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PROPERTIES AND RECENT PROGRESS IN OXIDE BASED THERMOELECTRIC MATERIALS

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Abstract

Advanced thermoelectric materials that can be used efficiently for energy conversion have received significant research interest for the last decade because of the mounting demand for sustainable and eco-friendly energy technologies. The main advantage of the thermoelectric materials is their capability to directly convert the waste heat into electrical energy which makes them highly promising for the recovery of waste heat from industrial processes, automotive systems and power generation applications. Oxide-based thermoelectric materials are interesting due to their high abundance, low cost, low mass density, excellent chemical and thermal stability, non-toxicity, and capability to work at higher temperatures in oxidizing conditions, among the different classes of thermoelectric materials. Although they are useful,

high thermoelectric efficiency is still hard to attain because of the interdependence of electrical conductivity, Seebeck coefficient and thermal conductivity. This review gives a thorough overview of the basic properties of oxide-based thermoelectric materials and the methods used to optimize these transport properties to improve the thermoelectric properties. Different synthesis and fabrication methods such as solid-state reaction, sol-gel, polymer solution, pressure-less sintering and spark plasma sintering are discussed and their effects on the material properties are explored. The developments of the systems that have been extensively studied, such as $\text{Ca}_3\text{Co}_4\text{O}_9$, SrTiO_3 and CaMnO_3 , over the last years are also summarized, including the effect of element doping and microstructural engineering. In addition, the review identifies the recent progress, current challenges and future research trends to enhance the figure of merit (ZT) and further extend the application of thermoelectric oxide materials to efficient and sustainable energy harvesting.

Keywords

Thermoelectric, Seebeck coefficient, electrical conductivity, Powerfactor, Thermal conductivity

INTRODUCTION

There are several issues with energy use in the globe today. Social and political instability is sharply increasing as a result of the global demand for energy. Over 60% of the energy lost globally is converted to heat. On the other hand, there is a growing demand for greenhouse gases especially CO_2 in the environment (1,2). Similarly, the effects of using fossil fuels on the ecosystem and climate change are become more concerning. Challenges to develop alternative technologies that can convert waste heat in to electrical energy plays key role in current days (3-5). It can reduce our dependent on fossil fuels and reduces greenhouse gas emission. Scientist worldwide are in search of such materials that can help to meet the increasing energy demands with minimal environmental impact(6-8). In several fields, materials with the ability to directly and reversibly transform thermal energy into electrical energy have sparked attention. Materials that possess these properties are called thermoelectric materials (TE). Home heating, automotive exhaust and industrial process can use TE materials(9-15). High-efficiency TE materials must be developed immediately for waste heat recovery, as this will have significant positive effects on the economy and the environment(16-25). It is highly applicable for remote applications in case of absence of any compressors or pumps especially

in space craft. Heat lost in engine coolant or exhaust gas can be used to produce electricity by using TE(26-35).

THERMOELECTRIC MATERIALS

Environmentally friendly energy conversion materials that are compact, highly reliable, pollutant-free, and feasible throughout a broad temperature range are called thermoelectric materials (36-42). Thermoelectric materials can be used to turn the vast amounts of waste heat produced by industrial processes, vehicle exhaust, and home heating into energy. It is critical to develop high-efficiency thermoelectric materials for waste heat recovery because they will have significant positive effects on the economy and the environment (43-54).

PROPERTIES OF TE:

To carry out such thermoelectric conversion, good TE materials should possess a few special qualities. The figure of merit (ZT), which is defined as the conversion efficiency of TE material, $ZT = \frac{S^2 \sigma T}{K}$. S, σ , T and K are Seebeck coefficient, electrical conductivity, Temperature and Thermal conductivity. $S^2 \sigma$ is the power factor. The relationship between Seebeck coefficient can be expressed as $S = \frac{8\pi^2 K_B^2}{3eh^2} m^* T \left(\frac{\pi}{3n} \right)^{2/3}$ Where k_B , e, h, m^* and n are Boltzmann constant, carrier charge, Planck's constant, effective mass and carrier concentration. Low thermal conductivity and high electrical conductivity are necessary to optimise ZT material's thermopower.

1. Electrical conductivity:

Electrical conductivity is given by, $\sigma = ne\mu$. Where μ and n are carrier mobility and carrier concentration Strongly doped semiconductors with carrier concentrations between 10^{19} and 10^{21} cm^{-3} are good TE materials. One kind of carrier should be chosen to guarantee a high Seebeck coefficient; mixing carriers can reduce thermopower. To obtain a single kind of carrier, materials with sufficient doping and energy bandgaps that allow for a good separation between n-type and p-type are selected. Consequently, semiconductors with an energy bandgap of less than 1 eV that are extensively doped are effective TE materials.

2. Effective mass:

Another contradiction arises from the charge carriers' effective mass, since a large effective mass results in limited electrical conductivity and high thermopower. The m^* refers to the density of states effective mass, which increases with flat, narrow bandgap with density of states at the Fermi surface, $\sigma = \frac{ne^2\tau}{m^*}$. Electrical conductivity results from heavy carriers moving with stronger velocities and, consequently, small mobilities, as m^* is linked to n . Effective mass and mobility have a complicated relationship that is influenced by anisotropy, electronic structure, and scattering mechanisms. Effective mass and the dominating charge carriers must be balanced in order to strike a compromise between high mobility and high effective mass.

3. Thermal conductivity:

Thermal conductivity in the thermoelectric materials comes from two sources

- (1) Electron and hole transporting heat (k_e)
- (2) Phonons travelling through the lattices (k_l)

$$k = k_l + k_e$$

$$k_e = LenuT$$

Since k_e is linearly proportional to electrical conductivity, decreasing k affect the electrical conductivity Lattice thermal conductivity is tuned to change thermal conductivity since reducing k has little to no improvement in ZT.

PHONON-GLASS-ELECTRON CRYSTAL

As ZT difficulty increases, the complex parameter relationship gets closer. A "phonon-glass-electron-crystal (PGEC)" model is a necessary component of high-quality thermoelectric materials. The characteristics of thermoelectric materials are described by this model. An ideal thermoelectric material is said to have both crystal-like electrical characteristics and glass-like thermal conductivity. The lattice thermal conductivities of glasses are poor. The idea of lowest thermal conductivity arises from the perception that thermal conductivity in glass is a random travel of energy through the lattice rather than quick transit via phonons. However, because they lack the necessary electron-crystal characteristics, they perform poorly as thermoelectrics. Thus, crystalline materials that scatter phonons without substantially altering electrical conductivity are good thermoelectric material. For a thermoelectric material to be capable of

such a conversion process, it must possess specific characteristics. The thermoelectric materials' conversion efficiency is correlated with the figure of merit (ZT), which is defined as

$$ZT = S^2 \sigma T / k$$

where, $S \rightarrow$ Seebeck coefficient ($\mu\text{V/K}$)

$\sigma \rightarrow$ Electrical conductivity ($\Omega^{-1}\text{cm}^{-1}$)

$k \rightarrow$ Thermal conductivity ($\text{Wm}^{-1}\text{K}^{-1}$)

$T \rightarrow$ Temperature (K)

$S^2 \sigma \rightarrow$ Power factor

RESEARCH PROGRESS ON THERMOELECTRIC MATERIALS

The 1950s saw remarkable advancements in the field of thermoelectrics. Bi_2Te_3 , PbTe , and SnGe bulk thermoelectric materials are examples of the first generation of thermoelectric materials that were created for room temperature applications. In 1960, solid solution formation and doping control were the main strategies for raising ZT. Global interest in the field of thermoelectrics was low between 1960 and 1990 (55-59).

With $ZT \sim 1$, the alloy family kept the best commercial material. Two distinct strategies have been developed over the last 20 years to find the next generation of high-performance thermoelectric materials. One is the synthesis and application of low dimensional thermoelectric material systems, and the other is the discovery and use of novel families of bulk materials with intricate crystal structures. High $ZT \sim 2.4$ at 300K has been recorded by $\text{Bi}_2/\text{Sb}_2\text{Te}_3$. However, at high temperatures, these substances become unstable and poisonous. As a result, the focus of the research had somewhat changed to oxides. Oxides' high chemical and thermal stability makes it possible to apply a significant temperature gradient across materials in air (60).

Oxides are distinguished by their structural, compositional, and chemical versatility. Oxides are inexpensive and environmentally benign. Metal oxides were not thought to have good TE at first, but studies on transition metal oxides showed promising results because of their strong electronic correlation, narrow bands, which resulted in strong spin and orbital fluctuations, and high degeneracy, which can occur in the d-electrons and is beneficial for enhancing TE. The most common oxide materials are p-type $\text{Ca}_3\text{Co}_4\text{O}_9$, n-type ZnO , SrTiO_3 , and CaMnO_3 .

The various manufacturing techniques employed and the potent thermoelectric outcomes attained in these materials in recent years are discussed in this review.

1. $\text{Ca}_3\text{Co}_4\text{O}_9$ (CCO):

CCO is a p-type semiconducting material well known for its electronic, magnetic and electro-optic properties. In the family of Cobalite, CCO has gained a special place due to its misfit layered structure. Its crystal structure consists of two different CdI_2 – type monoclinic structures. The middle layer consists of Ca and O. The others contain Ca and O. The substructure has the composition of Ca_2CoO_3 and is usually referred to as rock salt structure. Various techniques have been used to prepare CCO nanoparticles. The thermoelectric properties also show variation depending upon the fabrication techniques used and conditions of annealing and sintering. Various techniques used for the fabrication and their outcomes are given in this article.

i) Solid state reaction method:

The simplest yet effective method for the fabrications of CCO nanomaterials is the solid-state reaction method. CaCO_3 and Co_3O_4 are mixed for 5 mins at 400rpm in aagate ball. The powder obtained is heated at 850°C for 8 hours by varying the concentrations ($x=1,10,20$). Spark plasma sintering is processed. Decomposition of $\text{Ca}_3\text{Co}_4\text{O}_9$ to $\text{Ca}_3\text{Co}_2\text{O}_6$ is studied using TGA analysis, which shows two peaks at 911 and 965°C . All samples are *p*-type conductors with positive Seebeck coefficient. Electrical conductivity also shows increment with temperature and a higher ZT is obtained for pure CCO than the doped one. CaCO_3 and Co_3O_4 are mixed and calcined for 20 hours at 700°C . Pellets prepared were annealed at 900°C for 20 hours. Again, grounded and wood powders [1,1.05,0.15,0.25] were added to 1gm of CCO. The samples were sintered at different temperatures of 500°C and 900°C for 6 hours and 18 hours respectively. Structural analysis and thermoelectric studies were carried for all samples. Seebeck coefficient varies from $18\ \mu\text{V/k}$ to $144\ \mu\text{V/k}$ for $x=0$ and 0.15 at 800K . Among all the samples $\text{CCO}[0.15]$ shows high thermoelectric properties attaining $\text{ZT}=1.19$ at 800K .

ii) Pressure less sintering method:

Zirconia grinding media are used to combine CaCO_3 and Co_3O_4 with water. It is calcined twice at 900°C for 15 hours after drying. Samples were chilled to 900°C and then annealed at 900°C for 12, 24, and 72 hours after being fired in air at $1000\text{--}1300^\circ\text{C}$ for 6 hours. At 890°C and 940°C , TGA displays two peaks, signifying the breakdown into $\text{Ca}_3\text{Co}_2\text{O}_6$ and CaO at 940°C . The electrical conductivity of the 920°C sample is $56\ \text{S/cm}$ at 100°C , and the Seebeck

coefficient progressively rises from 130 to 160 $\mu\text{V}/\text{K}$ within the measured temperature range of 100-670 $^{\circ}\text{C}$. At 600 $^{\circ}\text{C}$, a ZT of 0.06 is recorded.

iii) Polymer solution method

$\text{Ca}[\text{CH}_3\text{CO}_2] \cdot \frac{1}{2}\text{H}_2\text{O}$ + $[\text{Co}(\text{CH}_3\text{CO}_2)_2 \cdot 4\text{H}_2\text{O}]$ were added in the distilled H_2O . Polyethyleneimine was added to the above solution. Partial evaporation take place in a rotary evaporator. The powder obtained was thermally heated twice at 750 and 800 $^{\circ}\text{C}$ for 12h and pelletized. Pellets prepared were annealed in air at 900 $^{\circ}\text{C}$ and 960 $^{\circ}\text{C}$ indicating the formation of $\text{Ca}_3\text{Co}_2\text{O}_6$. XRD studies reveals that $\text{Ca}_3\text{Co}_4\text{O}_9$ is the major phase accompanied by CaO , $\text{Ca}_y\text{Co}_{1-y}\text{O}$ and $\text{Ca}_3\text{Co}_2\text{O}_6$ for samples annealed for 24h. For further annealing time, number of secondary phases got decreased. Electrical resistivity got decreased with increase in temperature. The minimum resistivity values at room temperature is $15\text{m}\Omega\text{cm}$ for 96h annealed sample. For as prepared sample, Seebeck coefficient varies from 80 to $550\text{mV}\text{K}^{-1}$ for 400 and 800 $^{\circ}\text{C}$.

iv) Sol-gel method

$\text{Ca}(\text{NO}_3)_2$ and $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and citric acid were dissolved in distilled water with a metal ion concentration of 0.2~0.3 mol/liter solution was stirred and heated at 70 $^{\circ}\text{C}$ for 3h. The dried gel was grinded and calcined at different temperatures from 400 to 800 $^{\circ}\text{C}$ sintered by using SPS and CS techniques. XRD reveals that CCO appears when calcined at 600 $^{\circ}\text{C}$ as temperature is increased pure phase is obtained at 800 $^{\circ}\text{C}$. TGA reveals peaks at 251 $^{\circ}\text{C}$, 377 $^{\circ}\text{C}$, 627 $^{\circ}\text{C}$, and heavy one at 763 $^{\circ}\text{C}$, sharp endothermic peak exhibit at 956 $^{\circ}\text{C}$. electrical conductivity at room temperature for CS sample is $34\text{S}/\text{cm}$ and increased for 700 $^{\circ}\text{C}$. Power factor of CS and SPS are noted as 3.51×10^{-4} and $1.15 \times 10^{-4} \text{ W}/\text{m}^2\text{s}$ at 700 $^{\circ}\text{C}$. ZT values are noted as 0.16 and 0.052 at 700 $^{\circ}\text{C}$.

DOPING:

a) Bi doping

Bi doped CCO is prepared by using chemical sol-gel method. Bi doped CCO is prepared by using chemical sol-gel method. $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ + $\text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ + $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$. Ethylene glycol and polyethylene glycol is used to polymerize the solution. Nitric acid is added and stirred at 353K and gel is prepared and calcined at 923K for 4h and pellets are sintered at 1233K for 9h in a furnace with oxygen flow. Power factor of 22.5 and 23.8 is obtained for concentration of 0.2 and 0.3 of Bi. ZT of 0.16 at ZT of 0.16 at 823K is obtained for Bi doped with CCO prepared by spark plasma sintering method

b) Lanthanum doped

$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O} + \text{Ca}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O} + \text{La}(\text{NO}_3)_3$ are mixed and dissolved in distilled water. Precursors are calcined in a muffle furnace at 650, 700 and 750 °C for 5h to produce CCO powders. CCO/LaCCO 650 reveal weak signal corresponds to CaCo_2O_4 . No other phases were observed confirming the entry of La elements into the lattice of CCO. Power factor exhibits positive co-ordination with the temperature. LaCCO 700-900 having high power factor of $204.25 \mu\text{Wm}^{-1}\text{K}^{-2}$ at 600 °C three times higher than CCO. Improvement of K in 950 °C is due to density improvement compared with 900 °C samples. ZT reached 0.25 at 600 °C

c) Silver doping:

Silver doped CCO is prepared by using ball milling process and calcined at 1173K for 24h in air twice with an intermediate grinding. The prepared CCO mixed with different proportion of AgNPS [0, 0.5, 1.0, 1.5, 2.0]. XRD shows that all the samples are single phase. As AgNPS content grows higher impurity phase of CCO appears in XRD pattern. For pure CCO and AgNPS(0.2), conductivity of 74 S/cm and 85 S/cm is obtained at 700 K.

ZT of 0.1 at 700K is obtained.

d) Ba, La and Ag doped

Citrate sol-gel synthesis followed by spark plasma sintering is used for preparing $\text{Ca}_{2.9}\text{M}_{0.1}\text{Co}_4\text{O}_9$ [M=Ca, Ba, La, Ag]. Ca, Ba, La, Ag and Co were dissolved in an aqueous solution of citric acid. Ethylene glycol was added and solution was heated under continuous stirring at 358K in order to form precursor gel. The gel was dried at 393K in air for 24h and then heated at 1073K for 8h. Activation energy

2. SrTiO₃

In following years, the studies based on SrTiO₃ materials has expanded in wide range of fields. High power factor of $1.8 \text{ Wm}^{-1}\text{K}^{-1}$ is achieved for heavily La doped single crystal STO which increased the study of TE properties of STO. The electronic transport in SrTiO₃ can be tuned over a wide range of physical properties. The electrical conductivity of n-type STO materials can be achieved over a very broad range. Effective doping helps in achieving high ZT.

a) Pr doped SrTiO₃

SrCO_3 is added with Pr_2O_3 and TiO_2 mixed and made into pellets and calcined at 1300-1400 °C. The pellets are grinded, wrapped in graphite foil and again sintered by using SPS. Powerfactor of $1.3 \text{ Wm}^{-1}\text{K}^{-1}$ and $2 \text{ Wm}^{-1}\text{K}^{-1}$ is observed at 500 °C and 100 °C.

b) La doped SrTiO₃

La_2O_3 is mixed with TiO_2 and SrCO_3 using planetary ball milling for 60 mints and calcined at 1100 °C for 7 h in alumina crucible grounded and served. Pellets are sintered at 1500 °C. La

doped SrTiO₃ is prepared using SPS at 925, 1100 and 1200 °C. High ZT of 0.2 is reported for sample sintered and annealed at 500 °C. This is due to the high conductivity from 750 Scm⁻¹ to 400 Scm⁻¹.

c) Nb doped SrTiO₃

Nb doped SrTiO₃ is prepared by taking SrCO₃, La₂CO₃ and TiO₂ as starting materials mixed using an attrition mill for 60 min. calcined at 1373K for 3h. Pellets were prepared using 200 Mpa. Sintering at air/N₂. (Sr_{1-3x/2} La_x TiO₃) ZT is calculated for varying x. Highest ZT of 0.41 is calculated for x=0.125-0.175.

d) Titanium nitrate and Y

Y doped SrTiO₃ is prepared from calcination of Strontium Carbonate + Yttrium Oxide + Titanium oxide. Y doped SrTiO₃ and TiN powders is mixed. Pelletized under 47MPa and sintered at 1573K for 2hrs ZT of 0.26 at 1073 K.

e) La,Dy

La₂ + SrCO₃ + TiO₂ + Dy₂O₃ is mixed ball milled for 12 hrs. and dried pressed and pelletized, calcined at 1350 °C for 6hr in air. Pellets are smashed to fine powders, again pelletized and sintered at 1460 °C for 4 h to get La_{1-x}Dy_{0.1+x}Sr_{0.8}TiO₃ [x=0.02,0.05,0.08,0.10]. highest power factor of 1.9 e³ is obtained at 303 K.

f) Rare Earth

Multiple dopants method is also used to enhance the thermoelectric properties of SrTiO₃. Rare earth elements Y, La, Sm, Gd, Dy are doped simultaneously with SrTiO₃.

SrTiO₃ is mixed with TiO₂, Ti, Y₂O₃, La₂O₃, Sm₂O₃, Gd₂O₃ and Dy₂O₃. All are mixed and are made into pellets, sintering at 80mPa and 1873K for 4hrs. Thermoelectric studies are taken for Sr_{1-x}R_xTiO₃ by varying the concentrations from 0.05 to 0.2. ZT of 3.8 * 10⁻⁴ K⁻¹ is obtained for Sr_{0.9}Dy_{0.1}TiO₃ at 573 K.

3. CaMnO₃

Compared with, chalcogenides and skutterudites metal oxides good candidates for thermoelectric applications. due to their high thermal and chemical stability at high temperature in air, easy manufacture and low cost. But ionic bonding in metal oxides usually leads to a strong scattering of electrons by optical phonons, which results in low carrier mobility and thus generally makes for poor thermoelectric performance. For this reason, metal oxides have long been avoided in the search for good thermoelectric materials. In 1997, Na_xCo₂O₄, shows unexpected thermoelectric properties which made thermoelectric metal oxides highly attractive. Also, perovskite families have also been explored and considered as thermoelectric

oxides. Among them, SrTiO₃ is a good TE material, its TE properties and its variations with dopants are mentioned below.

i) Solid state reaction method

La³⁺, Y³⁺, Ce⁴⁺ were added to replace Ca²⁺ in CaMnO₃. Multi dopants were used to yield high efficiency by using simple solid state reaction method by taking CaCO₃, MnO₂, La₂O₃, CeO₂ and Y₂O₃ as mixing agents. They are mixed individually, calcined in air at 1273K for almost 12 hrs. They were pelletized and sintered at 1573K for 24 hrs. to obtain Ca_{1-x}La_xMnO₃, Ca_{1-x}Y_xMnO₃ and Ca_{1-x}Ce_xMnO₃. Thermoelectric results have been noted by varying the concentrations. The minimum resistivity has been noted for x=0.12 for La and Y doped and also for x=0.06 for Ce doped. Largest Seebeck coefficient of 500 to 600 μ VK⁻¹ is noted for CaMnO₃. A large ZT of is obtained for Ca_{0.9}La_{0.1}MnO₃ at 1000K.

ii) SAMARIUM DOPED CaMnO₃:

Sm doped CaMnO₃ is prepared by using sol-gel method. Ca_{0.1}Sm_{0.1}MnO₃ shows high power factor of 3.11 μ Wm-1K² at 800°C.

iii) Bi and Nb doped:

Bismuth and Niobium doped CaMnO₃ is prepared using solid state reaction method by taking CaCO₃ and MnO₂ as starting materials and grinded at 1373K. The prepared powders were mixed with Nb₂O₅ and Bi₂O₃ and calcined at 1373K. The powders were pelletized and sintered at 1573K for 12 hrs. Ca_{1-x}Bi_xMn_{1-y}Nb_yO₃ is prepared. Maximum power factor is obtained for x=y=0.04 and ZT~ 0.1 at 873K.

iv) Bi doped :

By using planetary ball milling method in an ethanol medium for 5hrs. from CaCO₃, MnO₂ and Bi₂O₃ calcined at 1173K for 10 hrs and again annealed at 1273K for 10hrs. Resultant powder was then again ball milled and pelletized. The pellets were sintered at 1423K for 10hrs and the results were studied varying the concentrations [0,0.02,0.03,0.04,0.06 and 0.10]. ZT of 0.25 is observed at 973K for x=0.03 and a high power factor of 4×10^{-4} is noted.

CONCLUSION

The global demand for sustainable energy and the energy and the environmental concern on the use of fossil fuel have imposed an impressing need for the advancement of alternative energy conversion technologies including thermoelectrics. On the road to improve thermoelectric material performance, we have established in the past years an arsenal of technical tools and ways to achieve low lattice thermal conductivity. There is a little overlap between lattice thermal conductivity reduction and power factor improvement and hence we should pay closer attention to the enhancement approaches with dual purpose. In this review

we have discussed various preparation techniques used and the powerfactors and ZT values obtained. In conclusion, thermoelectric research is an exciting field. It will also provide students of next generation with invaluable skill sets including an intimate knowledge on phonon and electron scattering. We feel that this review article is very timely and necessary in understanding the power factor of thermoelectric materials and hope that readers will find it very useful in their future research.

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