Odlični v znanosti 2013

SLOVENSKI 9. FORUM INOVACIJ

INOVATIVNI POTENCIAL SLOVENIJE

Oksidni termoelektriki:

več kot le še ena zelena energija

Odsek za raziskave sodobnih materialov k9 IJS

SPIRIT SLOVENIJA JAVNA AGENCIJA | I FEEL SLOVENIA

REPUBLIKA SLOVENIJA
MINISTRSTVO ZA GOSPODARSKI RAZVOJ IN TEHNOLOGIJO

JAVNA AGENCIJA ZA RAZISKOVALNO DEJAVNOST REPUBLIKE SLOVENIJE

Odlični v znanosti

CHEMISTRY OF MATERIALS

Article

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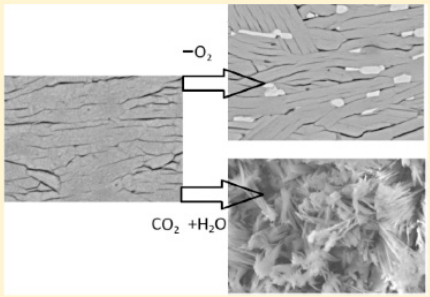
Chemical Decomposition as a Likely Source of Ambient and Thermal Instabilities of Layered Sodium Cobaltate

Damjan Vengust,*[,†] Bostjan Jancar,[†] Andreja Sestan,[†] Maja Ponikvar Svet,[‡] Bojan Budic,[§] and Danilo Suvorov[†]

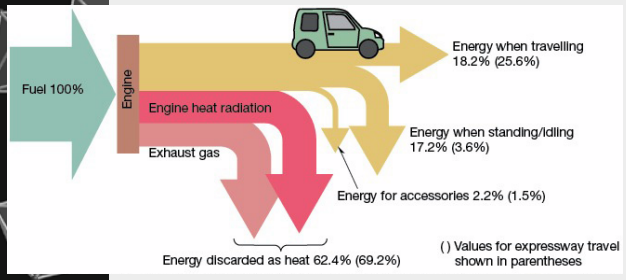
[†]Advanced Materials Department and [‡]Department of Inorganic Chemistry and Technology, Jozef Stefan Institute, Jamova 39, 1000 Ljubljana, Slovenia

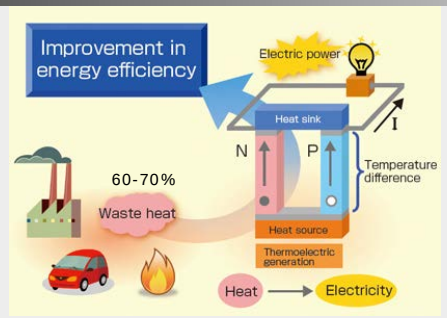
[§]Laboratory for Analytical Chemistry, National Institute of Chemistry, Hajdrihova 19, 1000 Ljubljana, Slovenia

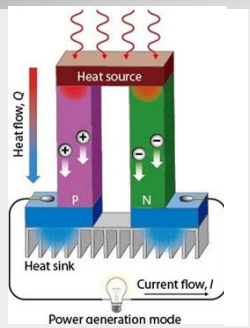
ABSTRACT: With the application of an oxygen atmosphere, we synthesized a highly textured sodium cobaltate, $Na_{0.75}CoO_2$. At the same time, we identified its peculiarities that influence the measured parameters to a degree that poses serious questions about this material's potential for use. We have systematically studied the influence of humidity on the ceramic pellets and identified the conditions under which the material completely deteriorates. By performing microstructural and thermal analyses, coupled with a determination of the evolved gases, we identified the chemical reactions that are involved in this process. In addition, we re-examined the performance of sodium cobaltate under the working conditions and found that the material behaves in a manner different from the expected manner. We have shown, in contrast to many other reports, that the oxygen vacancies do not play a very important role because the changes in the physical parameters can be attributed to the reduction of cobalt and consequently to the formation of CoO inclusions, which increases the amount of sodium in the sodium cobaltate lattice.

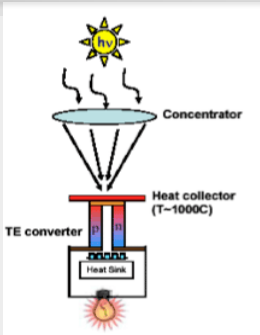


KEYWORDS: *thermoelectric oxide materials, hydrated $Na_{0.75}CoO_2$, oxygen vacancies, CoO*

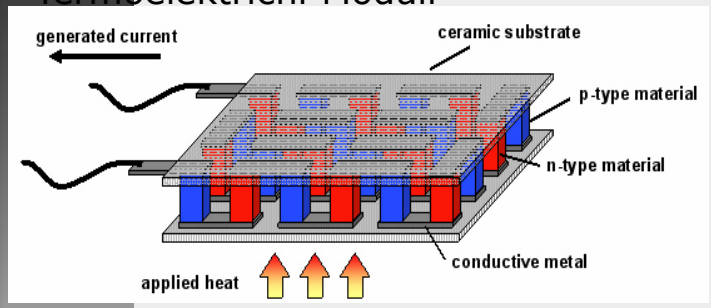


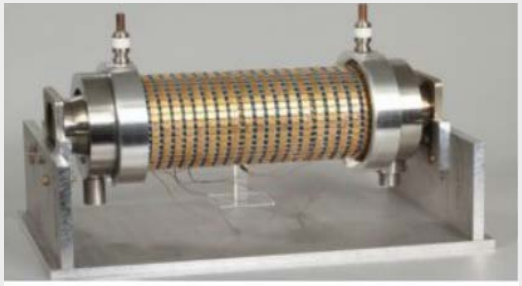






Termoelektrični Moduli

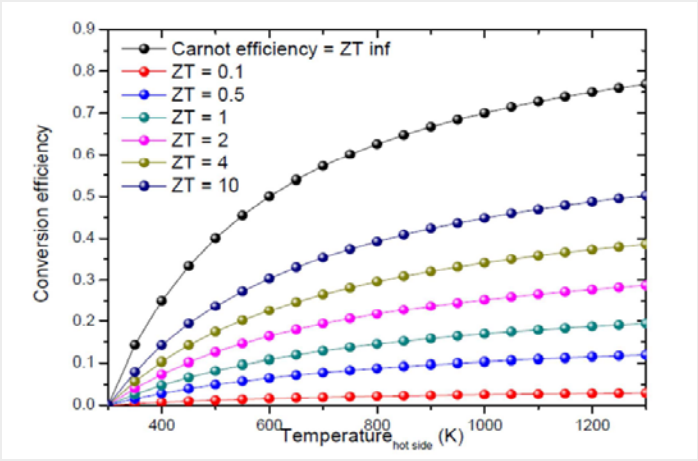


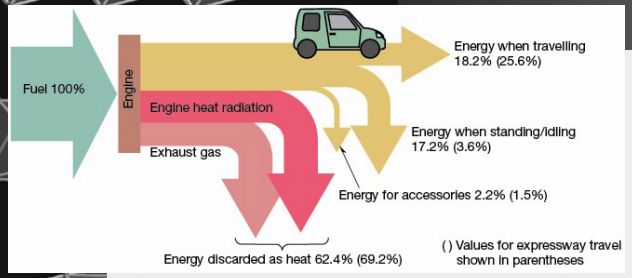


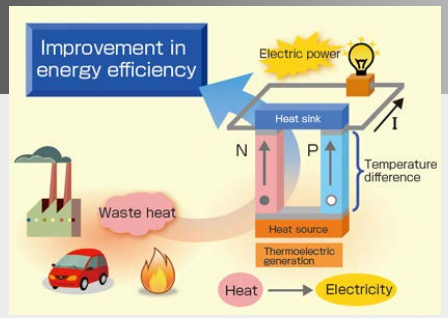
Thermoelektrični Materiali

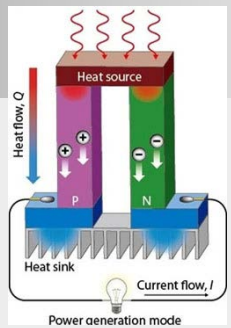
$$zT = \frac{\alpha^2 \sigma}{\lambda} T$$

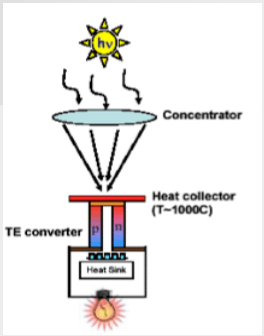
- Visok Seebeck–ov Koeficient
- Visoka Električna prevodnost
- Nizka Termična prevodnost





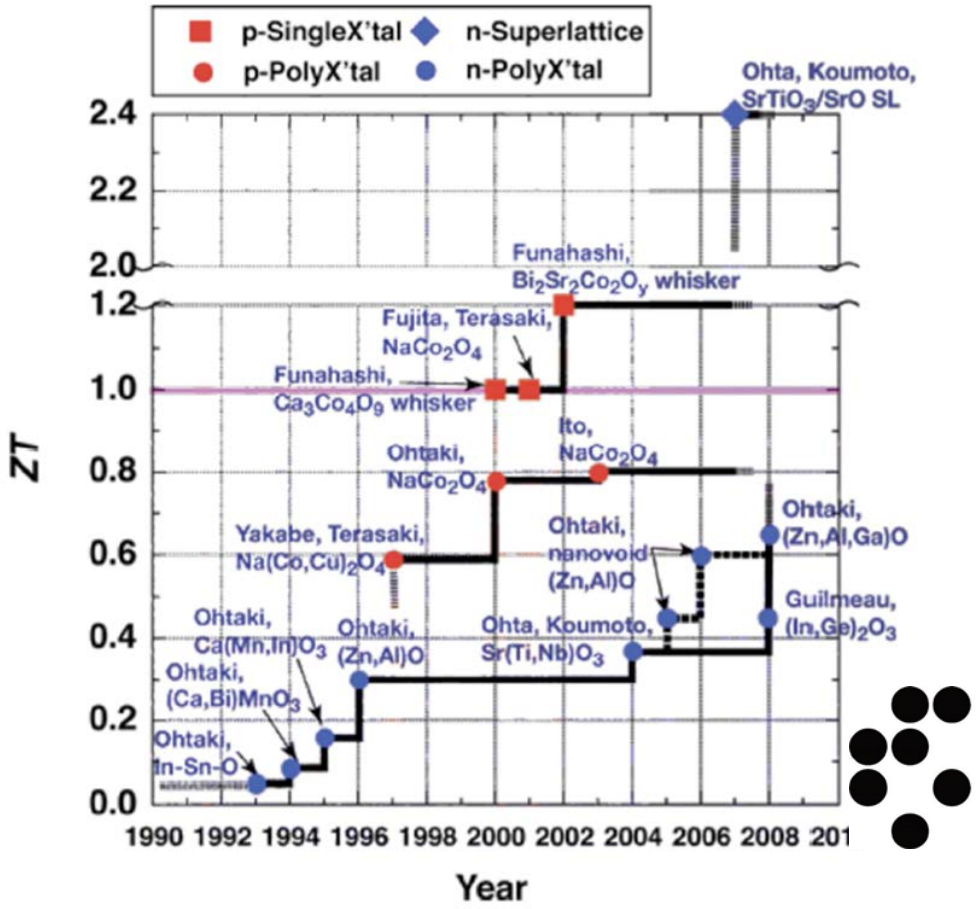


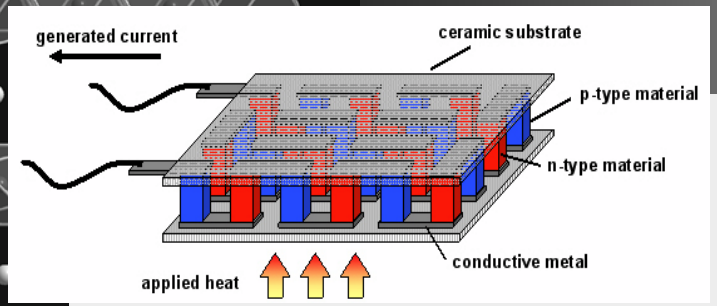


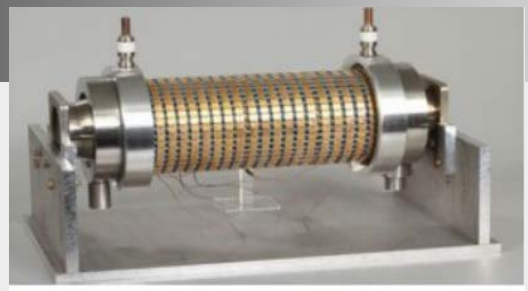


PbSe PbTe
$_zT \sim 2$

Oksidni termo-elektriki
???

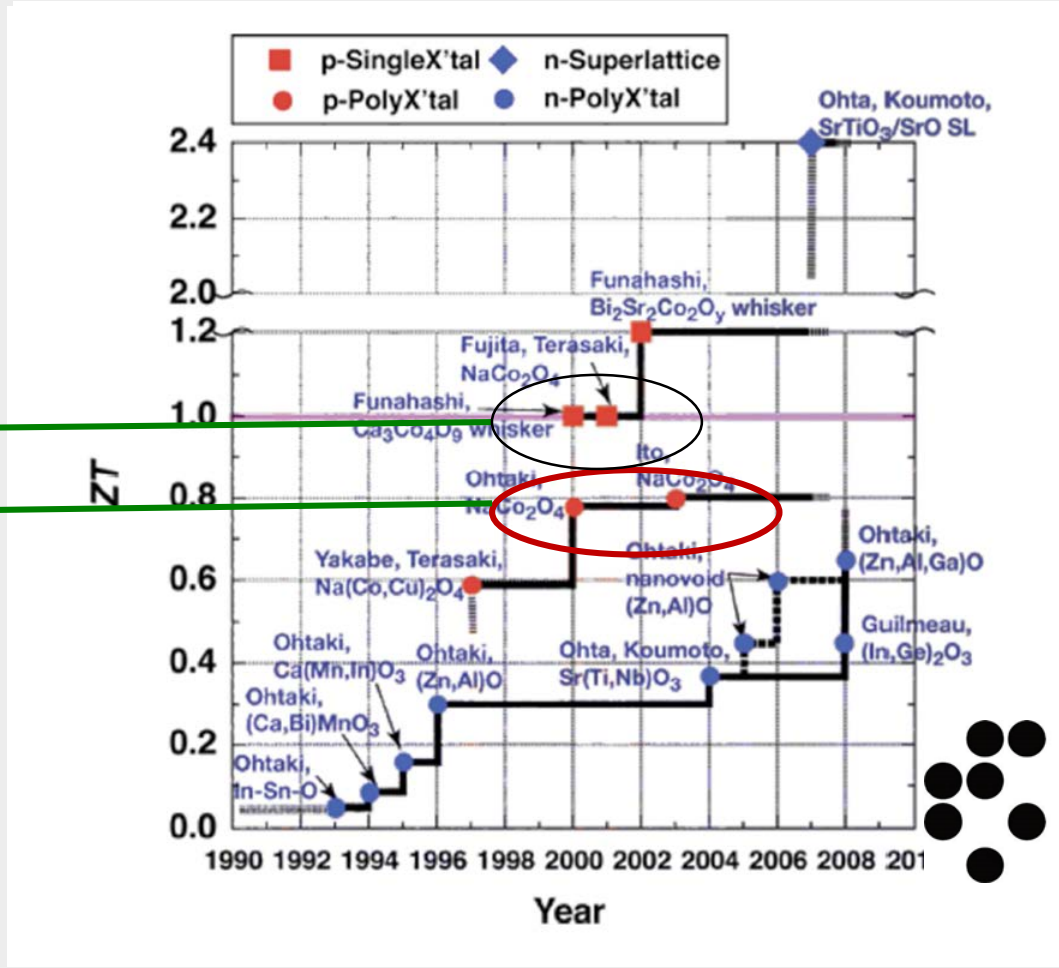






Monokristal

Keramika



Pogoji pri katerih pride do samo-urejanja

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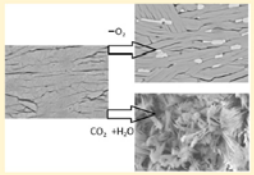
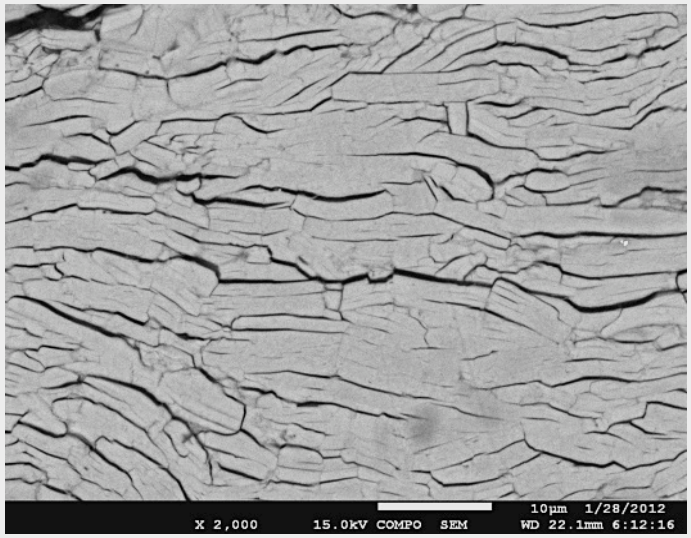
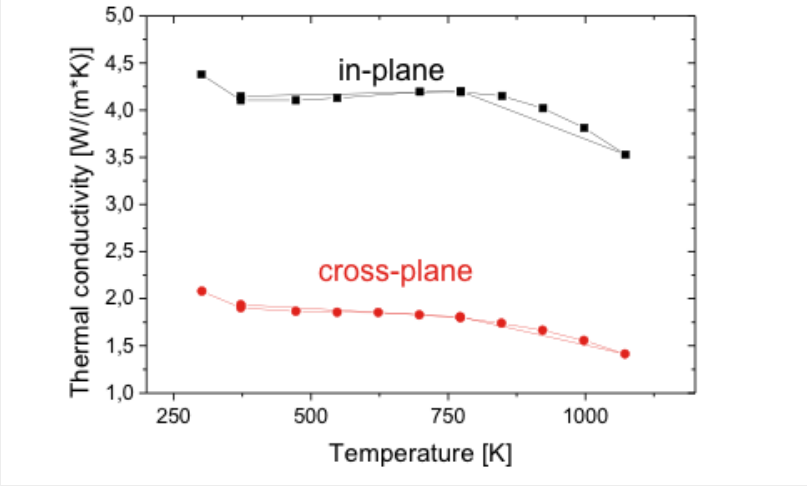
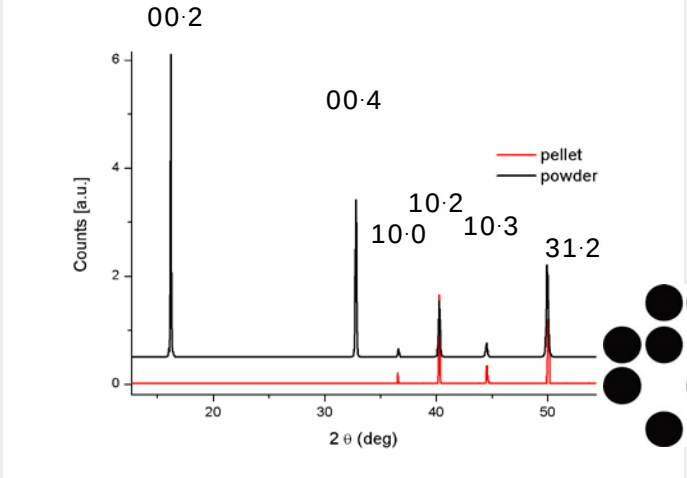


KEYWORDS: *thermoelectric oxide materials, hydrated $Na_{0.75}CoO_2$, oxygen vacancies, CoO*

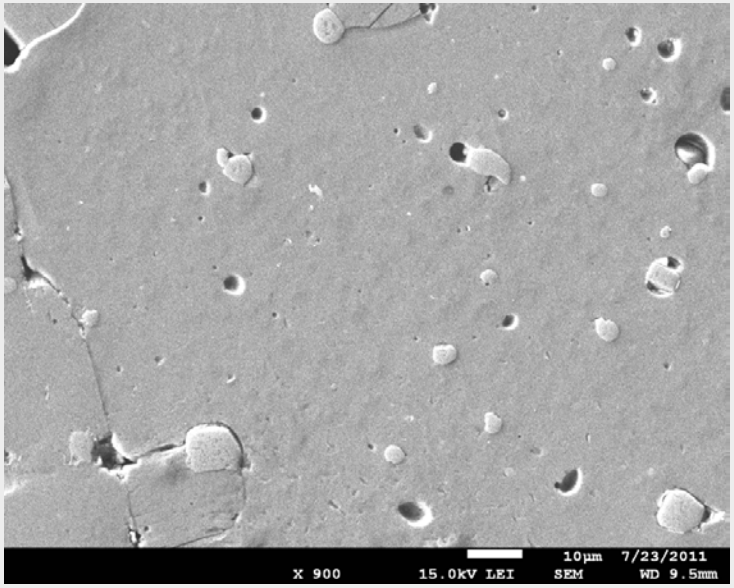


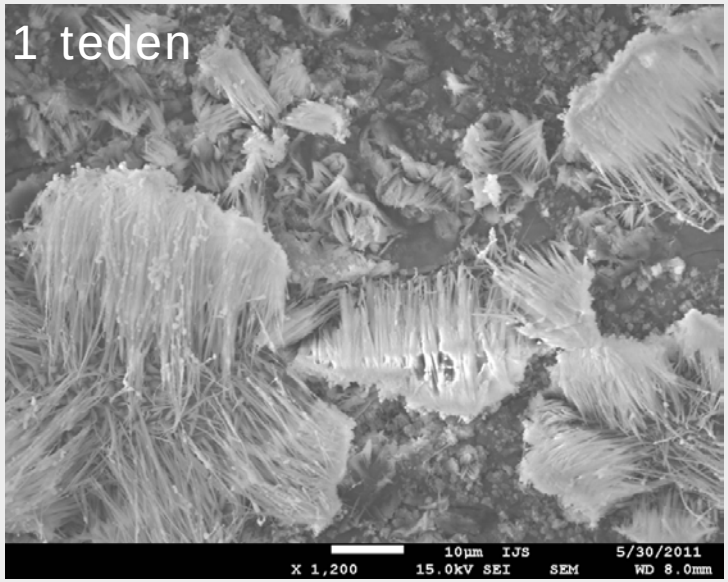
"in-plane"

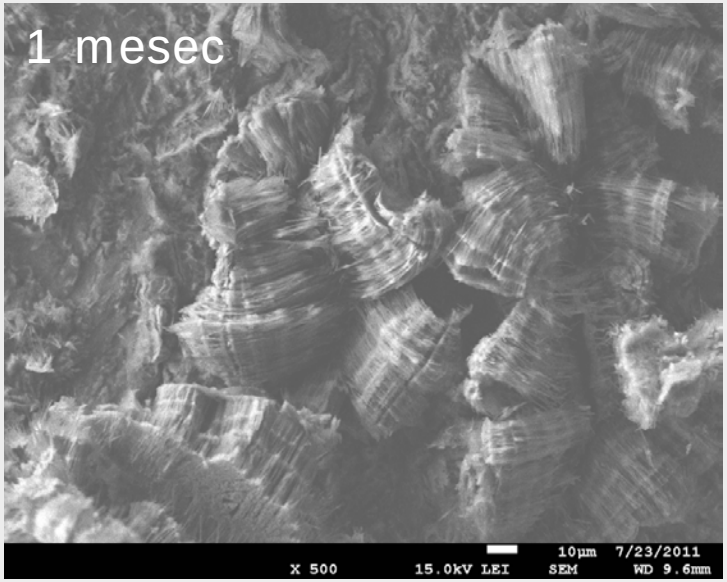




Kemijski mehanizmi razpada





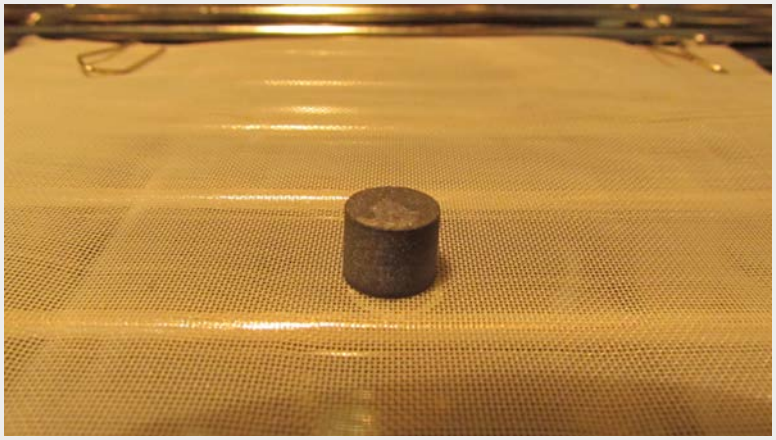


$$Na_xCoO_2 + 2yH_2O \rightarrow Na_{x-y}(H_3O)_yCoO_2 + yNaOH$$

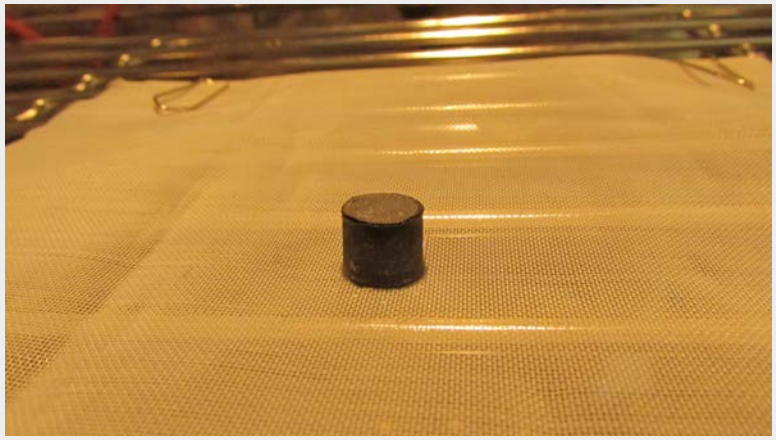
$$2NaOH + CO_2 \rightarrow Na_2CO_3 \cdot H_2O$$

$$3NaOH + 2CO_2 + H_2O \rightarrow Na_3(CO_3)(HCO_3) \cdot 2$$

Umetno staranje

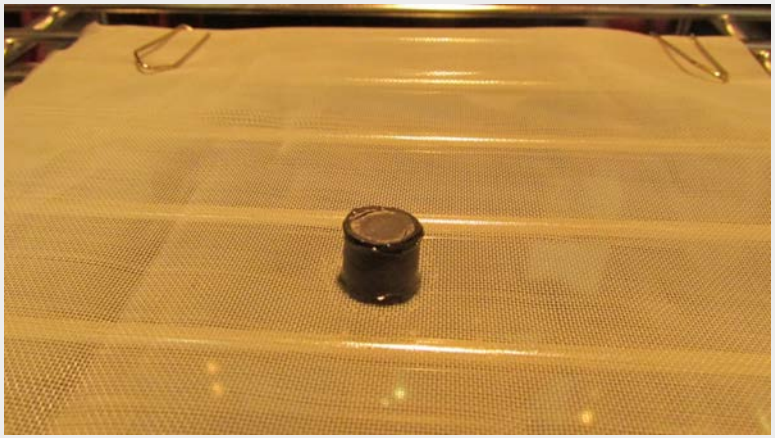


0 h



24h

T = 30ºC, Φ = 80%



48h

72h

Kompozitni material(razviti na našem odseku)

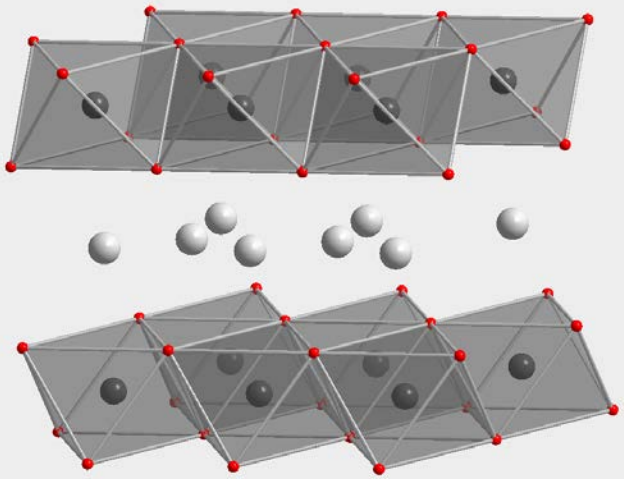
$Na_xCoO_{2+\delta}$

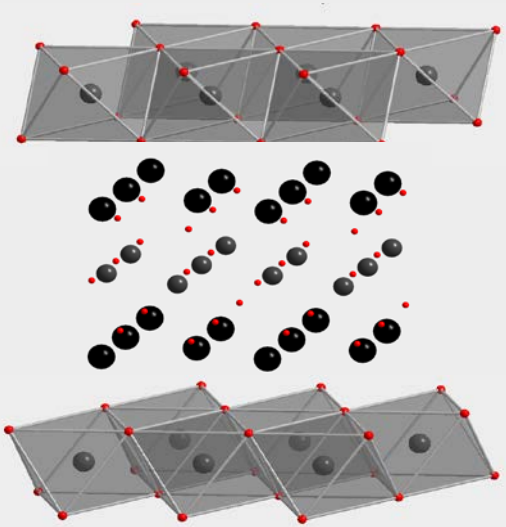
$Ca_3Co_4O_{9+\delta}$

1- single crystal
0.8 - ceramics

zT
@700ºC

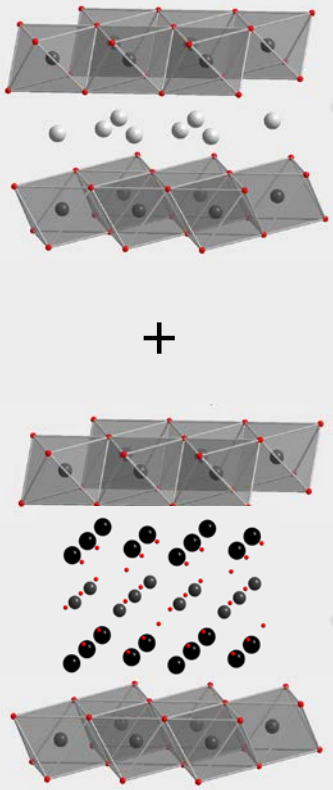
0.9 - single crystal
0.6 - ceramics

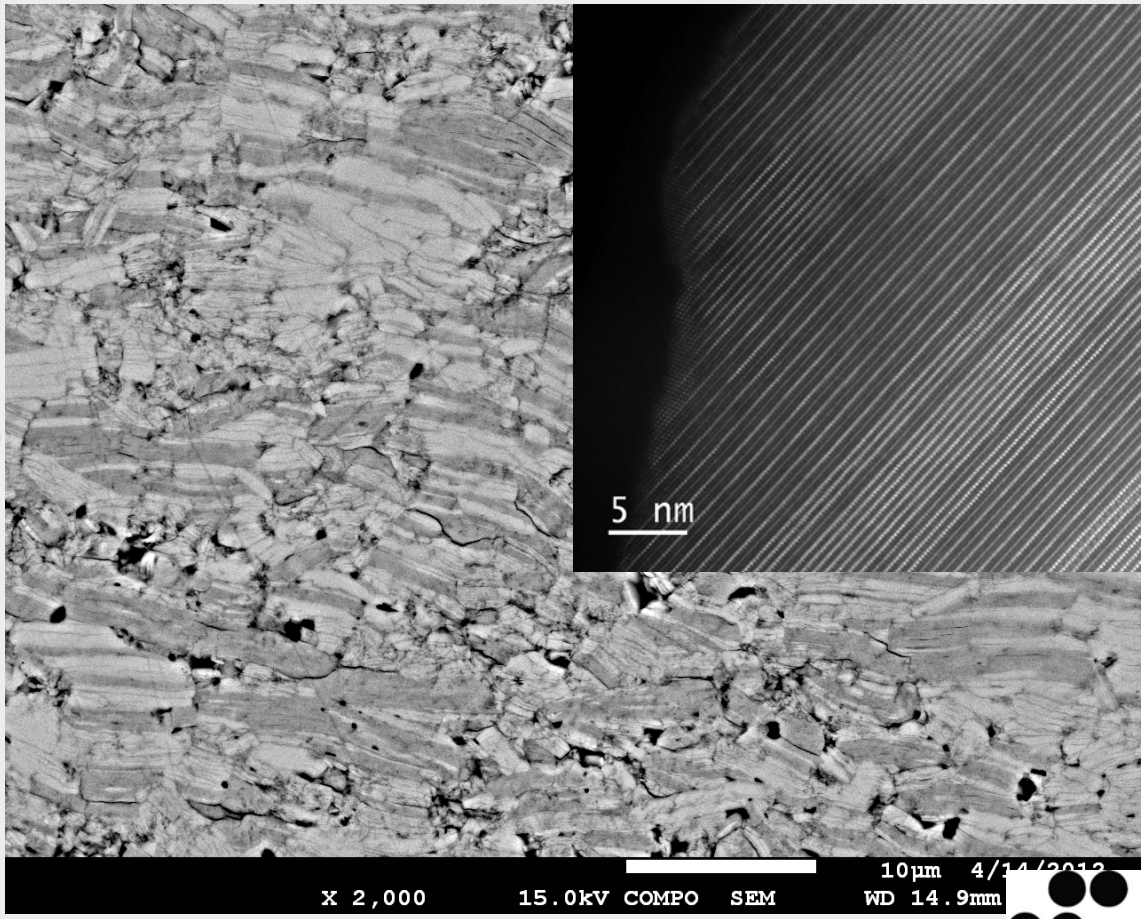




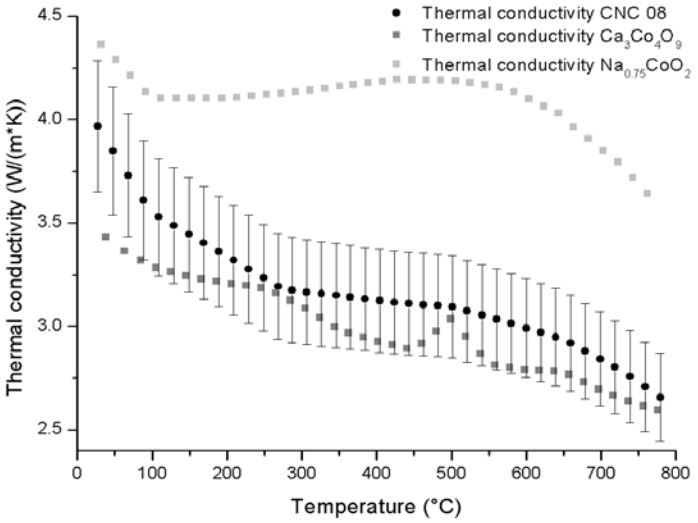
Pogoji pri katerih pride do samo-urejanja

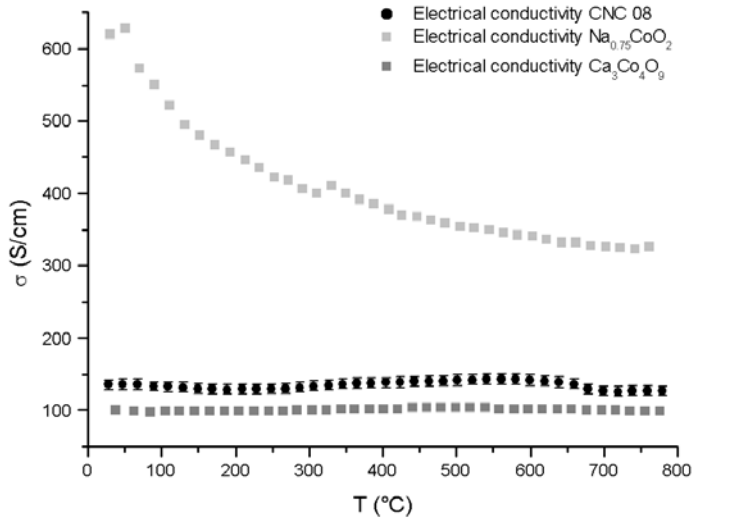
$Ca_{3-x}Na_xCo_4O_9$

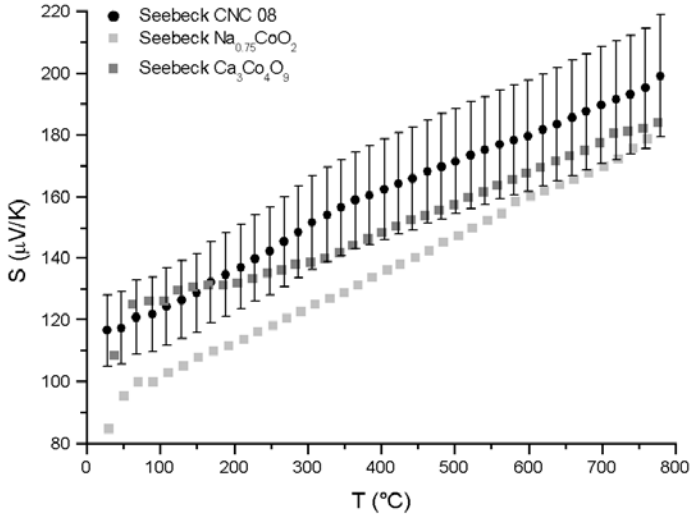


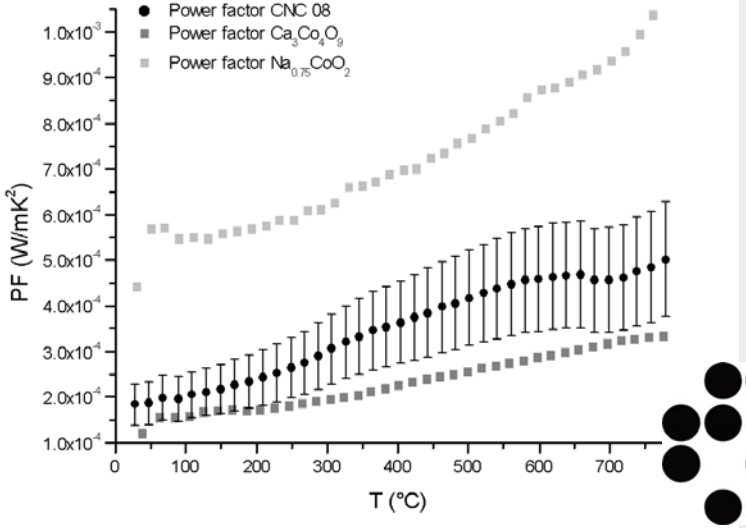


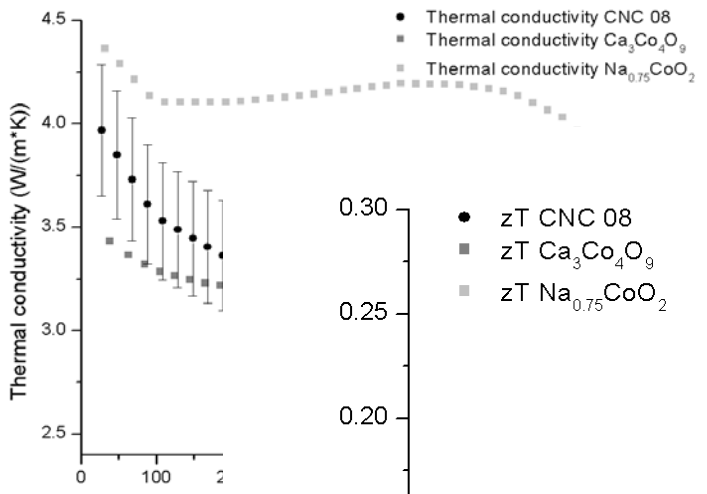
X = 0.3, 0.5, 0.8, 1.5, 2.5

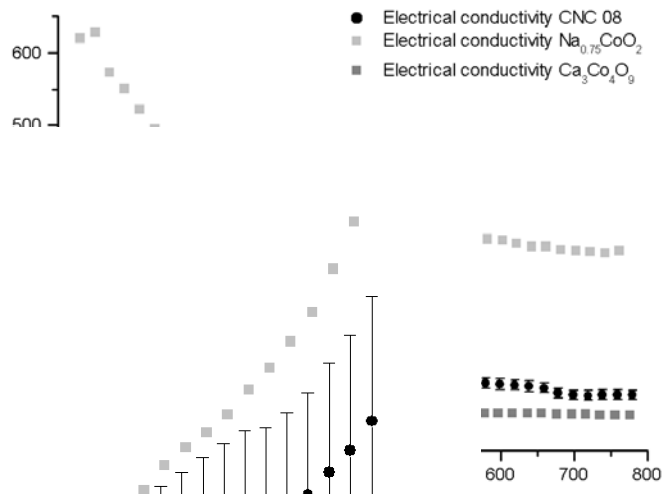

Thermal conductivity CNC 08
Thermal conductivity $Ca_3Co_4O_9$
Thermal conductivity $Na_{0.75}CoO_2$
Thermal conductivity (W/(m*K))
Temperature (°C)

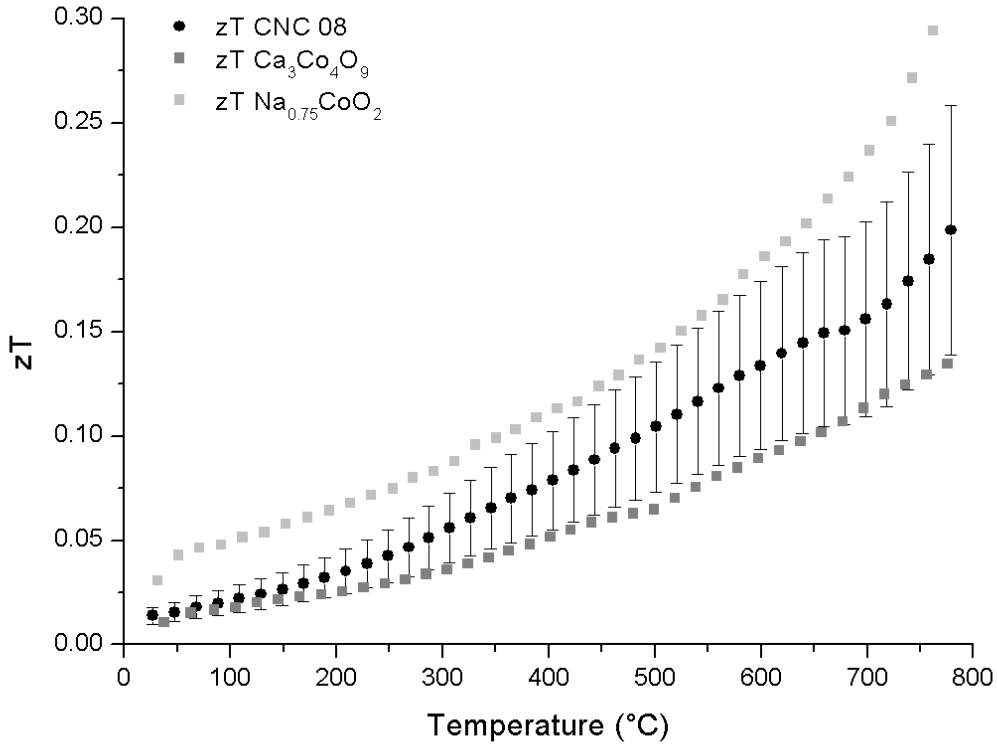

Electrical conductivity CNC 08
Electrical conductivity $Na_{0.75}CoO_2$
Electrical conductivity $Ca_3Co_4O_9$
σ (S/cm)
T (°C)

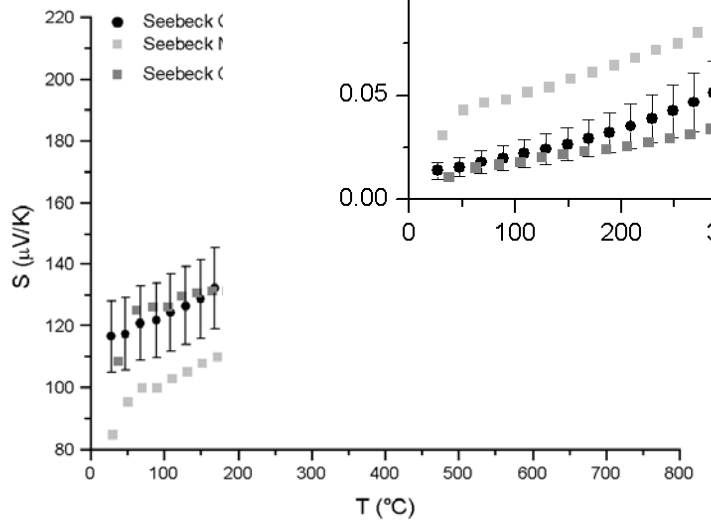

Seebeck CNC 08
Seebeck $Na_{0.75}CoO_2$
Seebeck $Ca_3Co_4O_9$
S (μV/K)
T (°C)

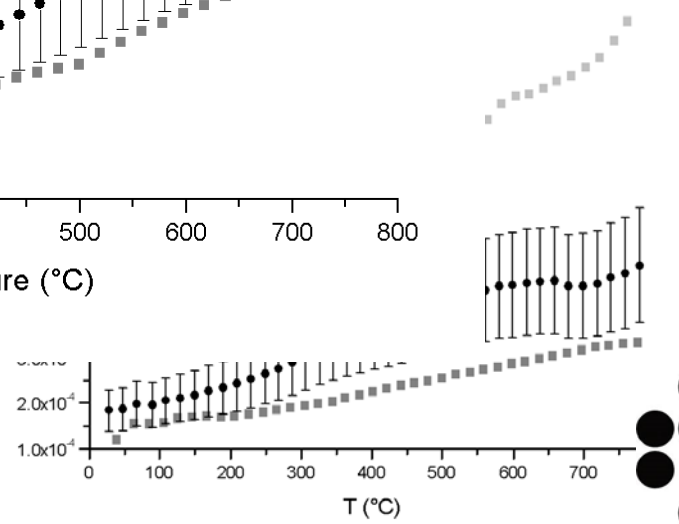

Power factor CNC 08
Power factor $Ca_3Co_4O_9$
Power factor $Na_{0.75}CoO_2$
PF (W/mK²)
T (°C)


Thermal conductivity CNC 08
Thermal conductivity $Ca_3Co_4O_9$
Thermal conductivity $Na_{0.75}CoO_2$
Thermal conductivity (W/(m*K))
4.5
4.0
3.5
3.0
2.5
0
100


Electrical conductivity CNC 08
Electrical conductivity $Na_{0.75}CoO_2$
Electrical conductivity $Ca_3Co_4O_9$
600
500
600
700
800

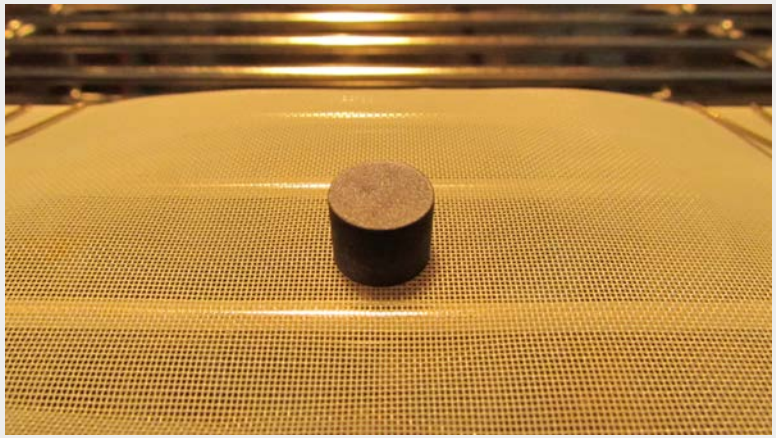

zT CNC 08
zT $Ca_3Co_4O_9$
zT $Na_{0.75}CoO_2$
zT
0.30
0.25
0.20
0.15
0.10
0.05
0.00
0
100
200
300
400
500
600
700
800
Temperature (°C)


Seebeck C
Seebeck N
Seebeck C
S (μV/K)
220
200
180
160
140
120
100
80
0
100
200
300
400
500
600
700
800
T (°C)

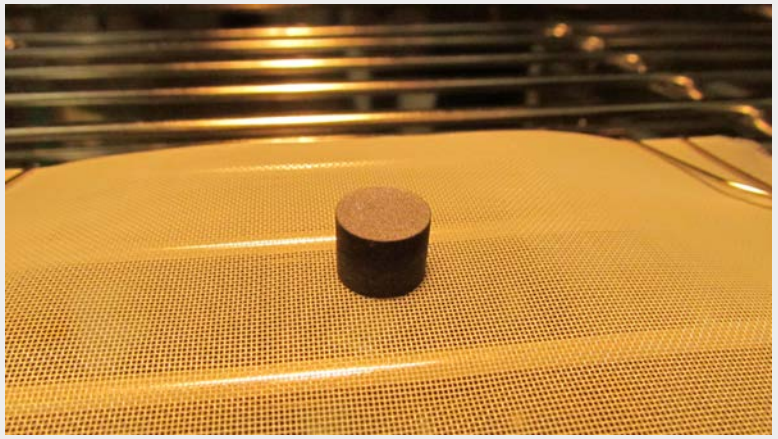

$2.0x10^{-4}$
$1.0x10^{-4}$
0
100
200
300
400
500
600
700
T (°C)

Umetno staranje vraščene faze

T = 30ºC, Φ = 80%

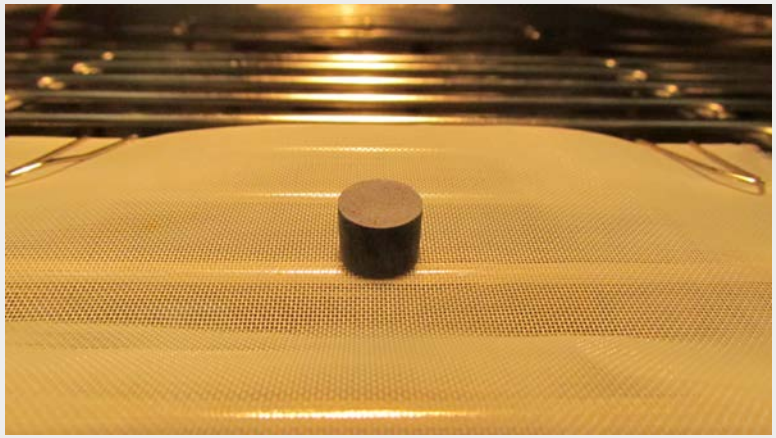


0 h

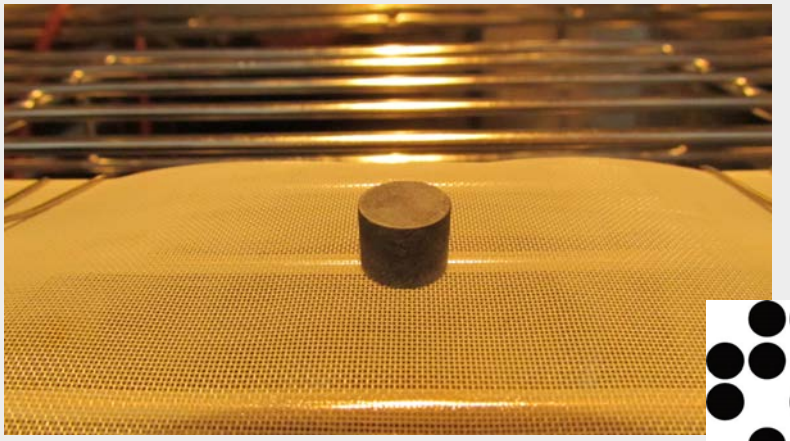


24h

!!!!!STABILNI!!!!



48h



72h

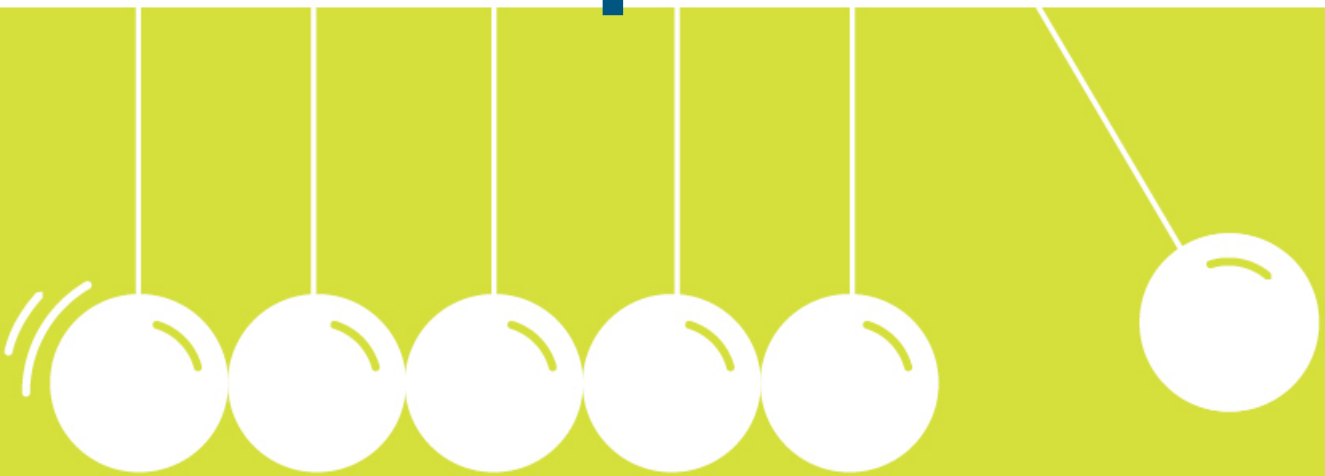
Zaključek

- Raziskali in opisali smo mehanizme razpada $Na_{0,75}CoO_2$ in dokazali, da je nezaščiten za visokotemperaturne termoelektrične aplikacije neprimeren.
- Ugotovili smo da lahko z sintezo kompozitnega TE na osnovi Na Ca koblatata učinkovito zavremo razpad. Usmerjenost oksidnih plasti in njihovo vraščanje med sintranjem še dodatno izboljša končne lastnosti takšnega materiala.

SLOVENSKI 9. FORUM INOVACIJ

INOVATIVNI POTENCIAL SLOVENIJE

Hvala za vašo pozornost



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