Introduction to Thermoelectric Oxides

Amal al-Wahish

Advance Solid state 672

Instructor: Elbio Dagotto

Spring 2009

Department of Physics and Astronomy,

University of Tennessee

wahish@utk.edu

(Dated: May 12, 2009)

Abstract

Since the Geothermal and solar heat can be directly converted into electricity by using thermoelectric generators, thermoelectric oxides are potential materials to improve the efficiency of these devices. This work give an introduction to the Thermoelectric Oxides materials, starting with the basic of thermoelectric laws, including Seebeck effect, Peltier effect, and Thomsone effect and Finally give examples of thermoelectric oxides and their properties.

I. INTRODUCTION

Thermoelectric Oxides (TE) are clean power generator without any adverse environmental affects, such as the release of exhaust gases or noise pollution caused by driving parts. Because TE are inexpensive, harmless, have thermal Durability, and chemical Stability at high temperature in air even at $1000K$. Oxide material are better than Chalcogenide material Such as Bi_2Te_3, for many practical applications by take in to account the previous characteristics.

A. Quick Historical Review

Several research groups have a goal of achieving higher performance thermoelectric materials for small-scale refrigeration or power generation. Refrigeration aspects include applications such as cooling electronics that can be handy in many electronic components and computer CPU cooling. In addition to Optoelectronics for enhanced performance, Such as cooling IR detectors and temperature stability of laser diodes . Thermoelectric power generation technologies (thermal-to-electrical conversion) are important in providing electrical power from heat gradients[1].

Recently Oxide materials are considered to be promising for future thermoelectric applications and candidate for devices, which can directly convert heat into electrical energy, electricity can be used for heat pumping or refrigeration by using Seebeck Effect.

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, Seebeck could have converted thermal energy into electricity with an efficiency of 3 percent which it is good percent in that time. From fig1, A and B different conductors are maintained at different temperatures T_1 and T_2 and $T_1 > T_2$ an open circuit electromotive force (emf), a potential V is developed

$$V = \alpha(T_1 - T_2) \tag{1}$$

Where 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[2].

In 1833, Peltier observed temperature changes in the vicinity of the junction between dissimilar conductors when a current passed but he couldn't explain this phenomena. 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. Return to Peltier Effect where the reverse situation is considered with an external emf source applied. The Peltier coefficient π is defined, for the same pair of conductors, by the relation:

$$\pi = \frac{q}{I} \tag{2}$$

Here q is the rate of heating or cooling at one of the junctions when an electric current I passes round the circuit. The Lack of interest and slow progress in thermoelectric application in era of electromagnetism, Where most of the researchers were interested in Electromagnetism. After thirteen years, W. Thomson or Lord Kelvin established a relationship between the Seebeck and Peltier coefficient and predicted the existence of a third thermoelectric effect. Thomson effect explained the heating or cooling in a single homogeneous conductor when a current passes along the conductor in the presence of a temperature gradient.

$$q = \beta I \Delta T \tag{3}$$

Where I is the current and β is the Thomson coefficient.

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

$$\frac{d\alpha_{ab}}{dT} = \frac{\beta_a - \beta_b}{T} \tag{4}$$

In 1911 Altenkirch gave satisfactory theory of thermoelectric generation and refrigeration and showed that good thermoelectric material should possess large Seebeck coefficient with low thermal conductivity, to retain the heat at the junction, and low electrical resistance to minimize Joule heating.The desirable characteristic were good represented by figure of merit which measure the Quality of the material for thermoelectric application is defined as Z [2].

$$Z = \frac{\sigma S^2}{\lambda} \tag{5}$$

Where σ is the electric conductivity

λ is the thermal conductivity

As it is clear from the previous equation the unit of Z is $1/K$. since Z is vary with T and for a given absolute temperature T, a useful non-dimensional figure of merit will be.

$$ZT = \frac{\sigma S^2}{\lambda} T \tag{6}$$

Power factor is

$$\sigma S^2 = \frac{S^2}{\rho} \tag{7}$$

Where ρ is the resistivity

Modern commercial Peltier devices exhibit a $ZT \approx 0.9$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 $ZT = 4$ [3].

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 Thermoelectric performance[1, 2].

B. Generating the Figure of Merit

If Load resistance R_L is connected across the cold ends of thermocouple arms a and b (Figure 2, position 2) a current will go through the circuit and deliver power to R_L. The efficiency of the generator is given by :

$$\varepsilon = \frac{\text{energy supplied to the load}}{\text{heat energy absorbed at hot junction}} \tag{8}$$

For special case when the thermal and the electric conductivities and Seebeck coefficients of a and b are constant within an arm , the efficiency can be written

$$\varepsilon = \frac{I^2 R_L}{\alpha_{ab} I T_1 + \lambda^{'}(T_1 - T_2) - \frac{1}{2} I^2 R} \tag{9}$$

Where $\lambda^{'}$ is the thermal conductance of a and b in parallel and R is the series resistance of a and b.

The maximum efficiency:

$$\varepsilon_{\max} = \left(\frac{T_1 - T_2}{T_1}\right) \frac{\sqrt{1 + Z_c T} - 1}{\sqrt{1 + Z_c T} + \frac{T_2}{T}} \tag{10}$$

Where T is the average of temperature given by:

$$T = \frac{T_1 + T_2}{2} \tag{11}$$

And the figure of merit of the couple is Z_c

$$Z_c = \frac{\alpha_{ab}^2}{R\lambda^{'}} \tag{12}$$

Let assume tha a and b have matched geometries which minimize the heat absorption, the the figure of merit can be written:

$$Z_c = \frac{\alpha_{ab}^2}{\left[\left(\frac{\lambda_a}{\sigma_a}\right)^{\frac{1}{2}} + \left(\frac{\lambda_b}{\sigma_b}\right)^{\frac{1}{2}}\right]^2} \tag{13}$$

In practical the two arms of the junction have similar material constants, so the figure of merit for a material is given by:

$$Z = \frac{\sigma S^2}{\lambda} \tag{14}$$

II. COMMON THERMOELECTRIC OXIDES

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 researcher's minds to explore high efficiency oxide materials. It was found that the power factor of a single crystal Na_xCoO_2 exceeded that of Bi_2Te_3. Na_xCoO_2 have a large thermoelectric power and a low resistivity in polycrystalline, see fig3. The crystal structure of

Na_xCoO_2 is shown in fig4, where the Na ion is randomly distributed with highly disordered insulating block occupy in the prism site between the CoO_2 blocks and the cobalt ion is in the center of a distorted oxygen octahedra with little vacancies[1].

In addition Cobalt Oxide systems have interesting magnetic properties as well as for possible analogies to colossal magnetoresistive manganite materials, or high superconducting transition temperature cuprate oxides. Is very interesting to study Na_xCoO_2 system, since the spin entropy has been found to play an essential role in the dramatically enhanced thermopower for large sodium content ($x \sim 0.7$), while magnetic ordering has been observed at high x, and at $x = 0.5$ where the system is a charge-ordered antiferromagnetic insulator. At small $x \sim 0.3$, the recent discovery of superconductivity in hydrated Na_xCoO_2 has been of particular interest with regard to the superconducting cuprates. The Co^{4+} ions are in the low-spin state and carry $S = 1/2$ so that quantum effects are maximal, while the underlying lattice is triangular rather than square like the cuprates. May be this case is new class of high-TC superconductors, but of course the nature and mechanism of superconducting pairing in this new class of materials is in the early stages of being addressed. The appropriate model may be a Mott insulator in two-dimensions, with $S = 1/2$ where quantum fluctuations are optimal. The Co spins would then play a critical role in forming Cooper pairs that might have triplet symmetry as in Sr_2RuO_4 or d-wave symmetry as in the cuprates. The traditional electron-phonon interaction may be establishing conventional s-wave pairing, with the possibility that the anharmonic motion of the hydrogen and oxygen ions might be playing a role in enhancing the superconducting properties, in a manner similar to MgB_2. The crystal structure of Na_xCoO_2 as a function of doping x, and related the structure to the observed physical properties has been studied by many research groups. The phase diagram as a function of Na doping is shown in the Fig5 below [4]. Where in March 2003 Takada et al. reported that $Na_xCoO_{2.y}H_2O$ ($x \sim 0.35, y \sim 1.3$) is a superconductor with a T_c of about $5K$. This compound consists of 2-dimensional CoO_2 separated by a thick insulating layer of Na^+ ions and H_2O molecules fig6.

On the other hand, $Ca_2Co_2O_5$ 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]. Another an efficient room-temperature thermoelectric oxides $La_{0.95}Sr_{0.05}CoO_3$,where J. Androulakis et P. reported that the investigated compound exhibits a very respectable room temperature

thermoelectric figure of merit value of 0.18.And not only show that oxides are promising candidates for thermoelectric cooling applications, but also point towards the need for careful theoretical calculations that will serve as a guide in producing the next generation of thermoelectric materials, shown in fig7 [5].

III. SUMMARY AND CONCLUSION

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 High thermal, chemical stability and No toxicity.

It is difficult to control an electronic system and a phonon system simultaneously in a single crystalline field, so most of TEO have a complex structure. 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.

---

[1] D. Rowe, *THERMOELECTRICS HANDBOOK,MACRO TO NANO* (CRC Press Taylor and Francis Group, LLC, Broken Sound Parkway NW, 2006).

[2] C. B. D.M. Rowe, *Modern Thermoelctrics* (Reston Publishing Company, Inc., Virginia, 1983), 1st ed.

[3] J. G. J. Androulakis, Pantelis Migiakis, APPLIED PHYSICS LETTERS **84**, 1099 (16 February 2004).

[4] Http://www.ncnr.nist.gov/staff/jeff/WaterSuperconductor.

[5] J. G. J. Androulakis, P. Migiakis, Applied Physics Letters **84**, 1099 (2004).

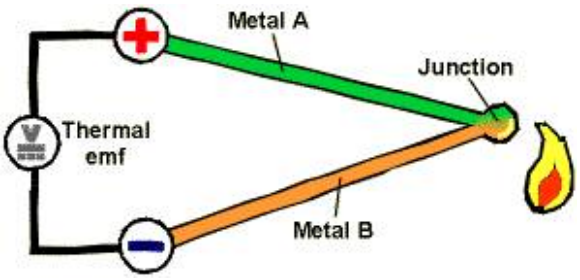

FIG. 1: Seebeck effect. Image: National Physical Laboratory, UK.

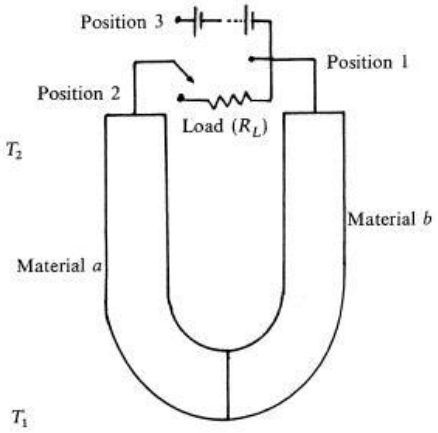

FIG. 2: Schematic thermoelectric device

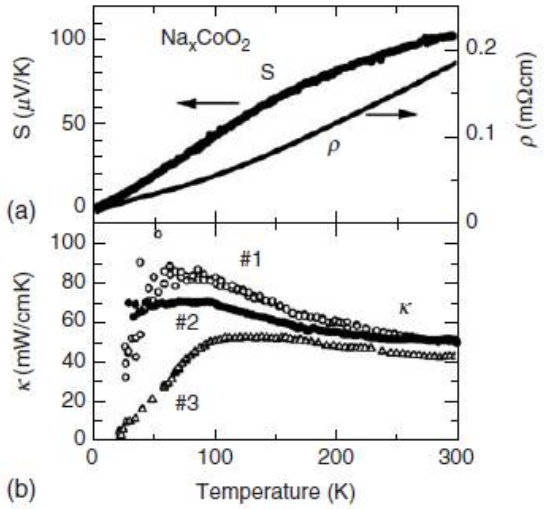

FIG. 3: Thermoelectric properties of Na_xCoO_2

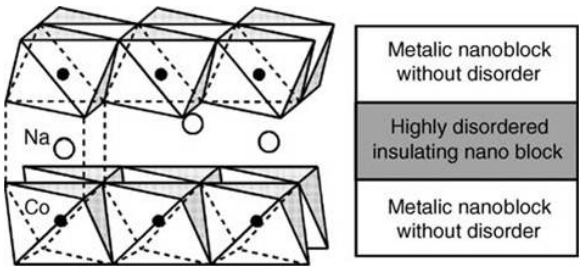

FIG. 4: Crystal Structure of Na_xCoO_2(left) and the corresponding nanoblock structure(right)[1]

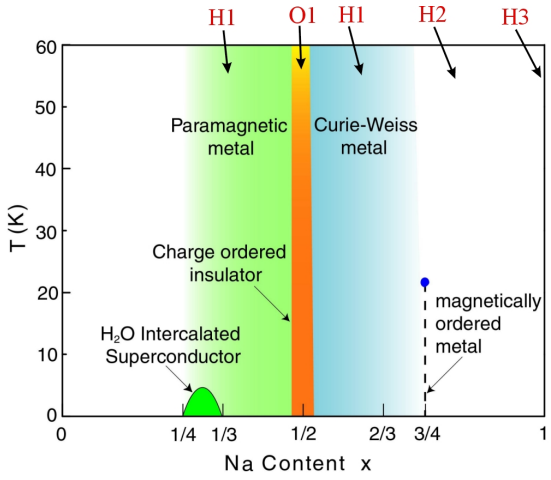

FIG. 5: Electronic phase diagram of Na_xCoO_2 as a function of the Na content x.

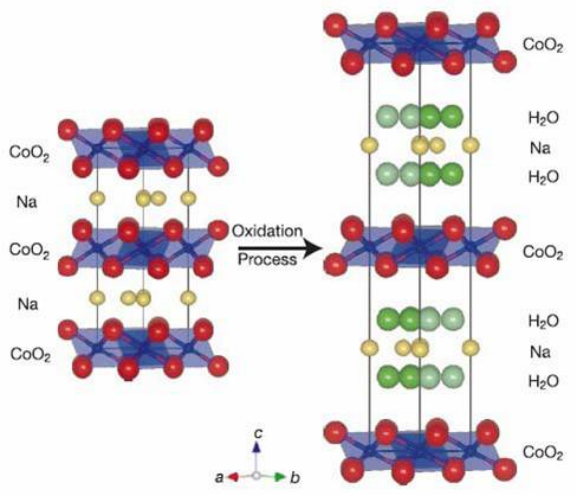

FIG. 6: The Crystal Structure of Hydrated Na_xCoO_2

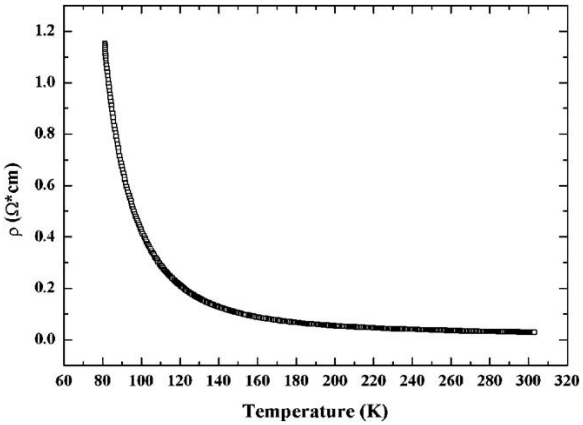

FIG. 7: Temperature dependence of the resistivity for the polycrystalline bar-shaped sample of $La_{0.95}Sr_{0.05}CoO_3$. Note that it exhibits a room temperature resistivity of 27 $m\Omega.cm$.