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Complex thermoelectric materials pdf

Due to growing global energy crises, the dangerous impact on the environment and the limited supply of fossil fuels, the need for an alternative energy source is significant. Thermoelectric materials have come to save the world from the growing energy crisis. Waste heat from motor vehicles and other electrical appliances can be used by generating electricity from it without adding more pollution to the atmosphere that is possible only with the help of thermoelectric materials. Thermoelectric materials have a wide range of applications ranging from small-scale production of electricity to their use in missiles and spacecraft. The thermoelectric phenomenon (TE) has three essential effects: Seebeck effect, Peltier effect and Thomson effect. The Seebeck effect is the direct conversion of heat into electricity (power generation), and the Peltier effect is just the opposite (cooling). For both results, it is necessary to form a junction between semiconductors of type n and p. Thomson effect, on the other hand, requires only one conductor carrying DC which when subjected to temperature gradient gives the absorption or evolution of heat. TE devices have the advantage over other conventional devices due to the on-the-go in-situ, noise-free service reliability, and exceptional. A TE module for both power generation and cooling consists of electrically connected thermocouples that include p and n semiconductors. For power generation, thermocouples are thermally connected in parallel and electrically in series. The efficiency of TE materials is regulated by its merit size figure $ZT = S^2\sigma T/\kappa$ which depends on both the electrical and thermal properties of the materials. S is the Seebeck coefficient that is given by the ratio of the voltage output to the temperature gradient (∇T), σ is electrical conductivity, and κ is thermal conductivity ($\kappa = \kappa_e + \kappa_l$, electronic thermal conductivity and lattice). The quantity $S^2\sigma$ is called the power factor and is associated with electrical transport. The thermodynamic efficiency of energy generation is given by [39, 40] T_c is the temperature of the cold side, T_h is the temperature of the hot side, ZT is the figure of merit, and T/T_h is Carnot efficiency. So big ZT and substantial difference between T_c and T_h is the key to increasing thermodynamic efficiency η . Improving the ZT of any material requires the σ and simultaneous reduction of κ , which simultaneously contradicts the Weidmann-Franz law. According to the Weidmann-Franz law, the ratio of σ to κ remains constant, implying that these two quantities cannot be increased at the same time and decreased respectively [41]. In order to improve ZT , some special strategies need to be used to reduce κ and increase σ in search of materials that can be better thermoelectric, it has been found that degenerate semiconductors can be potential thermoelectric materials, as is clear from Figure 1. Figure 1. This This shows the relationship between ZT and other parameters such as electronic conductivity σ , Seebeck S coefficient, thermopower α and electronic thermal conductivity κ_e , thermal conductivity of the lattice and total thermal conductivity κ . Download figure: standard high-resolution image image For degenerate semiconductors, S is given by [42] κ_B is Boltzmann's constant, h is constant Planck, m is the actual mass charge. It is clear that S increases with the decrease in the concentration of vector n . Electrical conductivity, on the other hand, is given $\sigma = ne$, where μ is the mobility of charge carriers. To increase the power factor, it is necessary to decouple the Seebeck coefficient and electrical conductivity because these two quantities depend on n in opposite ways. Also as a total thermal conductivity κ is the sum of electronic thermal conductivity κ_e and thermal conductivity lattice κ_l , both these parts of thermal conductivity must be examined separately. Ke is given by $L\sigma T$, where L is the Lorentz number. κ_e is directly proportional to the number of charge vectors n , and therefore it becomes difficult to reduce this part of thermal conductivity. Thermal conductivity lattice κ_l is given by $\kappa_l = Cv v_l$ [43], where Cv is the specific heat for unit volume, v is the speed of sound, l is phonon medium free path (mfp) and has little dependence on n . Therefore, to reduce thermal conductivity, strategies must be made mainly to reduce κ_l . Alter Cv and v is very difficult because these quantities are constant in case of solids. Thus, the primary objective is to minimize mfp of phonons and that also of long-wavelength phonons because the heat is carried mainly by long-wavelength phonons [44, 45]. Phonon mfp can be reduced by phony dispersion which can be induced by various approaches such as doping (also increases carrier concentration) [40, 46], nanostructure [45, 47], introducing fluid-like characteristics into solid crystals [48-50] and introducing rattling ions into cages as structures [51-53]. The mechanism of dispersal of the phony can be understood in Figure 2. Figure 2. Schematic diagram illustrating the mechanism of phonon dispersion and the electronic transport of hot and cold electrons within a thermoelectric material. Adapted from [54] with the permission of John Wiley and Sons. Download figure: Standard image High-resolution image The reduction of thermal conductivity of the lattice by the dispersion of phonons and not affect the transport of electrons can be achieved in materials that favor the concept of Phonon-Glass Electron-Crystal (PGEC), as proposed by Slack [55]. Heat is carried mainly by a wide range of phonons with variable average free paths [56]. The glasses have the lowest thermal conductivity because glasses, thermal conductivity can be considered as the random walk of energy through the lattice and not by the transport of phonon [43] while crystalline materials favor electrical conductivity. PGEC behavior in materials can be obtained by binding. Binding with isoelectronic elements (elements with the same electronic configuration) increases noise and helps in the dispersion of the phono on the sites and preserves the crystalline electronic structure. Complex crystalline structures show better PGEC behavior. Complexity may be due to disorder in unit cells or due to the complex cell of the unit. More complex structures have less lattice thermal conductivity. The reduction of thermal conductivity through disorder in the unitary cell is large in species such as clathrates [51] and skutterudites [52, 53]. CsBi4Te6 (which is the complicated alternative of Bi2Te3) has a low lattice thermal conductivity of 1.1 Wm-1K-1 due to a complex unit cell and thus improved ZT by 0.8 below room temperature [57, 58]. A very low thermal conductivity of 0.42 to 0.20 Wm-1K-1 in the temperature range from 300 to 837 K in K2Bi8Se13 is due to its large unit cell and complex anisotropic structure representing its high ZT of 1.3 to 873 K [59]. Recently, a new Cs4Cu3Bi9S17 semiconductor was found to have a low thermal conductivity of 0.71 Wm-1K-1 at room temperature and decreases to 0.46 Wm-1K-1 to 773 K [60]. With such a small thermal conductivity, this material can be a promising thermoelectric material. The low thermal conductivity is due to its complex 3D structure consisting of interconnected fragments of type Bi2Te3 and CdI3 [60]. Phon sound-phonous interaction is the main process to reduce the average free path of phonons and induce phony dispersion at high temperatures. There are two types of fonon-phonon interactions: a normal operation in which total momentum is preserved and a Umklapp process in which the entire momentum is not preserved. To achieve low thermal conductivity, all phonon dispersion processes must be used. The umklapp process is the dominant dispersion process at high temperatures, and at such temperatures the thermal conductivity of the lattice takes the form [61] \bar{M} denotes average mass per atom, V is the mean atomic volume, θ_D is the Debye temperature, and γ is the Gr neisen parameter which is the measure of the harmony of lattice vibrations and is given by $\gamma = \frac{1}{\alpha} \frac{\alpha}{\alpha} = \frac{1}{\alpha} \frac{\alpha}{\alpha}$ is the condition for little κ_l and is observed in materials with large coefficient of thermal expansion, module in isothermal bulk and low density. In addition, significant anharmonicity (considerable nonlinear dependence of force restoration on atomic displacement) is the key to an α that is generated by weak bonds and heavy elements. Large anharmonicity is observed in complex crystalline structures with large primitive cells and therefore lowering the thermal conductivity κ_l . Lattice is proportional to specific heat Cv s that can be reduced to liquid-containing materials such as ions in ion conductors. Ion conductors include molten sublattice (apart from solid sublattice) in which atoms can move freely throughout. Cv-specific heat in solid materials can be reduced to the limit the unique structural characteristics of ion conductors thus increasing the complexity of the crystal. This concept is called Phonon-Liquid Electron-Crystal (PLEC) which is used to explain the low thermal conductivity and high thermoelectric performance of Cu-based thermoelectric materials [48-50]. The PLEC is discussed in detail in section 3.3. Carrier mobility μ is inversely proportional to the actual mass of the charge vector band [62]. The Seebeck coefficient, on the other hand, is directly proportional to the actual mass density of the states [40, 42], and are related by equation [63]. In addition, and act in the opposite way when it comes to improving ZT because large (for flat bands) lowers the mobility of the carrier which in turn reduces electrical conductivity, while large increases the power factor. Therefore, it is necessary low to increase the thermoelectric performance of materials. This actual band mass effect on electrical properties is observed by n-type PbTe doping [64, 65, 65a] as shown in Figure 3. Figure 3. A higher effective mass in pbte la-dopata leads to a higher Seebeck coefficient (a) but to a lower ZT (b) in the entire temperature range. Adapted from [65a] with permission from The Royal Society of Chemistry. Download figure: Standard image High resolution image The maximum ZT image of thermoelectric material is determined by its quality factor given by [46, 63, 66, 67], which may have a higher value for a significant degeneration of the Nv band, low lattice thermal conductivity, small band effective mass and small deformation coefficient Σ . A potential differential coefficient Σ is necessary for the weak dispersion of charge vectors dominated by acoustic phonons [68-70] which allows high vector mobility without affecting the Seebeck coefficient. In the case where the system with two valence bands with the Seebeck coefficient and the conductivity of S_1 , σ_1 and S_2 , σ_2 respectively, the total coefficient seebeck is given by $S = \sigma_1 S_1 + \sigma_2 S_2 / (\sigma_1 + \sigma_2)$ and the total conductivity is given by $\sigma = \sigma_1 + \sigma_2$. As already mentioned, with the increase in the number of vectors (n), conductivity increases and the Seebeck coefficient decreases. The total Seebeck coefficient is closer to the value less than S for the two bands. To maintain the large value of the total coefficient seebeck S , the two bands must be aligned so that the Seebeck S coefficient is the same in the two bands, while the total conductivity is greater than the specific conductivity of one of the bands. Lead chalcogenes and their alloys are examples of complex band systems consisting of two bands in which, in addition to the main valence band L , there is another secondary valence band Σ [68, 69] as shown in Figure 4(a). Band convergence or overlap of light value band L and band of heavy Σ can increase gang degeneration in lead chalcogenes that can be by a higher concentration of doping. The position of the L bands Σ are the function of temperature. The L band lowers its position as the temperature rises while maintaining the position of Σ an almost constant band [69, 71] resulting in convergence of these bands, as shown in Figure 4(a). By converging the L and Σ bands, Nv of these two bands add up to increase the total degeneration of the band and thus increasing B leading to the increase in ZT as shown in Figure 4(c). In addition to band convergence, high Σ band also significantly improves the quality factor [71]. Band convergence can also be achieved in specific materials by increasing the crystalline symmetry of materials towards a more cubic arrangement [72]. In some cases, resonance levels are formed by dopants fused with the valence band which increase the Seebeck S coefficient especially at room temperature leading to the improvement of thermoelectric properties [73, 74] as shown in Figure 4(b). Electron resonance states strongly disperse charge vectors and thus reduce electronic mobility, thus reducing electrical conductivity. In order to benefit from resonance states, the Seebeck coefficient must thus be increased to overwhelm the damage caused by the reduction of electrical conductivity, as shown in Figure 4. (a) The relative energy of the valence bands in PbTe/0.85Se0.15. At 500 K the two valence bands converge, resulting in transport contributions from both L and Σ bands. C , conduction band; L , low degeneration hole band; Σ , high degeneration hole band. Adapted from [75] with permission from Springer Nature. (b), schematic representation of the density of the states of the main valence band in PbTe (dotted line) as opposed to that of multi-band and resonant doping. Resonance states and multiple bands increase the density of states and the Seebeck coefficient. Adapted by [68] with permission from John Wiley and Sons. (c), ZT in p-PbTe, which according to the calculation of the model can be enhanced by this band convergence effect ($L - \Sigma$) if properly doped, compared to each band alone (L and Σ). Adapted from [76] with the permission of Elsevier. Figure download: standard image High resolution image Thermoelectric performance can be significantly improved by the nanostructure of thermoelectric materials. Nanostructures such as nanowires, nanotubes, nanoforks, quantum wells, quantum dots, and superlattices show an improved power factor and reduced thermal conductivity compared to their bulk counterparts. The nanostructure can increase thermoelectric performance taking into account the two approaches. One is by strengthening the DOS near the Fermi level through quantum confinement, improving the power factor [77-79]. A the approach is that of the efficient dispersion of phonon at the edge of the grain due to their large mfp compared to electrons, thus decreasing the thermal conductivity of the lattice [44, 45, 47]. In the case of nanostructural thermoelectric materials, the thermal conductivity of the lattice is the fonon-electron dispersion mechanism that favors the dispersion of long-length phonons that carry heat. To reach the ZT peak, nanostructural thermoelectric materials require a high concentration of doping. At grain boundaries, minority low-energy carriers are scattered more strongly than energy-majority carriers, resulting in a more moderate bipolar transition [80, 81]. Due to this effect, nanostructure thermoelectrics show a higher Seebeck coefficient than their bulk counterparts at similar doping concentrations. In the case of 1D thermoelectric materials (nanowires), quantum confinement greatly improves thermoelectric performance compared to their 2D variants [82, 83]. Nanotubes show lower thermal conductivity than nanowires due to phonon dispersion on internal and external surfaces [82, 84, 85]. In the case of raw wires, sound resistance can cause an increase in the thermopower which in turn improves thermoelectric performance [86]. Nanocomposites show better thermoelectric properties due to their low lattice thermal conductivity due to the dispersion of phonon at interfaces between nearby nanoparticles, and the power factor is also larger than the constituent phases [87]. In the case of nano-inclusion thermoelectrics, the Seebeck S coefficient can be increased by filtering the energy [54, 88]. By combining all the mechanisms discussed above, there has been a significant reduction in the thermal conductivity of the lattice of thermoelectric materials since the last decade. Newly developed thermoelectric nanocomposites, copper-based thermoelectric materials and tin chalcogenides show significantly low lattice thermal conductivity, apart from complex material systems, as is clear from Figure 5. (a) Extremely low lattice thermal conductivity is reported in nanocomposites (SiGe/Si2 [89], Bi0.45Bi1.6Te3/Graphene [22], (PbTe)0.75(PbSe)0.20(PbS)0.05 [25]), copper-based thermoelectric materials (Cu2Se [23]) and tin chalcogenides (SnSe [90]) apart from complex material systems (InCo4Sb12 [10], Ba8Ga16Ge30 [19]) (Recent data). (b) Low lattice thermal conductivity is reported in complex material systems (nanocomposites in data up to 2008). Adapted from [58] with permission from Springer Nature. Comparing these two figures, it is clear that, in addition to complex material systems, the reduction in thermal conductivity of the lattice of other state-of-the-art thermoelectric alloys has been significant since the last decade. Download figure: Standard image High resolution image Table 1. Reference table of thermoelectric compound families, including structures and information on synthesis methods, Peak ZT with temperature. Thermoelectric compound structure synthesis method family [Refs] Example ZT (Range) Temperature Range (T) Skutterudites TX3. Cage Type Structure [1-12] La0.68Ce0.22Fe3.5Co0.5Sb12 (p-type), (p-type), (n-type), Ce0.92Fe4Sb12 (p-type), La0.29Co4Sb12 (n-type), Ca0.31Co4Sb12 (n-type) etc. 0.91-1.5 402-590 °C Clathrates [13-21] K6.5Ba1.5A9S137 (type-I), (K, Sr)24(Ga, Ge)136 (type-II) Ba8Cu5(Si, Ge, Sn)41 (type-I), Ba8Ni0.12Zn0.54Ga13.8 Ge31.56 (type-II), Sr7.92Ga15.04Sn0.35 Ge30.69 (type-I), Ba8Cu6S16Ge24 (type-I), Ba8Ga16Ge30 (type-I), etc. 0.4-1.14 317-627 °C Type I and Type II Binary chalcogenides Layered Structure [22 (a-f), 159 (c, d)] Bi2Se3, Bi2Te2.7Se0.3, BiSbSe3, Bi0.5Sb1.5Te3, Sb2Te3, Bi2(TeSe)3, Bi2Te2.85Se0.15, Bi0.4Sb1.6Te3Zn0 etc. 0.87-1.4 50-527 °C Copper Based [23] Cu1.99Ni0.01Se1.51, Li0.09Cu1.95e, Na0.05Cu0.95S, Cu1.85Ag0.15Sn0.99Ni0.1Se3, Cu2Se0.98Te0.02, Cu2Se0.92Sb0.08, Cu2Se/CNTs hybrid, Bi0.95Sb0.05CuSeO etc. 0.73-2.4 500-727 °C Lead Chalcogenides [24-26] Pb0.99Bi0.01Te 0.83-2.2 352-547 °C PbTe, 0.94Se0.06 Pb0.99Sb0.005 s Mg0.8Pb0.12Te0.88Se0.2 Pb0.98Ni0.02Te0.8Se0.2 Na0.02Ba0.06Pb0.94Te0.98Tl0.55e0.5 Pb0.995Sn0.005Te0.847Se0.150.003 etc. Tin chalcogenides [27-31] (a) Bi doped SnSe (single crystal), Na doped SnSe (single crystal and polycrystalline), SnSe+1%PbSe (polycrystalline), Sn0.92Ge0.08Se (polycrystalline), Zn0.01Sn0.99Se (polycrystalline), SnSe0.9Te0.1 (polycrystalline), Sn0.96Ge0.07Te, SnCd0.03Te/CdS SnCd0.03Te/ZnS etc. 0.6-2.2 27-600 °C Oxides [32, 33] Ca2.95Tb0.5Co4O9, Porous Ca3Co4O9, Bi1.8Pb0.2Ba2Co2O, SrTiO3, Cd0.99Ni0.01O, Zn0.9Cd0.1Sc0.0LO.015, Sr1-3x/2La1-xTiO3- δ 0.3-0.74 377-900 °C 0.125 \leq x \leq 0.175 etc. Mg2X compounds [34, 35] Mg1.96Al0.04Si0.97Bi0.03, Mg2.16Si0.45Sn0.53Sb0.013, Mg2Si0.6Sn0.38Bi0.02, Mg2Si0.53Sn0.4Ge0.05Bi0.02, Mg2Si0.53Sn0.4Ge0.5Sb0.0125, Mg2Sn0.73Bi0.02Ge0.25 etc. 1.0-1.4 400-600 °C Half-Heusler alloys [36-38] Hf0.25Zr0.75NiSn0.985Sb0.015, FeNb0.8Ti0.2Sb, FeNb0.88Hf0.12Sb, FeNb0.88Hf0.14Sb, Zr0.25Hf0.25Ti0.5NiSn0.994Sb0.006, FeNb0.84Hf0.17Ti0.06Sb, Zr0.5Hf0.5Co0.9Ni0.15b (Hf0.6Zr0.4)0.99V0.01NiSn0.995 etc. 0.83-1.5 500-927 °C The compounds with caged structures are better in showing the Phonon-Glass Electron-Crystal behaviour which focuses on conserving the electrical properties and reducing the lattice thermal conductivity. Typical cage compounds include Skutterudites and Clathrates. Both families of cage compounds have a cubic structure that favors good electronic transport. These compounds contain large voids in their picture. When these voids are filled with host atoms, they act as independent oscillators. Due to the large size of the voids, these oscillators vibrate with the most substantial amplitudes compared to the atomic displacement of structural atoms. This effect is called as a tinkling effect and due to this effect, low frequency resonant modes are formed. These resonance modes act as traps for low-frequency phonon and thus decrease the thermal conductivity of the lattice. It is also believed that the resonance modes formed are high-frequency modes that interfere with low-frequency phonon modes, thus decreasing the thermal conductivity of the lattice. Pattern. Rattles not only reduce the thermal conductivity of the lattice, but also improve electrical conductivity due to their electro-positivity.3.1.1. SkutteruditesThese are minerals with the general formula TX3 where T is the transition metal mainly Co, Rh or Ir and X is a pnictogen (group 15 element) mainly P, As or Sb. The structure of the skutterudites is cubic with the Space Group Im3 which was first described by Ofteidal in 1928. Binary skutterudite is filled with an electropositive element A (rare earth [91, 92], alkaline earth [77, 93] or alkali metals [92, 94]) to form the ternary skutterudite A2T8X24 which can also be described as half the unit cell AT4X12. The crystalline structure of skutterudites is shown in Figure 6(a). CoSb3-based Skutterudites are the most studied due to high mobility, low electrical resistance, high atomic masses, and good Seebeck coefficients [95, 96]. Despite having a high power factor, CoSb3 cannot achieve high ZT due to its high lattice thermal conductivity [97, 98]. The thermal conductivity of the lattice is significantly reduced by filling structural voids with appropriate filling elements. Filled antimony has the smallest thermal conductivity of the lattice due to the most significant cage and due to these larger cages, the vibration amplitude of a filled atom is stronger than in turn actively interfering with acoustic phonons [99]. In the case of CoSb3-based skutterudites if the atom or ion can serve as fillers or not, it depends on the difference in electronegativity between the filler and the sb atom of the picture. The most thermodynamically stable filled skutterudites are those in which the difference in electronegativity falls within the range $\Delta\chi$ 0.8 [100, 101]. CoSb3 ZT improved from 0.5 per un filled to 1.2 for partially filled CoSb3 due to reduced thermal lattice conductivity and improved electrical conductivity [77, 102]. The thermal conductivity of the lattice is reduced in skutterudites filled by the formation of Einstein-like vibrational modes resulting from the weak bond between fillers and skutterudite structure Sb atoms, thus dispersing the normal phonon modes of the structure with similar energies [77, 103]. Vibrational frequencies depend on the type of fillers in cages and rare earth metals have been found to have weaker vibrational frequencies followed by alkaline-earth metals producing average frequencies and higher vibrational frequencies are maintained by alkali metals [104], as shown in Figure 6. (a) The crystalline structure of filled CoSb3 skutterudites, green spheres are Sb atoms, red spheres are Co atoms, and black spheres are fillers. Adapted by [77, 103] with permission from Taylor and Francis. (b) Dependence on ZT per InxCo4Sb12 skutterudite ($x = 0.2, 0.6, 1.0$) [10]. Ristampato da [Khovaylo, V V, Korolkov, T A, Voronin, A I, Gorshenkov, M V e Burkov, A T (2017), J. Mater. Chem. A, 5(7), 3541-3546.] pubblicato dalla Royal Society of Chemistry. (c) (c) dependence of ZT for newly developed efficient skutterudites [105, 106, 6]. Download Figure: Standard Image High Resolution Image Introducing Fill Atoms into Cages, the thermal conductivity of the lattice is reduced and this reduction can be further increased by adding two or more filling atoms of different vibrational frequencies that will help in the significant increase of ZT as in multi-filled skutterudites Ba0.08La0.05Yb0.04Co4Sb12 with advanced ZT of 1.7 to 577 degrees

