Thermoelectric Materials Discovery Using Combinatorial Chemistry
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ABSTRACT
Transparent conducting oxides have been previously investigated for both bulk and thin film thermoelectric applications, and have shown promising results due to their thermal stability and electrical conductivity. Alloys of two or more transparent conducting oxides have been deposited using pulsed laser deposition (PLD) and combinatorial sputtering, and the resulting films were optimized for optical applications. In this study, thermoelectric materials were prepared by co-sputtering techniques, whereby a chemical gradient was formed across an alumina substrate that was patterned using photolithography to form hundreds of micro-thermocouples. The systems indium tin oxide (ITO), indium zinc oxide (IZO), and zinc tin oxide (ZTO) were investigated for this purpose and the resulting combinatorial libraries were rapidly screened to establish room temperature resistivity, Seebeck coefficient, and power factor as functions of both composition and heat treatment, in nitrogen and air ambients. Due to their chemical stability, oxidation resistance, and large Seebeck coefficients relative to metal thermocouples, these materials are ideal for temperature measurement or energy harvesting in harsh environments such as gas turbine engines.

INTRODUCTION
Thin film thermoelectric devices based on semiconducting oxides are being investigated for energy harvesting and temperature measurement in gas turbine engines used for propulsion and power generation. Thin film thermocouples for example have a rapid response time (less than one $\mu$s) and can be directly deposited onto the surface of components without the need for adhesives or surface preparation [1]. Furthermore, thin films add negligible mass to the components and thus, do not disturb the vibrational modes in smaller blades. Due to the existing thermal gradient across TBC coated turbine blades, it is possible to fabricate thermoelectric generators capable of powering active wireless transmitters.

Thermoelectric devices are characterized by a dimensionless figure of merit, $ZT$ which is defined according to eq. (1) as

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

where $\sigma$, $\kappa$, $S$, and $T$ are the electrical conductivity, thermal conductivity, Seebeck coefficient, and absolute temperature, respectively. Since thermal conductivity measurements are difficult to make on thin films, the thermoelectric power factor given by eq. (2) below is normally used to screen promising candidates for thermoelectrics,

$$\zeta = S^2 \sigma = ZT$$
Since conventional thermoelectrics such as PbTe, Bi₂Te₃, and SiGe either have relatively limited operating temperature ranges or cannot be used in oxidizing environments, significant research is being done to find alternative thermoelectric materials based on refractory oxides [2].

Several attempts have been made to replace platinum/rhodium based thermocouples, which cannot be used at temperatures above 800°C, due to dewetting of the platinum film and rhodium oxidation. However, these alternative thermocouple material systems have either had poor outputs or could not be used in oxidizing environments without employing protective coatings. For example, H. D. Bhatt et al. developed a La₃₋₀.xSrₓCoO₃ and a TiC-TaC thin film thermocouple that yielded stable output at temperatures up to 1350 K [3,4]. However, the reported Seebeck coefficients of the thermocouples in these studies were quite small and their operational temperatures were relatively low compared to the temperatures typically encountered in the hot sections of turbine engines. The thermoelectric powers of bulk oxides have also been investigated; however, the majority of these studies focused on discrete materials. For example, Ohtaki et al. [2] systematically analyzed the thermoelectric properties of Zn₁₋₀._xAlₓGaₓO produced by sintering ZnO, Al₂O₃, and Ga₂O₃ powders, in order to maximize ZT. A limited number of combinatorial studies using thin film libraries which contain thermocouples with continuously varying compositions have also been done using sputtering and PLD to characterize the thermoelectric properties of Zn₁₋₀._xAlₓO, (La₁₋₀._xCaₓ)VO₃, and (Ca₁₋₀._xBaₓ)₃Co₄O₉ films [4-7].

ITO, IZO, and to a lesser extent ZTO have been investigated as a transparent conducting oxide material by studying films prepared from single ceramic targets and by co-sputtering. Thermoelectric studies on bulk ZnO and In₂O₃ [(ZnO)ₘIn₂O₃] ceramics produced a maximum ZT value at m = 3, however, the authors only investigated a few compositions [8] and the thermoelectric properties of ITO and ZTO alloys were not optimized. In this study, co-sputtering techniques employing multiple targets were utilized to form a high resolution (less than 2 wt% variation per thermocouple) concentration gradient of ITO, IZO, and ZTO which depended on the relative distance from the two sputtering targets. Combinatorial chemistry techniques were used to rapidly screen the thermoelectric properties of the thermocouple libraries as a function of composition and heat treatment.

**EXPERIMENT**

Films in the systems In₂O₃:SnO₂, In₂O₃:ZnO, SnO₂:ZnO were deposited by rf co-sputtering using an MRC 3667 sputtering system in which the RF power and forward voltage were evenly split between two 15.2 cm diameter ceramic targets. For each system, seven hundred seventy thermoelements were patterned with platinum reference electrodes and bond pads using a 50 µm thick negative photoresist on a high purity (99.5%) alumina substrate to establish spatially dependent compositions. Immediately following, the entire process was repeated on an oxidized silicon wafer substrate and the thicknesses of the deposited films were measured using a Dektak IIA surface profilometer in order to determine film resistivity and power factor. The platinum bond pads and reference electrodes were sputtered from a high purity (99.99%) 100 mm diameter platinum target at a RF power of 300W and an argon pressure of 1.87 Pa for two hours resulting in a 3µm thick platinum film. The co-sputtered ITO, IZO, and ZTO films were fabricated by placing the masked alumina substrate between two simultaneously energized ceramic targets in 1.33 Pa argon pressure. Since relatively thick films are required for thermoelectric device applications, the oxide semiconductor films were deposited at 400W for twenty hours producing a nominal film thickness of 1.8 µm. The tuning parameters were
maintained throughout the sputtering run to preserve a uniform composition gradient. Prior to sputtering, a background pressure of less than $1.13 \times 10^{-4}$ Pa was achieved in the vacuum chamber. The targets were pre-sputtered onto shutters for 30 minutes in order to release trapped water vapor and remove cross contaminants derived from other targets. The substrate temperature was held at 25°C by water cooling during sputtering.

After deposition, the thin film thermocouples were heat treated in high purity nitrogen for 5 hours at 500°C then tested for thermoelectric output near room temperature. The thermoelectric power of each composition was tested by recording the voltage drop across the device while applying a constant temperature gradient of 7.7K with a hot probe, and the Seebeck coefficients were calculated by fitting the response to a second order autoregressive process. The surface temperatures of the hot and cold junction were verified using thin film type K thermocouples sputtered directly on the alumina wafer to determine the temperature gradient. The resistivities of the films were determined by measuring the resistance and thickness of each leg after deposition and subsequent heat treatments. Chemical composition of the co-sputtered films was determined using scanning electron microscopy (JEOL 5900 SEM) in conjunction with energy dispersive analysis of x-rays (EDS). The oxygen content of the most promising materials was determined using auger electron spectroscopy (AES) with a Perkin-Elmer 5500 multitechnique surface analyzer.

**DISCUSSION**

Figure 1 shows the thermoelectric power of In$_2$O$_3$, ZnO, and SnO$_2$ films upon thermal cycling to 1250°C. Despite their high Seebeck coefficients relative to indium oxide, films of intrinsic ZnO and SnO$_2$ had very noisy responses due to poor electrical conductivity. Furthermore, the hot junctions of the ZnO and SnO$_2$ films began to sublime at temperatures above 1100°C.

![Figure 1](image-url)  
*Figure 1* Thermoelectric power of (a) In$_2$O$_3$ vs Pt, (b) ZnO vs Pt, and (c) SnO$_2$ vs Pt as a function of temperature. Films were heat treated in nitrogen for five hours at 500°C and in air for one hour at 1000°C.
Furthermore, due to the high operating temperature of these devices, the charge carriers generated by oxygen vacancies are compensated, reducing the conductivity of the films. In the case of ZnO and SnO$_2$ films, this resulted in low power factor and noisy thermoelectric output. New candidates with improved properties were found by creating surface plots of Seebeck coefficient, resistivity, and composition as a function of position for the co-sputtered thermocouple libraries. The surface plots were superimposed on the combinatorial library, thereby creating maps to fully describe the thermoelectric properties in terms of chemical composition.

Figures 2 and 3 show thermoelectric maps for the systems In$_2$O$_3$:SnO$_2$ and In$_2$O$_3$:ZnO, describing the Seebeck coefficient and resistivity as a function of position. All films having a resistivity higher than 10$^3$ $\Omega$·cm were not considered. Since the Fermi level of indium oxide lies within the conduction band it is not surprising that thermoelements with relatively large indium content had the best conductivity in the IZO and ITO libraries [9]. Furthermore, In$_2$O$_3$ co-sputtered with both donor (Sn$^{4+}$) and acceptor (Zn$^{2+}$) ions exhibited a negative Seebeck coefficient at room temperature.

![Figure 2](image2.png)

**Figure 2** Maps showing the (a) thermoelectric response for a 7.7K $\Delta$T and (b) log resistivity of the nitrogen annealed In$_2$O$_3$:SnO$_2$ library.

SEM micrographs of the micro-thermocouples show the evolution of the microstructural changes in the films as a function of library position/composition (Fig. 4). The observed microstructures of the zinc oxide rich and indium oxide rich compositions were similar to those observed for co-sputtered IZO films [10]. Here, the indium oxide rich films (Fig. 4a and Fig. 4d) show sub-micrometer grains with a plate-like morphology with random orientation. Due to processing considerations, the substrate was maintained at a relatively low temperature during deposition, which resulted in poor crystallinity in these co-sputtered films [10]. This was evident in Figs. 4 (b) and (f) where no fine structure was observed.
Figure 3 Maps showing the (a) thermoelectric response for a 7.7K ΔT and (b) log resistivity of the nitrogen annealed In$_2$O$_3$:ZnO library.

Nanometer sized crystallites were observed in Fig. 4 (a), corresponding to In$_4$Sn$_3$O$_{12}$ (having 55 wt% In$_2$O$_3$ 45 wt% SnO$_2$), which exhibited a considerably finer grain microstructure than In$_2$O$_3$ doped with small amounts (< 10 wt%) of Sn or Zn. This is likely due to the fact that the In$_4$Sn$_3$O$_{12}$ phase is a high temperature phase (only stable above 1300°C [11]) in the In$_2$O$_3$-SnO$_2$ system, whereas ITO solid solutions doped with relatively small amounts of SnO$_2$ are stable down to room temperature.

Figure 4 SEM micrographs from IZO (a-c) and ITO (d-f) combinatorial libraries: (a) In$_2$O$_3$ (b) IZO (85/15) (c) ZnO (d) ITO (90/10) (e) ITO (55/45) (f) SnO$_2$
Candidate materials for both energy harvesting and temperature measurement were identified, as shown in table 1 and AES was performed on these compositions in order to verify the stoichiometry.

<table>
<thead>
<tr>
<th>Material</th>
<th>Seebeck ($\mu$V/°C)</th>
<th>Conductivity (Ω·cm)</th>
<th>Power Factor ($\mu$W/cm·K²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>80 wt% In$_2$O$_3$, 20 wt% SnO$_2$</td>
<td>95 $\mu$V/°C</td>
<td>0.013 Ω·cm</td>
<td>0.72 $\mu$W/cm·K²</td>
</tr>
<tr>
<td>55 wt% In$_2$O$_3$, 45 wt% SnO$_2$</td>
<td>240 $\mu$V/°C</td>
<td>0.32 Ω·cm</td>
<td>0.32 $\mu$W/cm·K²</td>
</tr>
<tr>
<td>85 wt % In$_2$O$_3$, 15 wt% ZnO</td>
<td>105 $\mu$V/°C</td>
<td>0.0065 Ω·cm</td>
<td>1.69 $\mu$W/cm·K²</td>
</tr>
<tr>
<td>63 wt% In$_2$O$_3$, 37 wt% ZnO</td>
<td>420 $\mu$V/°C</td>
<td>0.475 Ω·cm</td>
<td>0.37 $\mu$W/cm·K²</td>
</tr>
<tr>
<td>68 wt% ZnO, 32 wt% SnO$_2$</td>
<td>260 $\mu$V/°C</td>
<td>0.28 Ω·cm</td>
<td>0.2399 $\mu$W/cm·K²</td>
</tr>
<tr>
<td>37 wt% ZnO, 43 wt% SnO$_2$</td>
<td>480 $\mu$V/°C</td>
<td>15.8 Ω·cm</td>
<td>0.015 $\mu$W/cm·K²</td>
</tr>
</tbody>
</table>

Table 1 Comparison of various chemistries in the systems In$_2$O$_3$:ZnO and In$_2$O$_3$:SnO$_2$ and their thermoelectric properties at room temperature, as identified by combinatorial screening.

CONCLUSION

Thousands of micro thermocouples, each with unique compositions in a binary conducting oxide system, were characterized in terms of Seebeck coefficient, electrical conductivity, and power factor. Based on these results, six new compounds were identified that are promising candidates for harsh environment thermocouples and thermoelectric devices for energy harvesting. Based on these findings, precursor powders were developed for plasma sprayed thermoelectric generators.

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REFERENCES

Data Mining-Aided Crystal Engineering for the Design of Transparent Conducting Oxides

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ABSTRACT

The purpose of this paper is to accelerate the pace of material discovery processes by systematically visualizing the huge search space that conventionally needs to be explored. To this end, we demonstrate not only the use of empirical- or crystal chemistry-based physical intuition for decision-making, but also to utilize knowledge-based data mining methodologies in the context of finding p-type delafossite transparent conducting oxides (TCOs). We report on examples using high-dimensional visualizations such as radial visualization combined with machine learning algorithms such as k-nearest neighbor algorithm (k-NN) to better define and visualize the search space (i.e. structure maps) of functional materials design. The vital role of search space generated from these approaches is discussed in the context of crystal chemistry of delafossite crystal structure.

INTRODUCTION

Crystal structure of materials is closely linked with its final property [1]. In this regard, the ability to understand structural factors governing desired properties is critical in better designing functional materials. However, one of the current challenges in finding functional materials arises from the lack of tools to explore the huge search space. A good example is the discovery process for advanced TCOs due to the extremely huge search space from the many possible combinations from the periodic table to meet the TCO requirements.

There are two main approaches to handle huge search space. One is a combinatorial high-throughput synthesis and materials informatics to synthesize and interpret composition spreads, respectively [2, 3]. The other approach is to directly define the search space for TCOs such as structure mappings based on the concept of crystal chemistry [4]. While the former have been modernized successfully, the latter is still considered as a classical tool for identifying search space of materials. An example of the latter for designing new TCO includes identifying the role of the cations by Shannon et al in the 1970’s to the phase stability, chemical bonding, and transport properties [5, 6]. The starting point of their approach was a classical bivariate structure field map consisting of ionic radii of A and B sites of the delafossite ABO$_2$ (ex. A=Cu, Ag, Pd, Pt; B=Co, Cr, Fe, Ga, In) structure [4], which were successfully revisited by Marquardt et al. later for exploring p-type TCOs [7]. This delafossite structure map was again noteworthy to the TCO community in the 2000s because only a few p-type TCOs such as Cu$_2$O have been developed so far [8], and there is much that still needs to be explored.

Nevertheless, the approaches of the latter are inconclusive to elucidate interrelationships between structural factors and electrical/optical properties because two structural parameters used in the classical structure maps are usually not enough to fully delineate relationships of structural factors and performance of TCOs and therefore there is a need to systematically explore their inherent inter-complexities between multivariate structural factors.
APPROACHES

To solve the addressed issues here for oxide discovery as a TCO application, we revisit classical bivariate ABO\textsubscript{2} structure maps and modify them as modernized multivariate search spaces for ultimately finding potential p-type TCOs. We aim at fundamentally changing the conventional processes for TCO design to rational approaches by mainly focusing on a way to reduce the search space and simultaneously explore design routes in the space.

Structural aspects of ABO\textsubscript{2} delafossites for p-type TCOs

The delafossite structures have several advantages as the candidates for p-type TCO. For instance, tetrahedral coordinations of oxide ions reduce the non-bonding characteristics of the oxide ions, which lead to the delocalizations of the holes at the valence band edges. This layered structure enhances the bandgap enlargement and the low coordination number of the A ions is more effective to introduce comparable energy levels of Ad\textsuperscript{10} to those of O2p [9, 10].

Database of ABO\textsubscript{2} compounds

The search space includes selection of elements for multinary metal oxides with possible structures such as delafossites (ABO\textsubscript{2}) as well as available compositions for alloys based on literature survey. Following the scheme of Marquardt et al. [7], A and B are systematically mutated by coordination classes of ABO\textsubscript{2} compounds (i.e. AVI B\textsubscript{1/2}VI B\textsubscript{1/2}VI O\textsubscript{2}, A\textsuperscript{IV}B\textsubscript{1/2}IV B\textsubscript{1/2}IV O\textsubscript{2}, A\textsuperscript{VIII}B\textsubscript{1/2}VII B\textsubscript{1/2}VII O\textsubscript{2}, and A\textsuperscript{VII}B\textsubscript{1/2}VI B\textsubscript{1/2}VI O\textsubscript{2}) and the delafossites in ABO\textsubscript{2} compounds include AB\textsubscript{1/2}III B\textsubscript{1/2}III O\textsubscript{2}, AB\textsubscript{2/3}IV B\textsubscript{1/3}V O\textsubscript{2}, AB\textsubscript{2/3}IV B\textsubscript{1/3}V O\textsubscript{2}, and A(B\textsuperscript{III}, B\textsuperscript{IV})O\textsubscript{2}.

While we mainly used an inorganic material database, the so-called atomwork of National Institute for Materials Science in Japan, for structural information, TCO related electrical and/or optical properties were also collected from the literature [7, 9, 11-37]. Data of ABO\textsubscript{2} compounds compiled from published databases consists of the different experimental data as well as theoretical calculations. When identical choices of A and B with the same final form of compounds such as film or bulk are available from multiple resources, we considered both. If the data history is different (such as theoretical/experimental data or dissimilar experiments), we treated the data as additional samples while carefully checking the difference between theoretical calculations and experiments. The results from theoretical calculations for TCO system agree well with experimental data. Therefore, the origin of TCO data is not critical, but rather the optimization of radial visualizations from various structural classifiers to study new hypothetical p-type TCOs.

Figure-of-merit of ABO\textsubscript{2} structure maps

With two (sometimes three) carefully chosen physical factors, structure maps can be regarded as the first step of the materials design processes because they ensure that each compound is spatially located by its structure type [1, 38]. In this regard, it is possible to search stable phases of hypothetical materials. The figure-of-merit of structure maps can be defined as the ability to separate different structure types. However, it is a formidable task to choose appropriate physical factors to meet the above requirements of structure maps. With the aid of data mining techniques, there has been a study for developing multivariate structure maps.
without any *a priori* assumption of which two parameters are to be selected [38]. However, the approach of principal component analysis (PCA) that was used in that study can only be used when our data sets have no missing data points since it treats data as a matrix for eigenvalue decomposition. Instead, in our approach we demonstrate other data mining aided approaches such as high-dimensional visualization that are more robust to missing data.

**High-dimensional visualization for multivariate structure maps**

The next stage of the data-driven TCO discovery process is to map out a set of multidimensional points onto low dimensional space using high-dimensional visualization. In this way, the multivariate search space provides more possibility to identify various governing structural factors that determines performance of TCO, the degree of the relative impact of factors, and interdependency between factors are extracted.

1) **Radial visualization as high-dimensional data representation**

As a high-dimensional visualization tool, we utilize a radial visualization in a way that the multiple variables are equally laid out on the circumference of the circle (Figure 1(a)). This visualization uses the concept of Hooke’s law such that a data point for a sample sits in a circle and it is connected with virtual springs. The spring constant \( k_i \) is the scaled data value in each variable. The position of each data point is assigned at the equilibrium position where the sum of spring forces is zero. The location of each data point is assigned at the equilibrium position where the sum of spring forces is zero. The mathematical foundations and some features of radial visualization can be found in literature [39, 40].

2) **k-nearest neighbor (k-NN) algorithm to optimize radial visualization**

While the advantage of radial visualization over any other dimension reduction techniques such as PCA is the direct use of original data sets, the display of radial visualization highly depends on the layout of the variables. Moreover, when we show I variables of total M variables, the possible projections of I variables are \( \frac{M!}{((M-I)!)I!} \) and each selection of I variables produce different radial projections of \( \frac{(I-1)!}{2} \) [41, 42]. In our approach, we use k-NN algorithm to evaluate usefulness of radial projections created by changing the order of multiple variables as Leban *et al.* suggested [41]. As shown in Figure 1(b), k-NN algorithm searches the patterns for the k-training samples that are closest to the unknown samples in high-dimensional space. The unknown sample is assigned the most common class (i.e. structure types in this study) among its k-nearest neighbors. To this end, we calculate the accuracy of k-NN on positional information generated from radial visualization. The accuracy is estimated using the leave-one-out cross validation methods such that each data is classified in terms of structure types while other samples participate in the prediction of structure types. The computational details are beyond the scope of this paper but the reader is referred to the literature for more information [41-44].

**RESULTS AND DISCUSSIONS**

Generated ABO\(_2\) structure maps by radial visualization are shown in Figure 2. The top-left projection may be most useful for assigning structure types of hypothetical ABO\(_2\) compounds since it most clearly separates ABO\(_2\) compounds with different structures. Figure 3(a) is an example of a radial structure map consisting of five structural factors. From the locations of each data point, delafossites have higher values of \( M_A \).
Figure 1. (a) A schematic of radial visualization for representing a point having 8 variables. (b) A procedure for finding interesting projections via k-NN algorithm in radial visualization. Note that the structure type of each sample (ex. marked with star-shaped) is assigned in a given order of variables for radial visualization. Here, when k=5, the four nearest neighbors are class of “circle”, while one is class of “triangle”. Therefore, the star-marked sample is assigned as “circle” class.

Figure 2. Exemplary ABO$_2$ structure maps generated by radial visualization and k-NN algorithms. The used notations in Figure 2 and Figure 3 are R$_4$ and R$_6$: Shannon’s ionic radius of A and B, a and c: lattice parameter of a- and c-axis, $M_A$, $M_{B1}$, and $M_{B2}$: Mendeleev sequential number of A and B, $f_{B1}$, $f_{B2}$: fraction of B, and V: volume of unit cell. B$_1$ and B$_2$ were devised to deal with complex delafossites in the database (see the section of database of ABO$_2$ compounds).