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# Investigation of the transport properties and compositions of the

 $Ca_2RE_7Pn_5O_5$  series (*RE* = Pr, Sm, Gd, Dy; *Pn* = Sb, Bi)

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# Abstract

The Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> phases (*RE* = Pr, Sm, Gd, Dy; *Pn* = Sb, Bi) were successfully prepared from high temperature reactions at 1225-1300°C. These phases maintain the same structure types as the parent *RE*<sub>9</sub>*Pn*<sub>5</sub>O<sub>5</sub> phases, except for a Ca/*RE* mixing. The study and preparation of these phases was motivated by the desire to shift the metallic type properties of the parent *RE*<sub>9</sub>*Pn*<sub>5</sub>O<sub>5</sub> phases to a level more suitable for thermoelectric applications. Electrical resistivity measurements performed on pure, bulk samples indicated all phases to be narrow band gap semiconductors or semimetals, supporting the charge balanced electron count of the Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> composition. Unfortunately, all samples are too electrically resistive for any potential usage as thermoelectrics. Electronic band structure calculations performed on idealized *RE*<sub>9</sub>*Pn*<sub>5</sub>O<sub>5</sub> structures revealed the presence of a pseudogap at the Fermi level, which is consistent with the observed electrical resistivity and Seebeck coefficient behavior.

**Keywords**: rare-earth antimonide oxides; rare-earth bismuthide oxides; crystal structure; thermoelectric properties; electronic structure.

# Introduction

One of the reemerging areas of research in the development of alternate forms of energy is the study of new and more efficient thermoelectric materials. While most of the early thermoelectrics obtained the figure-of-merit  $ZT \sim 1$ , theoretical studies performed in the 1990s suggested improvements in ZT through the decoupling of the electrical conductivity and Seebeck coefficient by forming quantum nanostructures with reduced dimensionality.<sup>1-3</sup> Although not

intended, the major advancements in thermoelectric efficiency have instead arisen from the reduction of thermal conductivity by nanostructuring.<sup>4</sup> Such notable gains in efficiency have ushered in a new age of research into thermoelectrics, and a doubling of efficiency ( $ZT \sim 2$ ) among the state of the art materials, such as PbTe-SrTe.<sup>5</sup> As such, there is a great deal of motivation to discover new materials with intrinsically attractive properties that may push the boundaries of thermoelectric efficiency even further.

Devices containing thermoelectric materials are capable of performing heating and cooling, depending on the direction of the applied current, as well as being able to convert waste heat into a usable form of electricity.<sup>6</sup> Thermoelectrics offer several advantages over other competing energy sources including long operation hours, scalability, quietness, and versatility. To obtain the most suitable balance of these properties in a single phase, narrow band gap semiconductors and semiconductors are targeted for thermoelectric applications as they possess electrical properties corresponding to an optimized power factor  $\alpha^2 \sigma$ . The lattice thermal conductivity  $\kappa_1$  of a thermoelectric material must also be kept as low as possible, so structures containing soft bonds, heavy atoms, and site disorder are popular choices.Unfortunately, thermoelectrics suffer from low efficiencies due to the tradeoffs between Seebeck coefficient  $\alpha$ , electrical conductivity  $\sigma$ , and charge carrier thermal conductivity  $\kappa_e$  (Equation 1).

$$ZT = \frac{\alpha^2 \sigma}{k_l + k_e} \tag{1}$$

A number of methods are then applied to reduce thermal conductivity further, mostly by doping and nanostructuring.

One of the more noteworthy strategies for the design of a good thermoelectric is the design of a natural superlattice structure, in which electrically conductive and phonon scattering properties are accomplished in separate portions of the lattice. This approach is advantageous for thermoelectricity since it allows for the tuning of one property without affecting the other. As such, a natural superlattice structure may display a phonon-glass electron-crystal (PGEC)-type behavior, as postulated by Slack.<sup>7</sup> Several successful thermoelectric materials, such as Ca<sub>1-</sub>  $_{\rm x}Yb_{\rm x}Zn_2Sb_2^{-8}$  and Na<sub>x</sub>Co<sub>2</sub>O<sub>4</sub><sup>9, 10</sup> display natural superlattice type structures, and have been shown to achieve good *ZT* values.

As per the natural superlattice approach, we have turned our attention on rare-earth pnictide oxide phases. Ideally, we may achieve good thermoelectric properties from a natural

superlattice type structure containing the electrically conductive and thermally insulating frameworks of rare-earth pnictides and rare-earth oxides, respectively. The presence of heavy rare-earth and pnictogen elements and the added structural complexity introduced by chemical fusion of different sublattices would also serve to heavily reduce thermal conductivity. In particular, the  $RE_9Pn_5O_5$  series is of special interest, since it displays natural superlattice-type structures, with alternating slabs of  $RE_5Pn_5$  and  $RE_4O_5$  stacked along the *c* direction.<sup>11, 12</sup> The pristine  $RE_9Pn_5O_5$  phases have been shown to behave as metals, owing to their unbalanced electron counts, which renders them unsuitable as thermoelectrics. Additionally, these phases are very air sensitive, requiring great precautions for usage and handling. Our group has studied the incorporation of carbon into these phases in the past in an effort to stabilize their structures and form charge balanced phases for the purpose of thermoelectricity, but we were unable to achieve a pure, stable sample.<sup>13</sup>

Our studies on the Ca $RE_3$ SbO<sub>4</sub> and Ca<sub>2</sub> $RE_8$ Sb<sub>3</sub>O<sub>10</sub> phases<sup>14</sup> motivated us to explore calcium substitution in the  $RE_9Pn_5O_5$  phases. By a simple electron counting scheme, a charge balanced  $(Ca^{2+})_2(RE^{3+})_7(Pn^{3-})_5(O^{2-})_5$  formula would exist if the  $RE_9Pn_5O_5$  structure would tolerate calcium/rare-earth mixing. Verily, we have shown that the Ca<sub>2</sub> $RE_7Pn_5O_5$  phases do in fact exist, demonstrating that calcium substitution simultaneously improves the stability and maintains the structure of the parent  $RE_9Pn_5O_5$  phase while also eliminating its metallic-type conduction. In this work, we present the details of the synthetic approach, structural and compositional analyses, physical property measurements, and electronic structure calculations of the Ca<sub>2</sub> $RE_7Pn_5O_5$  phases.

## **Experimental**

#### **Synthesis**

Samples were made using high-purity *RE* metals (*RE* = Pr, Sm, Gd, Dy; 99.9 wt.% or better, SmartElements), calcium metal (99.98 wt.% Alfa Aesar), antimony metal (99.999 wt.%, CERAC Inc.), *RE*<sub>2</sub>O<sub>3</sub>, (99.99 wt.%, Rhône-Poulenc for *RE* = Sm, Gd, Dy; 99.9 wt.% Alfa Aesar for *RE* = Pr), and calcium oxide (99.99 wt. %, CERAC). The *RESb* and *REBi* binary phases were first prepared as precursors to avoid the use of elemental antimony and bismuth, which are volatile at high temperatures. These samples were prepared in an argon-filled glove box by mixing stoichiometric amounts of *RE* and Sb/Bi. The *RESb* samples were pressed into pellets

while the *REBi* samples were not. All samples were sealed below 10<sup>-4</sup> torr in evacuated silica ampoules of 10 to 15 cm in length. The silica tubes were carbon coated to avoid reaction between *RE* and silica. The *RESb* samples were heated in a box furnace at 600°C for 12 hours, then at 850°C for 48 hours. The *REBi* samples were heated at 235°C for 12 hours, then at 350°C for 12 hours, and finally at 850°C for 48 hours. The resulting powder was ground and pressed into a pellet within an argon-filled glove box. The pellets were then sealed in silica tubes and heated at 850°C for 48 hours. Black, solid chunks of rare-earth antimonides and rare-earth bismuthides were obtained in this manner, and the purity of each sample was confirmed by X-ray powder diffraction experiments.

Preparation of the Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> samples (RE = Pr, Sm, Gd, Dy) was accomplished by mixing stoichiometric amounts of calcium oxide, rare-earth sesquioxide  $(RE_2O_3)$ , and RESb/REBi precursors in an argon-filled glove box. All samples were consolidated with the use of a hydraulic press, and were subsequently sealed in tantalum ampoules with the use of an arc melter. This method allows for high temperature reactions with no oxidation, sample loss, or reaction with the container. High-temperature reaction conditions were accomplished through the use of an induction furnace. The tantalum ampoules containing samples were placed in a molybdenum susceptor, which was heated under dynamic vacuum below  $10^{-4}$  torr by radio frequency induction from a water-chilled copper coil. The Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> samples were heated for 18 hours at 1300°C and 1225°C, respectively. Upon completion of heat treatments, samples were allowed to cool for one hour before removal. The Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> samples were obtained as shiny, molten chunks. Decomposition of the Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> samples due to moisture after at least 48 hours was confirmed by X-ray powder diffraction. Thus, all samples were stored in an evacuated dessicator filled with drierite, which was observed to maintain sample purity for several months. A summary of all samples prepared is presented in Table 1.

Table 1. Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> samples prepared by high-temperature synthesis in an induction furnace

(Pn = Sb, Bi).

System	RE used	Loading composition	Temperature used	State
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$Ca_2RE_7Sb_5O_5$	Pr, Sm, Gd	$2CaO + 5RESb + RE_2O_3$	1300°C	Light gray, molten
Ca <sub>2</sub> RE <sub>7</sub> Bi <sub>5</sub> O <sub>5</sub>	Gd, Dy	$2CaO + 5REBi + RE_2O_3$	1225°C	Dark gray, molten

#### **X-ray Single Crystal Diffraction**

Single crystals picked up from the samples were analyzed on a Bruker SMART Apex II diffractometer using  $MoK_{\alpha}$  radiation. Intensity corrections for Lorentz and polarization effects were performed with the SAINT program.<sup>15</sup> A multi-scan absorption correction was applied based on the crystal shape determined by optical face indexing. Due to an ordering of vacancies, a five-fold supercell for each structure is created (when compared to the parent Sc<sub>2</sub>Sb-type structure), which in turn resulted in twinning for all crystals except Ca<sub>2</sub>Dy<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub>. All data sets except Ca<sub>2</sub>Dy<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> were detwinned using the TWINABS program to eliminate intensity bias due to overlapping reflections. Crystal structures were determined and solved using the SHELX software.<sup>16</sup> The final refinements of the twin crystals were performed using the hkl5-type files containing intensities of both twinned components. A summary of the refinement results is presented in Table 2. All  $Ca_2RE_7Pn_5O_5$  phases crystallize in the P4/n space group, much like the analogous  $RE_9Sb_5O_5$  phases. Upon inspection, it was observed that there was an unusually large amount of electron density on the normally vacant 2a sites in each structure from the twinned crystal (except for the Ca<sub>2</sub>Dy<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> crystal that was not twinned). Most likely, this extra electron density stems from the twinning interfaces that place RE/Ca atoms almost exactly in the center of square voids (i.e. the 2a site), and such phenomenon has been observed in the parent  $RE_9Pn_5O_5$ structure<sup>12</sup>. This conclusion is supported by the fact that an additional electron density is not found in the non-twinned Ca<sub>2</sub>Dy<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> crystal. Additionally, the presence of Ca or *RE* atoms on the 2a site would offset the stoichiometry and charge balance of the  $Ca_2RE_7Pn_5O_5$  phases. However, we could not prove with absolute certainty that the extra electron density is the artifact of the twinning, or it is real and in fact leads to twinning. As a result, we report the crystal structures below with the artifact peak as a residual electron density peak. Further information on the crystal structures can be found in the Supporting information and may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax (49)

7247-808-666; email crysdata@fiz.karlsruhe.de), by quoting the CSD depository numbers 429690 - 429692 for Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and 429693 - 429694 for Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub>.

	$Ca_2Pr_7Sb_5O_5$	Ca <sub>2</sub> Sm <sub>7</sub> Sb <sub>5</sub> O <sub>5</sub>	$Ca_2Gd_7Sb_5O_5$	Ca2Gd7Bi5O5	Ca <sub>2</sub> Dy <sub>7</sub> Bi <sub>5</sub> O <sub>5</sub>
Refined composition	$\begin{array}{c} Ca_{2.11(5)}Pr_{6.89(5)}Sb_5\\ O_5\\ \end{array}$	$\begin{array}{c} Ca_{2.01(4)}Sm_{6.99(4)}Sb_5\\ O_5 \end{array}$	$\begin{array}{c} Ca_{1.98(2)}Gd_{6.98(2)}Sb_{5}\\ O_{5} \end{array}$	$\begin{array}{c} Ca_{2.39(5)}Gd_{6.61(5)}Bi_{5}\\ O_{5}\end{array}$	$\begin{array}{c} Ca_{2.09(3)}Dy_{6.91(3)}Bi_5\\ O_5 \end{array}$
Space group	<i>P</i> 4/n	<i>P</i> 4/n	P 4/n	<i>P</i> 4/n	<i>P</i> 4/n
Radiation			Mo $K_{\alpha}$ (0.71073 nm)		
Scan mode			$\omega$ and $\phi$		
Temperatur e			296(2) K	2	
Crystal dimensions (mm)	0.080 x 0.066 x 0.053	0.072 x 0.064 x 0.058	0.077 x 0.070 x 0.062	0.083 x 0.068 x 0.061	0.115 x 0.094 x 0.049
a (Å)	10.223(1)	10.067(1)	9.992(1)	10.102(1)	9.9996(1)
<b>c</b> (Å)	9.138(2)	9.011 (2)	8.976(2)	9.027(2)	8.9341(2)
Volume (Å <sup>3</sup> )	955.1(3)	913.2(3)	896.2(3)	921.2(3)	893.34(2)
Twin fractions	0.531/0.469(3)	0.512/0.488(2)	0.506/0.494(2)	0.501/0.499(3)	N/A
$p_{\text{calc}} (\text{g/cm}^3)$	6.015	6.622	6.938	8.147	8.668
Ζ	2	2	2	2	2
Index ranges	$-13 \le h \le 14$ $0 \le k \le 20$ $0 \le l \le 18$	$0 \le h \le 20$ -13 $\le k \le 14$ -18 $\le l \le 0$	$0 \le h \le 20$ -13 $\le k \le 14$ -17 $\le l \le 0$	$0 \le h \le 20$ -13 $\le k \le 14$ -18 $\le l \le 0$	$-19 \le h \le 17$ $-20 \le k \le 19$ $-17 \le l \le 17$
$2\theta \max$	90.80°	90.76°	90.82°	90.90°	90.64°
Measured reflections	23235	44532	28980	35183	36098
Unique reflections	3314	3850	3786	3934	3757
Reflections used	3918	9464	5120	6235	1848
Number of parameters	50	51	51	51	50
Twinning artifact el. density <sup>a</sup> , e/Å <sup>3</sup>	15.45	11.475	5.424	21.497	N/A
Max/min el. density <sup>b</sup> , e/Å <sup>3</sup>	4.29/-3.32	3.65/-4.13	4.01/-2.72	4.29/-4.47	4.35/-2.84
Goodness- of-fit on  F <sup>2</sup>	1.020	1.024	1.048	1.138	1.017

**Table 2.** Crystallographic and refinement data for the Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> crystals.

R indices	$R_{1} (>4\sigma) = 0.0543$ $wR_{2} = 0.1195$ $R_{1} (all data) = 0.1547$	$R_1 (>4\sigma) = 0.0467$ $wR_2 = 0.0881$ $R_1 (all data) =$ 0.0938	$R_1 (>4\sigma) = 0.0326$ $wR_2 = 0.0637$ $R_1 (all data) = 0.0711$	$R_{1} (>4\sigma) = 0.0533$ $wR_{2} = 0.897$ $R_{1} (all data) = 0.1183$	$R_{1} (>4\sigma) = 0.0383$ $wR_{2} = 0.0822$ $R_{1} (all data) = 0.0682$
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<sup>a</sup> The largest residual electron density peak in these structures, except for  $Ca_2Dy_7Bi_5O_5$ , is an artifact of the twinning these crystals display.

 $^{\rm b}$  The second largest electron density peak, except for Ca\_2Dy\_7Bi\_5O\_5 where the largest peak is reported.

#### **X-ray Powder Diffraction**

Each sample under study was analyzed by X-ray powder diffraction on a PANalytical X'Pert Pro instrument using  $CuK_{\alpha 1}$  incident radiation and an X'Celerator detector. Approximately 50 mg of sample was ground up using a mortar and pestle and deposited on a zero-background Si holder. The data were collected in the  $2\theta$  range between  $20^{\circ}$  and  $70^{\circ}$  and analyzed using the Rietveld refinement method (Rietica program<sup>17</sup>) to determine sample purity and lattice constants. The structural parameters obtained from the single crystal solutions were used for the refinements, and site occupancies for calcium and rare-earth were fixed.

## Electron Microprobe Analysis (EPMA)

The samples of interest were mounted in discs of epoxy resin one inch in diameter and approximately 10 mm in thickness. Polishing was accomplished using a Struers Rotopol-31 unit with a Struers RotoForce-4 revolving sample holder. The final step of polishing used a solution of diamond dust of approximately 1 µm in size. Quantitative elemental analysis of the samples was performed by electron probe microanalysis (EPMA) using wavelength-dispersive (WDS) X-ray spectroscopy (model JXA-8500F, JEOL). CaSiO<sub>3</sub>, PrB<sub>6</sub>, SmB<sub>6</sub>, Gd<sub>3</sub>Ga<sub>5</sub>O<sub>12</sub>, DyP<sub>5</sub>O<sub>14</sub>, antimony metal, and bismuth metal were used as standards to determine the concentration of oxygen, Ca, Pr, Sm, Gd, Dy, Sb, and Bi in the samples, respectively.

#### **Thermoelectric Measurements**

Pure samples of  $Ca_2RE_7Pn_5O_5$  (*RE* = Pr, Sm, Gd, Dy; *Pn* = Sb, Bi) were prepared, pressed, sealed in evacuated silica ampoules, and annealed at 500°C for three days. Powder Xray diffraction analysis confirmed no decomposition or generation of impurities by these methods. Once annealed, samples were cut into bars of approximately 8 × 2 × 2 mm in dimensions using a kerosene lubricant to avoid sample oxidation, and were subsequently stored in an argon atmosphere. Thermoelectric measurements were carried out on a Quantum Design

Physical Property Measurement System (PPMS). Platinum leads were attached on the rectangular bars using Epo-Tek H20E silver epoxy. The contacts for all samples were cured under a stream of ultra-high purity Ar inside a tube furnace.

#### **Electronic Band Structure Calculations**

The electronic structures of all samples for which a crystal could be obtained and solved were calculated using the tight-binding, linear-muffin tin orbital method<sup>18</sup> with the atomic sphere approximation (TB-LMTO-ASA) as implemented in the Stuttgart program.<sup>19</sup> All 4*f* electrons were considered as core electrons. Exchange and correlation were treated by the local density approximation (LDA).<sup>20</sup> A scalar relativistic approximation<sup>21</sup> was employed to account for all relativistic effects except spin-orbit coupling. Overlapping Wigner-Seitz cells were constructed with radii determined by requiring the overlapping potential to be the best approximation to the full potential, according to the atomic sphere approximation (ASA). Automatic sphere generation<sup>22</sup> was performed to construct empty spheres to be included in the unit cell in order to satisfy the overlap criteria of the TB-LMTO-ASA model. The X-ray single crystal data, including lattice parameters and atomic coordinates, were used as the model for calculations. The Ca/RE sites in Ca<sub>2</sub>RE<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>RE<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> structures with no changes in atomic parameters (such approach neglects a size difference<sup>23</sup> between Ca<sup>2+</sup> and RE<sup>3+</sup>).

#### **Results and Discussion**

#### **Phase Formation and Stability**

In a previous study by our group, the  $RE_9Sb_5O_5$  phases were reacted with carbon in an effort to yield a charge balanced, stable phase (assuming C<sup>4-</sup> was present). In most cases, however, a pure sample could not be obtained, and all samples were observed to be highly air sensitive.<sup>13</sup> Instead, we have determined that stabilization by calcium addition is more practical. Our experiments revealed that sample compositions of Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> may yield air stable, pure phases through high temperature reaction conditions. Site mixing of calcium and rare-earth is accomplished in all Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> phases due to similar atomic radii<sup>23</sup>; this strategy was also employed in the discovery of the Ca*RE*<sub>3</sub>SbO<sub>4</sub> and Ca<sub>2</sub>*RE*<sub>8</sub>Sb<sub>3</sub>O<sub>10</sub> phases.<sup>14</sup>

The stable nature of the  $Ca_2RE_7Pn_5O_5$  phases most likely results from the charge balanced electron formula achieved by substitution of trivalent  $RE^{3+}$  with divalent  $Ca^{2+}$ . Due to

the mixing of calcium and rare-earth, as well as the potential for off-stoichiometry, a Ca<sub>5-x</sub> $RE_{5+0.667x}$ Sb<sub>5</sub>O<sub>5</sub> compositional series with varying amounts of calcium and rare-earth may exist. However, our studies concluded that all samples of this series share the same Bragg peak positions in their powder X-ray diffraction data, suggesting that there is an optimal composition of calcium and rare-earth that is most stable. We then determined that the Ca<sub>2</sub> $RE_7Pn_5O_5$ stoichiometry yielded the most pure samples, indicating this system is thermodynamically driven to a charge balanced phase. Thus, our synthetic approach was able to yield pure Ca<sub>2</sub> $RE_7Sb_5O_5$ phases for the RE = La - Dy, and pure Ca<sub>2</sub> $RE_7Bi_5O_5$  samples for late members of the RE = Gd -Dy series (Ca<sub>2</sub> $RE_7Bi_5O_5$  samples containing early RE were observed to form (Ca, $RE_2$ )<sub>2</sub>BiO<sub>2</sub>).

High temperature reactions in an induction furnace are necessary to form pure  $Ca_2RE_7Pn_5O_5$  samples. Phase formation was observed to occur for all temperatures between 1200°C and 1600°C, although temperatures of 1300°C and 1225°C were determined to be the most suitable for obtaining pure samples of  $Ca_2RE_7Sb_5O_5$  and  $Ca_2RE_7Bi_5O_5$ , respectively. Gray, molten products are obtained for the  $Ca_2RE_7Pn_5O_5$  samples, with the  $Ca_2RE_7Bi_5O_5$  samples being slightly darker in tone. A set of experiments performed on the pristine  $RE_9Pn_5O_5$  samples confirmed their instability, with samples tarnishing in air after a few minutes and full decomposition in air after 24-48 hours. In contrast, the  $Ca_2RE_7Pn_5O_5$  phases were observed to be stable in dry air or argon, although still reactive in moist air, with noticeable decomposition occurring after 48 hours. Thus, storage in an argon-filled glovebox or evacuated desiccator was deemed to be necessary in order to prevent the loss of sample integrity.

#### Structural determination and analysis

The basic frameworks of the Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> phases are identical to the *RE*<sub>9</sub>*Pn*<sub>5</sub>O<sub>5</sub> series. Based on the single crystal data, all Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> phases adopt the tetragonal *P*4/*n* symmetry, assuming an oxygen-stuffed, rare-earth deficient derivative of the Sc<sub>2</sub>Sb-type structure.<sup>24, 25</sup> Each Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> phase contains site mixing of calcium and rare-earth. These phases consist of NaCl-type (Ca/*RE*)<sub>5</sub>*Pn*<sub>5</sub> slabs stacked along the *c* direction and separated by (Ca/*RE*)<sub>4</sub>O<sub>5</sub> layers containing (Ca/*RE*)<sub>4</sub>O and (Ca/*RE*)<sub>5</sub>O polyhedra (Figure 1). One fifth of all calcium/rare-earth sites with respect to the Sc<sub>2</sub>Sb structure are vacant in the parent *RE*<sub>9</sub>*Pn*<sub>5</sub>O<sub>5</sub> phases; these ordered vacancies form the basis of the superstructure with respect to the original *P*4/*nmm* cell and occur in the (Ca/*RE*)<sub>4</sub>O<sub>5</sub> layers, forming ordered, empty channels along the *c* direction.<sup>12</sup> The existence of the *P*4/*n* phase was also confirmed by X-ray powder diffraction experiments based on the presence of characteristic weak (220) and (221) reflections, which are observed for the P4/n superstructure but not the P4/nmm structure.



**Figure 1.** The Ca<sub>2</sub> $RE_7Pn_5O_5$  structure viewed along the *b* and *c* direction (left and right, respectively). Twinning interfaces result in electron density located in the empty channels along the *c* direction.

According to the single crystal diffraction data, each phase (except  $Ca_2Dy_7Bi_5O_5$ ) displays reticular merohedral twinning with  $^{1}/_{5}$  of all reflections shared between domains. In order to obtain reliable diffraction intensities, each data set (except for  $Ca_2Dy_7Bi_5O_5$ ) had to be detwinned with the TWINABS program, yielding corrected intensities that could be used to solve the crystal structure of one twin component. The resulting data sets were solved with good *R* factors and yielded atomic parameters comparable to those in the original  $RE_9Pn_5O_5$  structures. However, one major difference was observed: each of the crystal solutions, apart from the nontwinned  $Ca_2Dy_7Bi_5O_5$ , had residual electron density on the normally vacant 2a site. Since the pristine  $RE_9Pn_5O_5$  phases do not contain rare earth atoms on these sites, we assume these sites to be indeed vacant. As mentioned before, this electron density can be attributed the twinning interfaces in the crystal, and is supported by the fact that the non-twinned  $Ca_2Dy_7Bi_5O_5$  crystal does not have this property.

#### **Compositional analysis**

Unfortunately, our crystallographic models of the  $Ca_2RE_7Pn_5O_5$  phases make it difficult to obtain an accurate composition due to the calcium and rare-earth mixing. Thus, we performed electron microprobe analysis on all samples in order to verify their compositions. The results are presented below in Table 3.

	$Ca_2Pr_7Sb_5O_5$	$Ca_{2.11(5)}Pr_{6.89(5)}Sb_5O_5$	$Ca_{2.13(6)}Pr_{6.89(4)}Sb_{5.00(4)}O_{6.92(6)}$
$Ca_2RE_7Sb_5O_5^a$	$Ca_2Sm_7Sb_5O_5$	$Ca_{2.01(4)}Sm_{6.99(4)}Sb_5O_5$	$Ca_{2.03(5)}Sm_{7.00(3)}Sb_{5.00(3)}O_{6.47(5)}$
	$Ca_2Gd_7Sb_5O_5$	$Ca_{1.98(2)}Gd_{6.98(2)}Sb_5O_5$	$Ca_{2.16(6)}Gd_{6.92(3)}Sb_{5.00(3)}O_{5.75(6)}$
$C_{0}$ , $PF_{-}P_{1}$ , $O^{a}$	$Ca_2Gd_7Bi_5O_5$	$Ca_{2.39(5)}Gd_{6.61(5)}Bi_5O_5$	$Ca_{2.07(5)}Gd_{6.95(3)}Bi_{5.00(3)}O_{5.99(6)}$
Ca <sub>2</sub> <i>KL</i> <sub>7</sub> D15O5	$Ca_2Dy_7Bi_5O_5$	$Ca_{2.09(3)}Dy_{6.91(3)}Bi_5O_5$	$Ca_{2.11(6)}Dy_{6.93(4)}Bi_{5.00(3)}O_{5.75(6)}$

**Table 3.** Comparison of experimentally determined compositions of Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> samples derived from X-ray diffraction and EPMA experiments.

X-ray diffraction results

EPMA results

<sup>a</sup> The Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> samples were normalized to compositions containing five antimony/bismuth atoms.

The EPMA data for all samples revealed atomic amounts no greater than three standard deviations from the loading compositions. The calcium amounts were consistently higher than expected, which is perhaps due to the fact that the  $K_{\alpha}/K_{\beta}$  peaks of calcium and the  $L_{\alpha}/L_{\beta}$  peaks of antimony overlap. The oxygen amounts were also well above the expected values, which can be attributed to oxidation from surface polishing. No tantalum signals were observed in any of the data sets. Based on the EPMA, we believe that all samples under study maintain the loading compositions without any significant fluctuations.

#### **Physical Properties and Electronic Structure**

Loading composition

Phase

The pure  $Ca_2RE_7Sb_5O_5$  and samples displayed an Arrhenius-type decrease in electrical resistivity with temperature, suggesting that these phases are semiconductors (a bump in the  $Ca_2Pr_7Sb_5O_5$  data at lower temperatures occurs due to an antiferromagnetic transition). Conversely, the  $Ca_2RE_7Bi_5O_5$  phases displayed a linear decrease in electrical resistivity with temperature (Figure 2). These types of behavior directly contrast with the parent  $RE_9Pn_5O_5$  phases, which were reported to have metallic-type conduction.<sup>11</sup> Thus, by reducing the electron count, we did succeed in removing the metallic-type electrical resistivity behavior with respect to the parent  $RE_9Pn_5O_5$  structures and achieved activation energies on the order of about 0.04-0.06 eV in  $Ca_2RE_7Sb_5O_5$  (Table 4). In the case of  $Ca_2RE_7Bi_5O_5$ , the electrical resistivity decreases

with temperature (similar to semiconductors) but the decrease is linear as opposed to exponential in semiconductors. We could not establish the origin of such non-Arrhenius behavior, but a similar trend was observed in some disordered semimetallic systems due to the electron-electron correlations.<sup>26,27</sup> Additionally, electrical resistivity at low temperatures is much lower for  $Ca_2RE_7Bi_5O_5$ , suggesting a larger metallic character, likely due to the greater orbital overlap of bismuth versus antimony. Overall, the  $Ca_2RE_7Pn_5O_5$  phases display similar or lower electrical resistivity than most other rare-earth pnictide oxide phases studied by our group so far. However, these electrical resistivities (around 0.1-2  $\Omega$  cm at room temperature) are still too great for any thermoelectric applications.



**Figure 2.** Electrical resistivity data for the  $Ca_2RE_7Pn_5O_5$  samples: a)  $Ca_2Pr_7Sb_5O_5$ , b)  $Ca_2Sm_7Sb_5O_5$ , c)  $Ca_2Gd_7Sb_5O_5$ , d)  $Ca_2Dy_7Sb_5O_5$ , e)  $Ca_2Gd_7Bi_5O_5$ , and f)  $Ca_2Dy_7Bi_5O_5$ .

	$Ca_2RE_7Pn_5O_5$ samples.	
Sample	Room temperature electrical resistivity	Activation energy
Ca <sub>2</sub> Pr <sub>7</sub> Sb <sub>5</sub> O <sub>5</sub>	1.92 Ω cm	0.058 eV
Ca <sub>2</sub> Sm <sub>7</sub> Sb <sub>5</sub> O	$1.51 \ \Omega \ \mathrm{cm}$	0.048 eV
Ca2Gd7Sb5O	$1.52 \ \Omega \ \mathrm{cm}$	0.042 eV
Ca <sub>2</sub> Dy <sub>7</sub> Sb <sub>5</sub> O	$1.53 \ \Omega \ \mathrm{cm}$	0.033 eV

 Table 4. Room temperature electrical resistivity and activation energy data for selected

 Co. BE. Dr. O. complex

Ca2Gd7Bi5O5	0.151 Ω cm	n/a
$Ca_2Dy_7Bi_5O_5$	$0.108 \ \Omega \ cm$	n/a

Seebeck coefficient measurements ( $\alpha$ ) on the Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> samples revealed a near-linear dependence of  $\alpha$  on temperature, with  $\alpha$  approaching zero as T  $\rightarrow$  0 for all samples (Figure 3), which is indicative of heavily doped (degenerate) semiconductors and semimetals. The Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> samples display larger Seebeck coefficients than the Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> samples, which correlates well with their electrical resistivity. The Ca<sub>2</sub>*Pr*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>Sm<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> phases also display a curvature in their Seebeck coefficient data with increasing temperature, which could arise from contributions from electrons and holes in a complex multiband structure. Small variations between samples with respect to calcium/rare-earth amounts could also greatly affect the dominant charge carrier type. The nature of this type of conduction may also explain why Ca<sub>2</sub>Gd<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> is *p*-type while Ca<sub>2</sub>Gd<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> is *n*-type (albeit weakly). Unfortunately, the Seebeck values obtained from our experiments are far lower than those observed from benchmark materials ( $\alpha \ge 150 \ \mu V \ K^{-1}$ ), making thermoelectric applications unlikely.

The thermal conductivity for  $Ca_2RE_7Pn_5O_5$  is dominated by the lattice contribution, since even for the electrically most conductive  $Ca_2Gd_7Bi_5O_5$  the electronic thermal conductivity is below  $10^{-2}$  Wm<sup>-1</sup>K<sup>-1</sup> at the highest measured temperature of 375 K. At low temperatures, the thermal conductivities of all  $Ca_2RE_7Pn_5O_5$  samples rapidly increase with temperature, which is due to the  $T^3$  dependence in their heat capacities (Figure 4). After reaching the maximum the thermal conductivities of the  $Ca_2RE_7Sb_5O_5$  phases slowly decline due to the Umklapp scattering. The  $Ca_2RE_7Bi_5O_5$  phases have less pronounced peaks in their thermal conductivities at low temperatures, which is likely due to a short phonon free path resulting form the small particle size and significant grain boundaries. This short phonon free path can also explain a relatively small effect of the Umklapp scattering on the thermal conductivity of  $Ca_2RE_7Bi_5O_5$  at higher temperatures.



**Figure 3.** Seebeck coefficient data for the  $Ca_2RE_7Pn_5O_5$  samples: a)  $Ca_2Pr_7Sb_5O_5$ , b)  $Ca_2Sm_7Sb_5O_5$ , c)  $Ca_2Gd_7Sb_5O_5$ , d)  $Ca_2Dy_7Sb_5O_5$ , e)  $Ca_2Gd_7Bi_5O_5$ , and f)  $Ca_2Dy_7Bi_5O_5$ .



**Figure 4.** Thermal conductivity data for the  $Ca_2RE_7Pn_5O_5$  samples: a)  $Ca_2Pr_7Sb_5O_5$ , b)  $Ca_2Sm_7Sb_5O_5$ , c)  $Ca_2Gd_7Sb_5O_5$ , d)  $Ca_2Dy_7Sb_5O_5$ , e)  $Ca_2Gd_7Bi_5O_5$ , and f)  $Ca_2Dy_7Bi_5O_5$ .

Electronic band structure calculations performed on the idealized  $RE_9Pn_5O_5$  structures reveal the presence of a noticeable pseudogap (density of states  $\neq 0$ ) at the Fermi level, corresponding to a charge balanced electron formula (80 –e/f.u. for Ca<sub>2</sub> $RE_7Pn_5O_5$ ). Such a distribution of states would be expected to yield semimetallic-like behavior with no activation energy in the electrical resistivity. However, the Ca<sub>2</sub> $RE_7Sb_5O_5$  samples display semiconductor behavior, which suggests the presence of Ca in their structure leads to a small band gap. In case of Ca<sub>2</sub> $RE_7Bi_5O_5$ , the Ca incorporation does not open a band gap and this effect combined with an atomic disorder likely leads to an unusual behavior of the electrical resistivity. Presence of the

pseudogap at 80 -e/f.u. indicates that the system is thermodynamically driven to a charge balanced Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub> formula when calcium is introduced. For all phases, the valence band is dominated by the *Pn p* states immediately below the Fermi level, and the states in the conduction band are dominated by the *RE d* states. As with many other rare-earth pnictide oxide structures, the density of states approaching the Fermi level becomes quite small, which may explain the relatively high electrical resistivity values.



**Figure 5.** Calculated electronic band structures for the Ca<sub>2</sub>Gd<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> structure (left) and Ca<sub>2</sub>Gd<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> structure (right).

## Conclusions

Substituting rare earth with calcium in  $RE_9Pn_5O_5$  was shown to yield pure, chargebalanced Ca<sub>2</sub> $RE_7Pn_5O_5$  phases upon high temperature reactions. Samples of Ca<sub>2</sub> $RE_7Pn_5O_5$  were observed to be much more stable versus the corresponding  $RE_9Pn_5O_5$  phases when prepared by similar methods, although the former are still moisture sensitive. X-ray powder and single crystal diffraction experiments confirmed that the Ca<sub>2</sub> $RE_7Pn_5O_5$  phases crystallize in the same P4/nstructure type as the parent  $RE_9Pn_5O_5$  phases, and in most cases display the same twinning laws. The acquired X-ray single crystal data suggested residual electron density on the 2*a* site, which we argue is an artifact of the reticular merohedral twinning.

Electrical resistivity and Seebeck coefficient measurements performed on pure  $Ca_2RE_7Pn_5O_5$  samples yielded semiconducting behavior for  $Ca_2RE_7Sb_5O_5$  phases and a linear decrease in resistivity for  $Ca_2RE_7Bi_5O_5$  phases, in contrast to the metallic nature of the parent  $RE_9Pn_5O_5$  structures. Unfortunately, the electrical resistivity and Seebeck coefficient values are

not ideal for thermoelectric applications. The calculated electronic structures of idealized  $RE_9Pn_5O_5$  suggest semimetallic densities of states, which appear to be modified by the Ca incorporation as seen from the experimental data.

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**Supporting Information.** Additional crystallographic data, magnetic data, and electronic structures are presented.

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Highlights

- The *RE*<sub>9</sub>*Pn*<sub>5</sub>O<sub>5</sub> structure may be stabilized with calcium substitution in the form of Ca<sub>2</sub>*RE*<sub>7</sub>*Pn*<sub>5</sub>O<sub>5</sub>.
- The  $Ca_2RE_7Pn_5O_5$  phases maintain the parent *P* 4/*n* structure, albeit with Ca/*RE* mixing.
- The Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> phases behave as semiconductors while the Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub> phases are semimetal with electron-electron correlations.
- Electronic structure calculations yield a semimetal-like density of states for both Ca<sub>2</sub>*RE*<sub>7</sub>Sb<sub>5</sub>O<sub>5</sub> and Ca<sub>2</sub>*RE*<sub>7</sub>Bi<sub>5</sub>O<sub>5</sub>.