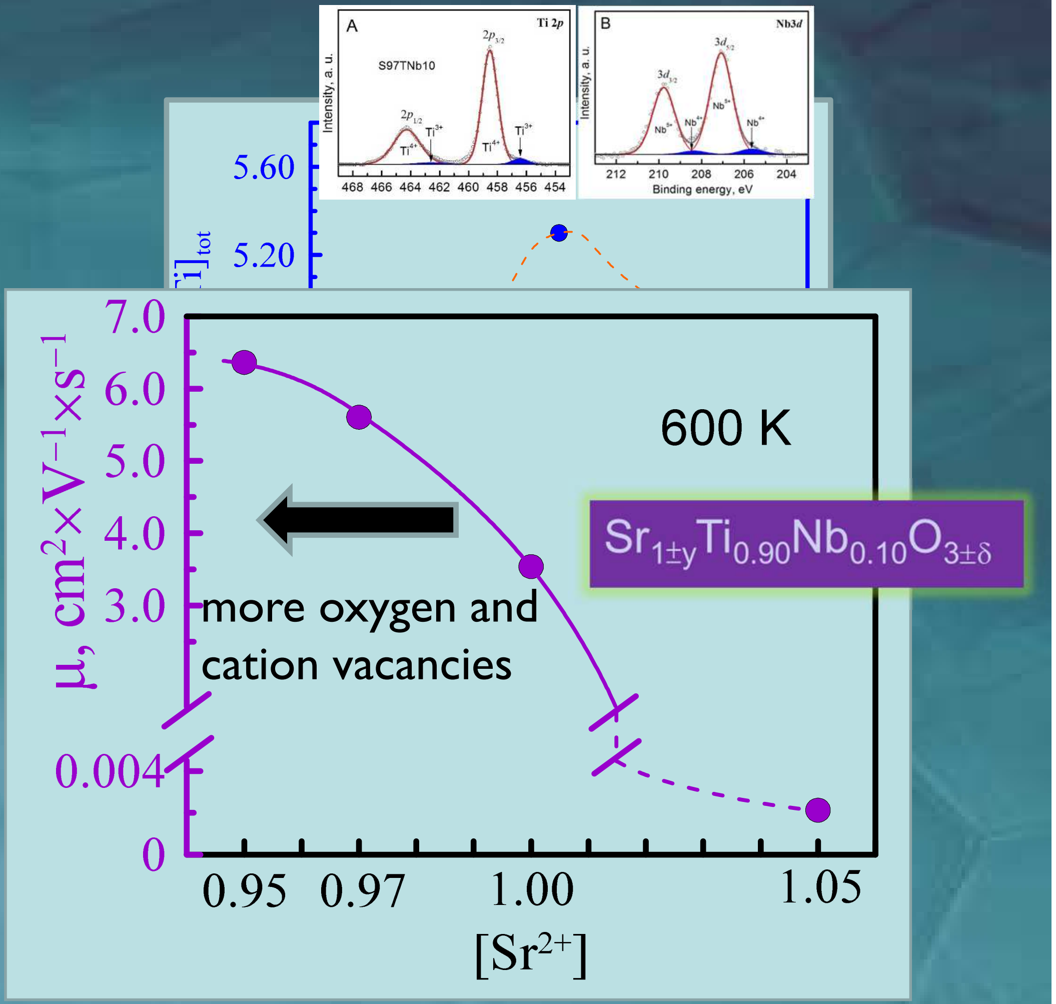
more

$V_O^{\bullet\bullet}, V_{Sr}''$

SrTiO$_3$ – effects of cation deficiency

- introducing A-site deficiency is favorable for enhancing the mobility of the charge carries

$Sr_yTi_{0.90}Nb_{0.10}O_{3\pm\delta}$



more oxygen and cation vacancies

$Sr_{1\pm y}Ti_{0.90}Nb_{0.10}O_{3\pm\delta}$

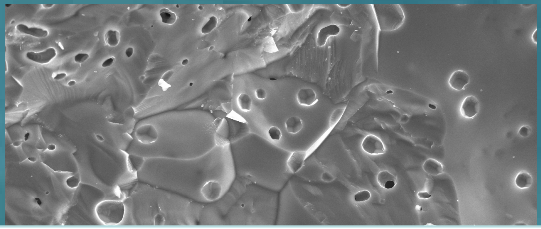
A.V. Kovalevsky, M.H. Aguirre, S. Populoh, S.G. Patrício, N.M. Ferreira, S.M. Mikhalev, D. P. Fagg, A. Weidenkaff and J. R. Frade, ***J. Mater. Chem. A*****, *2017***, *vol. 5, pp. 3909-3922.*

$SrTiO_3$ – redox-promoted composites

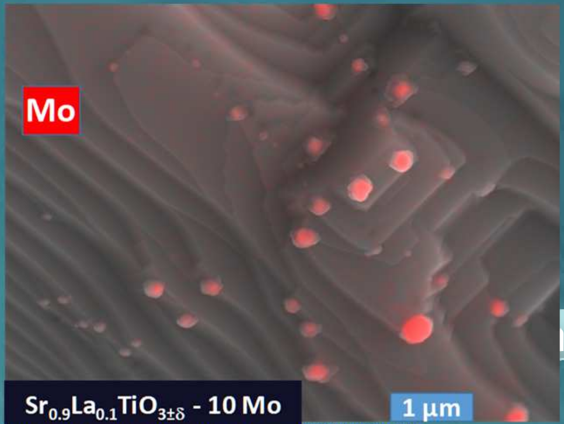
$(Sr,La)TiO_{3\pm\delta}$ + MoO_3 **OX** → $(Sr,V_{Sr}'',La)Ti(Mo)O_{3\pm\delta}$ + $SrMoO_4$ **RED** → Mo + $(Sr,V_{Sr}'',La)TiO_{3\pm\delta}$ + $SrMo(Ti)O_{3\pm\delta}$

composite lattice

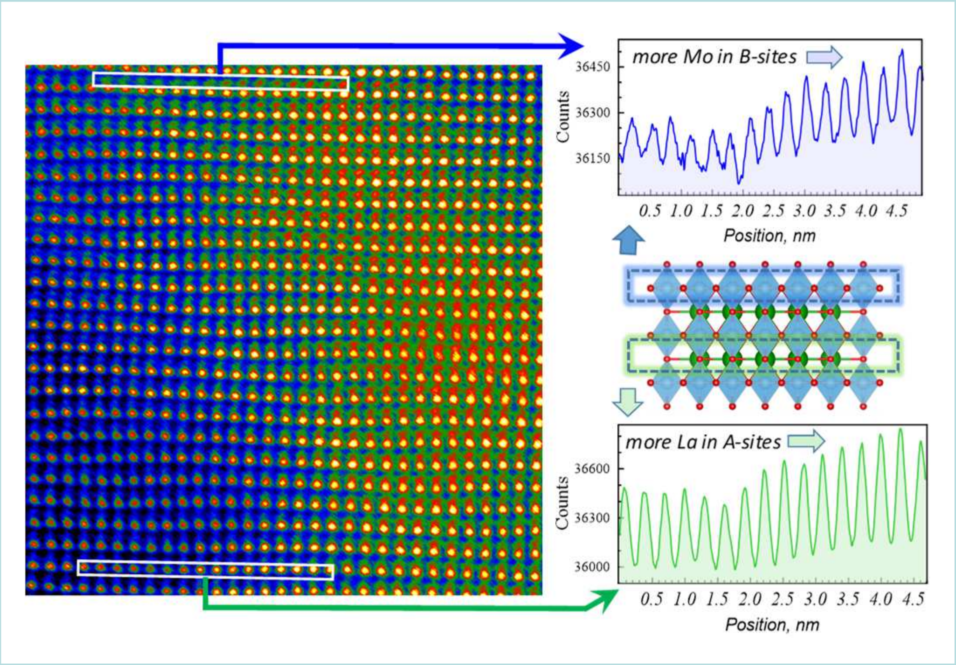
Ox

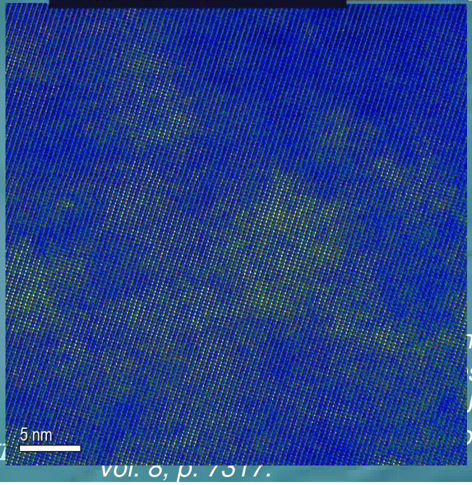


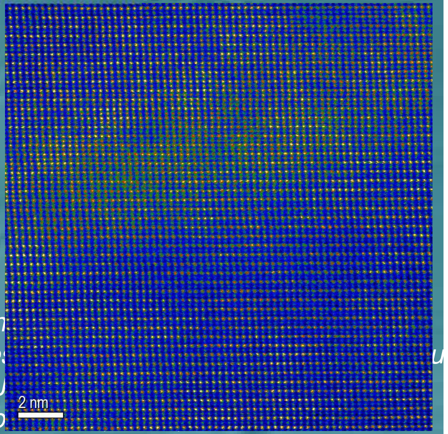
H_2



Red (Mo)





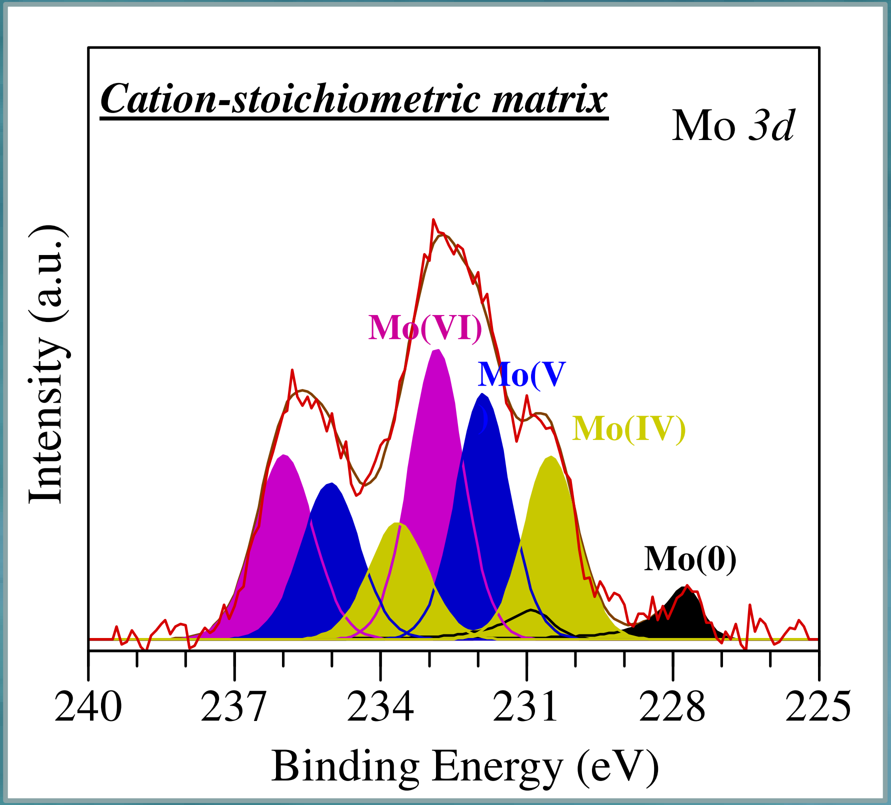


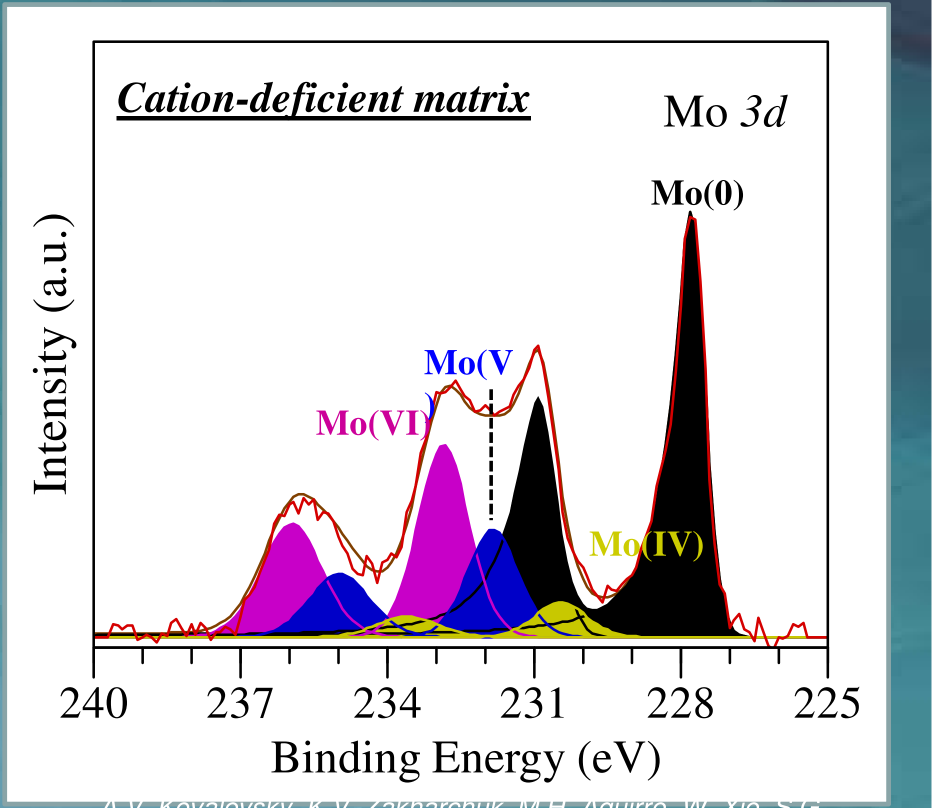
vol. 8, p. 7317.

$SrTiO_3$ – redox-promoted composites

$(Sr,V_{Sr}^{''},La)TiO_{3\pm\delta}$ + $SrMo(Ti)O_{3\pm\delta}$ + Mo

Redox composition?

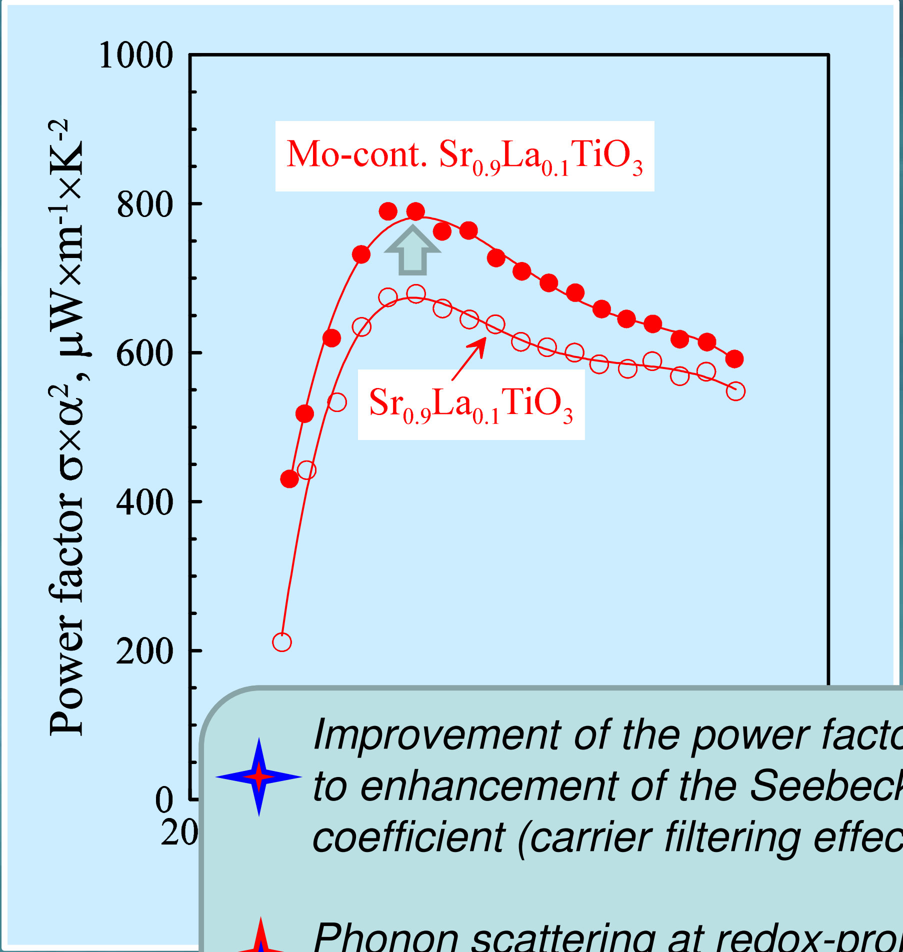




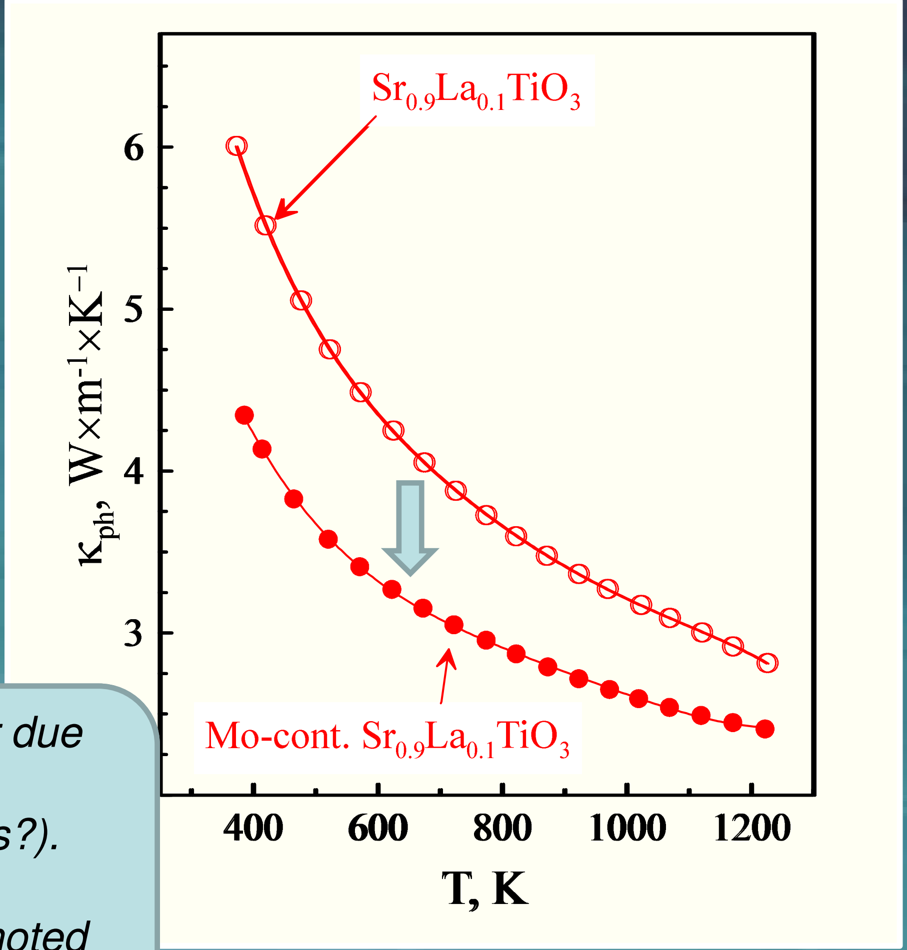
A.V. Kovalevsky, K.V. Zakharchuk, M.H. Aguirre, W. Xie, S.G. Patrício, N.M. Ferreira, D. Lopes, S.A. Sergiienko, G. Constantinescu, S.M. Mikhalev, A. Weidenkaff, J.R. Frade, Redox engineering of strontium titanate-based thermoelectrics, 2020, ***J. Mater. Chem. A****, vol. 8, p. 7317.*

$SrTiO_3$ – redox-promoted composites

Power factor PF=σ×α²



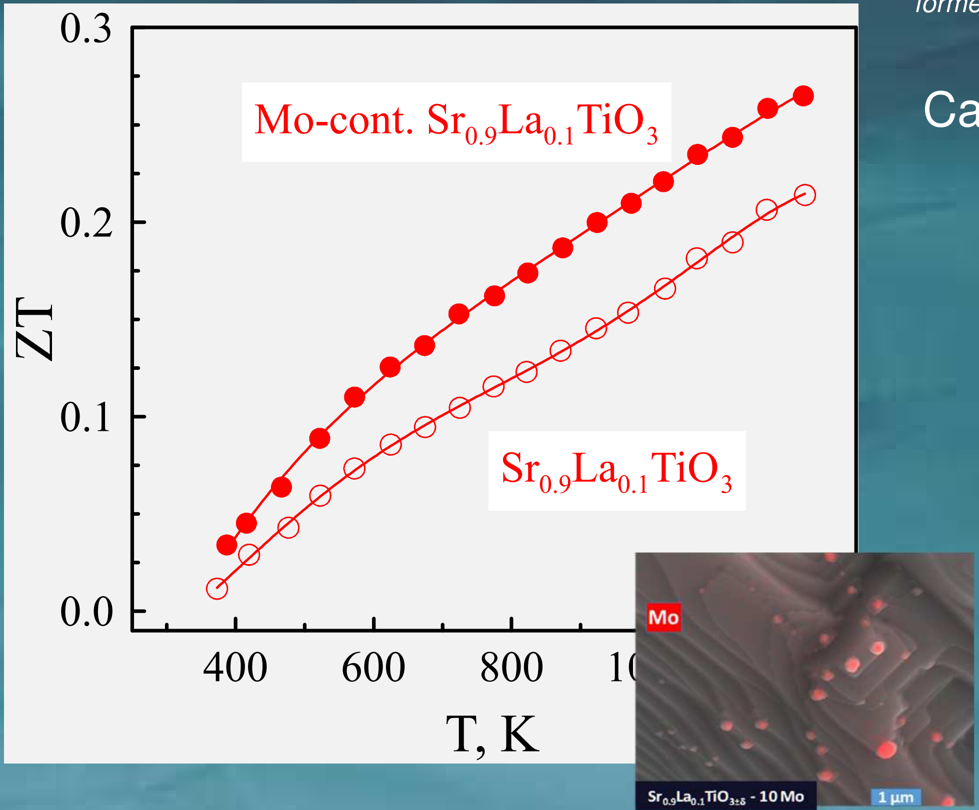
Thermal conductivity



- *Improvement of the power factor due to enhancement of the Seebeck coefficient (carrier filtering effects?).*
- *Phonon scattering at redox-promoted interfaces.*

Kovalevsky, K.V. Zakharchuk, M.H. Aguirre, W. Xie, S.G. Patrício, Ferreira, D. Lopes, S.A. Sergiienko, G. Constantinescu, S.M. Mikhalev, A. Weidenkaff, J.R. Frade, Redox engineering of strontium titanate-based thermoelectrics, 2020, ***J. Mater. Chem. A****, vol. 8, p. 7317*

$SrTiO_3$ – redox-promoted composites

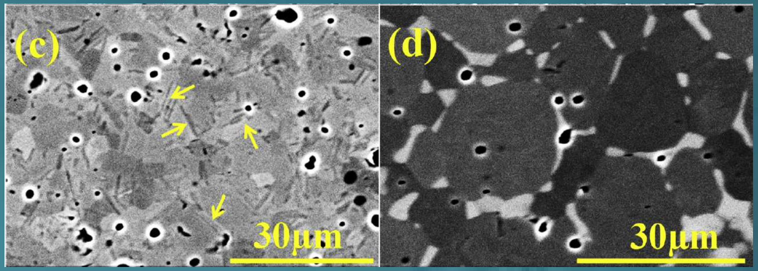


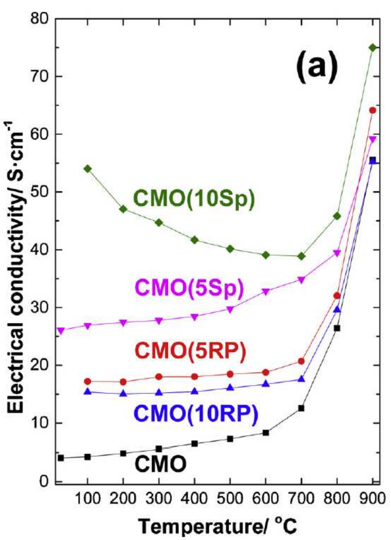
*A.V. Kovalevsky, K.V. Zakharchuk, M.H. Aguirre, W. Xie, S.G. Patrício, N.M. Ferreira, D. Lopes, S.A. Sergiienko, G. Constantinescu, S.M. Mikhalev, A. Weidenkaff, J.R. Frade, Redox engineering of strontium titanate-based thermoelectrics, 2020, **J. Mater. Chem. A**, vol. 8, p. 7317.*

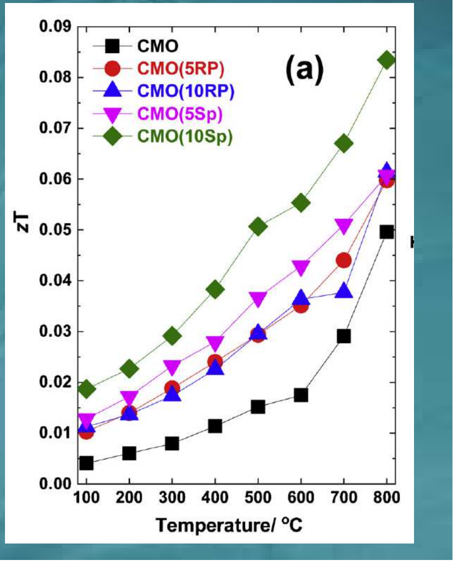
S. Prakash Singh, N. Kanas, T. Desissa, M.-A. Einarsrud, T. Norby, K. Wiik, Thermoelectric properties of non-stoichiometric $CaMnO_{3-\delta}$ composites formed by redox-activated exsolution, J. Europ. Ceram. Soc. 40 (2020) 1344.

$$CaO+MnO_2 \xrightarrow{Red} Ca_{1-x}Mn_xO\text{(rock-salt)}$$

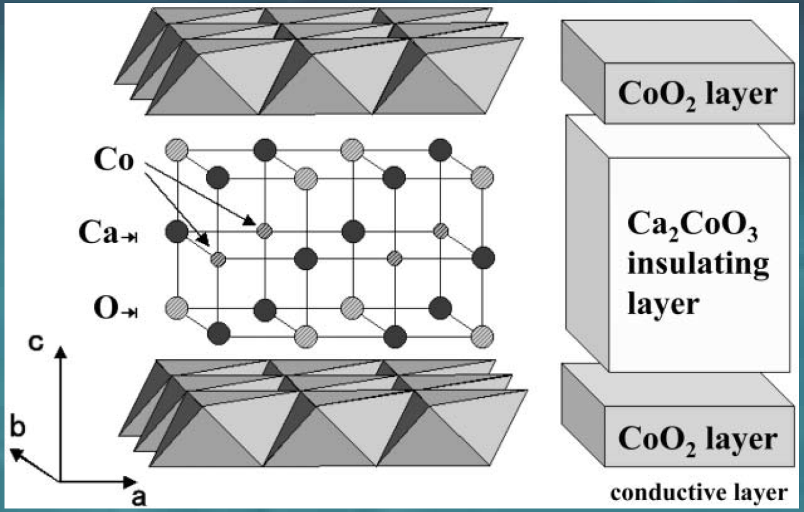
$$\xrightarrow{Ox} \mathbf{CaMnO_3}+Ca_4Mn_3O_{10}+CaMn_2O_4$$







$Ca_3Co_4O_3$ – redox-promoted composites

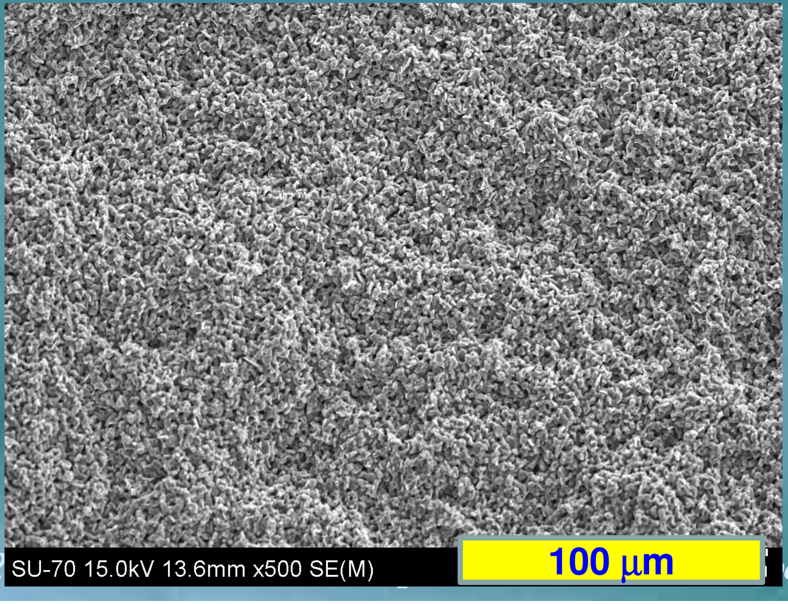


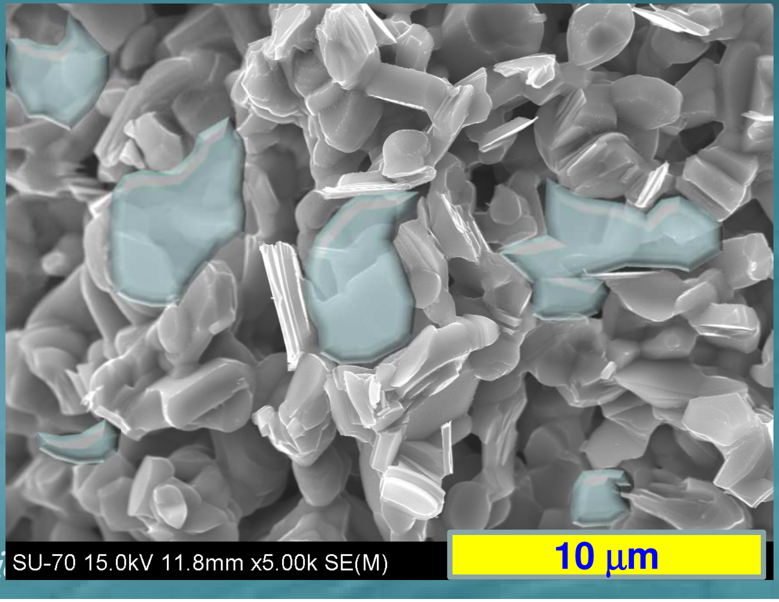
$Ca_3Co_4O_9$

natural superlattice with promising TE properties

A. C. Masset, C. Michel, A. Maignan, M. Hervieu, O. Toulemonde, F. Studer, B. Raveau and J. Hejtmanek, **Phys. Rev. B**, 2000, 62, 166; Y. Miyazaki, M. Onoda, T. Oku, M. Kikuchi, Y. Ishii, Y. Ono, Y. Morii and T. Kajitani, **J. Phys. Soc. Jpn.**, 2002, 71, 491–497.

High grain anisotropy – low densification





$Ca_3Co_4O_3$ – redox-promoted composites

$Ca_3Co_4O_9$ powder

+

Co (met.) powder

OX

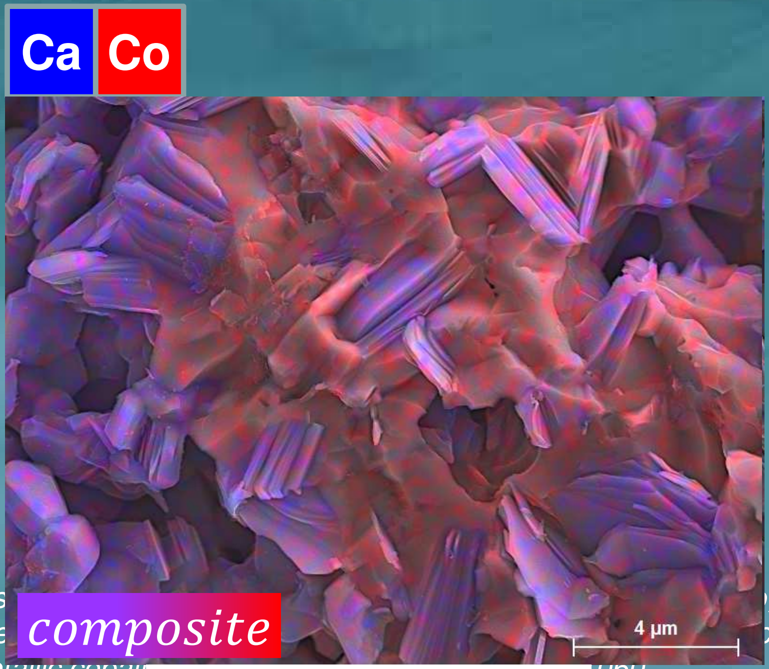
$\xrightarrow[900ºC\ (2h)]{}$

$Ca_3Co_4O_9$ matrix

+

Co_3O_4 filler

composite ceramics

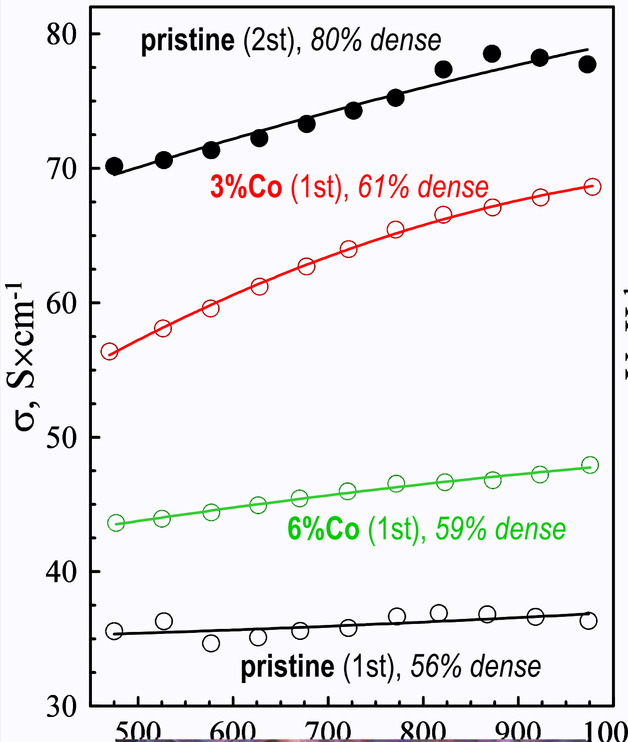


$Ca_3Co_4O_9 + Co_3O_4$

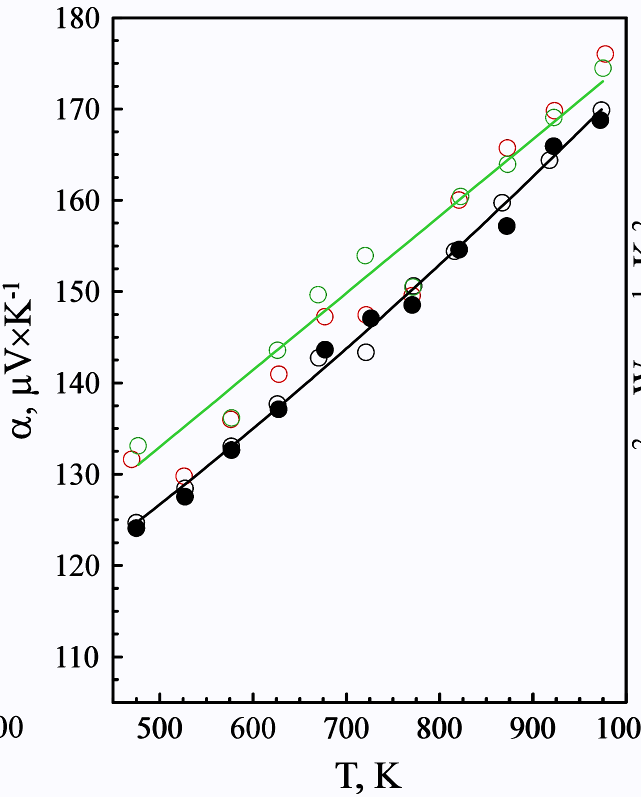
G. Constantines … , P. Amirkhizi, J.R. Frade, A.V. Kovalevsky, Re … cal performance in $Ca_3Co_4O_9$ materials by metallic cobal … 060.

$Ca_3Co_4O_3$ – redox-promoted composites

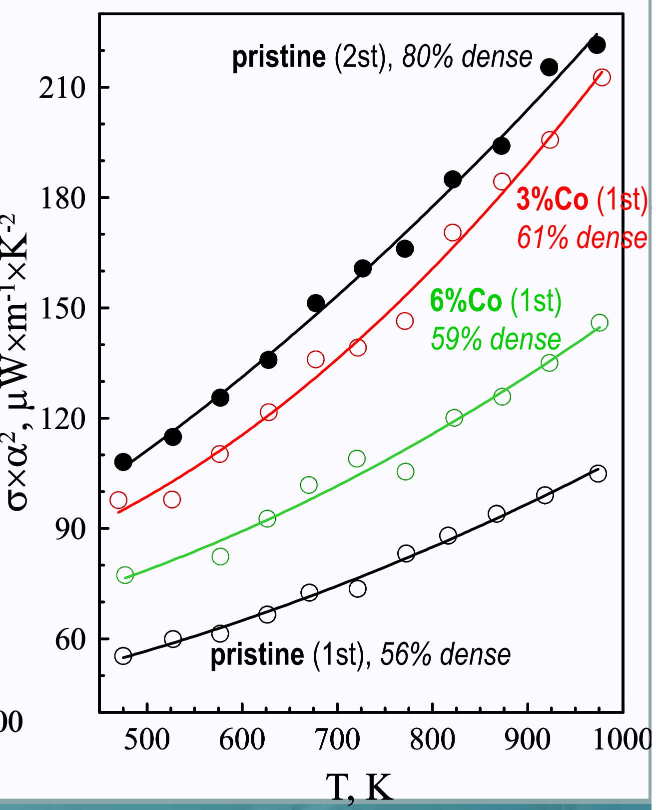
Electrical conductivity

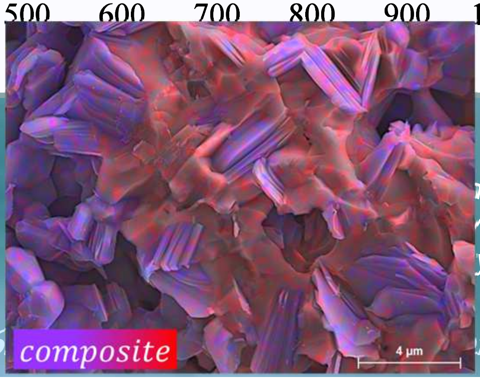


Seebeck coefficient



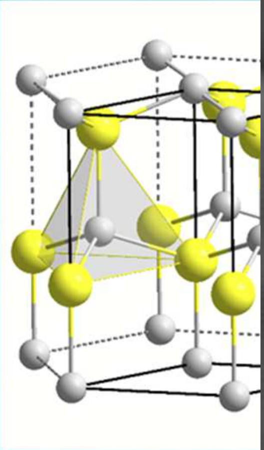
Power factor

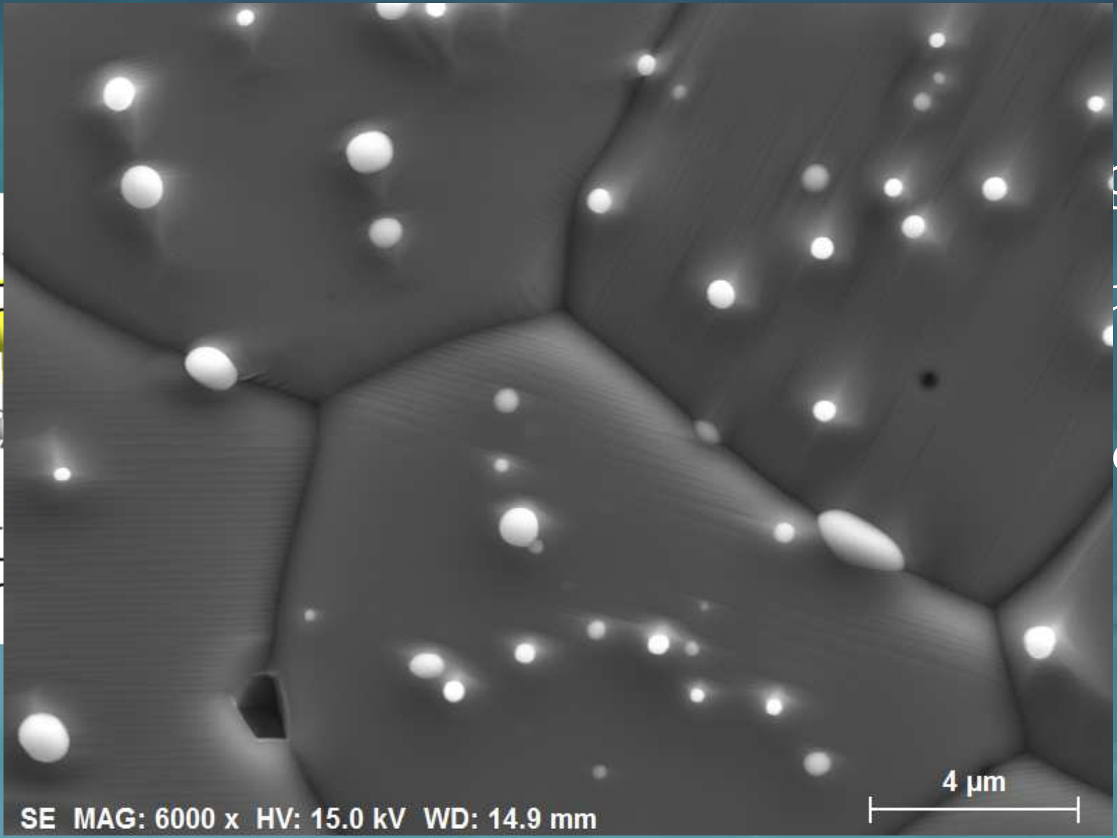




tinescu, A.R. Sarabando, Sh. Rasekh, D. Lopes, S. Sergiienko, P. Amirkhizi, J.R. Frade, A.V.
, Redox-promoted tailoring of the high-temperature electrical performance in $Ca_3Co_4O_9$
*y metallic cobalt addition, **Materials**, 2020, 13, p. 1060.*

ZnO – self-organization in composites





plications:

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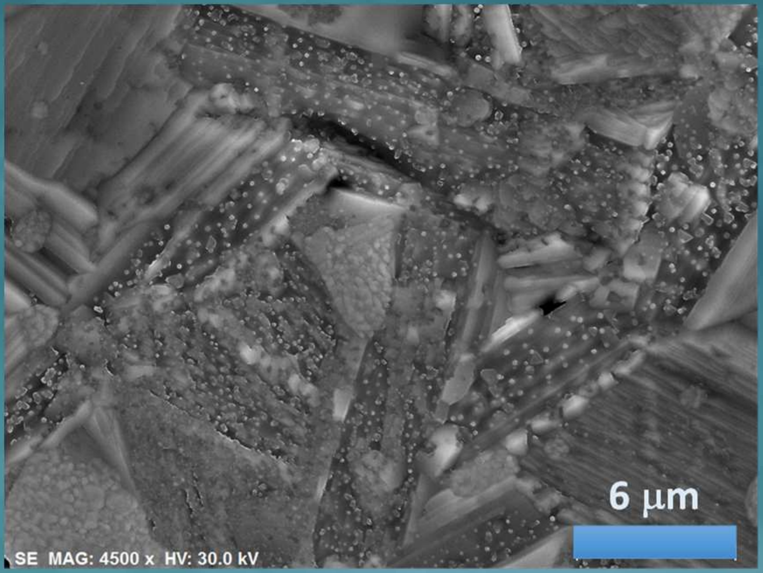
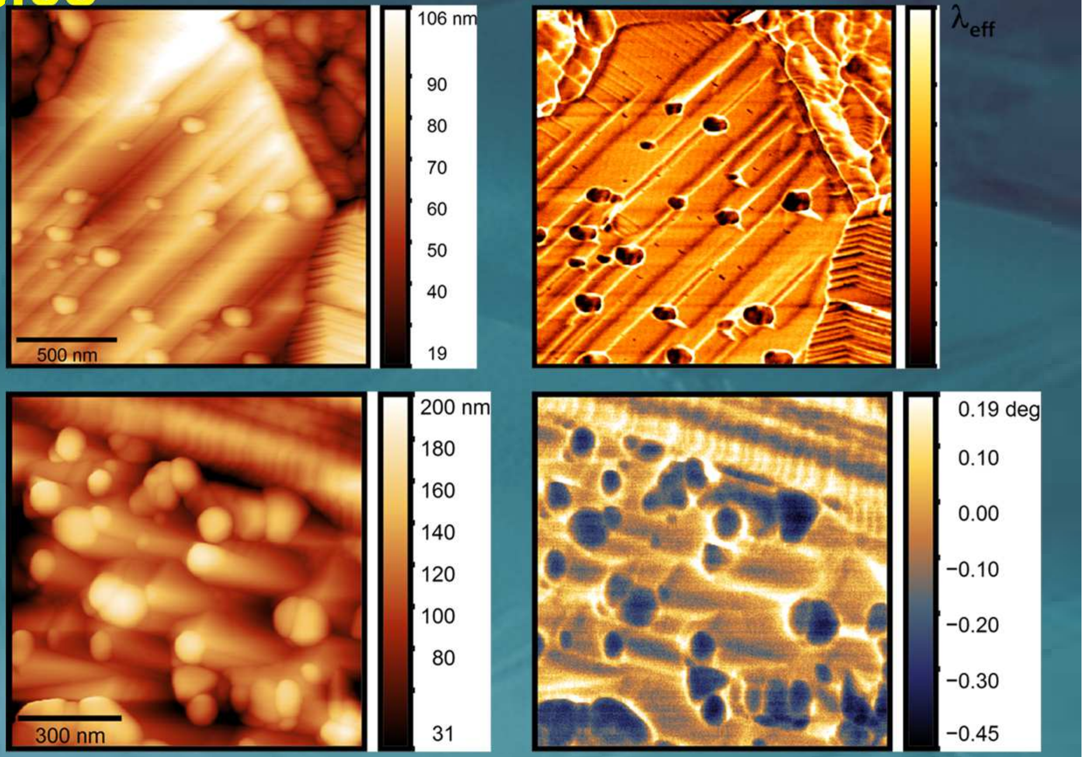
ductivity

Nanocomposite formed by an addition of external nanoparticles

ZnO – self-organization in composites

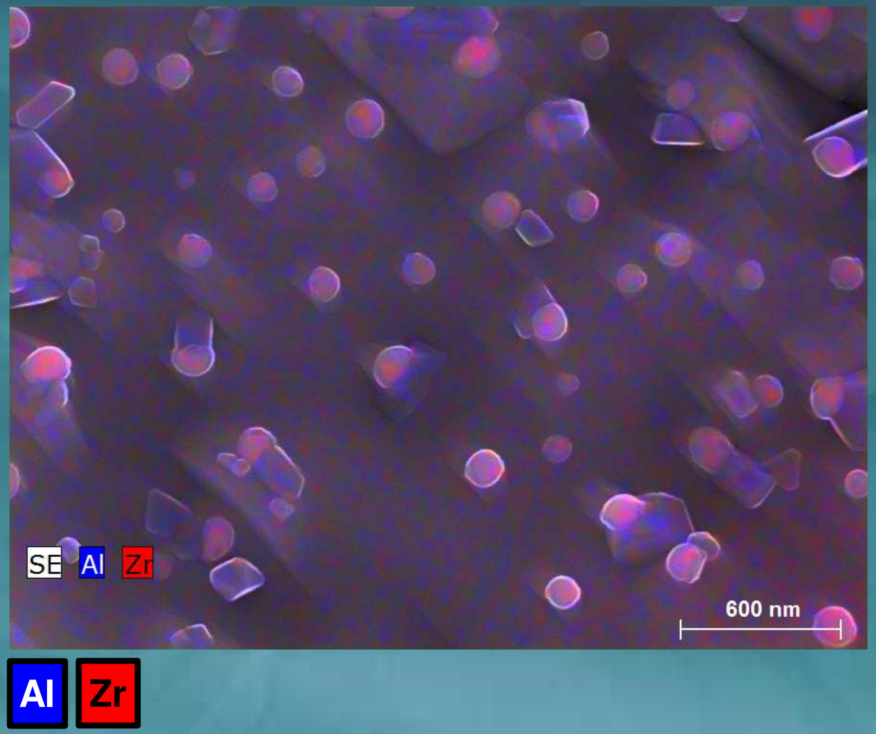
Zn(Al)O + ZrO_2 nanoparticles

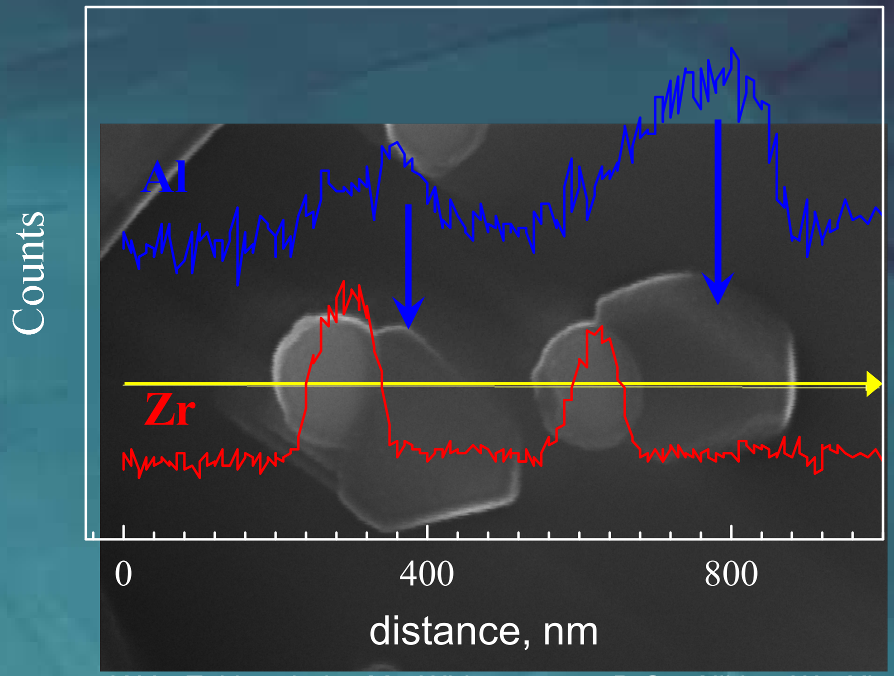




K.V. Zakharchuk, M. Widenmeyer, D.O. Alikin, W. Xie, S. Populoh, S.M. Mikhalev, A. Tselev, J.R. Frade, A. Weidenkaff, A.V. Kovalevsky, A self-forming nanocomposite concept for ZnO-based thermoelectrics, ***J. Mater. Chem. A****, 2018, vol. 6, pp.13386-13396.*

ZnO – self-organization in composites



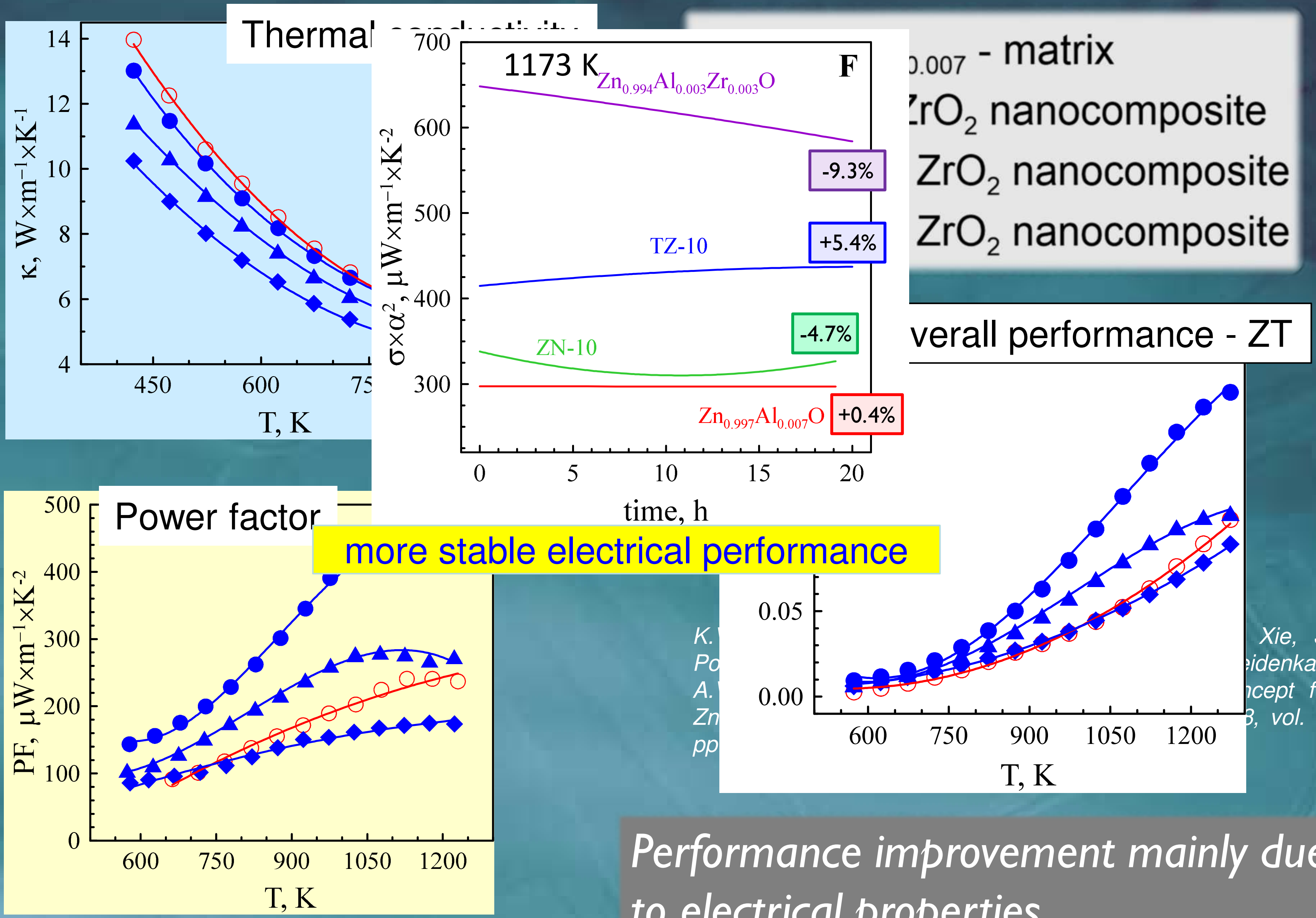


K.V. Zakharchuk, M. Widenmeyer, D.O. Alikin, W. Xie, S. Populoh, S.M. Mikhalev, A. Tselev, J.R. Frade, A. Weidenkaff, A.V. Kovalevsky, A self-forming nanocomposite concept for ZnO-based thermoelectrics, ***J. Mater. Chem. A****, 2018, vol. 6, pp.13386-13396.*

Self-forming composite….

$Zn(Al)O+ZrO_2 \rightarrow Zn(Al,Zr)O+ZnAl_2O_4$

ZnO – self-organization in composites



.007 - matrix

rO$_2$ nanocomposite

ZrO$_2$ nanocomposite

ZrO$_2$ nanocomposite

more stable electrical performance

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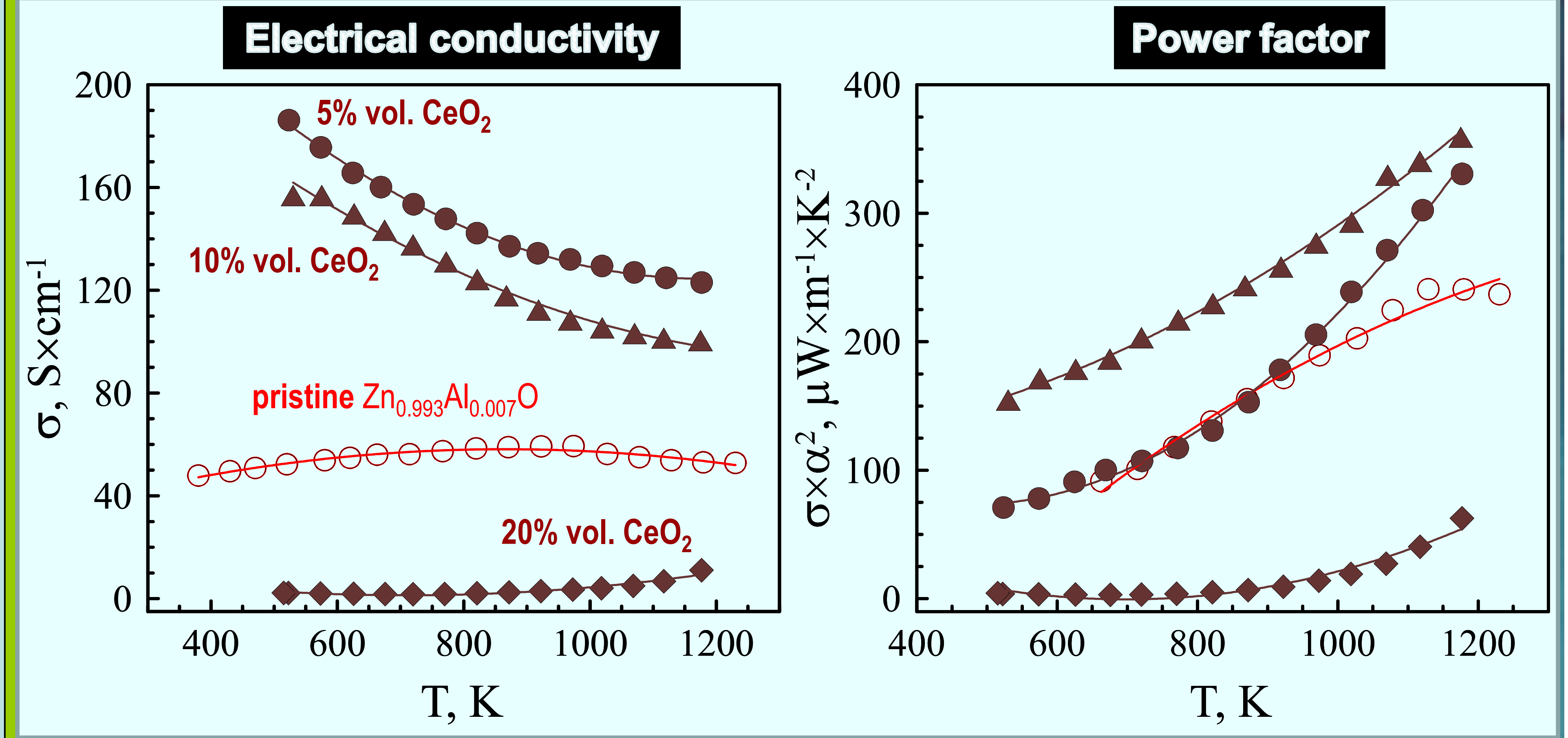
Po ... eidenkaff,
A.V ... ncept for
Zn ... B, vol. 6,
pp

Performance improvement mainly due to electrical properties…

ZnO – self-organization in composites

Zn(Al)O + CeO_2 nanoparticles

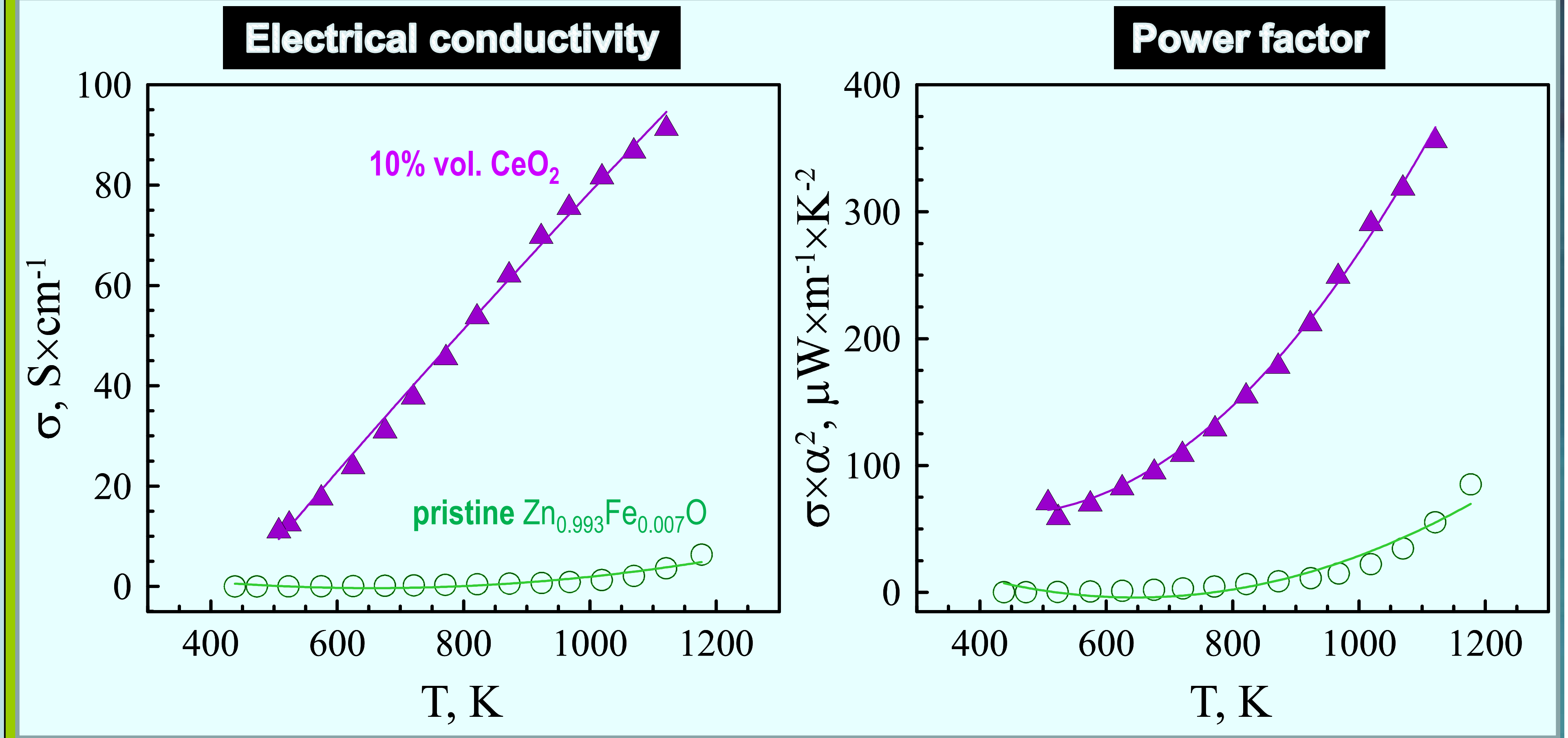
Mixing and high-temperature sintering



ZnO – self-organization in composites

$Zn(Fe)O + CeO_2$ nanoparticles

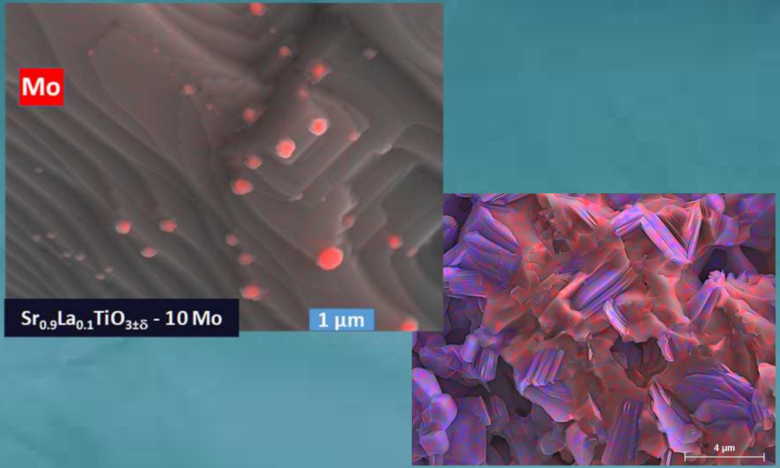
Mixing and high-temperature sintering



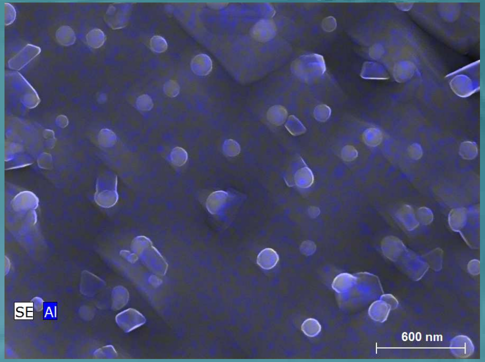
Conclusions

Oxides do offer additional possibilities for designing good thermoelectrics

- Unique redox properties



- Complex behavior on substitution and self-organization



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COMPETE
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