The Solid Solution Yb_{2-x}Ca_xCdSb₂: Structure, Thermoelectric Properties, and Quality Factor

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Abstract

Solid solutions of $Yb_{2,x}A_xCdSb_2$ (A = Ca, Sr, Eu; $x \le 1$) are of interest for their promising thermoelectric properties. Of these solid solutions, Yb_{2-x}Ca_xCdSb₂ has end members with different crystal structures. Yb₂CdSb₂ crystallizes in the polar space group of Cmc2₁ whereas Ca₂CdSb₂ crystallizes in the centrosymmetric space group *Pnma*. Other solid solutions, Yb₂. $_xA_xCdSb_2$ (A = Sr, Eu), crystallize in the polar space group for $x \le 1$, and compositions with $x \ge 1$ have not been reported. Both structure types are composed of corner sharing CdSb₄ tetrahedra condensed into sheets that differ by the stacking of the layers. Single crystals of the solid solution $Yb_{2-x}Ca_xCdSb_2$ (x = 0 to 1) were studied to elucidate the structural transition between the Yb₂CdSb₂ and the Ca₂CdSb₂ structure types. For $x \le 1$, the structures remain in the polar space group, $Cmc2_1$. As the Ca content is increased, a positional disorder arises in the intralayer cation sites (Yb2/Ca2) and the Cd site resulting in the CdSb4 tetrahedral chain inverting. This phenomenon could be indicative of an intergrowth of the opposing space group. The thermoelectric properties of polycrystalline samples of $Yb_{2-x}Ca_xCdSb_2$ ($x \le 1$) were measured from 300-525 K. The lattice thermal conductivity is extremely low (0.3 – 0.4 W/m K) and the Seebeck coefficients are high $(100 - 180 \,\mu\text{V/K})$ across the temperature range. Phonon dispersion curve calculations demonstrate a minimum in the thermal conductivity for the x = 0.3composition. The low thermal conductivity stems from the acoustic branches being confined to low frequencies, and large number of phonon scattering channels provided by the localized optical branches. The thermoelectric quality factor of the Yb_{1.7}A_{0.3}CdSb₂ (A = Ca, Sr, Eu) series has been calculated and predicts that the A = Ca, Sr solid solutions may not improve with carrier concentration optimization but that the Eu series is worthy of additional modifications. Overall, the x = 0.3 compositions provide the highest zT as they provide the best electronic properties with the lowest thermal conductivity.

Introduction

Yb₂CdSb₂ and other Zintl phases with the A₂MPn₂ composition are of interest for thermoelectric (TE) applications due to their low thermal conductivity and high TE power factor.^{1–6} These properties result in a high dimensionless figure of merit, $zT = S^2T/\rho\kappa$, where S is the Seebeck coefficient, ρ is electrical resistivity, and κ is thermal conductivity. TE materials are used to fabricate TE generators, which function by connecting a *p*-type leg and *n*-type leg thermally in parallel and electrically in series across a temperature gradient. The charge carriers diffuse from the hot side to the cold side of the device, producing a voltage difference. In particular, Yb₂CdSb₂ is of interest as it has an ultralow thermal conductivity, < 0.6 W/mK, high Seebeck coefficient, > 100 μ V/K, and low electrical resistivity, < 4 m Ω -cm, at room temperature. Additionally, Yb₂CdSb₂ has structural similarities to other high *zT* Zintl phases.^{7–11}

Yb₂CdSb₂ and Ca₂CdSb₂ are both known Zintl phases that crystallize in the orthorhombic space groups Cmc2₁ and Pnma,¹² respectively, Figure 1. The building units of Yb₂CdSb₂ and Ca₂CdSb₂ are identical, but the compounds are not isostructural primarily because of the way the layers are stacked. Both structures exhibit infinite layers of CdSb₄ corner-shared tetrahedra. In both structure types, the two crystallographically distinct Yb polyhedra have different local coordination environments where the Yb1 atom is found in a distorted octahedron and the Yb2 atom coordination is best described as a square pyramid with Cd atoms capping the adjacent edges of the pyramid. The Ca₂CdSb₂ structure type has a center of symmetry so the layer stacking can be described as AA⁻¹AA⁻¹, where A⁻¹ indicates the layer related by an inversion center. The Yb₂CdSb₂ structure type does not have a center of symmetry so the layer stacking can be described as AAAA. A recent study, starting from the Ca rich side of Ca_{2-x}Yb_xCdSb₂ suggests that both electronic and size-factors play a role in determining the structure type.¹³ Yb²⁺ and Ca²⁺ ions are nearly the same size, with Yb²⁺ considered to be slightly larger in a 6coordination site (difference of $\Delta r = 0.02$ Å). Site preferences were investigated for size or electronic factors employing density functional theory (DFT), crystal orbital Hamilton population,¹⁴ electron localization function diagrams and electronic factor criterion based on QVAL values (the match between the Q value of an atomic site and the electronegativity of the atom occupying that site; a way of defining atomic charges) and site volumes.^{13,15–17}

Another important distinction between the two crystal structures is in the distances between the Yb1-Yb1 and Ca1-Ca1 atoms. In the Yb₂CdSb₂ structure these distances are the same, but in the Ca₂CdSb₂ structure the distances are different with one longer and one shorter than the distance in the Yb₂CdSb₂ structure. The change in structure type has been attributed to bonding interactions between the cation and the $[CdSb_2]^{4-}$ layers, where the interlayer Yb1-Sb interactions become much weaker upon changing the symmetry from $Cmc2_1$ to $Pnma.^1$ A second hypothesis attributes the structure change to a bonding interaction provided by the symmetrical Yb-Yb distances.¹³



Figure 1. **Left**: Yb₂CdSb₂ structure in the *Cmc*2₁ space group viewed down the *a*-axis. **Right**: Ca₂CdSb₂ structure in the *Pnma* space group viewed down the *b*-axis. The long axis is viewed vertically in both structures.

The solid solution of Yb_{2-x}Eu_xCdSb₂, $x_{max} \sim 1$ has been synthesized and maximum *zT* of 0.7 at 525 K when x = 0.36 is reported.¹⁸ This is almost a 30% increase in zT compared to the parent compound, Yb₂CdSb₂.¹⁸ The resulting high *zT* is largely a result of the massive drop of thermal conductivity and the preservation of the large Seebeck coefficient of the parent phase. Calcium has a similar effective ionic radii to Yb and is isovalent with respect to both Yb and Eu.¹⁹ Calcium is also earth abundant, and in p-type Zintl phases, replacing Yb²⁺ with Ca²⁺ typically reduces carrier concentration, leading to higher Seebeck, higher resistivity, and lower thermal conductivity.^{20–23} In some systems this allows for a higher *zT*. However, unlike the Eu²⁺ containing analog, which does not form an Eu₂CdSb₂ compound, the end member of Ca₂CdSb₂ is stable, although crystallizing in a different space group.

The work described herein builds upon the compositional and structural change of Yb₂. _xCa_xCdSb₂ from *Cmc*2₁ to *Pnma*.^{12,13} Single crystal structures of an expanded compositional range have been studied at low temperatures revealing site disorder with increased Ca content. The synthesis of pure phase powders and the impact of Ca²⁺ substitution for Yb²⁺ on the TE properties is presented. Additionally, for the composition with the highest *zT*, the effects of Sr substitution were explored. The thermoelectric quality factor is calculated to provide insight towards the best compositional materials to investigate for further optimization.

Methods

Synthesis. Single-crystal samples were synthesized similarly to that reported for Yb₂CdSb₂.¹ All manipulations were carried out in argon- or nitrogen-filled gloveboxes or under vacuum to minimize oxidation. The elements in the respective 2-*x* Yb, *x* Ca, Cd, 2 Sb, and 10 Pb molar ratio to provide a total weight of 5 g (Yb pieces, Metall Rare Earth Limited, 99.99%; Ca Dendrites, Sigma, 99.99%; Cd shot, Alfa Aesar, 99.95%; Sb shot, Alfa Aesar, 99.99%; Pb granules, Mallinckrodt, 99.99%) were loaded in a 5 mL Canfield alumina crucible set.²⁴ The crucible set was placed into fused silica tubes and sealed under <100 mTorr of vacuum. The sealed tube was placed upright in a box furnace and heated at a rate of 120°C/h to 960°C, held for 96 hrs, and then slowly cooled at a rate of 2°C/h to 500°C. Once at 500°C, the sample was inverted, and the molten lead was removed by centrifugation. Finally, black-colored, reflective plate-like crystals of Yb_{2-x}Ca_xCdSb₂ were observed as the product by opening the reaction vessel in a N₂-filled glovebox equipped with an optical microscope.

Bulk samples were synthesized via mechanical milling and spark plasma sintering (SPS). Yb was filed into small pieces using a metal rasp and combined with the elements in a ratio of 2-*x* Yb, *x* Ca, 1.08 Cd, and 2 Sb (sources: Yb pieces, Metall Rare Earth Limited, 99.99%; Ca Dendrites, Sigma, 99.99%; Cd shot, Alfa Aesar, 99.95%; Sb shot, Alfa Aesar, 99.99%). A slight excess of Cd was added in order to compensate for loss to the walls in the mill. The combined elements (total 3 g) were milled 2 x 30 minutes in a stainless steel vial (5 mL) with WC₂ end caps with 2 balls (8 mm) and the vial was scraped between milling to form a homogenous free flowing powder. The powder (~2.7 g) was sieved with a 100 mesh filter, loaded into a graphite die (12.7 mm ID, 30 mm OD, 30 mm height) and transferred to a Dr. Sinter-Lab SPS-211LX instrument for densification. Prior to initiating the heating profile, the chamber was evacuated to ~10 Pa, and a force of 2 kN was applied. The die was heated to 550°C and the force was increased to 8 – 10.5 kN to react and densify the powder into a pellet.

Single Crystal X-ray Diffraction. Single-crystal X-ray diffraction (XRD) data were collected from the dark silver reflective needle-like crystals at 100 K using a Bruker Apex-II Dual source Cu and Mo diffractometer with CCD detector, Mo Kα radiation, or a D8 VENTURE Photon100 Kappa Dual source Mo/Cu diffractometer with a CCD detector, Mo Kα radiation.

Only the highest-symmetry Bravais lattice suggested for the refined unit cell parameters was selected for each collected crystal. The frames were integrated by using SAINT program within APEX III version 2017.3-0. Non-centrosymmetric space group $Cmc2_1$ (No. 36) was suggested by XPREP based on the analysis of systematic absences for samples x = 0, 0.13, 0.21 0.39, 0.66, and 0.80. The centrosymmetric space group Pnma (No. 62) was suggested by XPREP based on the analysis of systematic absences for samples x = 0.97, 1.25, and 1.50. The structure was determined using direct methods, and difference Fourier synthesis was used to assign the remaining atoms (SHELXTL version 6.14). For all structures the occupancies of the Yb and Ca were allowed to freely refine until the composition was stable and then the occupancies were fixed for a final refinement cycle.

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Powder X-ray Diffraction. Powder X-ray diffraction (PXRD) was performed on pieces of the pressed pellets that had been ground into powders and loaded onto a zero-background holder. PXRD was collected with a Bruker D8 Eco Advance Powder X-ray diffractometer with Cu K α radiation (λ = 1.54060 Å) with a 2 θ range from 10° to 80° with a step size of ~0.02° and a scan rate of 1s/step utilizing a Lynx-EX detector. The peaks from the bulk reaction product were

identified via peak matching as Yb₂CdSb₂ and YbCd₂Sb₂ and Rietveld refinements were performed using GSAS-II²⁵ to determine unit cell parameters and weight percentages of any impurity phases present.

Electron Microprobe Analysis (EMPA). Polycrystalline samples were enclosed in epoxy and polished to provide flat surfaces for analysis. The polished samples were coated with carbon. Microprobe analysis was performed by using a Cameca SX-100 electron microprobe microanalyzer with wavelength dispersive spectrometers. The characteristic X-rays generated by samples were analyzed by wavelength dispersive spectroscopy (WDS) to determine the compositions of samples. X-ray intensities of Yb, Ca, Cd, and Sb were compared with those of calibrated Yb₁₄MnSb₁₁, CaSiO₃, Cd, and Sb for quantitative analysis. At least 10 different points with a spot size of 1 µm were analyzed for each sample. The sample compositions were determined and summarized in Supporting Information (SI), **Table S1** and **Figure S1**.

Thermoelectric Properties. The thermoelectric properties were measured on > 91% dense samples for *x* = 0, 0.3, and 0.5 and > 87% dense for *x* = 0.2. Thermal diffusivity (D) measurement was conducted on the pellet from 300 K to 525 K on a Netzsch LFA-457 unit. The pellet surfaces were polished flat and parallel and coated with graphite. The measurement was conducted under a dynamic argon atmosphere with a flow rate of 50 mL/min. Thermal conductivity was calculated using the equation $\kappa = D \times \rho \times C_p$ where heat capacity was estimated using the Dulong-Petit law.

A Linseis LSR-3 instrument was employed to measure the Seebeck coefficient and electrical resistivity via a four-probe method from 325 K to 525 K under a helium atmosphere on a bar-shaped sample. The sample which had been previously measured on the LFA instrument was cut into an approximately $2 \times 2 \times 10$ mm bar using a Buehler diamond saw and polished before measurement. The probe distance was 8 mm. All thermoelectric data (**Figure S2**) were fit with third order polynomials for easier viewing of the data and calculating *zT*.

Density Functional Theory Calculations.

Electronic structure, phonon dispersion relations and thermal transport were computed by firstprinciples DFT with the generalized gradient approximation Perdew-Burke-Ernzerhof (PBE) functional,²⁶ using the Quantum-Espresso package.²⁷ Core electrons are treated implicitly through projector augmented wave (PAW) pseudopotentials^{28,29} and the valence electronic wavefunctions are expanded in a plane-wave basis set with a kinetic energy cutoff of 45 Ry. The Kohn-Sham orbitals are integrated on a $2 \times 4 \times 1$ Monkhorst–Pack mesh of k-points.³⁰ Structural and cell relaxations are performed using a quasi-Newton optimization algorithm with a convergence criterion of 10^{-6} Ry/Bohr for the maximum residual force component. The convergence threshold for electronic self-consistent calculation was 10^{-15} Ry.

The semi-classical Boltzmann transport theory with constant relaxation time approximation has been employed to evaluate the electron transport properties, as implemented in PAOflow code.³¹ For these calculations the electronic structure is calculated over a finer 8 x 16 x 4 k-point mesh. Kohn-Sham orbitals are projected on atomic wavefunctions to construct an effective Hamiltonian that is used to compute transport coefficients. In the Boltzmann transport theory, the carrier relaxation time (τ) is treated as an empirical parameter. The choice of τ does not affect the calculation of the Seebeck coefficient, but both the electrical conductivity and the electronic thermal conductivity depend linearly on it. Since we do not have an estimate of τ for

Yb_{2-x}Ca_xCdSb₂, we have used a value of 5 fs for all the solid solutions considered. This arbitrary choice is justified *a posteriori*, by the agreement between the calculated and the measured power factor.

Harmonic second order interatomic force constants (IFCs) and phonon dispersions were computed using density-functional perturbation theory (DFPT)³² with 2×4×2 mesh of q-points. The threshold for the iterative calculation of the perturbed Kohn–Sham wavefunctions was set to 10^{-16} Ry. Anharmonic third order IFCs were computed by finite differences ($\Delta x = 0.01$ Å), in a 2 × 2 × 2 supercell, with a cutoff interaction distance up to the 6th shell of neighbors. Translational invariance of the anharmonic force constants was enforced using the Lagrangian approach.³³ With the second and third order IFCs, the thermal conductivity was computed by solving the phonon Boltzmann transport equation (BTE) with an iterative self-consistent algorithm, using the ShengBTE code³³ with q-point grids up to $12 \times 19 \times 5$, considering both three-phonon and isotopic scattering.³⁴

The agreement between theory and experiments obtained in previous works on analogous systems^{13,35} suggests that this computational approach is suitable to study electronic and phononic transport in $Yb_{2-x}Ca_xCdSb_2$.

Results and Discussion.

Single Crystal. Single crystals of $Yb_{2-x}Ca_xCdSb_2$ with x = 0, 0.13, 0.27, 0.39, 0.66, 0.8, 0.97, 1.25, and 1.48 were synthesized by flux reaction. The atomic coordinates in the unit cell and full crystallographic information Tables are listed in SI,**Tables S2 – S3**.

Figure 2 illustrates the trend in lattice parameters of the solid solution as a function of Calcium content. As the amount of Calcium is increased in the structure, the a-axis increases through x = 0.39. From x = 0.39 to x = 0.8 the *a*-lattice parameter remains the same and decreases linearly after the structure changes from Cmc2₁ to Pnma around a 1:1, Yb:Ca ratio, Figure 2A. The *b*-axis increases linearly until the structure change. After the structure change, the *b*-axis remains constant, Figure 2B. The *c*-axis continues to increase linearly from x = 0 to 2, Figure **2C**. The volume of the structure increases linearly until the structure transition. After the structure transition, the volume increases linearly with a smaller slope suggesting that the cation substitution have little effect on the structure in this regime, **Figure 2D**. The lattice parameters for Ca₂CdSb₂ and solid-solution lattice parameters from Xie et al. and Kim et al. are added for reference.^{12,13} The lattice parameters of Kim et al. are consistent with this study except for a slight difference in the Yb_{0.75}Ca_{1.25}CdSb₂ (here) vs Yb_{0.67}Ca_{1.33}CdSb₂ (Kim et al.) structure. The observed lattice parameter and volume expansions are accurately reproduced by first principles calculations, which however systematically predict slightly lower density (~2%) than experiments. Specifically, calculations predict a 4.3 Å³ expansion for x = 0.5 and 7 Å³ for x =1.0, with respect to the reference Yb₂CdSb₂ crystal.



Figure 2. (**A**) *Cmc2*₁ *a*-lattice parameter and *Pnma b*-lattice parameter for the solid-solution Yb₂₋ _xCa_xCdSb₂. (**B**) *Cmc2*₁ *b*-lattice parameter and *Pnma c*-lattice parameter for the solid-solution Yb_{2-x}Ca_xCdSb₂. (**C**) *Cmc2*₁ *c*-lattice parameter and *Pnma a*-lattice parameter for the solidsolution Yb_{2-x}Ca_xCdSb₂. (**D**) Volume for the solid-solution Yb_{2-x}Ca_xCdSb₂. Where Ca₂CdSb₂ structure from Xia *et al.*¹² is indicated with an open red square, the Ca_{2-x}Yb_xCdSb₂ solid-solution from Kim *et al.*¹³ are shown as X's, the calculated theoretical volumes are triangles. The *Cmc2*₁ data are indicated in black and the *Pnma* data are in red. Data collected at 100 K, this work; at RT, Kim *et al.*¹³ and 120 K, Xia *et al.*.¹²

For the structures of the solid solution with compositions x = 0.27, 0.66, 0.8, 0.97, 1.25, and 1.48 there is excess electron density around the Yb2/Ca2 and Cd1 sites which is modeled by a Ca3 and Cd2 site (shown in **Figure 3B** and **3C**). In the x = 0.39, there is a slight electron density around these sites; however, convergence of the refinement of the Ca3/Cd2 sites was never achieved and the structure solution is of good quality without accounting for disorder modeled

by the additional Ca3/Cd2 sites. The site disorder in the Cmc2₁ structure type is illustrated in Figure 3 where the Cd1 site shifts slightly causing the Yb2 site to shift. A similar shifting, but in opposite directions in the *Pnma* structure type is illustrated in SI, Figure S3. The new Ca3 site (near Yb2/Ca2 intralayer site) refines as solely occupied by Ca for the structural solutions in the *Cmc2*¹ space group and partially occupied by Yb for the solutions in the *Pnma* space group. The shifting of the Ca3/Cd2 sites results in a flipping of direction the CdSb₄ chains modulating the layers and occurs in <6% of the overall structure, Figure 4. The addition of the positional disorder was attempted in all crystals of the solid solution, with and without the Ca3/Cd2 site, and the best refinements are presented. It is possible that there is some intergrowth between the AA and the AA⁻¹ ordered layers resulting in an average structure best refined by partial occupancy. To conclusively determine whether the disorder can be attributed to an intergrowth of the stacking layers from the two polymorphs, further investigation with HRTEM and electron diffraction is necessary. As shown in Figure 4, both the Yb1 and Yb2 sites are occupied by Ca in all the solid solutions; however, the Yb1 site (interlayer site, octahedral coordination) is occupied with a larger fraction of Ca than the Yb2 site (intralayer site, square pyramidal coordination). Kim et al. also saw a higher % occupancy on the Yb1 site as compared to the Yb2 site and the site preference has been identified as mainly an electronic effect, as the preference correlates with electronegativity and the QVAL of the Yb2 (intralayer site) with surrounding atoms.¹³ Additionally, the Yb1 site volume is larger than the Yb2 site volume and also when the six-coordinate coordinate Yb²⁺ (1.02 Å) is replaced by Ca²⁺ (1.0 Å).^{19,36} As illustrated by Kim et al.¹³ and in **Figure 5**, the *Cmc*2₁ structure type has a single A1-A1 (A₂MPn₂) bond distance. For example, the Yb1-Yb1 bond distance is 4.635 Å in Yb₂CdSb₂ and 4.659 Å in Yb_{1.2}Ca_{0.8}CdSb₂. The 4.659 Å Yb1-Yb1 distance is similar to the 4.67 Å bond distance reported for the Yb_{1,12}Ca_{0,88}CdSb₂ structure.¹³ The *Pnma* structure has one longer and one shorter A1-A1 distance. For reference, Yb_{1.03}Ca_{0.97}CdSb₂, the A1-A1 (A = Yb/Ca) site has distances of 4.463 Å and 4.881 Å versus 4.464 Å and 4.907 Å in the Ca₂CdSb₂ reported structure.¹ The shorter A1-A1 bond has been described as having an energetically unfavorable antibonding character just below the E_F in their crystal orbital Hamilton population curve causing an energetically favorable shift from the Pnma to Cmc2₁ crystal structures with the increased fraction of the larger Yb²⁺.¹³



Figure 3. Shifting of the Cd1 and Yb2 sites results in a flipping of the CdSb₄ chain in ~2% of the overall structure above x = 0.6 for Yb_{2-x}Ca_xCdSb₂. (A)The majority of the structure with Yb2 and Cd1 atomic positions. (B) The shifting of Cd1 atomic position to the Cd2 atomic position and the Yb2 atomic position shifting to the Ca3 atomic position (pink). (C) The minority of the structure showing the Ca3 and Cd2 atomic positions.



Figure 4. The % occupancy of the $Yb_{2-x}Ca_xCdSb_2$ as a function of *x* for each of the cation sites.



Figure 5. The Yb1 – Yb1 and Ca1 – Ca1 distances are plotted as a function of increasing Ca content for Yb_{2-x}Ca_xCdSb₂. The Ca₂CdSb₂ data are from Xia et al.¹²

The Ca content correlates with the average Yb/Ca-Sb bond distance, and increases with increasing *x*, **Figure 6A**. Yb1 and Yb2 are plotted on separate *y*-axes due to Yb1 having a larger starting average bond distance; however, they are plotted with the same magnitude of change on the axis for easy comparison. Initially, the change in bond distance increases similarly, but as the Ca content increases the Yb1 site continues to increase while there is a slight drop in the Yb2-Sb bond distance as the structure changes from *Cmc2*₁ to *Pnma*. The average Ca3-Sb bond distances remains unchanged as Ca content increases. The polyhedral volumes are presented in a similar fashion, with the Yb1 and Yb2 polyhedra volumes presented on opposite y-axes, but with the same order of magnitude for easy comparison between the volume changes, **Figure 6B**. The Yb1 and Yb2 polyhedra volume show a similar trend as the average bond distances with the Yb1 polyhedron increasing more than the Yb2 polyhedron with increasing *x*. The fact that the Yb1 polyhedra having a larger rate of change in volume follows from the higher Ca occupancy on that site. The Ca3 polyhedral volume is unchanged as Ca content increases.



Figure 6. (**A**) Average Yb/Ca-Sb bond distances as a function of Ca content (*x*) for Yb₂₋ _{*x*}Ca_{*x*}CdSb₂. (**B**) Average Yb/Ca polyhedral volume as a function of Ca content. The Yb1 site is represented by red squares, the Yb2 site is represented by blue triangles, and the Yb3 site is represented by blue circles. The open symbols represent average distances and polyhedra volumes from Xia et al.¹² Additionally, both y-axes are plotted with the same magnitude of change to allow comparison between the change in Yb1 and Yb2.

As shown in **Figure 7A** the Cd1-Sb1-Cd1 angle increases with the addition of Ca from a minimum of $115.53(3)^{\circ}$ (Yb₂CdSb₂) to a maximum of 116.65° (Ca₂CdSb₂), while the Cd1-Sb2-Sb1 angle slightly increases to a maximum of $110.26(6)^{\circ}$ (Yb_{1.61}Ca_{0.39}CdSb₂) to a minimum of 109.26° (Ca₂CdSb₂). Sb2 links the tetrahedra into chains and Sb1 links the chains into sheets. In **Figures 7B** and **7C**, the bond distances of the two types of CdSb₄ bonds increase as a function of Ca content.



Figure 7. (**A**) Average Cd1-Sb1-Cd1 and Cd1-Sb2-Cd1 bond angles. (**B**) One type of Cd1-Sb1 bond distance plotted with the Cd1-Sb2 bond distance. (**C**) The second type of Cd1-Sb1 bond distance. The bond angles are plotted with the same change along the *y*-axes. All bond distances are plotted with the same change along the *y*-axes. The red squares correspond to the right *y*-axis and the blue squares correspond to the left *y*-axis. The open squares are angles and bond distances from Xia et al.¹²

Single crystal samples of Yb_{1.34}Ca_{0.66}CdSb₂, Yb_{1.03}Ca_{0.97}CdSb₂, and Yb_{0.52}Ca_{1.48}CdSb₂ were ground into powders to check for co-crystallization of *Cmc2*₁ and *Pnma* polymorphs. Since these compositions were close to the transition from *Cmc2*₁ to *Pnma*, it is possible that the two polymorphs could be found for the single crystal samples prepared via flux. The refinements and refinement statistics are provided in SI, **Figures S4** – **S6** and **Tables S4** – **S6**. The best refinements are from the related single crystal structures PXRD pattern for the complementary reaction. Therefore, from PXRD and Rietveld refinement, it is unlikely that these compositions contain both polymorphs of Yb_{2-x}Ca_xCdSb₂; however, the disorder observed in single crystal XRD refinement suggests small amounts of polymorphism, ~ 6%, a percentage that may not be visible via PXRD.

Thermoelectric Characterization and Theory.

 $Yb_{2-x}Ca_{x}CdSb_{2}$

The PXRD patterns for the solid solutions of the bulk samples synthesized via mechanical milling and SPS are shown in **Figure 8** where the hkl's (002) and (132) are shown to highlight the shifting of the unit cell parameters with the incorporation of Ca. The Rietveld refinements are summarized in **Figure S7A-D** and **Table S7**. The Rietveld refinements initially yielded >10% R statistics with small quantities of YbCd₂Sb₂, Yb₂O₃, and Cd as impurities. From the difference curve, three broad peaks are noticeable at 29.13°, 34.28°, and 42.14° and can be seen in **Figure 8**. In GSAS II, these were added as background peaks for the refinement. After additional cycles, five smaller broad peaks were noticeable in the difference curve at 24.15°, 49.48°, 53.71°, 59.01°, and 64.63°. Modeling all 8 peaks as background results in good refinement statistics for all samples, <10%. Due to the broadness of these peaks, exact peak positions are difficult to attain making indexing of unit cell parameters challenging and inaccurate. The broadness of the peak is likely due to a small amount of impurity with small or highly strained grains;³⁷ however, an additional phase was not identified in SEM or with EMPA. The lattice parameters show a linear increase from x = 0 to 0.5, **Figure S8**.



Figure 8. PXRD patterns for $Yb_{2-x}Ca_xCdSb_2$ compositions prepared as powders. Calculated Yb_2CdSb_2 PXRD pattern is shown for comparison.

Figure 9 provides the total and lattice thermal conductivity of the Yb_{2-x}Ca_xCdSb₂ series. As Ca replaces Yb in the structure the thermal conductivity is decreased (**Figure 9A**). As expected for this structure type, the thermal conductivity is very low for x = 0, consistent with that reported by Cooley et al.¹⁸ In all compositions, with the addition of Ca, there is a significant drop in the thermal conductivity. This is presumably due to a combination of enhanced anharmonicity and alloy scattering. In the Yb_{1.7}Ca_{0.3}CdSb₂ sample there is a small decrease just before 350 K that is believed to be the melting of a minor unidentified impurity. Thermal conductivity was measured first, the sample polished and cut into a bar for Seebeck/resistivity and no transitions are apparent. Therefore, the slight impurity was removed in the initial measurement and does not affect the subsequent measurements. The x = 0.2 has the lowest thermal conductivity, **Figure 9B**, the

Ca substituted samples have decreased lattice thermal conductivity compared to the parent compound, in part, a result of alloy scattering. However, similar to the total thermal conductivity, they do not follow an expected trend where lattice thermal conductivity is expected to decrease as a function of increasing *x*. The perplexing thermal conductivity trend suggested that other factors aside from alloy scattering are important and need to be considered.



Figure 9. (A) Thermal conductivity and (B) lattice thermal conductivity versus temperature for the Yb_{2-x}Ca_xCdSb₂ solid-solution.

Experimental thermal conductivity is low and the trend suggested other factors, aside from alloy scattering, that are important to the decreased thermal conductivity; therefore, theoretical calculations were employed to probe the origin and provide insight to the dependency on *x*. The thermal conductivity calculations at 300 K show that the lowest κ_{ave} occurs for Yb_{1.75}Ca_{0.25}CdSb₂ at 0.36 W/mK, **Table 1**, consistent with what is observed experimentally. The thermal conductivity increases at Yb_{1.5}Ca_{0.5}CdSb₂ and then decreases again when the composition undergoes a phase transition from *Cmc*2₁ to *Pnma*. The decrease in thermal conductivity at *x* = 0.25 agrees with the experimental measurements, even if our first-principles calculations are carried out for pure crystals and do not account for alloy scattering. The detailed analysis of harmonic and anharmonic phonon properties accounts for this unusual thermal conductivity trends. The phonon dispersion relations for Yb_{2-x}Ca_xCdSb₂, computed along the high-symmetry k-point path of the orthorhombic Bravais lattice, are plotted in **Figure 10A** for *x* = 0, 0.25, 0.5.

Adding Ca to pure Yb₂CdSb₂ engenders new optical modes at ~6 THz, but it does not modify significantly the low-frequency acoustic phonons. However, Ca substitution increases the anharmonic phonon scattering rate for phonons below 3 THz, which are those that mostly contribute to heat transport in these materials (Figure 10B, C). The minimum of κ at $x \sim 0.20$ -0.25 is observed also in the calculations which then provide support and interpretation to the experiment. Figure 10B shows that in our calculations the scattering rate is maximized by the x = 0.25 composition. This composition corresponds to the lowest compositional symmetry within the unit cell (1 substitutional Ca out of 2 formerly equivalent Yb sites). Breaking this symmetry gives rise to new phonon modes, such as the flat branch at ~ 1 THz (purple line in **Figure 10A**). which enhance the phonon scattering phase space and reduce κ_{ph} . Adding another Ca (x = 0.25), restores the former symmetry within the cell and reduces the scattering channels. This effect stems from the reduced symmetry of the Ca-substituted compounds which engender a larger number of viable channels for three-phonon scattering. Anharmonic scattering has its maximum efficiency for the x = 0.25 composition, and it eventually decreases at x = 0.50, thus leading to the observed minimum of thermal conductivity. In experimental samples, mass disorder would further increase phonon scattering rates thus lowering the overall lattice thermal conductivity. Additionally, based on the disorder model (~2%) observed in some of the single crystal refinements, described in Figure 3, it is possible that there are small domains of stacking polymorphs, reinforcing the anomalous trend observed in thermal conductivity.



Figure 10. Phonon dispersion relations (A), anharmonic scattering rates (B) and cumulative thermal conductivity as a function of frequency (C) for $Yb_{2-x}Ca_xCdSb_2$. Compounds with Ca concentration x = 0 (blue), x = 0.25 (purple) and x = 0.50 (cyan) are displayed.

Table 1. Calculated avera	ge thermal conductivit	y for Yb _{2-x} Ca _x CdSb ₂	$x_2(x = 0, 0.25, 0.5, 1.0)$
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x	κ _{ave} (W/mK)			
0	0.58			
0.25	0.36			
0.5	0.49			
1.0	0.42			

The Yb_{1.7}Ca_{0.3}CdSb₂ and Yb_{1.5}Ca_{0.5}CdSb₂ compositions have increased Seebeck coefficients, with Yb_{1.5}Ca_{0.5}CdSb₂ having the largest Seebeck coefficient, (**Figure 11**) while the Yb_{1.8}Ca_{0.2}CdSb₂ remains unchanged. These results were investigated computationally by calculating the band structures for x = 0, 0.25, and 0.5, **Figure 12A**. The parent compound and the x = 0.25 band structures are nearly indistinguishable, while the Ca = 0.5 exhibits differences attributed to the opening of the gap, shifting and broadening of the second valence band below the Fermi level, leading to an increase in the hole effective mass. These results suggest that the Seebeck coefficient should change very little with the addition of 0.25 Ca; therefore, the x = 0.2 sample Seebeck is likely to resemble the x = 0 parent sample, presuming there is little difference in defect concentration or structure. In turn, the opening of the band gap and the broadening of the valence band, obtained by adding more Ca, lead to an increase of the Seebeck coefficient, which is however compensated by an increase of electrical resistivity, without improvement of the thermoelectric power factor ($PF = S^2/\rho$) (**Figure 12B,C**).



Figure 11. Seebeck coefficient versus temperature (K) for the Yb_{2-x}Ca_xCdSb₂ solid-solution.



Figure 12. Band structure (A), Seebeck coefficient -S - (B) and power factor -PF - (C) of Yb_{2-x}Ca_xCdSb₂ (x = 0, 0.25, and 0.5) obtained from electronic structure calculations and the semi-empirical Boltzmann transport equation. Both S and PF are directional properties, however, to compare to experimental measurements on pellets, the reported values are averaged over the three directions in space.

The resistivity increases systematically with the addition of calcium, as expected (**Figure 13**). However, there is a very large increase for the Yb_{1.5}Ca_{0.5}CdSb₂ sample; increasing by more than a factor of 2 at 525 K. These results follow a trend observed for other Ca substituted Zintl phases. In both Yb_{14-x}Ca_xMnSb₁₁ and Yb_{1-x}Ca_xCd₂Sb₂ the Seebeck coefficient is enhanced and electrical resistivity increases with the addition of Ca. For example, the electrical resistivity of Yb_{1-x}Ca_xCd₂Sb₂ increases across the entire solid-solution along with the Seebeck coefficient until x = 0.8.²⁰ The optimized properties of Yb_{1-x}Ca_xCd₂Sb₂ provided a max *zT* of ~1 at 650 K with an x = 0.4.²⁰ Overall, concurrently with observed thermal conductivity minimum, this electronic effect leads to an increase in *zT* for a small amount of dopant, but as the amount of calcium is increased the electrical resistivity becomes too large and ultimately the *zT* is lower for those compositions.²⁰⁻²³



Figure 13. Electrical resistivity as a function of temperature for the Yb_{2-x}Ca_xCdSb₂ solid-solution.

Figure 14 provides the *zT* for the Yb_{2-x}Ca_xCdSb₂ solid-solution. Yb_{1.7}Ca_{0.3}CdSb₂ has a slightly increased *zT* of 0.53 at 525 K over that of the Yb₂CdSb₂ composition with a *zT* of 0.50 at 525 K. While the Yb_{1.5}Ca_{0.5}CdSb₂ sample has the highest Seebeck and the lowest thermal conductivity, the large increase in resistivity leads to an overall decrease in *zT* to 0.44 at 525 K. If we employ the model that has been proposed to explain the structural changes from Kim et al.,¹³ it is likely that for *x* = 0.3, the slightly larger Yb1-Yb1 distance is contributing to the density of states and giving rise to the high Seebeck coefficient while the electrical resistivity is low enough due to the delocalized nature of that bonding. As additional Ca is added to the solid solution, the benefits of the Yb1–Yb1 bonding interaction is lessened until it is no longer important for mobility and the resistance is no longer optimized. Additionally, Kim et al.¹³ illustrates the slightly different coordination environments from the Sb1 and Sb2 distances and angles. As illustrated in **Figure 5**, in the two types of Cd1-Sb1 distances and the Cd1-Sb2 distance, there is a larger jump in the distance from the *x* = 0.13 to the *x* = 0.27 which could be signaling an optimization in the bonding of the CdSb₄ tetrahedra.



Figure 14. *zT* of the Yb_{2-x}Ca_xCdSb₂ solid-solution.

With the increase in *zT* of the Yb_{1.7}Ca_{0.3}CdSb₂ composition, the Sr containing phase was synthesized and investigated to see if the higher *zT* in Yb_{1.7}Eu_{0.3}CdSb₂ could be attributed to size or electronic effects. If size was the main contributing factor, a similar or lower *zT* than that for the Ca phase is expected since Sr²⁺ has a similar, but slightly smaller size compared to Eu²⁺. Similar to the Eu²⁺ solid solution (Yb_{2-x}Eu_xCdSb₂), Sr²⁺ should prefer the interlayer A1 over the intralayer A2 site and provide lower mobility as it decreases the bonding within the Yb1-Sb octahedra. The phase purity and thermoelectric properties of Yb_{1.7}Sr_{0.3}CdSb₂ are presented in **Figures S7E, S9 – S11, Tables S7 – S8**. The thermal conductivity decreases to a nearly identical value as the *x* = 0.3 sample in the Ca system, described above. The Seebeck coefficient is increased at RT to ~200 µV/K. However, the electrical resistivity with the Sr dopant is increased by ~350 %. The increase in resistivity negates any benefit gained by the decrease in thermal conductivity and the increase in Seebeck coefficient in the final *zT*.

For the Yb_{2-x}A_xCdSb₂ (A = Ca, Eu) solid solutions described herein, the x = 0.3 samples are the samples with the largest zTs. The increased zT in these Ca samples is attributed to optimized bonding with regards to (Yb/A)1-(Yb/A)1 in the (Yb/A)1-Sb octahedra; however, the bonding was not examined in the Eu-alloyed samples. In the Eu samples, the increased zT can be attributed to the decreased resistivity while maintaining a low thermal conductivity and high Seebeck coefficient. It is a combination of optimization of the electronic contributions and thermal conductivity that give rise to a good zT in a material.³⁸ The potential of a material can be evaluated based on the thermoelectric quality factor which combines the electronic and lattice thermal conductivity.³⁹ The potential for further improvement can then be predicted based on the limited number of samples experimentally investigated. In order to determine if it's possible

to increase the zT of Yb_{2-x}A_xCdSb₂ (A = Ca, Sr) further, calculations of the thermoelectric quality factor³⁹ were performed. A material's quality factor is described by $B = \left(\frac{k_B}{e}\right)^2 \frac{\sigma_{E_0}}{\kappa_L} T$, where k_B is the Boltzmann constant, e is the electron charge, σ_{E_0} is a transport coefficient, and κ_L is lattice thermal conductivity. The power of the thermoelectric quality factor in determining properties inherent to a material is due to the removal of the dependance on carrier concentration that determines *zT*. The thermoelectric quality factor provides an analysis of transport data using an effective mass model (even without explicitly determining the effective mass) and without having to perform the numerical integration of the Fermi function.³⁹ That is, the thermoelectric quality factor can be parameterized by the electronic chemical potential (related to carrier concentration) and lattice thermal conductivity. Table 2 summarizes the chemical potentials and the thermoelectric quality factors for Yb₂CdSb₂, Yb_{1.7}Ca_{0.3}CdSb₂, Yb_{1.7}Sr_{0.3}CdSb₂, Yb_{1.7}Eu_{0.3}CdSb₂, and Yb_{1.5}Ca_{0.5}CdSb₂ at 525 K. Using these values, the compositions were placed onto the zT vs chemical potential graph in **Figure 15**. The predicted zT s based on quality factor coincide with the measured values suggesting that the thermoelectric quality factor can provide a measure for whether a material can be further improved towards the highest zTby changing the chemical potential. In the case of Yb₂CdSb₂, there is little room for improvement with changing chemical potential. An ideal dopant would increase the quality factor and then the chemical potential could be further optimized. For Yb_{1.7}Ca_{0.3}CdSb₂, the quality factor is almost unchanged, but the chemical potential is shifted to the left. Hence, there is little room for improvement. An increase in the amount of Ca in the solid solution to Yb_{1.5}Ca_{0.5}CdSb₂, decreases the quality factor and changes the chemical potential. The quality factor is also decreased for Yb_{1.7}Sr_{0.3}CdSb₂. In the case of Yb_{1.7}Eu_{0.3}CdSb₂, the quality factor is increased and there is room for improvement in zT. This may be attributed to the fact that the A1-A1 bonding can be enhanced in the Eu-containing phase and contribute to bonding within the CdSb layers and therefore to the chemical potential.

Table 2	Calculated	reduced	chemical	potential	and	quality	factor	from	thermo	electric
propertie	es.									

Composition	Reduced Chemical Potential (η)	Quality Factor (β)
Yb ₂ CdSb ₂	0.4706	0.1689
Yb _{1.7} Ca _{0.3} CdSb ₂	-0.4210	0.1773
Yb _{1.7} Sr _{0.3} CdSb ₂	-0.6910	0.1478
Yb _{1.7} Eu _{0.3} CdSb ₂	0.5380	0.3271
Yb _{1.5} Ca _{0.5} CdSb ₂	0.2450	0.0458



Figure 15. Thermoelectric quality factor and chemical potential plotted for $Yb_{2-x}A_xCdSb_2$ (A = Ca, Sr, Eu) compositions. The solid solutions are indicated by the colored circles shown in Table 2, filled gray: Yb_2CdSb_2 , filled red: $Yb_{1.7}Ca_{0.3}CdSb_2$, filled blue: $Yb_{1.7}Sr_{0.3}CdSb_2$, filled red: $Yb_{1.5}Ca_{0.5}CdSb_2$. The *zT* vs chemical potential graph is reprinted from [*Appl. Phys. Rev.* **2018**, *5* (2). https://doi.org/10.1063/1.5021094.], with the permission of AIP Publishing.³⁹

Conclusions

The solid-solution of Yb_{2-x}Ca_xCdSb₂ was prepared and the transition from *Cmc2*₁ to *Pnma* occurs at ~1:1 Yb:Ca. Ca substitutes on both cation sites, but primarily in the intralayer site. As the Ca content increases, the structure exhibits stacking faults that can be modeled as disorder in the Yb2/Ca2 and Cd1 sites. The amount of disorder is less than 6% compared to the majority structure but may assist in phonon scattering giving rise to the low thermal conductivity that is observed. Phonon dispersion curve calculations provide additional evidence for the low thermal conductivity, showing a minimum in the thermal conductivity for the *x* = 0.3 composition. A combination of the acoustic modes being confined to low frequencies, the optical modes having low group velocities, and the optical modes intersecting with the acoustic branches creating phonon scattering channels support the experimentally observed low thermal conductivity. Similar to that reported for Yb_{2-x}Eu_xCdSb₂,¹⁸ there is an increase in *zT* for the *x* = 0.3, Yb_{1.7}Ca_{0.3}CdSb₂, composition. Unlike Yb_{2-x}Eu_xCdSb₂, the Yb_{2-x}Ca_xCdSb₂ solid-solution results in an increase in both electrical resistivity and Seebeck coefficient at *x* = 0.3. Yb_{1.7}Sr_{0.3}CdSb₂ was also prepared and the thermoelectric properties investigated in order to determine whether

electronics or size was an important constituent of the higher *zT* reported for Yb_{1.7}Eu_{0.3}CdSb₂.¹⁸ Based on the thermoelectric quality factor there is little room for improvement expected with carrier concentration modification for the Ca or Sr substituted phases. However, it may be possible to further improve the TE properties of the Yb_{1.7}Ca_{0.3}CdSb₂ by changing the electronics (bonding and Fermi level) via substitution onto the Cd or Sb sites.

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Notes

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Supporting Information

Experimental details and supporting figures: (PDF): EMPA of polycrystalline samples, Experimental thermoelectric data and fittings, Full Crystallographic Tables and Atomic Coordinates, Shifting of the Cd1 and Yb2 sites for the *Pnma* structure, Rietveld refinements of polycrystalline samples and ground single crystalline samples, Yb_{2-x}Sr_xCdSb₂ EMPA, PXRD, and TE data.

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Synopsis: $Yb_{2-x}Ca_xCdSb_2$ solid solution transitions from the *Cmc*2₁ to *Pnma* space group at x = 1 and the Yb(Ca) metal-metal distances distort into a long-short distance with increasing x. Phonon dispersion curve calculations demonstrate a minimum in the thermal conductivity for the x = 0.3 composition, consistent with experiment.