Introduction to Oxide Thermoelectric

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Course: Solid state 672
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Outline

- 1-Why we are interested in Thermoelectric Oxides?
- 2-Historical review
- 3-Thermoelectric and Thermomagnetic Effects
- 3.1-Seebeck Effect
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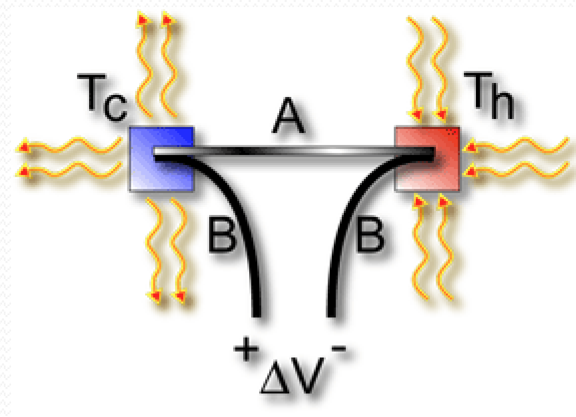
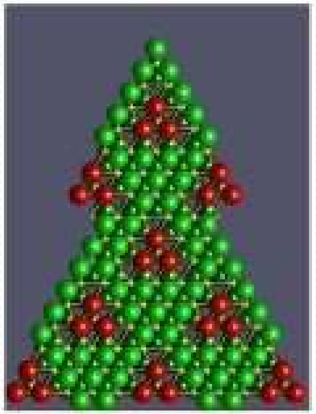
- Example of Thermoelectric Oxides
- Conclusion and Summary
- References.



Why?

- Oxide materials are considered to be promising for future thermoelectric applications

- Thermoelectric materials are candidates for devices, which can directly convert heat into electrical energy, electricity can be used for heat pumping or refrigeration by using Seebeck Effect.



- Clean Power generator without any adverse environmental affects, such as the release of exhaust gases or noise pollution caused by driving parts.

- Because of their thermal Durability and chemical Stability, Oxide material are better than Chalcogenide material Such as Bi_2Te_3, which one of the more effective materials for thermoelectric energy conversion.

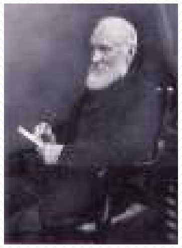
A Quick Historical review

- In 1821, Seebeck discovered that a voltage appears when two different conductors are joined together and the junction is heated and if compass needle placed in the vicinity of closed loop , it deflect. The phenomenon has long been used in the measurement of temperature.
- In the same year, he could have converted thermal energy into electricity with an efficiency of 3 percent.

- In 1833, Peltier observed temperature changes in the vicinity of the junction between dissimilar conductors when a current passed.

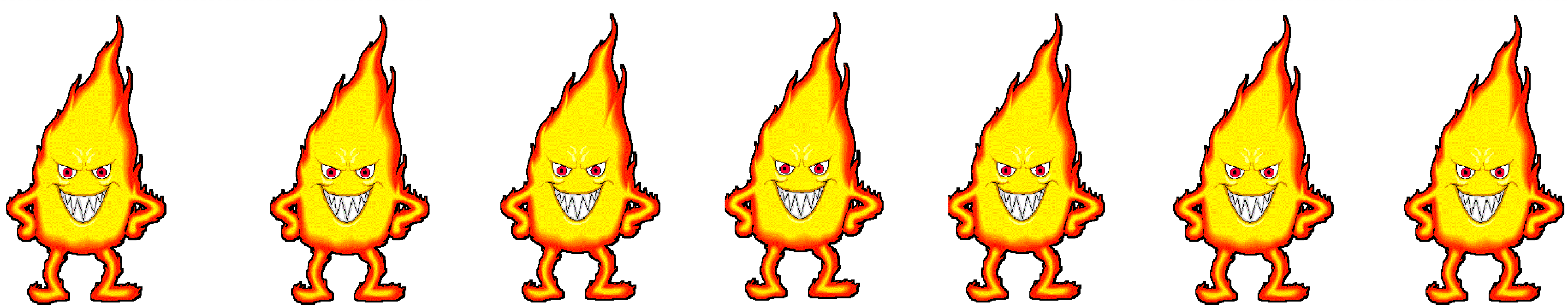
- In 1838, lenz explain the true nature of Peltier effect, Lenz concluded that, depending on the direction of Current flow, heat is absorbed or generated at a junction between two conductors.
- Lenz demonstrated his explanation by freezing water at a bismuth-junction and melting the ice by reversing the direction flow.

- Lack of interest and slow progress in thermoelectric application, era of electromagnetism.
- In 1851 W.Thomson established a relationship between the Seebck and Peltier coefficient and predicted the existence of a third thermoelectric effect, Thomsone effect .



- In 1909 and 1911 Altenkirch gave satisfactory theory of thermoelectric generation and refrigeration and showed that good thermoelectric material should possess large Seeback coefficient with low thermal conductivity, to retain the heat at the junction, and low electrical resistance to minimize Joule heating[1].

- Oxide materials had been ignored for a long time by the thermoelectric community, but the discovery of Na_xCoO_2 as a strong candidate thermoelectric material in 1997 lit a fire in the researchers' minds to explore high efficiency oxide materials[2].



- It was found that layer-structured Oxide $NaCo_2O_4$ was a highly effective thermoelectric material, and the dimensionless figure of merit ZT of single crystal of $NaCo_2O_4$ was shown to exceed unity, which standard value for practical applications .

- Ca $_2Co_2O_5$ and related materials were found to be excellent thermoelectric materials.

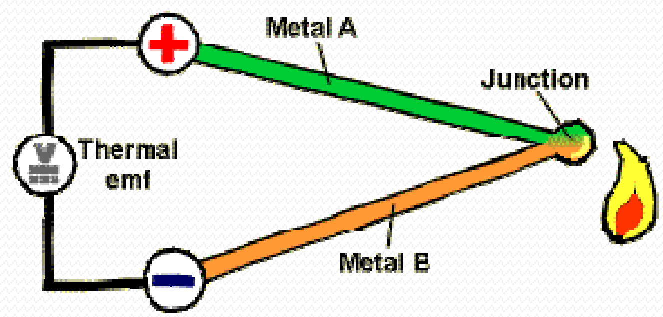
- These new Oxide thermoelectric materials are all p-type semiconductors. In general, n-type materials are not as effective as p-type oxides[3].

Thermoelectric and Thermomagnetic Effects

- Seeback Effect
- A and B are maintained at different temperatures T_1 and T_2 and T_1 is grater than T_2 an open circuit electromotive force (emf), V is developed

$$V = \alpha(T_1 - T_2)$$

- α is the symbol for the Seebeck coefficient, S is also sometimes used and the Seebeck coefficient referred to as the thermal emf or thermopower.



- Peltier Effect
- The reverse situation is considered with an external emf source applied. The Peltier coefficient is defined, for the same pair of conductors, by the relation:

$$\pi = \frac{q}{I}$$

- Here q is the rate of heating or cooling at one of the junctions when an electric current I passes round the circuit.

- Thomson Effect

- It relates to the rate of generation of reversible heat q which results from the passage of a current along a portion of a single conductor along which there is a temperature difference ΔT. Providing the temperature difference is small,

- where β is the Thomson coefficient.

$$q = \beta I \Delta T$$

- The Kelvin Relationships
- The above three thermoelectric coefficients are elated by the Kelvin relationships:

$$\frac{d\alpha_{ab}}{dT} = \frac{\beta_a - \beta_b}{T}$$

- The Quality of the material measured by the Figure of Merit for thermoelectric devices is defined as

$$ZT = \frac{\sigma S^2}{\lambda} T$$

- where σ is the electrical conductivity, λ is the thermal conductivity, and α or S is the Seebeck coefficient or thermopower

Power factor is

$$\sigma S^2 = \frac{S^2}{\rho}$$

- Modern commercial Peltier devices exhibit a *ZT of ≈0.9 at room temperature which corresponds* to a Carnot efficiency of 10%. It is noteworthy to mention that for solid-state home-refrigeration to be realized thermoelectric devices with a Carnot efficiency of 30% are needed, i.e., thermoelectric materials should be used with *ZT≥4 [4]*.

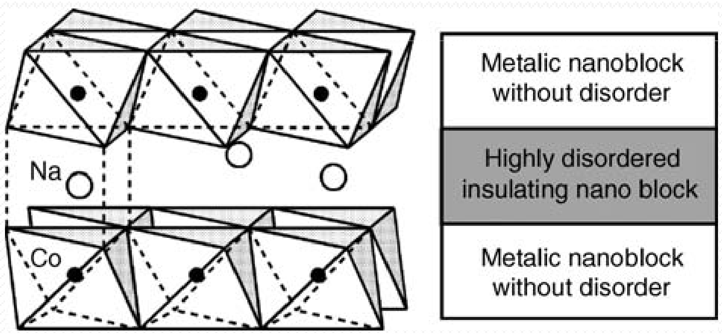
- In order to achieve a high figure-of-merit, we have to be able to control both electron and phonon transport to realize high electrical conductivity, large thermopower, and low thermal conductivity simultaneously this can only be done in a complex crystalline field such as Layered cobalt oxides like sodium cobaltite and calcium cobaltite.

- In these oxides, CoO_2 nanosheets possessing a strongly correlated electron system serve as electronic transport layers, while sodium ion nanoblock layers or calcium cobalt oxide misfit layers serve as phonon scattering regions to give low thermal conductivity. Thus, if more than two kinds of unit nanoblocks with different compositions and symmetries are integrated into hybrid crystals or superlattices, each block can play its own role to generate a specific function and hence electron system and phonon system can be independently controlled, and these functions are combined to give rise to high TE performance

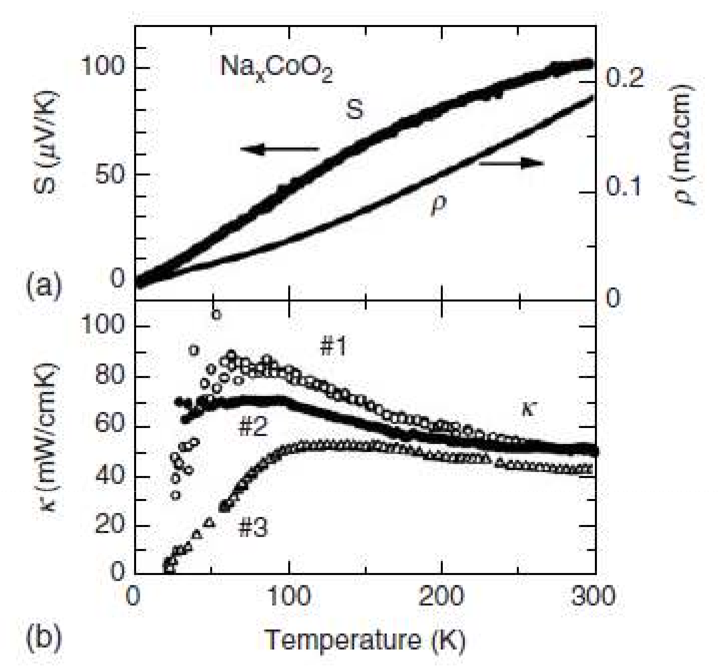
COMMON TE OXIDES

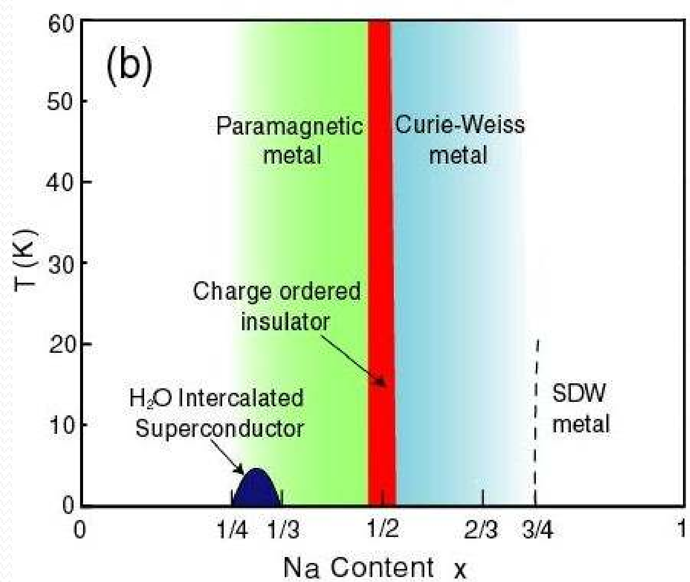
Na_xCoO_2

- large thermoelectric power and a low resistivity in polycrystalline
- The power factor of a single crystal Na_xCoO_2 exceeded that of Bi_2Te_3



Crystal structure of Na_xCoO_2 and the corresponding nanoblock structure





Thermoelectric properties of Na$_x$CoO$_2$

-ρ =200 μΩ cm at 300 K(is metallic)

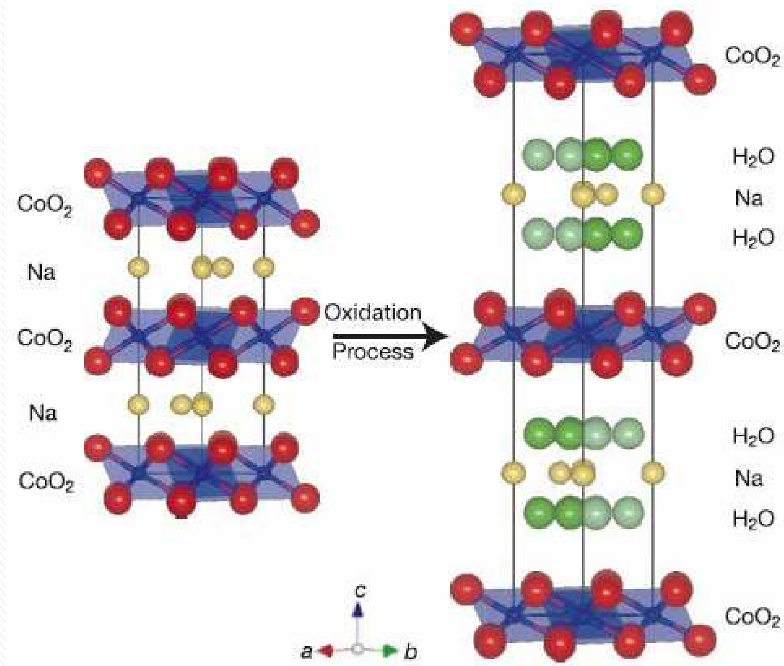
-The thermopower (S) is large (100 μV K at 300 K)

-The power factor=50 μ W K^{-2} cm^{-1} at 300 K.

- ZT reached unity at 800 K

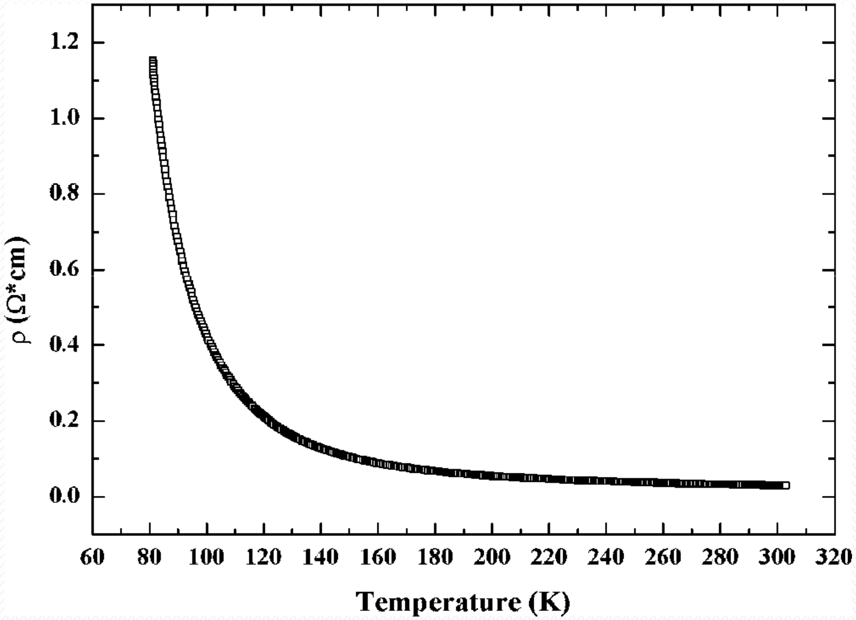
Electronic phase diagram of Na$_x$CoO$_2$ as a function of the Na content x.

Very recently, superconductivity at , 5 K has been discovered in H_2O-absorbed Na_xCoO_2 (x = 0.35) This is the first superconductor in Co oxides, and many researchers have rushed into this field.



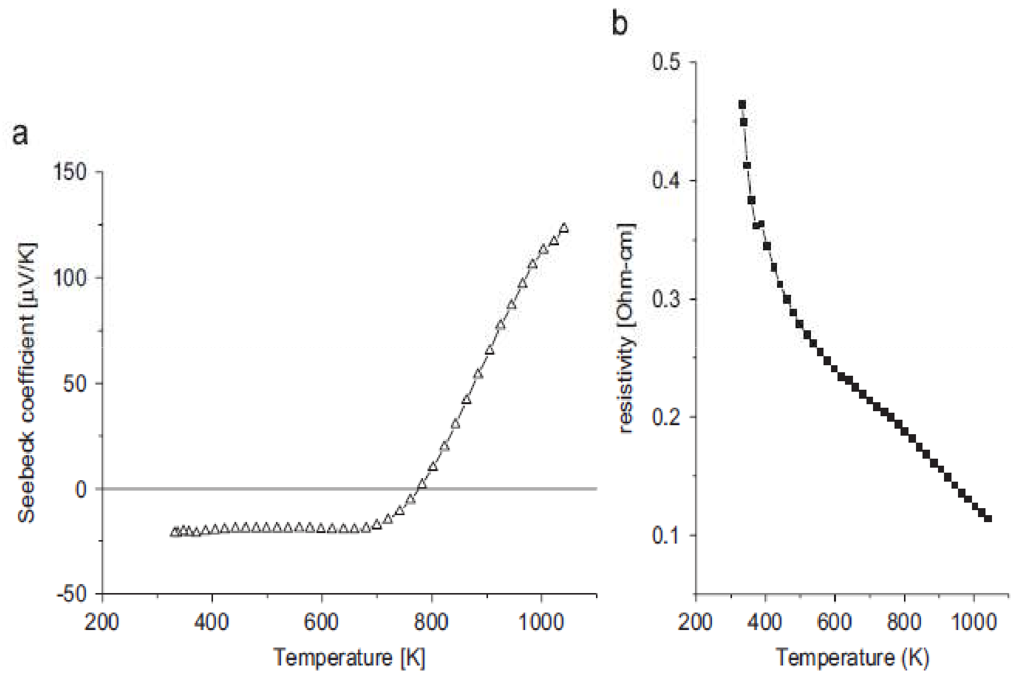
In March 2003 Takada *et al.* *reported that* $Na_xCoO_{2.y}H_2O$ *(x ~ 0.35, y ~ 1.3) is a superconductor with a* T_c *of about 5 K. This compound consists of 2-dimensional* CoO_2 *separated by a thick insulating layer of* Na^+ *ions and* H_2O *molecules.*

- $La_{0.95}Sr_{0.05}CoO_3$, an efficient room-temperature thermoelectric oxide[4]



Temperature dependence of the resistivity for the polycrystalline bar-shaped sample of $La_{0.95}Sr_{0.05}CoO_3$. Note that it exhibits a room temperature resistivity of 27 mΩcm.

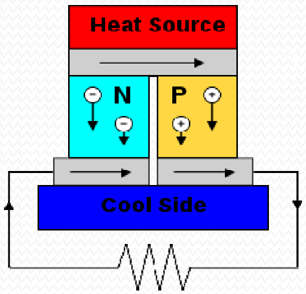
• $La_{0.8}Ca_{0.2}MnO_3$



Thermopower (a) and resistivity (b) in the temperature range $300\,K < T < 1200\,K$ of the LCMO thin film.

Conclusion and Summary

- Challenges to create novel oxide thermoelectric have been motivated recently and extensive investigations from various viewpoints of materials design are being carried out.
- The Seebeck and Peltier effects are thermodynamic phenomena offering alternative pathways for power generation and refrigeration based solely on solid state elements
- Geothermal and solar heat can be directly converted into electricity by using thermoelectric generators.
- The use of geothermal or solar heat as energy source for a thermoelectric generator is an attractive and environmentally clean (CO_2-free) proposal to generate electrical power
- Thermoelectric Oxides are
- 1-High thermal and chemical stability
- 2-No toxicity
- It is difficult to control an electronic system and a phonon system simultaneously in a single crystalline field.



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