2026 Volume: 02 Issue: 06 www.ijrpa.com ISSN 2456-9995 Review Article

International Journal Research Publication Analysis

Page: 01-27

A COMPREHENSIVE REVIEW OF THE STRUCTURE AND ELECTRICAL-THERMAL PROPERTIES OF NOVEL THERMOELECTRIC MATERIALS

Adindu C. Iyasara[1*], Geoffrey O. Okafor[2], John N. Nweke[3], Dumpe K. Barinem[4], Nobert O. Osonwa[1], Henry I. Eneh[4], Ikechukwu C. Agha [4],Ngozi F. Okereke[5], Patrick O. Nwosibe[5], Arinzechukwu S. Okolo[6], Muhammed O. Ibrahim[7]

[1]Department of Ceramic and Glass Technology, Akanu Ibiam Federal Polytechnic, Unwana, Nigeria.

[2]Department of Mechanical Engineering Technology, Akanu Ibiam Federal Polytechnic, Unwana, Nigeria.

[3]Department of Electrical/Electronics Engineering Technology, Akanu Ibiam Federal Polytechnic, Unwana, Nigeria.

[4]Department of Mechanical Engineering Technology, Federal Polytechnic, Ngodo, Isiochi, Nigeria.

[5]Department of Petroleum and Gas Engineering, Federal Polytechnic, Ngodo, Isiochi, Nigeria.

[6]Department of leadership and Management-project Management, University of Derby, United Kingdom.

[7]Department of Electrical/Electronics Engineering Technology, Federal Polytechnic, Nyak, Shedam, Nigeria.

Article Received: 7 May 2026
Article Revised: 27 May 2026
Published on: 17 June 2026

***Corresponding Author: Adindu C. Iyasara**
Department of Ceramic and Glass Technology, Akanu Ibiam Federal Polytechnic, Unwana, Nigeria.

DOI: https://doi-doi.org/101555/ijrpa.7659

ABSTRACT

Novel thermoelectric (TE) materials are increasingly centered on oxide ceramics because of their excellent thermal stability, oxidation resistance, environmental compatibility, and abundance of constituent elements. In contrast, conventional thermoelectric non-oxidematerials such as bismuth telluride, and lead telluride exhibit unfavorable properties such as instability at high temperatures with scarce and toxic raw materials that constitute an environmental hazard. Novel TE materials showcase diverse crystal architecturesincluding

wurtzite (e.g. ZnO), perovskite (e.g. $SrTiO_3$), layered cobaltite (e.g. $NaCo_2O_4$) and oxychalcogenide (e.g. BiCuSeO) structures that strongly influence carrier transport and phonon scattering. This review paper comprehensively examines the structure, electrical conductivity, Seebeck coefficient and thermal conductivity of selected novel oxide thermoelectric materials, emphasizing how defect chemistry, aliovalent doping, nanostructuring, and composite design improve the thermoelectric figure of merit (ZT). Recent studies have demonstrated that oxides can achieve competitive thermoelectric performance while maintaining outstanding chemical and mechanical durability, making them attractive for waste heat recovery in industrial furnaces, automotive systems, and energy harvesting in renewable energy technological applications.

KEYWORDS: Thermoelectric materials, crystal structure, Seebeck coefficient, thermal conductivity, figure of merit.

1. INTRODUCTION

A substantial fraction of industrial energy is lost as heat with potential for recovery through thermoelectric conversion (Snyder & Toberer, 2008). Oxide thermoelectrics offer chemical and thermal stability, noon-toxicity, and mechanical robustness, making them suitable for high temperature applications (Koumoto et al, 2010). The discovery of high thermoelectric performance in $NaCo_2O_4$ single crystals marked a turning point for oxide-based devices (Terasaki et al, 1997). Other oxide systems such as $Ca_3Co_4O_9$, $SrTiO_3$ and ZnO have been investigated extensively for their ability to combine large Seebeck coefficients with acceptable electrical conductivity at elevatedtemperatures (Ohtaki et al, 1996; Liu et al, 2023). These materials also compatible with scalable ceramic processing methods, including solid-state reaction (SSR), sol-gel synthesis, and spark plasma sintering (SPS) (Koumoto& Mori, 2013).

Thermoelectric effects – Seebeck,Peltier and Thomson effects are governed by charge and heat transport in solids (Rowe, 2018). The efficiency of thermoelectric materials is commonly described by the dimensionless figure of merit (ZT), given by:

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

where S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature at which the properties are measured and $k = k_L + k_E$(Tritt and Subramanian, 2006) is the total thermal conductivity. k_L and $k_E$are the lattice thermal conductivity and electronic thermal conductivity, respectively.

For a high ZT to be achieved, the following parameters are essential (Tritt and Subramanian, 2006; Wood,1988; Sales, 1998; Nolas and Poon, 2006):

1. Large Seebeck coefficient to produce a required high voltage for a given temperature difference.
2. High electrical conductivity to minimise losses through electrical heating (Joule heating), and
3. Low thermal conductivity to restrict diffusion of heat across the device by maintaining a large thermal gradient.

Oxides often exhibit high lattice thermal conductivity due to strong ionic bonds, but defect chemistry or engineering reduce the total thermal conductivity while maintaining favorable electronic transport (Koumoto et al, 2010; Liu et al, 2023). The phonon-glass electron-crystal (PGEC) concept guides oxide thermoelectric design, aiming for glass-like thermal conductivity and crystal-like electrical conductivity (Slack, 1995).

2. NOVEL THERMOELECTRIC MATERIALS

As stipulated by Ioffe's theory, oxides are unsuitable for TE applications due to their strong, mixed ionic and covalent bonds, possession of high lattice thermal conductivityand lower carrier mobility resulting in low electrical conductivity (Terasaki, 2013). However, there is a strong empirical evidence that oxide thermoelectrics containing transition-metal oxides are novel alternative materials to the current intermetallic (conventional) TE materials. Generally, oxides are inert, non-toxic, light weight, cheap, possess small thermal expansion with high melting point, hence promising TE candidates for high temperature applications (Funahashi, 2009; Tomeš et al, 2010).

Novel thermoelectric materials are expected to exhibit increased ZT and large power factor (PF) compared to conventional thermoelectric non-oxide materials. Basic novel thermoelectric materials include p-type $Na_xCo_2O_4$ [comparable to $(Bi, Sb)_2(Te, Se)_3$] and n-type rare-earth (RE) doped $SrTiO_3$ based compositions that have been reduced in N_2/5 % H_2 gas mixtures (Terasaki, Sasago and Uchinokura, 1997). The recognition of Novel thermoelectric materials (oxides) as potential TE materials particularly p-type oxides when Terasaki*et al (1997)*in their study showed that layered cobalt oxide, $Na_xCo_2O_4$ exhibited a high electrical conductivity ($\sigma \approx 500$ S/m) and a large Seebeck coefficient ($S \approx 100$ μV/K). This landmark opened the window for further investigations of other oxides for TE

applications. This breakthrough opened the window for further research into other oxides for TE applications.

Transition metal-oxides for TE applications are classified into wide-band-gap semiconductor, perovskite-based, layered cobalt oxides and oxychalcogenides(Nag and Shubha, 2014)and recently oxides with adaptive structures(Kieslich et al, 2016). A discussion of structures and thermoelectric properties of some of these promising classes of TE oxides will be reviewed.

2.1. Wurtzite Oxides – ZnO

Crystal Structure of ZnO

Zinc (II) oxide (ZnO) is a wide band gap semiconductor and a promising candidate for TE applications. It is also known as a transparent conducting oxide, TCO (Karvonen, Tomes and Weidenkaff, 2011) with a wurtzite crystal structure belonging to a hexagonal system (Onodera and Takesada, 2012). In the hexagonal lattice of ZnO (Figure 1), each Zn ion is surrounded by four O^{2-} ions in a tetrahedral configuration to form ZnO_4 groups. It possesses a wide band gap of 3.44 eV at low temperature (Janotti and De Walle, 2009; Mang, Reimann, and Riibenacke, 1995). Stoichiometric ZnO is an intrinsic semiconductor (insulator) but exhibits n-type conductivity due to excess Zn atoms and the structure is as shown below.

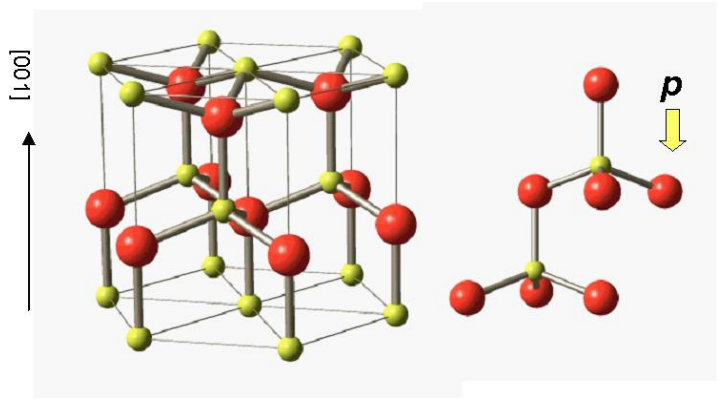

Figure 1. Wurtzite crystal structure of ZnO. Zn^{2+} ions are in red and O^{2-} in yellow.

Thermoelectric Properties of ZnO

The strategy to enhance the TE efficiency of zinc (II) oxide lies in the reduction of the Zn-O ionic bonds to increase the carrier mobility. A single crystal ZnO and Al-doped ZnO samples were found to possess a carrier mobility of ~ 200 cm^2/Vs and 80 cm^2/Vs, respectively at room temperature (Wanger and Helbig, 1974). A study of $ZnO_{0.98}Al_{0.02}O$ thin films showed a ZT ~ 0.3 at 1273 K with a PF of 1.5 x 10^{-3} W/m. K^2(Karvonen, Tomes and Weidenkaff, 2011). An improved ZT (0.4) at 773 K (Ohtaki, Maehara, and Shige, 2003) was obtained in

Al-doped ZnO using nanoparticles of carbon or organic polymer (void forming agent). The enhancement of the TE performance of the Al-doped ZnO is attributed to the compression of the c/a lattice ratio of crystal due to the Al doping (Wiff et al, 2009).

Co-doping has been identified as an effective mechanism in the promotion of TE performance of ZnO. A reported research has shown ZT = 0.47 and 0.65 at 1000 and 1273 K, respectively for an Al-Ga dual doped ZnO ($Zn_{0.96}Al_{0.02}Ga_{0.02}O$).

ZnO possesses a very high thermal conductivity when compared to other thermoelectric oxides. It has k = 54 W/m.K for single crystals and k = 40 W/m.K for polycrystalline samples (Wanger and Helbig, 1974) at room temperature. Therefore, the effective means of reducing this high thermal conductivity without compromising the power factor, PF is a fundamental research challenge.

2.2. Perovskite Oxides – $SrTiO_3$

Strontium titanate, $SrTiO_3$ (STO) is the n = 1 end member of the Ruddlesden-Popper (RP) phases with formula $SrO_{n-1}(SrTiO_3)_n$ (n = integer) and particularly when doped with Nb has received considerable attention as a thermoelectric n-type oxide (Koumoto, 2010). Bhattacharya et al(2014)highlighted notable transport properties of $SrTiO_3$ to include quantum paraelectricity, induced ferroelectricity, superconductivity, correlation between superconductivity and ferromagnetism, piezoelectricity, photo-catalytic activity, and thermoelectricity. Moreover, strontium titanate was the first discovered superconducting ternary oxide(Dawson, Freeman, Hardinga, and Sinclair, 2013). It is a non-toxic, chemically stable in air with a high melting temperature (2080 ^oC) thereby making it a promising candidate for TE applications at high temperatures (Koumoto, 2010).

Crystal structure of $SrTiO_3$

Pure $SrTiO_3$ (STO) crystallizes in an ideal cubic perovskite structure at room temperature with a lattice parameter, a ~ 3. 905 Å (space group = Pm-3m) and a wide band gap, E_g of ~ 3.2 eV (Bhattacharya et al, 2014;Benthem, Elsasser, and French, 2001). STO undergoes a phase transformation from cubic (Pm-3m) to tetragonal (I4/mcm) structure at a temperature below 105 K as a result of the rotation of the TiO_6 octahedra within the structure (Bhattacharya et al, 2014; Dawson, Freeman, Hardinga, and Sinclair, 2013 and Migliori et al,1993).

Perovskites are ternary compounds with the general formula ABX_3 where “A” and “B” are two different cations in equal ratio (with A > x2 the ionic radius of B) and “X” is an anion,

which is usually oxygen (O). In an ideal cubic $SrTiO_3$ structure, "A" represents Sr^{2+} and "B" is the smaller Ti^{4+} ion. Sr^{2+} ions occupy the corner positions of the cube, while the Ti^{4+} ions occupy the centre with O^{2-} (X) anions located at the edge centres of the cubic unit cell (Adams, 2010). The schematic of cubic perovskite structure of $SrTiO_3$ is shown in Figure 2. As shown in the structure of $SrTiO_3$(Figure 2), Sr^{2+} cations are arranged in cubo-octahedral coordination and are surrounded by twelve O^{2-} anions. The Ti^{4+} ions are surrounded by six O^{2-} anions which leads to the formation of TiO_6 octahedra. By the introduction of dopant into the lattice, distortions from cubic to lower symmetries (size incompatibility) may occur.

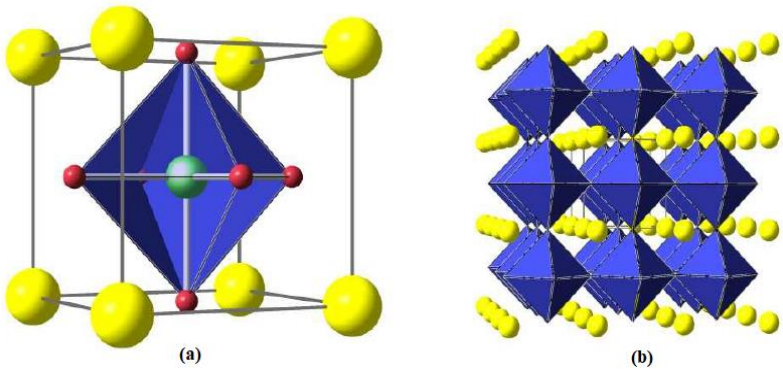

Figure 2. Crystal structure of cubic perovskite $SrTiO_3$ at room temperature showing the (a) octahedral coordination of Ti^{4+} cation and (b) corner sharing array of TiO_6octahedra(Adams, 2010). Sr^{2+} ions are in yellow, Ti^{4+} ions in green and O^{2-} ions in red.

The measure of stability (degree of distortion) within the structure of perovskite-type ABO_3 is defined by the Goldschmidt tolerance factor, t (Adams, 2010; Müller, 2007):

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \qquad 1.0$$

where r_A, r_B and r_O are the ionic radii of atoms "A", "B" and oxygen, respectively. For an ideal cubic perovskite such as $SrTiO_3$, t = 1, r_A = 1.44 Å, r_B = 0.605 Å and r_O = 1.40 Å. Lower symmetries are adopted when t < 1 or t > 1. This deviation from t = 1 results in distortion from the ideal perovskite structure.

Electronic structure of $SrTiO_3$

The Ti^{4+} ion in $SrTiO_3$ is a typical transition metal oxide having a d^0 electron configuration. Donor doping of $SrTiO_3$ is thought to partially fill its conduction band with electrons which results in a transition from d^0 state to d^1 electron configuration (Ti^{3+}) thereby increasing the

carrier concentration of the lattice. Undoped $SrTiO_3$ is a band insulator at room temperature with a large band gap (3.2 eV) separating the valence from the conduction band (Hill,2002). Due to the six-fold coordination of Ti^{4+} ions by O^{2-} anions, octahedral field splitting of Ti-3d states (five degenerate d-band) occurs (Ravichandran, 2011; Ravichandran et al, 2010). Figure 3 shows the schematic spatial (three-dimensional) distribution of the octahedral crystal field (Ravichandran, 2011).

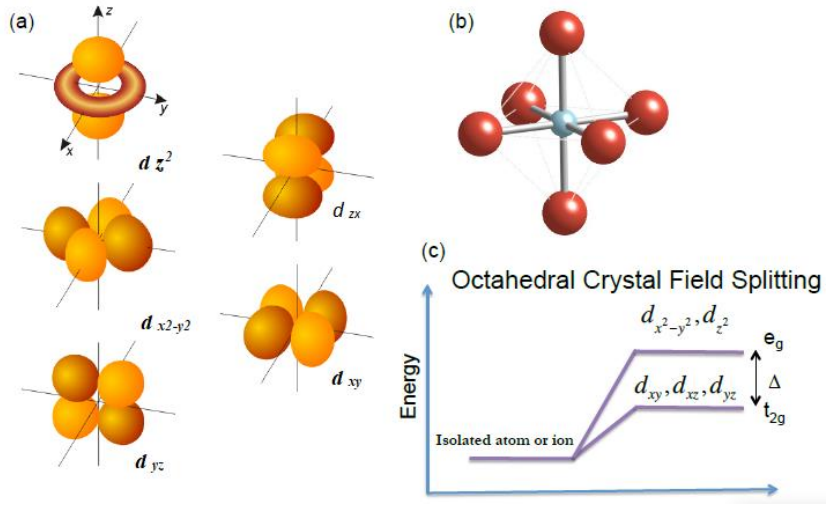

Figure 3. Diagrammatic representation of (a) spatial distribution of d-orbitals (b) oxygen octahedral cage around Ti^{4+} (c) d-band energy splitting due to the octahedral crystal field (Ravichandran, 2011).

Thermoelectric properties of $SrTiO_3$

Doped and/or reduced $SrTiO_3$ ceramic materials have recently shown increased conductivity sufficient for thermoelectric applications (Dawson, Freeman, Hardinga, and Sinclair, 2013). Upon doping either at A-site or B-site and/or creation of oxygen vacancies, $SrTiO_3$ undergoes a transformation to semiconductor (Bhattacharya et al, 2014) producing n-type carriers and if sufficient O is removed it becomes metallic in character. Doped and oxygen deficient strontium titanate ($SrTiO_{3-\delta}$) has been reported to exhibit Seebeck coefficients ($|S| \sim 200 - 300$ μV/K), low resistivity ($\rho < 5$ μΩ/cm) at 750 K due to the carrier electrons possessing high effective mass, m* of (~ 6-10)m_e attributed to its d-band nature and significant high PF ~ 0.8 – 1.3 W/m. K^2(Bhattacharya et al, 2014; Koumoto, 2010 and Dehkordi et al, 2014). For example, n-type La-doped $SrTiO_3$ single crystals are reported to have high PF of 3.6 x 10^{-3} W/m. K^2 at room temperature attributed to high carrier concentration, comparable to Bi-Te alloys(Li, Lin, and Zhou, 2009). However, at 773 K, a decrease in ZT (0.15) occurs in the doped $SrTiO_3$ single crystals because of its inherent high thermal conductivity (Wang et al,

2009; Okuda, Nakanishi, Miyasaka, and Tokura, 2001;Muta, Kurosaki, and Yamanaka, 2005).The high thermal conductivity in $SrTiO_3$ and other oxides emanates from the contribution of the lattice thermal conductivity (k_L). $SrTiO_3$ and other related oxides are also susceptible to oxygen uptake (reoxidation) in air when reduced and oxygen-loss in reducing atmospheres at high temperatures(Kumar, Barasheed, and Alshareef, 2013). Nonetheless, promising n-type thermoelectric properties have been reported in $SrTiO_3$ doped with Nb, W, La, Ce, Pr, Nd, Sm, Gd, Dy and Yb(Kieslich et al, 2016).

Doped $SrTiO_3$ exhibits high carrier mobility and large effective mass due to its d-band structure thereby causing the observed high electrical conductivity and Seebeck coefficient. Despite the reported high S, high σ and large PF, the ZT remains low due to its high k compared with non-oxide TE materials (Liu et al, 2013). It has been widely studied in terms of different dopants, doping mechanisms, and processing conditions (Srivastava et al, 2016). ZT value of 0.27 at 1073 K was obtained in the study of La- and Nb-doped $SrTiO_3$ single crystals (Ohta, Nomura, Ohta, and Koumoto, 2005). $Sr_{1-x}La_xTiO_3$ ($0 \leq x \leq 0.1$) single crystals were studied by Okuda, Nakanishi, Miyasaka, and Tokura (2001) and a large PF of 3600 μW/m. K^2 was observed at room temperature. Improved TE properties (k ~ 3 W/m. K, ZT = 0.37) at 1000 K have been reported in an epitaxial Nb-doped strontium titanate ($SrTi_{0.8}Nb_{0.2}O_3$) films (Wang et al, 2009; Ohta et al, 2005). Kovalevsky *et a (2014)* studied RE-doped $Sr_{0.9}R_{0.1}TiO_{3-\delta}$ (R = Dy, Sm, Nd) ceramics in reduced atmosphere and obtained an optimised ZT of 0.42 at 1190-1225 K. Recently, Lu *et al* obtained a similar result with a ZT = 0.41 at 973 K from their La-doped, A-site deficient strontium titanate sample ($Sr_{1-3x/2}La_xTiO_3$; x = 0.15) processed in 5% H_2/N_2 reduced atmosphere (Bilc et al, 2016; Lu et al, 2016).

Co-doping has been suggested to enhance thermoelectric properties of $SrTiO_3$ ceramics. La-doped and Dy-doped $SrTiO_3$ ceramics ($La_{0.1}Sr_{0.9}TiO_3$ and $Dy_{0.1}Sr_{0.9}TiO_3$) showed maximum ZTs of 0.17 at 673 K (k ~ 3.4 W/m.K, 1073 K) and 0.22 at 573 K (k ~ 2.2 W/m.K), respectively (Muta, Kurosaki, and Yamanaka, 2003; Han, Sun, and Song, 2017). Co doping with La and Dy ($La_{0.1}Sr_{0.83}Dy_{0.07}TiO_3$) (Wang et al, 2010; Wang and Wang, 2013) resulted in a reduced k (2.5 W/m.K) and a high ZT = 0.36 at 1045 K. Enhanced thermoelectric properties have been reported for La-Nb doped $SrTiO_3$ ceramics. Wang *et al*(2013) in the study of La-Nb co-doped $SrTiO_3$ obtained a significant improved power factor and Seebeck coefficient when compared to La-doped $SrTiO_3$ which is attributed to energy filtering effect of grain boundaries. An increase in electrical conductivity is observed in the study of Nb-doped $La_{0.05}Sr_{0.95}TiO_3$(Wang et al, 2009). Recently, Iyasara et al (2022) in the study of La-Sm A-

site co-doped deficient $SrTiO_3$ obtained a significant improved ZT (0.30 at 973 K) and reduced thermal conductivity (k = 2.7 W/m.k at 973 K) which are attributed to the application of a strongly reducing atmosphere in the processing of the materials hence, provided a promising route to further enhance the thermoelectric properties of titanate-based ceramic materials.

Apart from A and/or B-site doping, co-doping, ionic doping mechanism (A/B-site cation vacancy), generation of oxygen vacancies and processing under reducing conditions, incorporation of graphene or graphene oxide (GO), metallic elements or creation of second phases have been suggested as potential routes in improving the thermoelectric properties of doped $SrTiO_3$ based ceramics. Improvement in TE performance due to addition of graphene have been observed in conventional materials (non-oxides) (Feng et al, 2013; Dong et al, 2013), organic (polymeric) materials (Liu, Wang, Yin, and Jiang, 2014; Xu, Chen, and Qiu, 2013) and RE-doped $SrTiO_3$ ceramics (Lin et al, 2015; Okhay et al, 2018). In the study by Lin *et al (*2015), incorporation of small amount of graphene into La-doped $SrTiO_3$ (LSTO) composites and sintered in Ar/H_2 reducing gas produced final materials with multiphase structures and nano grains. As a result of the reduced thermal conductivity and improved power factor, the highest ZT (0.36 at 1023 K) was achieved by adding 0.6 wt. % graphene, which is adjudged to be over 280 % higher when compared to pure LSTO.

Layered Cobaltites – $NaCo_2O_4$

Crystal structure of $NaCo_2O_4$

The crystal structure of Na_xCoO_2 ($NaCo_2O_4$) is a hexagonal layered structure with an alternating stack of Na^+ ions and sheets of CoO_2 along the c-axis (Figure 4) (Nag and Shubha, 2014). The CoO_2 sheets serve as electronic crystal thereby maintaining high electrical conductivity while the Na^+ ion blocks function as phonon scattering boundaries resulting in low k(Nag and Shubha, 2014). Due to the phonon glass-electron crystal (PGEC) behaviour of Na_xCoO_2, its structure type is known as nano-block integration. The large Seebeck coefficients at high temperatures associated with Na_xCoO_2 and other layered cobalt oxides due to the low spin state of Co^{3+} and Co^{4+} are as a result of the CoO_2 sheets in the structure (Koshibae, Tsutsui, and . Maekawa, 2000).

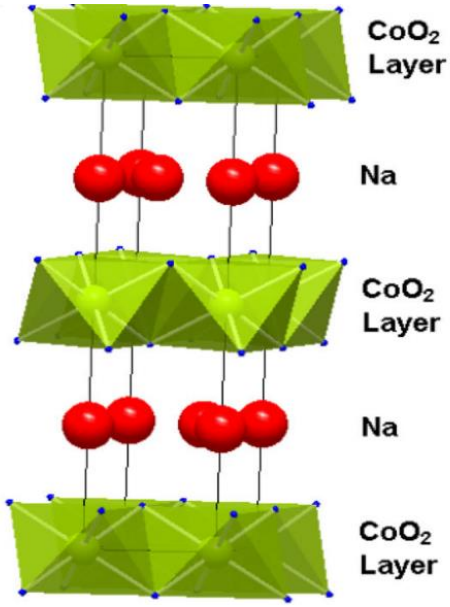

Figure 4. Hexagonal crystal structure of $NaCo_2O_4$ layered cobalt oxide(Nag and Shubha, 2014).

Thermoelectric properties of $NaCo_2O_4$

The short MFP associated with layered structured materials due to phonon scattering at the interfaces between the layers result in low k, hence better candidates for TE applications. Therefore, there is a prospect for layered-structure cobalt oxides as TE materials. Prime p-type oxides for thermoelectric applications are alkaline based layered cobalt oxides (Doumerc, 2009;Fergus,2012). They are found to exhibit large Seebeck coefficients due to low spin state of Co^{3+} (Fergus,2012). These layered cobaltites derive a path for conduction due to the presence of CoO_2 planes while the interconnected points or interfaces between the layers and other parts of the structure inhibit heat flow via lattice phonons. Prominent amongst these layered cobaltites are $Ca_3Co_4O_9$ (Fergus,2012; Ohta, Sugiura, and Koumoto, 2008; Li, Lin, and Zhou, 2009), and $NaCo_2O_4$(Fergus,2012).

Single crystal Na_xCoO_2 shows a thermal conductivity between 4 and 5 W/m.K at 300 K with largeSeebeck coefficient (100 μV/K), low resistivity (200 μΩcm) and a resulting PF value of 50 $\mu W/K^2.cm$ (Terasaki, Sasago, and Uchinokura, 1997; Nag and Shubha, 2014). A high ZT ≈ 1 at 800 K has been reported for a single crystal Na_xCoO_2 sample with a high PF and a low thermal conductivity (Nag and Shubha, 2014; Fergus, 2012). Unlike single crystal Na_xCoO_2, the polycrystalline ceramic Na_xCoO_2 shows a high resistivity which results in ZT = 0.8 at 1000 K (Fujita, Mochida and Nakamura, 2001). It is observed that at high temperatures, Na_xCoO_2 becomes unstable because it tends to absorb moisture in air (a situation known as hygroscopy) while the constituent Na vaporises (degrades) at above 800

°C. This, therefore, limits the TE application of Na_xCoO_2 at elevated temperatures. This drawback notwithstanding, the huge success recorded in TE study of Na_xCoO_2 has led to the exploitation of other layered cobalt oxides such as $Ca_3Co_4O_9$ and $Bi_2Sr_2Co_2O_9$. The crystal structure of $Ca_3Co_4O_9$ is similar to Na_xCoO_2 except that its CoO_2 planes are separated with layers of a distorted rock-like structure (CaO) as shown in Figure 5. ZT values of 1.2 to 2.9 at 873 K(Funahashi et al, 2000) and ZT ≥ 1.1 at 1000 K (Funahashi and Shikano,2002) have been reported for $Ca_3Co_4O_9$ single crystals and $Bi_2Sr_2Co_2O_9$ whiskers, respectively.

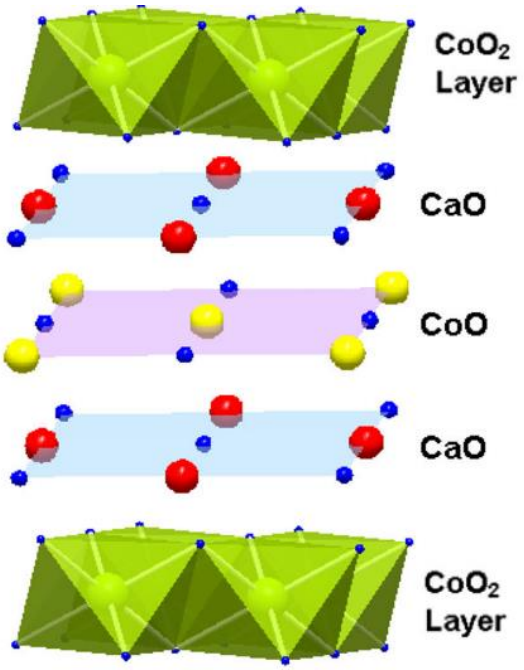

Figure 5. Crystal structure of layered $Ca_3Co_4O_9$ oxide (Nag and Shubha, 2014).

Oxychalcogenides – BiCuSeO

Crystal structure of BiCuSeO

BiCuSeO is a potential p-type TE material, and the oxide with highest known ZT (Kumar and Schwingenschlo, 2016). It is a non-toxic quaternary oxychalcogenide with a tetragonal crystal structure (space group P4/nmm) (Shao et al, 2016; Liu et al, 2011). The crystal structure is composed of alternately stacked layers of insulating oxide $(Bi_2O_2)^{2+}$ and the conductive selenide $(CuSe_2)^{2-}$(Wu, 2014;Kumar and Schwingenschlo, 2016; Liu et al, 2011)as shown in Figure 6. The layered crystal structure enhances phonon scattering at the interface (leading to low k), exhibits weak bonding, and contains heavy elements. BiCuSeO possesses k of 0.4 – 0.5 W/m.K at 900 K(Kumar and Schwingenschlo, 2016; Shao et al, 2016;) and k ≤ 1 at room temperature (Kumar and Schwingenschlo, 2016; Li et al, 2012; Ding et al, 2015).

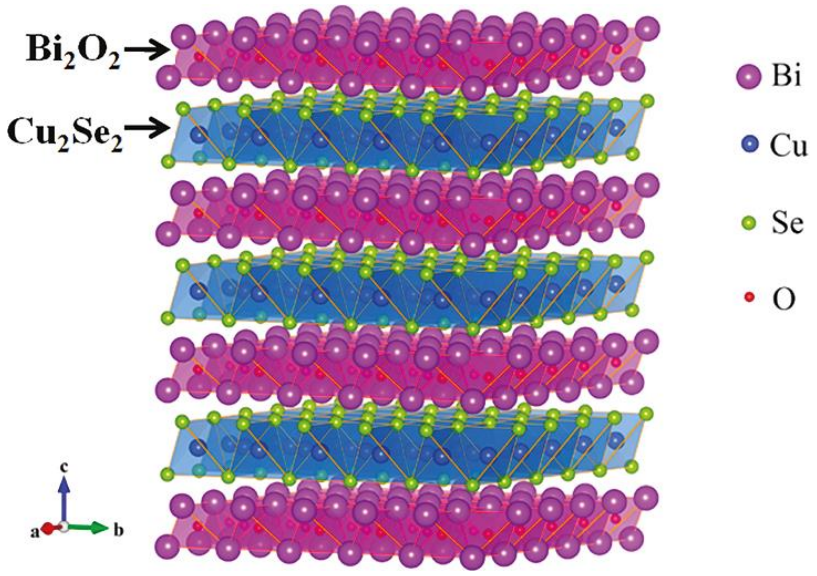

Figure 6. Tetragonal crystal structure of BiCuSeO (space group P4/nmm) (Liu et al, 2011).

Thermoelectric properties of BiCuSeO

Empirical studies and research have shown that BiCuSeO has a good TE properties with σ ≥ 4000 S/m, S ≥ 200 μV/K and k = 0.5 W/m. K with a ZT = 0.7 at 773 (Li, Lin, and Zhou, 2009; Kumar and Schwingenschlo, 2016; Liu et al, 2011). A high ZT (0.76) has been reported in BiCuSeO in which the Sr^{2+} is substituted for Bi^{3+} in $(Bi_2O_2)^{2+}$layer(Zhao et al, 2010). Liu *et al* (2011)enhanced the TE of BiCuSeO properties by introducing Cu deficiencies or holesinto the $(CuSe_2)^{2-}$selenidelayers. In this study, Cu deficient $BiCu_{0.975}SeO$ gave an σ = 3000 S/m, S = 273 μV/K, k = 0.5 W/m. K and a high ZT = 0.81 at 923 K. A further study was reported by Ding et al (2015) for a heavily Ba-doped BiCuSeO ($Bi_{1-x}Ba_xCuSeO$) in which a ZT ~ 1.1 at 923 K was obtained. Finally Bilcet al (2015); Zhaoet al (2014) and Barreteau et al(2014) achieved a ZT ≈ 1.4 at 923 K which remains to date the highest reported for p-type TE oxides.

Tetragonal Tungsten Bronze Oxides

Tetragonal tungsten bronze (TTB) structure materials such as $Nb_{8-x}W_{9+x}O_{47}$(Krumeich, Hussain, Bartsch, and Gruehn, 1995; Krumeich, 1995; Krumeich, Wörle, and Hussain, 2000) and W-Nb-O alloy systems (Winter and Clarke, 2007; Gaultois, Douglas, Sparks, and Seshadri, have been found to share similar structures with Magneli oxides. Na_xWO_3 was first reported in 1824 by Wöhler(Dickens and Whittingham, 1968)but Magneli was the first to determine its structure using x-ray diffraction(Magneli,1949; Zhu et al, 2015). Since this discovery, numerous compounds have been shown to crystallise with the TTB structure. The

main elements or cations common in TTBs include alkali/alkali earth, rare earth, and transition metals (Arnold and Morrison, 2009; Fang, Gong, Gebru, and Yuan, 2014).

TTB Structure

Tetragonal tungsten bronze (TTB) oxide ceramics are the largest class of dielectrics after perovskites(Zhu et al, 2015). The TTB structure is a complex framework lattice with a distorted, corner-sharing oxygen-octahedra ($B1O_6$ and $B2O_6$) which form three different interstices/tunnels or sites (Zhu et al, 2015; Fang, Gong, Gebru, and Yuan, 2014). These tunnels are square (also called perovskite), A1 with a coordination number of 12, pentagonal, A2 with 15-coordinated sites and trigonal/triangular (which is the smallest channel) C containing 9-coordinated sites. A typical TTB structure is represented with the general formula:

$$[A1_2A2_4C_4][B1_2B2_8]O_{30} \qquad 2.0$$

Generally, the A1 and A2 sites are occupied by metal cations of alkali/alkaline earth elements, p-block elements (e.g. Pb, Bi) or RE elements. C-sites are narrow and can be empty in most TTB compounds or occupied by small cations like Li^+. B octahedra sites are often occupied by Ti^{4+}, Nb^{5+} and Ta^{5+}. Because of the capacity to accommodate large cations and possession of great flexibility (or degrees offreedom) for tuning the chemical composition, the TTB family shows excellent properties for diverse applications (Zhu et al, 2015; Lin et al,2014). These include electro-optic, pyroelectric, piezoelectric, semiconductivity (and metallic conductivity), superconductivity and high permittivity. A prototype TTB crystal structure showing the sites and the corner-sharing oxygen octahedra is presented in Figure 7.

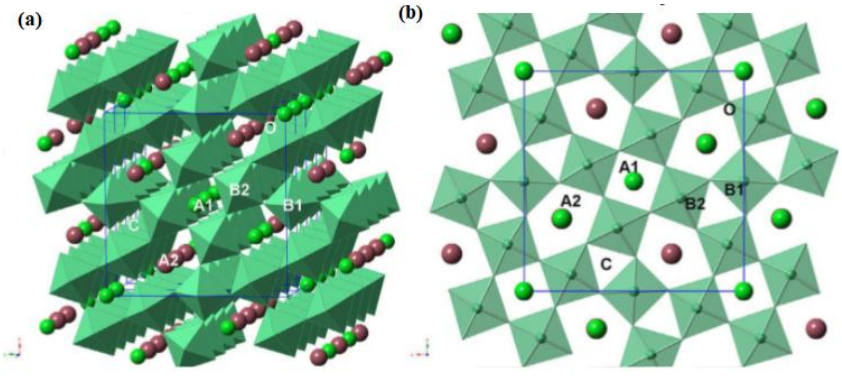

Figure 7. (a) Tilted view of a prototype tetragonal tungsten bronze (TTB) structure showing multiple unit cells and the corner-sharing oxygen octahedra (b) a-b plane projection (// c-axis) illustrating the tunnels described by the corner-sharing oxygen octahedral (Chan et al, 2017).

Thermoelectric Properties of TTB Oxides

Oxides are potential TE materials due to their cheapness or abundance, non-toxicity and high chemical and/or physical stability when subjected to high temperatures. However, high crystallographic symmetry (and small unit cells) associated with oxides lead to high thermal conductivity and low ZT (Heinrich et al, 2015). In order to improve the TE efficiency via lowering of the thermal conductivity, materials with intrinsic phonon scattering centres such as Magneli phases and TTBs have recently attracted attention (Krumeich,1998;Heinrich et al, 2015)[192]. The CS planes and the natural disorder inherent in Magneli phases and TTBs are regarded as intrinsic nanostructures and serve as barriers to phonon propagation.

The TE properties of $Na_{8-x}W_{9+x}O_{47-\delta}$ (x = 0, 0.075, 0.1, 1, 2) TTB compounds were investigated (Kieslich et al, 2016;Heinrich et al, 2015) with compositions exhibiting stability up to 1323 K, low thermal conductivity (1.6-2.0 W/m.K) , and high S = -240 μV/K (indication of n-type) at room temperature. The highest PF = 0.8 μW/cm. K^2 and maximum ZT = 0.043 at 973 K were observed in $Nb_6W_{11}O_{47-\delta}$ (x = 2). The highest ZT (0.043) for $Na_{8-x}W_{9+x}O_{47-\delta}$ obtained in this study is very low compared to other n-type oxides, but the high Seebeck coefficient and very low thermal conductivity recorded show the potential of TTBs for TE applications. Lee *et al*(2010)[210] and Li *et al (*2015) independently investigated the TE performance of single crystal $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ TTB compounds and reported a high PF (200 μW/m.K^2) at 516 K parallel to c-axis and a ZT > 0.5 along the c-direction (Chan et al, 2017). In a related study of TE properties of $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ single crystal and ceramics, k = 1.92 W/m.K (400 K), PF = 40.8 μW/cm.K^2 (550 K), ZT = 1.12 (550 K) for single crystals; and k = 2.28 W/m.K (550 K), PF = 7 μW/cm.K^2 (550 K), ZT = 0.17 (550 K) for ceramics (Lee, Bock, Trolier-McKinstry, and Randall, 2012). In the recent study of the TE properties of $Nb_{8-x}W_{9+x}O_{47}$ (0<x<5) TTB ceramics, S = -95 μV/K, k = 2.6 W/m.K and ZT = 0.2 at 1173 K were reported for $Nb_4W_{13}O_{47}$ (x = 4) composition (Cerretti et al, 2017).

3. APPLICATIONS AND FUTURE PROSPECTS

Novel thermoelectric materials (oxide thermoelectrics) have attracted considerable attention for high-temperature energy conversion because of their superior thermal stability, oxidation resistance, environmental friendliness, and mechanical durability. Unlike, conventional thermoelectric materials (non-oxide materials), novel TE materials can operate reliably in oxidizing atmospheres and harsh industrial conditions at exceeding 800 K, making them particularly suitable for large-scale waste heat recovery applications (Koumoto et al, 2010; Hebert et al, 201).

One of the most significant applications of oxide thermoelectrics is industrial waste heat recovery. Large quantities of heat generated in steel manufacturing, cement production, glass processing, petrochemical refining, and thermal power plants are dissipated into the environment. Oxide thermoelectric generators can convert part of this waste heat directly into electricity without moving parts, thereby improving overall energy efficiency and reducing greenhouse emissions. Oxides such as calcium cobalt oxide and strontium titanate are particularly promising for these applications because they maintain stable transport properties at elevated temperatures (Koumoto& Mori, 2013).

Automotive thermoelectric generators also present a rapidly growing area of interest, internal combustion engines lose a substantial fraction of fuel energy through exhaust heat. Oxide thermoelectric modules integrated into exhaust systems could partially recover this heat and improve fuel efficiency. Because novel thermoelectric materials are chemically stable under oxidative and high-temperature conditions, they possess clear advantages over conventional thermoelectric compounds for long-term automotive operation (Snyder & Toberer, 2008).

Another emerging applications is in renewable energy systems, particularlyconcentrated solar power and geothermal technologies. Oxide thermoelectrics can withstand the high operating temperatures associated with solar thermal collectors and geothermal reservoirs. Their robustnessand resistance to thermal degradation make them suitable for continuous energy harvesting in remote or extreme environments (Liu et al, 2023).

Oxide thermoelectric materials are also increasingly explored for aerospace and space technology applications. Spacecraft, satellites, and remote sensing systems require durable power-generation materials capable of operating under severe thermal cycling conditions.

In microelectronics and sensor technologies, oxide thermoelectrics are being investigated for self-powered sensors and wearable energy-harvesting devices. Advances in thin-film deposition methods, nanostructuring and flexible ceramic composites have enabled the fabrication of miniaturized thermoelectric devices capable of powering low-energy electronics. Transparent conducting oxides such as Indium oxide and doped ZnO are especially attractive because of their optical transparency and electrical conductivity (Koumoto et al, 2010).

The future prospects of oxide thermoelectrics depend largely on overcoming the challenge of simultaneously achieving high electrical conductivity and low thermal conductivity. Several emerging research directions show considerable promise. These include nanostructured oxides, high entropy oxides, defect and band structure engineering, artificial intelligence and

computational materials design, and advanced ceramic processing (Liu et al, 2023; Sarkar et al, 2019; Pei et al, 2012).

CONCLUSION

The growing global demand for sustainable energy technologies and efficient energy utilization has intensified research into thermoelectric materials capable of directly converting waste heat into useful electrical power. Among the numerous classes of thermoelectric materials investigated over the past several decades, oxide materials have emerged as the most promising categoryof novel thermoelectric materials because of their remarkable thermal stability, oxidation resistance, environmental compatibility, mechanical robustness, abundance of constituent element and non-toxicity. Hence making them highly attractive for practical industrial energy recovery applications.

This review has demonstrated that the thermoelectricperformance of oxide materials is fundamentally governed by the intricate relationship among crystal structure, electronic transport, and thermal transport properties. Various oxide crystal systems such as wurtzite structure of ZnO, perovskite architecture of $SrTiO_3$and layered misfit structure of $NaCoO_4$ exhibit distinctive electronic band structures and phonon transport characteristics that directly influence their thermoelectric behaviour.

In summary, novel thermoelectric materials have evolve from relatively low-performance thermoelectric materials into a highly strategic class of advanced functional materials for next-generation energy technologies.Continued interdisciplinary research combining ceramic technology, Solid-state physics, materials chemistry, electronic engineering, nanotechnology and computational engineering is expected to significantly improve the efficiency and commercial viability of oxide thermoelectric systems. With sustained scientific innovation and technological development, oxide thermoelectrics are poised to play a major role in global efforts toward cleaner energy production, improvedenergy efficiency, and environmentally sustainable industrial development.

REFERENCES

1. Abanti Nag & Shubha, V. (2014). Oxide thermoelectric materials: A structure-property relationship. *Journal of Electronic Materials,* 43(4), 962–977.
2. Adindu C. Iyasara., Zhilun Lu., Whitney L. Schmidt., Derek C. Sinclair., & Ian M. Reaney.(2022). Effects of Processing Strategies and La+Sm Co-Doping on the Thermoelectric Performance of A-Site-Deficient $SrTiO_{3-\delta}$ Ceramics.Crystals , 12, 1622.

3. Adrian P. Jones., Terry C. Williams, & Frances Wall. (1996). *Rare Earth Minerals: Chemistry, Origin and Ore Deposits*. United Kingdom: Chapman and Hall.
4. Anderson Janotti & Chris G Van De Walle (2009). Fundamentals of zinc oxide as a semiconductor. *Reports Prog. Phys.*, 72, 126501, 29.
5. applications. Springer
6. Arash Mehdizadeh Dehkordi, Sriparna Bhattacharya, Taghi Darroudi, Jennifer W Gra, Udo Schwingenschlo, Husam N Alshareef, & Terry M Tritt. (2014). Large Thermoelectric Power Factor in Pr-Doped $SrTiO_{3-}$. *Chem. Mater.*, 26(7), 2478−2485.
7. Barreteau, C., Pan, L., Amzallag, E., Zhao, L.D., Bérardan, D & Dragoe,N. (2014). System as good thermoelectric materials Layered oxychalcogenide in the Bi – Cu – O – Se system as good thermoelectric. *Semicond. Sci. Technol.*, 29(6), 1–11.
8. Begoña Abad, Irene Alda, Pablo Díaz-Chao, Hiroshi Kawakami, Albert Almarza, David Amantia, David Gutierrez, Laurent Aubouy, & Marisol Martín-González. (2013). "Improved power factor of polyaniline nanocomposites with exfoliated graphene nanoplatelets (GNPs). *Journal of Materials Chemistry A*, 1(35), 10450–10457.
9. Bhattacharya, S., Mehdizadeh A, Dehkordi., Tennakoon, S., Adebisi, R., Gladden, J.R., Darroudi,T., Alshareef, H.N., & Tritt, T.M. (2014). Role of phonon scattering by elastic strain field in thermoelectric $Sr_{1-x}Y_xTiO_{3-\delta}$. *Journal of Applied Physics,* 115(22).
10. Bin Feng, Jian Xie, Gaoshao Cao, Tiejun Zhu, & Xinbing Zhao. (2013). Enhanced thermoelectric properties of p-type $CoSb_3$/graphene nanocomposite. *J. Mater. Chem. A*, 1(42), 13111–13119.
11. Biprodas Dutta, Jugdersuren Battogtokh, David Mckewon, Igor Vidensky, Neilanjan Dutta, & Ian L. Pegg. (2007). Thermoelectric Properties of $NaCo_{2-x}Fe_x O_y$. *Journal of Electronic. Materials,* 36(7), 746–752.
12. Cerretti,G., Schrade, M., Song, X., Balke, B., Lu, H., Weidner, T., Lieberwirth, I., Panthöfer, M., Norby, T & Tremel, W. (2017). Thermal stability and enhanced thermoelectric properties of the tetragonal tungsten bronzes $Nb_{8-x}W_{9+x}O_{47}$ ($0 < x < 5$). *J. Mater. Chem. A*, 5(20), 9768–9774.
13. Christophe P. Heinrich, Matthias Schrade, Giacomo Cerretti, Ingo Lieberwirth, Patrick Leidich, Andreas Schmitz, Harald Fjeld, Eckhard Mueller, Terje G. Finstad, Truls Norby, & Wolfgang Tremel. (2015). Tetragonal tungsten bronzes $Nb_{8-x}W_{9+x}O_{47-\delta}$: optimization strategies and transport properties of a new n-type thermoelectric oxide. *Mater. Horizons*, 2(5), 519–527.

14. Daniel, I Bilc., Calin, G Floare., Liviu, P Za., Sorina Garabagiu, Sebastien Lemal, & Philippe Ghosez. (2016). First-Principles Modeling of $SrTiO_3$ Based Oxides for Thermoelectric Applications. *J. Phys. Chem. C*, 120, 25678−25688.
15. Dawson, J.A., Li, X., Freeman, C.L., Hardinga, J.H., & Sinclair, D.C. (2013). The application of a new potential model to the rare-earth doping of $SrTiO_3$ and $CaTiO_3$. *Journal of Materials Chemistry C*, 1(8), 1574–1582.
16. Deepanshu Srivastava, Colin Norman, Feridoon Azough, Marion C. Schafer, Emmanuel Guilmeau, Demie Kepaptsoglou, Quentin M. Ramasse, Giuseppe Nicotrad, & Robert Freer, Tuning the Thermoelectric Properties of A-site Deficient $SrTiO_3$ Ceramics by Vacancies and Carrier Concentration. *Phys. Chem. Chem. Phys.*, 18, 26475–26486.
17. Deepanshu Srivastava, Colin Norman, Feridoon Azough, Marion C. Schäfer, Emmanuel Guilmeau, & Robert Freer. (2018), Improving the thermoelectric properties of $SrTiO_3$-based ceramics with metallic inclusions. *J. Alloys Compd.*, 731, 723–730.
18. Dickens, P.G & Whittingham, M.S. (1968). The tungsten bronzes and related compounds. *Q. Rev. Chem. Soc.*, 22(1), 30–44.
19. Donna C. Arnold & Finlay D. Morrison. (2009). B-cation effects in relaxor and ferroelectric tetragonal tungsten bronzes. *J. Mater. Chem.*, 19(36), 6485.
20. Doumerc,J.P., Blangero, M., Pollet, M., Carlier, D., Darriet, J., Berthelot, R., Delmas, C., & Decourt, R. (2009). Transition-metal oxides for thermoelectric generation. *Journal of. Electronic Materials.*, 38(7),1078–1082.
21. Dragos Neagu & John T. S Irvine. (2010). Structure and Properties of $La_{0.4}Sr_{0.4}TiO_3$ Ceramics for Use as Anode Materials in Solid Oxide Fuel Cells. *Chem. Mater.*, 22(6), 5042–5053.
22. Fangzhuan Liu, Lingyu Wang, Qinjian Yin, & Bo Jiang. (2014). Optimization of thermoelectric figure of merit in poly(p-phenylenediamine)/exfoliated graphene nanosheets composites," *RSC Adv.*, 4(93), 51558–51568.
23. Frank Krumeich, Michael Wörle, & Altaf Hussain. (2000). Superstructure and twinning in the tetragonal tungsten bronze-type phase $Nb_7W_{10}O_{47}$. *J. Solid State Chem.*, 149(2), 428–433.
24. Frank Krumeich. (1998). Order and Disorder in Niobium Tungsten Oxides of the Tetragonal Tungsten Bronze Type. *Acta Crystallogr. Sect. B Struct. Sci.*, 54(3), 240–249.
25. Fu Li, Jing-Feng Li, Li-Dong Zhao, Kai Xiang, Yong Liu, Bo-Ping Zhang, Yuan-Hua

Lin, Ce-Wen Nana, & Hong-Min Zhu. (2012). Polycrystalline BiCuSeO Oxides as a Potential Thermoelectric Material. *Energy Environ. Sci.*, 5, 7188–7195.

26. Fujita, K., Mochida, T., & Nakamura, K. (2001). High Temperature Thermoelectric Properties of $Na_xCoO_{2-\delta}$ Single Crystals. *Japanese Journal of Applied Physics,* 40, 4644.
27. Funahashi, R., Matsubara, I., Ikuta, H., Takeuchi, T., Mizutani, U., & Sodeoka, S. (2000). An oxide single crystal with high thermoelectric performance in air. *Japaneese Journal of Applied Physics,* 39 (11B), Part 2, L1127–L1129.
28. George, S Nolas & Joe Poon. (2006). Recent Developments Thermoelectric Materials. *MRS Bull.*, 31, 1–7.
29. Gerhard Henning Olsen (2016). Ferroelectric Tungsten Bronzes. Norwagian University of Science and Technology.
30. Goldschmidt, V.M. *Geochemistry*. (1958). Oxford, Clarendon Press.
31. Gregor Kieslich., Giacomo Cerretti., Igor Veremchuk., Raphaël P. Hermann., Martin Panthöfer., Juri Grin., and Wolfgang Tremel.(2016). A chemists view: Metal oxides with adaptive structures for thermoelectric applications. *Phys. Status Solidi Appl. Mater. Sci.*, 213(3), 808–823.
32. Hejtmanek, J. (2000). Misfit.Layered cobaltite with an anisotropic giant magnetoresistance: $Ca_3Co_4O_9$ as a thermoelectric material. Physical Review B, 62(1), 166-175.
33. Hezhu Shao, Xiaojian Tan, Guo Qiang Liu, Jun Jiang, & Haochuan Jiang. (2016). A first-principles study on the phonon transport in layered BiCuOSe. *Sci. Rep.*, 6, 1–9.
34. Hiroaki Muta, Ken Kurosaki, & Shinsuke Yamanaka. (2004). Thermoelectric properties of doped $BaTiO_3$-$SrTiO_3$ solid solution. *Journal of Alloys Compounds*, 368(1–2), 22–24.
35. Hiroaki Muta, Ken Kurosaki, & Shinsuke Yamanaka. (2005). Thermoelectric properties of reduced and La-doped single-crystalline $SrTiO_3$. *Journal of Alloys Compound.*, 392(1–2), 306–309.
36. Hiroaki Muta, Ken Kurosaki, & Shinsuke Yamanaka.(2003). Thermoelectric properties of rare earth doped $SrTiO_3$. *Journal of Alloys Compound.*, 350(1–2), 292–295.
37. Hiromichi Ohta, Kenji Sugiura, and Kunihito Koumoto.(2008). Recent Progress in Oxide Thermoelectric Materials: p-Type $Ca_3Co_4O_9$ and n-Type $SrTiO_3$-. 47(19), 8429–8436.
38. Hongchao Wang & Chunlei Wang. (2013). Thermoelectric properties of Yb-doped

$La_{0.1}Sr_{0.9}TiO_3$ ceramics at high temperature. *Ceram. Int.*, 39(2), 941–946.

39. Hosono, H., &Koumoto, K (2007).Giant thermoelectric Seebeck coefficient of a two-dimensional electron gas in SrTiO3.Nature Materials, 6(2), 129-1334.
40. Ichiro Matsubara, Ryoji Funahashi, Masahiro Shikano, Kei Sasaki, & Hiroyuki Enomoto. (2002). Cation substituted $(Ca_2CoO_3)_xCoO_2$ films and their thermoelectric properties. *Appl. Phys. Lett.*, 80(25), 4729–4731.
41. Ichiro Terasaki. (2013). Layered Cobalt Oxides: Correlated Electrons for Thermoelectrics, in *Thermoelectric Nanomaterials: Materials Design and Applications.*, K. Koumoto and T. Mori, (Eds). Berlin Heidelberg: Springer, Springer Series in Materials Science, 182, 51–70.
42. Janina Molenda, Claude Delmas, & Paul Hagenmuller. (1983). Electronic and electrochemical properties of Na_xCoO_{2-y} cathode. *Solid State Ionics*, 9(10), 431–435.
43. Jason Chan. (2015). Study of Filled Tungsten Bronze Strontium Barium Niobate for Thermoelectric Applications. M.Sc Thesis, Pennsylvania State University, US.
44. Jason H. Chan, Jonathan A. Bock, Hanzheng Guo, Susan Trolier-McKinstry, & Clive A. Randall. (2017). Filled oxygen-deficient strontium barium niobates. (2017). *Journal of American Ceramic Society*,100(2), 774–782.
45. Jayakanth Ravichandran, Wolter Siemons, Dong-wook Oh, Justin T Kardel, Arvind Chari, Herman Heijmerikx, Matthew L Scullin, Arun Majumdar, Ramamoorthy Ramesh, & David G Cahill.(2010). High temperature thermoelectric response of double-doped $SrTiO_3$ epitaxial films. *Sci. Technol.*, 6.
46. Jayakanth Ravichandran. (2011). Thermal and Electrical Transport in Oxide Heterostrucutures. PhD, Thesis, University of California, Berkeley.
47. Jeffrey W. Fergus. (2012). Oxide materials for high temperature thermoelectric energy conversion. *Journal of European Ceramic Society,* 32(3), 525–540.
48. Jiao Han, Qiu Sun, & Ying Song (2017). Enhanced thermoelectric properties of La and Dy co-doped, Sr-deficient $SrTiO_3$ ceramics. *Journal of Alloys Compounds*, 705, 22–27.
49. Jing Li, Jiehe Sui, Yanling Pei, Celine Barreteau, David Berardan, Nita Dragoe, Wei Cai, Jiaqing He, & Li-Dong Zhao. (2012). A high thermoelectric figure of merit ZT > 1 in Ba heavily doped BiCuSeO oxyselenides. *Energy Environmental Science*, 5(9), 8543.
50. Jingdu Dong, Wei Liu, Han Li, Xianli Su, Xinfeng Tang, & Ctirad Uher. (2013). In situ synthesis and thermoelectric properties of PbTe-graphene nanocomposites by utilizing

a facile and novel wet chemical method. *J. Mater. Chem. A*, 1(40), 12503–12511.

51. Jinglei Xiang & Lawrence T. Drzal.(2012). Templated growth of polyaniline on exfoliated graphene nanoplatelets (GNP) and its thermoelectric properties. *Polymer.*, 53(19), 4202–4210.
52. Jingxuan Ding, Ben Xu, Yuanhua Lin, Cewen Nan, & Wei Liu. (2015). Lattice vibration modes of the layered material BiCuSeO and first principles study of its thermoelectric properties. *New Journal of Physics.*, 17, 083012.
53. Jun Wang, Bo Yu Zhang, Hui Jun Kang, Yan Li, Xinba Yaer, Jing Feng Li, Qing Tan, Shuai Zhang, Guo Hua Fan, Cheng Yan Liu, Lei Miao, Ding Nan, Tong Min Wang, & Li Dong Zhao (2017). Record high thermoelectric performance in bulk $SrTiO_3$ via nano-scale modulation doping. *Nano Energy*, 35, 387–395.
54. Klaus Van Benthem, Elsasser, C & Roger H French. (2001). Bulk Electronic Structure of $SrTiO_3$: Experiment and Theory. *J. Appl. Phys.*, 90, 6156–6164.
55. Kongli Xu, Guangming Chen, & Dong Qiu. (2013). Convenient construction of poly(3,4-ethylenedioxythiophene)-graphene pie-like structure with enhanced thermoelectric performance," *Journal of Materials Chemistry A*, 1(40), 12395–1239.
56. Koshibae, W., Tsutsui, K., & Maekawa, S. (2000). Thermopower in cobalt oxides. *Phys. Rev. B - Condens. Matter Mater. Phys.*, 62(11), 6869–6872.
57. Koumoto, K., Mori, T. (Eds.) (2013). Thermoelectric nanomaterials: Materials design and
58. Koumoto, K., Wang, Y., Zhang, R., Kosuga, A., &Funahashi, R. (2010). Oxide thermoelectric
59. Kovalevsky, A.V., Populoh, S., Patricio, S.G., Thiel, P., Ferro, M.C., Fagg, D.P., J R Frade, J.R., & Weidenkaff, A. Design of $SrTiO_3$-Based Thermoelectrics by Tungsten Substitution, *Journal of Physical Chemistry C,* 119(9), 4466−4478.
60. Kovalevsky, A.V., Yaremchenko, A.A., Populoh, S., Thiel, P., Fagg, D.P., Weidenkaff, A & Frade, J.R. (2014). Towards a high thermoelectric performance in rare-earth substituted $SrTiO_3$: effects provided by strongly-reducing sintering conditions. *Phys. Chem. Chem. Phys.*, vol. 16, no. 48, pp. 26946–26954, 2014.
61. Krumeich, F. (1995). Oxidation-Products of $Nb_7W_{10}O_{47}$ - A Transmission Electron-Microscopy Study. *J. Solid State Chem.*, 119(2), 420–427.
62. Krumeich, F., Hussain,A., Bartsch, C & Gruehn, R. (1995). Preparation and Structure of Niobium Tungsten-Oxides $(Nb,W)_{(17)}O_{-47}$ with Mixed-Valency. *Zeitschrift fur Anorg. und Allg. Chemie*, 621(5), 799–806.

63. Kumar, S & Schwingenschlo, U. (2016). Lattice thermal conductivity in layered BiCuSeO. *Phys. Chem. Chem. Phys.*, 18,19158–19164.
64. Kun Lin, Yangchun Rong, Hui Wu, Qingzhen Huang, Li You, Yang Ren, Longlong Fan, Jun Chen, & Xianran Xing. (2014). Ordered Structure and Thermal Expansion in Tungsten Bronze Pb_2 $K_{0.5}Li_{0.5}Nb_5O_{15}$. (2014). *Inorg. Chem.*, 53(17), 9174–9180.
65. Kunihito Koumoto, Yifeng Wang, Ruizhi Zhang, Atsuko Kosuga, & Ryoji Funahashi. (2010). Oxide Thermoelectric Materials: A Nano Structuring Approach. *Annu. Rev. Mater. Res.*, 40, 363–394.
66. Lassi Karvonen;, Petr Tomes;, and Auke Weidenkaff, (2011). Thermoelectric performance of perovskite- type oxide materials Materials. *Mater. \matters*, 6(4), 92–99 .
67. Li Hanbo, Zheng Ganhong, Dai Zhenxiang, Yuan Zhenheng, Wang Haiqiu, & Ma Yongqing.(2014). Thermoelectric properties of $Sr_{0.9}La_{0.1}TiO_3$and $Sr_{2.7}La_{0.3}Ti_2O_7$ with 15% Ag addition. *J. Rare Earths*, 32(4), 314–319.
68. Li-dong Zhao, Jiaqing He, David Berardan, Yuanhua Lin, & Jing-feng Li. (2014). BiCuSeO oxyselenides : new promising thermoelectric materials. *Energy Environ. Sci.*, 7, 2900–2924.
69. Lihua Zhang, Tsuyoshi Tosho, Noriyuki Okinaka, & Tomohiro Akiyama. (2007). Thermoelectric Properties of Combustion Synthesized and Spark Plasma Sintered $Sr_{1-X}R_xTiO_3$ (R = Y, La, Sm, Gd, Dy, $0<X\leq0.1$). *Mater. Trans.*, 48(8), 2088–2093.
70. Liu, J., Wang, C.L., Li, Y., Su, W.B., Zhu, Y.H., Li, J.C & Mei, L.M. (2013). Influence of rare earth doping on thermoelectric properties of $SrTiO_3$ ceramics. *J. Appl. Phys.*, 114(22), 20.
71. Liu, Y., Zhi, J., Li, W., Yang, Q., Zhang, L., & Zhang, Y. (2023). Oxide materials for
72. M.-H. Whangbo, E. Canadell, P. Foury, & J.-P. Pouget. (1991). Hidden Fermi surface nesting and charge density wave instability in low-dimensional metals. *Science (80-.).*, 252, 96–98.
73. Magneli, A. (1949). The Crystal Structure of Tetragonal Potassium. *Ark Kemi*, 1(3), 213–221.
74. Mang, A., Reimann,K & St. Riibenacke. (1995). Band Gaps, Crystal-Field Splitting, Spin-Orbit Coupling, and Excition Binding Energies in ZnO under Hydrostatic Pressure. *Solid State Commun.*, 94(4), 251–254.
75. Masset, A.C., Michel, C., Maignan, A., Hervien, M., Toulemonde, O., Studer, F., Raveau, B., &

76. materials: Nanostructuring approach. Annual Review of Materials Research, 40, 363-394.

77. Mengjie Qin, Feng Gao, An Min Wang, Chaochao Zhang, Qingqing Zhang, & Li Wang. (2016). Fabrication and High-Temperature Thermoelectric Properties of Ti-Doped $Sr_{0.9}La_{0.1}TiO_3$ Ceramics. *Ceramic International*, 42(1)5.

78. Mengjie Qin, Feng Gao, Gaogao Dong, Jie Xu, Maosen Fu, Yu Wang, Mike Reece, & Haixue Yan. (2018). Microstructure characterization and thermoelectric properties of $Sr_{0.9}La_{0.1}TiO_3$ ceramics with nano-sized Ag as additive. *J.Alloys Compd.*, 762, 80–89.

79. Michael R. Winter & David R. Clarke. (2007). Oxide materials with low thermal conductivity. *Journal of American Ceramic Society*, 90(2), 533–540.

80. Michael W. Gaultois, Jason E. Douglas, Taylor D. Sparks, & Ram Seshadri.(2015). Single-step preparation and consolidation of reduced early-transition-metal oxide/metal n-type thermoelectric composites. *AIP Adv.*, 5(9).

81. Michitaka Ohtaki, Kazuhiko Araki, & Kiyoshi Yamamoto. (2009). High thermoelectric performance of dually doped ZnO ceramics. *Journal of Electroic Materials*, 38(7), 1234–1238.

82. Michitaka Ohtaki, Sayaka Maehara, & Shinichirou Shige. (2003). Thermoelectric Properties of Al-doped ZnO Sintered with Nanosized Void Forming Agents in *22nd lnternational Conference on Thermoelectrics*, 171–174.

83. Migliori, A., Sarrao, J.L., William M. Visscher., Bell, T.M., Ming Lei., Fisk, Z & Leisure, R.G.(1993). Resonant ultrasound spectroscopic techniques for measurement of the elastic moduli of solids. *Phys. B*, 1(183), 1–24.

84. Müller, U. (2007). *Ionic Compounds, in Inorganic Structural Chemistry*, Second Edi. United Kingdom: John Wiley & Sons, Ltd, Chichester.

85. Naoki Iwagami, Hajime Nagata, Isao Sakaguchi, & Tadashi Takenaka. (2016). Diffusion behavior of Ag electrodes into $(Bi_{1/2}Na_{1/2})TiO_3$ ceramics. *Journal of the Ceramic Society of Japan*, 124(6) 644–647.

86. Naoki Wakiya, Jui-kai Wang, Atsushi Saiki, Kazuo Shinozaki, & Nobuyasu Mizutani. (1999). Synthesis and Dielectric Properties of $Ba_{1-x}\ R_{2x/\ 3}Nb_2O_6$ (R : Rare Earth) with Tetragonal Tungsten Bronze Structure. *Journal of European Ceramic Society*, 19, 1071–1075.

87. Ngai, K.L & Reinecke, T.L. (1978). Structural instabilities and superconductivity in the alkali tungsten bronzes. *J. Phys. F Met. Phys.*, 8(1), 151–160.

88. Nicola A. Hill. (2002). Density Functional Studies of Multiferroic Magnetoelectrics.

Annu. Rev. Mater. Res., 32(1), 1–37, 2002.

89. Ohta, H., Kim, S., Mune, Y., Mizoguchi, T., Nomura, T., Nakanishi, Y., Ikuhara, Y., Hirano, M.,
90. Oide,Y., Miyazaki, Y., Ono, Y., X Y Huang, X. Y., & Kajitani,T. (2006). Thermogravimetric Study and High-Temperature Thermoelectric Properties of $[Ca_2(Co_{1-x}A_x,)_{03}]_{0.62}CoO_2$, in *2006 International Conference on Thermoelectrics*, 402–405.
91. Okuda, T., Nakanishi, K., Miyasaka, S & Tokura, Y. Large Thermoelectric Response of Metallic Perovskite: $Sr_{1-x}La_xTiO_3$ ($0 \leq x \leq 0.1$). *Phys. Rev. B*, 63, 1131041–1131044.
92. Olena Okhay, Sebastian Zlotnik, Wenjie Xie, Krzysztof Orlinski, Maria J. Hortiguela Gallo, Gonzalo Otero-Irurueta, Antonio J.S. Fernandes, Dorota A. Pawlak, Anke Weidenkaff, & Alexander Tkach. (2018). Thermoelectric performance of Nb-doped $SrTiO_3$ enhanced by reduced graphene oxide and Sr deficiency cooperation," *Carbon* ., 143, 215–222.
93. Olena Okhay, Sebastian Zlotnik, Wenjie Xie, Krzysztof Orlinski, Maria J. Hortiguela Gallo, Gonzalo Otero-Irurueta, Antonio J.S. Fernandes, Dorota A. Pawlak, Anke Weidenkaff, & Alexander Tkach. (2019). Thermoelectric performance of Nb-doped $SrTiO_3$ enhanced by reduced graphene oxide and Sr deficiency cooperation. *Carbon* ., 143, 215–222.
94. Onodera, A & Takesada, M. (2012). Electronic Ferroelectricity in II-VI Semiconductor ZnO in *Advances in Ferrolectrics*, P.-B. A, Ed. Intech.
95. Ozdogan, K., Upadhyay,M Kahaly., Alshareef, H.N & Schwingenschögl, U. (2012). Anomalous enhancement of the thermoelectric figure of merit by V co- doping of Nb-$SrTiO_3$. *Appl. Phys. Lett*., 100(19) , 1931101-1931104.
96. Petr Tomeš, Matthias Trottmann, Clemens Suter, Myriam Heidi Aguirre, Aldo Steinfeld, Philipp Haueter, and Anke Weidenkaff. (2010). Thermoelectric oxide modules (TOMs) for the direct conversion of simulated solar radiation into electrical energy. *Materials (Basel),*3(4), 2801–2814.
97. properties of Al-doped ZnO as a promising oxide material for high- temperature thermoelectric conversion. *Journal of Materials. Chemistry,* 7, 85–90.
98. Qiang Li, Zhiwei Lin, & Juan Zhou. (2009). Thermoelectric materials with potential high power factors for electricity generation. *Journal of Electronic Materials,* 38(7), 1268–1272.
99. Ranga, M.R Raju & Choudhary,R.N.P.(2003). Diffuse phase transition in

$Sr_5RTi_3Nb_7O_{30}$ (R=La, Nd and Sm). *J. Phys. Chem. Solids*, 64(5), 847–853.

100. Ruth Margaret Adams. (2010). Structure-composition-property Relations in B-site Deficient Hexagonal Perovskite Systems. PhD Thesis, University of Huddersfield, UK.
101. Ryoji Funahashi & Masahiro Shikano. (2002). $Bi_2Sr_2Co_2O_y$ whiskers with high thermoelectric figure of merit. *Appl. Phys. Lett.*, 81(8), 1459–1461.
102. Ryoji Funahashi. (2009). Oxide thermoelectric power generation. Thermoelectrics Applications Workshop, San Diego, CA, September 29 - October 1. Retrieved from*https://www.energy.gov/eere/vehicles/2009-thermoelectrics-applications-workshop-1*
103. Sales, B. C. (1998). Electron Crystals and Phon lLasses: A new Path to Improved Thermoelectric Materials. *MRS Bull.*, 23(1),15–2.
104. Sarath Kumar, S.R., Abeer, Z Barasheed, & Alshareef, H.N. (2013). High Temperature Thermoelectric Properties of Strontium Titanate Thin Films with Oxygen Vacancy and Niobium Doping. *Appl. Mater. Interfaces*, 5(15), 7268–7273.
105. Shin Ichi Shamoto, Yuki Hasegawa, & Tsuyoshi Kajitani. (2006). Two-Dimensional Sodium Fluctuation at High Temperatures in High-Temperature Thermoelectric Material γ-$Na_{0:7}CoO_2$. *Japanese Journal of Applied Physics, Part 1 Regul. Pap. Short Notes Rev. Pap.*, 45(8), 6395–6397.
106. Shingo Ohta, Takashi Nomura, Hiromichi Ohta, & Kunihito Koumoto. (2005). High-temperature carrier transport and thermoelectric properties of heavily La- or Nb- doped single crystals," *J. Appl. Phys.*, vol. 97, no. 3, pp. 0341061–0341064, 2005.
107. Shingo Ohta, Takashi Nomura, Hiromichi Ohta, Masahiro Hirano, Hideo Hosono, & Kunihito Koumoto. Large thermoelectric performance of heavily Nb-doped $SrTiO_3$ epitaxial film at high temperature. *Appl. Phys. Lett.*, 87, 092108.
108. Slack, G.A. (1995). New materials and performance limits for thermoelectric cooling.
109. Smirnov, M & Saint-Grégoire, P. (2013). An innovative approach to structural instabilities in tetragonal tungsten bronze crystals through the concept of rigid unit modes. *Condens. Matter*, 1–22.
110. Snyder, G.J., &Toberer, E.S. (2008). Complex thermoelectric materials. Nature Materials, 7(2),
111. Soonil Lee, Rudeger H.T. Wilke, Susan Trolier-Mckinstry, Shujun Zhang, & Clive A. Randall. (2010). $Sr_xBa_{1-x}Nb_2O_{6-\delta}$ Ferroelectric- thermoelectrics: Crystal anisotropy, conduction mechanism, and power factor. *Appl. Phys. Lett.*, 96(3), 4–7.
112. Terasaki, I. (2005). Thermoelectric materials in layered transition-metal oxides, in *24th*

International Conference on Thermoelectrics, 301–306.

113. Terasaki, I., Sasago, Y., & Uchinokura, K. (1997). Large thermoelectric power in $NaCo_2O_4$ single crystals. *Phys. Rev. B*, 56(20), R12685–R12687.
114. Terry M Tritt & Subramanian, M.A. (2006). Thermoelectric Materials, Phenomena, and Applications : A Bird's Eye View. *MRS Bull.*, 31, 188–198.
115. Tomoaki Tanaka, Shin Nakamura, & Shuichi Iida.(1994). Observation of Distinct Metallic Conductivity in $NaCo_2O_4$. *Japanese Journal of Applied Physics*, 33(4B), L581–L582.
116. Toshiki Tsubota, Michitaka Ohtaki, Koichi Eguchi, & Hiromichi Arai. (1997). Thermoelectric
117. properties of Al-doped ZnO as a promising oxide material for high- temperature thermoelectric conversion. *Journal of Materials. Chemistry,* 7, 85–90.
118. Venkatesh, J & Murthy, V.R.K. (1999). Microwave dielectric properties of (Ba, Sr)$(Zn_{1/3}Ta_{2/3})O_3$ dielectric resonators, in *Materials Chemistry and Physics 58 (3)*, Elsevier B.V., 276–279.
119. Wang, H. C., Wang, C.L., Su, W.B., Liu, J., Peng, H., Zhang, J.L., Zhao, M.L., Li, J.C., Yin, N., & Mei, L.M. (2009). Substitution effect on the thermoelectric properties of reduced Nb-doped. *Journal of Alloys Compound.*, 486, 693–696.
120. Wang, H.C., Wang, C.L., Su, W.B., Liu, J., Peng, H., Sun, Y., Zhang, J.L., Zhao, M.L., Li, J.C., Yin,N & Mei, L.M. (2011). Synthesis and thermoelectric performance of Ta doped $Sr_{0.9}La_{0.1}TiO_3$ ceramics. (2011). *Ceramics International*, 37(7), 2609–2613.
121. Wang, H.C., Wang, C.L., Su, W.B., Liu, J., Zhao, Y., Peng,Y.H., Zhang, J.L., Zhao, M.L., Li, J.C., Yin, N & Mei, L.M. Enhancement of thermoelectric figure of merit by doping Dy in $La_{0.1}Sr_{0.9}TiO_3$ ceramic. *Mater. Res. Bull.*, 45(7), 809–812.
122. Wanger, P and Helbig, R. (1974). The Hall Effect and the Anisotropy of the Mobility of the Electrons in ZnO. *J Phys Chem Solids*, 35, 327–335.
123. Wiff, J.P., Kinemuchi, Y., Kaga, H., C Ito, and K Watari, "Correlations between thermoelectric properties and effective mass caused by lattice distortion in Al-doped ZnO ceramics," *J. Eur. Ceram. Soc.*, vol. 29, pp. 1413–1418, 2009.
124. Wood, C. (1988). Materials for thermoelectric energy conversion," R*eports on Progress in Physics*, 51, 459–539.
125. Xiao Li Zhu, Xiao Qiang Liu, & Xiang Ming Chen. (2011). Crystal Structure and Dielectric Properties of $Sr_5RTi_3Nb_7O_{30}$ (R=La, Nd, Sm, and Eu) Tungsten Bronze Ceramics. *Journal American of Ceramic Society,* 94(6), 1829–1836.

126. Xiao Zhang & Li-dong Zhao. (2015). Thermoelectric materials : Energy conversion between heat and electricity. *Journal of Materials*, 1(2), 92–105.

127. Yi Li, Jian Liu, Chun-Lei Wang, Wen-Bin Su, Yuan-Hu Zhu, Ji-Chao Li, & Liang-Mo Mei, Thermoelectric properties of $Sr_{0.61}Ba_{0.39}Nb_2O_{6-\delta}$ ceramics in different oxygen-reduction conditions. *Chinese Phys. B*, 24(4), 047201.

128. Yifeng Wang, Xiaoyan Zhang, Liming Shen, Ningzhong Bao, Chunlei Wan, Nam Hee Park, Kunihito Koumoto, & Arunava Gupta. (2013). Nb-doped grain boundary induced thermoelectric power factor enhancement in La-doped $SrTiO_3$ nanoceramics. *J. Power Sources*, 241, 255–258.

129. Yong Liu, Li-dong Zhao, Yaochun Liu, Jinle Lan, Wei Xu, Fu Li, Bo-ping Zhang, & David Berardan. (2011). Remarkable Enhancement in Thermoelectric Performance of BiCuSeO. *Journal of American Chemical Society,* 133, 20112–20115.

130. Yu Jiao Fang, Gao Shang Gong, Zerihun Gebru, & Song Liu Yuan. (2014). Effects of A1 site occupation on dielectric and ferroelectric properties of $Sr_4CaRTi_3Nb_7O_{30}$ (R = Ce, Eu) tungsten bronze ceramics. *Chinese Phys. B*, 23(12).

131. Yue Lin, Colin Norman, Deepanshu Srivastava, Feridoon Azough, Li Wang, Mark Robbins, Kevin Simpson, Robert Freer, & Ian A. Kinloch. (2015). Thermoelectric Power Generation from Lanthanum Strontium Titanium Oxide at Room Temperature through the Addition of Graphene. *ACS Appl. Mater. Interfaces*, 7(29), 15898–15908.

132. Zhao, L.D., Berardan, D., Pei, Y.L., Byl, C., Dragoe, N., Zhao, L.D., & Berardan, D. (2010). $Bi_{1-x}Sr_xCuSeO$ oxyselenides as promising thermoelectric materials. *Appl. Phys. Lett.*, 97, 0921181–0921184.

133. Zheng, G.H., Dai, Z.X., Li, H.B., Wang, H.Q., Li ,Y.Q., Xu, X.F., Huang, B.T., Ma, Y.Q., & Li, G. (2014). Improving the Thermoelectric Properties of $Sr_{0.9}La_{0.1}TiO_3$ by Ag Addition.*Journal of Low Temperature Physics*, 174, 128–135.

134. Zhilun Lu, Huairuo Zhang, Wen Lei, Derek C. Sinclair, & Ian M. Reaney (2016). High-Figure-of-Merit Thermoelectric La-Doped A-Site-Deficient $SrTiO_3$ Ceramics. *Chem. Mater.*, 28(3), 925–935.

135. Zhu, X., Fu,M., Stennett, M.C., Vilarinho, P.M., Levin, I., Randall, C.A., Gardner, J., Morrison, F. D. & Reaney, I.M. (2015). A Crystal-chemical framework for relaxor versus normal ferroelectric behavior in tetragonal tungsten bronzes. *Chem. Mater.*, 27(9), 3250–3261.