

# MATERIALS DISCOVERY: STRATEGIES TO DOWNSELECT RADIATION DETECTION MATERIALS USING PERFORMANCE-BASED METRICS

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## ABSTRACT

Materials informatic approaches offer new options for accelerating the development of semiconducting gamma detection materials. The ability to identify promising materials from large numbers of candidate material compositions and *a priori* curtail less fruitful inquiry is based upon the ability to construct robust models for property estimation. Informatic-defined approaches relate atomic-level composition and structure to performance-directed properties for property estimation. To downselect to a smaller number of more likely materials, the estimated potential of a candidate composition is assessed against a series of performance metrics for a semiconducting detection material. Design rules based on structure-property relationships and candidate analysis offer an assessment of property trade-offs and the validity of perceived design constraints. For the II-VI semiconductor class (e.g.,  $\text{CdTe} + \text{ZnTe} \rightarrow \text{CdZnTe}_2$ ), the initial number of candidate compositions is over 700 which undergoes a 90% reduction upon application of density, band gap and mobility property screens. Many of these surviving materials lie outside the classical compositions associated with wide-band-gap semiconductors, and employ transition-metal or even group IA and IIA elements.

## INTRODUCTION

The identification of new semiconducting material compositions for gamma-radiation detection both has proven to be time-consuming and elusive [1-3]. Elemental semiconductors such as silicon and germanium are limited in number, and tuning their properties for room-temperature radiation detection is largely a matter of doping and processing techniques. The variation in properties afforded by different compositions of compound semiconductors offer more options to tailor properties in accordance with detector applications. However to date compound semiconductors have proven expensive to synthesize with sufficient crystal size and purity, and carrier transport performance metrics such as the carrier mobility/lifetime product are far lower than for elemental materials.

These challenges motivate an interest in techniques that can identify *a priori* those gamma detection materials most likely to be fruitful when prototyped in the laboratory [4,5]. Along with the directly generating candidate systems of interest, we seek design rules that offer guidance as to why particular materials classes perform well (or poorly). Design rules can be used to assess the accuracy of informatics-based results, as well as to provide ideas on how, or if, a sub-optimal system (properties/materials) might be improved. Finally, these rules give an indication of property trade-offs and whether they are intrinsic or might potentially be circumvented.

Here we describe the current state of our informatics-based search for new semiconducting gamma detection materials. Our early-stage screens suggest that there are new materials worthy of synthetic prototyping. Auxiliary analysis of the models and screens underlying our approach also illuminate reasons, beyond pure synthetic difficulty, why it has been historically challenging to identify a truly satisfactory semiconducting gamma detection compound.

## METHODS AND DISCUSSION

Candidate material screening has several requirements: 1) target set of desired properties; 2) knowledge base of materials compositions containing relevant physical properties, 3) a set of initial materials compositions; and 4) structure-property relationships (SPRs) for the properties to be considered. Once target properties have been identified, the initial material set is generated and passed sequentially through each available SPR to arrive at a candidate list for possible synthetic prototyping. Separately, patterns in the candidate output, and properties of the SPRs, are analyzed for design rules.

Table 1: Key target properties for semiconducting gamma radiation detection materials.

Property	Rank	Desired Range [CZT value]	Advantages
Band gap	1+	1.4 – 3 eV [1.5-2.2]	Carrier numbers; background signal
Density	1	> 6 g/cm <sup>3</sup> [5.8]	Stopping Power
Electron mobility	1	> 1000 cm <sup>2</sup> /Vs [~1200-2000]	Charge Collection
Carrier lifetime	1	>10 <sup>-5</sup> sec [~ 10 <sup>-5</sup> sec]	Charge Collection
Crystal structure	2	Cubic [cubic]	Synthetic
Phase thermodynamics	1-2	Single phase [Multiple]	Synthetic
Defect solubility	1-2	n- and p-dopeable; low defect concentrations	Synthetic

The electronic properties for the compounds discussed in this study were primarily assembled from standard reference sources (NIST, Landolt-Bornstein); with specific additions for alkali halide, alkaline earth halides, binary semiconductors [6], ternary I-III-VI<sub>2</sub> and II-IV-V<sub>2</sub> compound [7,8] and insulating ternaries [9] compounds. Structural data for this study was assembled from the Inorganic Crystal Structure Database [10]. For our investigations the target properties of a successful candidate would track the widely investigated properties of cadmium zinc telluride (CZT) [1, 11], and are listed in Table 1. Currently our focus has been upon the critical properties of band gap, density, and carrier mobility; we are currently in the process of developing models for carrier lifetime.

This program has focused to date on the inorganic semiconducting materials classes seen in Table 2. The candidate counts for each class are derived by considering allowed cations and anions, accommodating the requirements of stoichiometry, and removing several radioactive elements unsuitable for a gamma-detecting application.

Table 2: Candidate semiconducting gamma radiation detection materials broken into four materials classes. Composition key: A-cation, B-anion; TM-main row transition metals.

Class	Description	Parent Formula	Composition Variation	Candidate Numbers	Examples
1	II-VI	A-B; (A1-A2)B <sub>2</sub>	A= Group IIa, IIb, TM(2+) elements B= Group VIa	770	CdTe CdZnTe <sub>2</sub>
2	III-V	A-B; (A1-A2)B <sub>2</sub>	A= Group IIIa, IIIb, TM(3+) elements B= Group Va	555	GaAs InGaAs <sub>2</sub>
3	I-III-VI <sub>2</sub>	A-B-C <sub>2</sub>	A= Group Ia, Ib, TM(1+) B= Group IIIa, IIIb, TM(3+) C= Group VIa	705	CuInSe <sub>2</sub>
4	II-IV-V <sub>2</sub>	A-B-C <sub>2</sub>	A= Group IIa, IIb, TM(2+) B= Group IVa, IVb, TM(4+) C= Group Va	975	CdGeAs <sub>2</sub>

Robust materials selection imposes some general guidance on the development and application of the candidate-screening SPRs. First, because crystal structures are not known prior to synthesis, screening SPRs should have "structureless" inputs, without reference to crystal coordinates or implicit three-dimensional inputs such as space groups or c/a ratios. Second, where possible, SPRs should be based on physical inputs, rather than solely on empirical correlations. Physically-based models permit more reliable extrapolation, provide design rules that are physically-based, and are more transparent to later scrutiny. Third, some properties, particularly electronic transport properties, are characterized by low-quality data during early laboratory prototyping. An attempt must be made in screening to project to the "ultimate" properties that might be expected after years of synthetic effort. Finally, we observe that in some cases the set of generated candidates may be insensitive to particular SPR details. This can be valuable for limiting the amount of input information required to construct a model, but also for focusing modeling effort on design-constraining material properties.

For our screens, we employ a band-gap model patterned after the work of Ruoff [12,13] that relates atomic properties such as partial charge, atomic radius, and polarizability to the band gap. Our model does not depend on details of the 3D structure, and exhibits a mean error of ~0.4 eV. For density, a rather simple categorical model suffices, indicating whether the material is roughly 5.8 g/cm<sup>3</sup> or greater, or less than this amount. Rough density estimates are generally insensitive to details of structure for many inorganic materials; a simple estimate can be made by using

atomic radii, accounting for formal charge, and applying a generic packing factor. While this model performance is limited, it is adequate to separate very light materials from heavier ones, and to explain why certain materials classes such as binary III-Vs are not strongly represented in the final candidate list.

Mobility presents a more complex modeling problem, both because there are many scattering mechanisms that lead to finite mobility, and because early-stage synthetic prototypes exhibit very low room-temperature carrier mobilities, due to crystal defects. The quantity of real interest for this design is an 'ultimate' mobility, which would apply to a pure synthetic system with minimal defects. (Such a 'pure' system might be 5-10 years in the making--one reason why accurate informatics assessments of good detection material systems are valuable.) In identifying a theoretical construct to associate with the ultimate mobility, we look to the excellent results obtained for wide-band-gap semiconductors such as CdTe using the optical (polaron) component of the mobility. The polaron mobility closely matches the room-temperature mobility of CdTe [14]. Our calculations for wide-band-gap semiconductors such as GaAs (estimated electron mobility 3000-5000 cm<sup>2</sup>/V.s) show semi-quantitative agreement with experiment (<8500 cm<sup>2</sup>/V.s [15]) for highly-purified systems. Here we adopt the polaron electron mobility as our screen for ultimate mobility, while acknowledging other mechanisms may play a role in restricting mobility.

Theoretical estimates of the polaron mobility have been extensively studied, and calculational methods are summarized by Mahan [16]. Based on Mahan [16] and Szigetti [17], the mobility tracks the difference of the reciprocal static and optical dielectric properties ( $\frac{1}{\epsilon_0} - \frac{1}{\epsilon_\infty}$ ), reflects the effective charge difference between anion and cation in the material. As seen in Figure 1, for the moderate values of effective electron mass encountered in wide band gap semiconductors, the charge separation dominates the behavior of mobility, and one may construct an approximate screen based on the effective charge separation. We use such a model here. We comment that in the future this model can be altered by either of two considerations: 1) a class of low-defect systems is identified for which the optical/polaron mobility is found to be only a minor factor in determining room-temperature mobility, or 2) materials are identified which exhibit anomalously-low effective electron masses. To date we are aware of no such circumstances.

As part of the down-selection strategy, design rules showing the trade-offs between properties offer additional guidance beyond the pure generation of new candidate materials. First, consider the correlation between band gap and mobility. It is often stated that band gap and mobility are inversely related through a connection to the effective electron mass which is also consistent with tight binding calculations and perturbation theory definition of effective mass [16,18]. Figure 2 shows a plot of several properties, including known effective electron masses, as a function of band gap. Consistent with this picture, we have identified *no correlation* between  $m_e$  and the band gap  $E_g$  for *wide-band-gap* semiconductors. Our design rules suggest that there is indeed a connection between band gap and mobility, but for a different reason: band gap and "ultimate" mobility are both associated with charge separation. As charge separation increases, band gap generally increases, while mobility generally decreases (often dramatically). The result is that *increasing* the band gap through a composition change presents design challenge unless

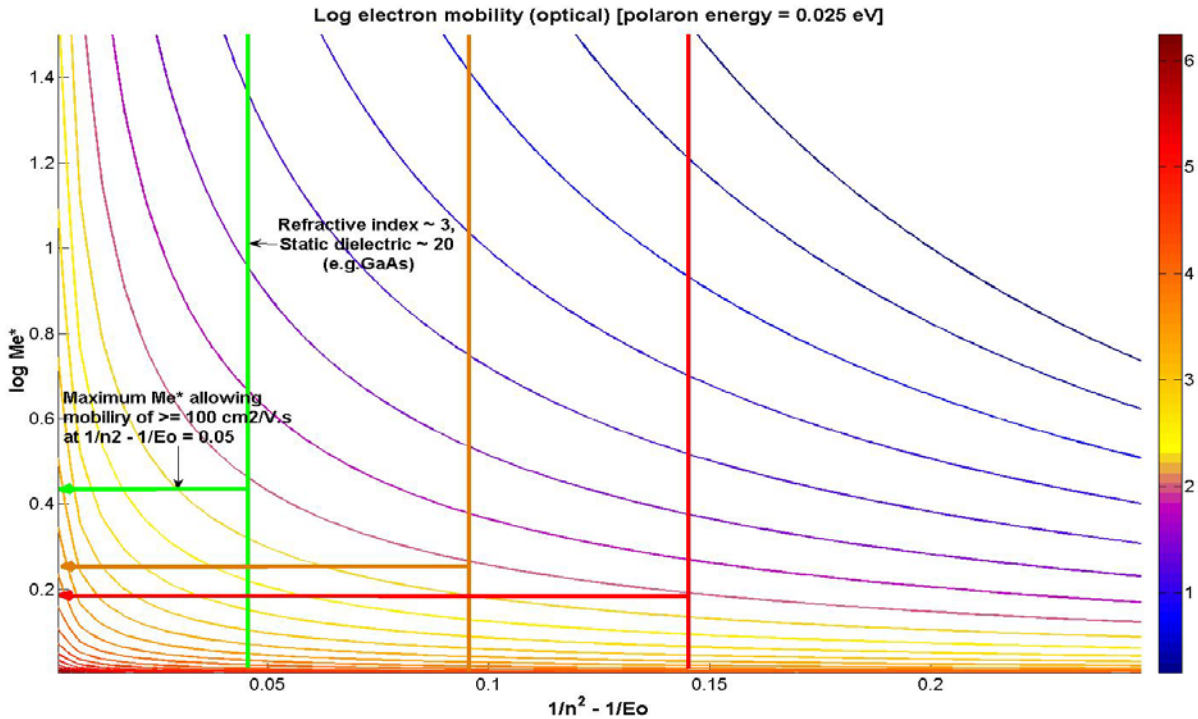


Figure 1: The dependence of polaron (optimal) mobility on dielectric constants and effective electron mass. The horizontal axis relates directly to the effective charge separation between cation and anion. Low charge separations are required to achieve good polaron mobility for the effective electron masses found in most wide-band-gap semiconductors.

the initial mobility is also very large. On the other hand, *decreasing* the band gap through composition changes is far less constrained, and often enhances ultimate mobility.

The potential correlation between density and band gap needs closer examination. The data shown in Figure 2 strongly infer that band gap and density are anti-correlated for semiconducting systems. This seems reasonable, as low-band-gap materials are typically associated with heavy-atom systems such as HgTe, while 'lighter' systems generally have higher band gaps. However, more detailed analysis of the assembled data set yields a different interpretation.

The apparent discrepancy between expectation and assembled data can be resolved by factoring the data underlying Figure 2 in the manner seen in Figure 3. The apparent correlation results from the collected types of semiconductors examined to date, and does not indicate a broad generality for connecting band gap and density. Indeed, because the underlying individual models for band gap and density are simple and physical, they should be trusted to prevail over the "obvious" but misleading Figure 2.

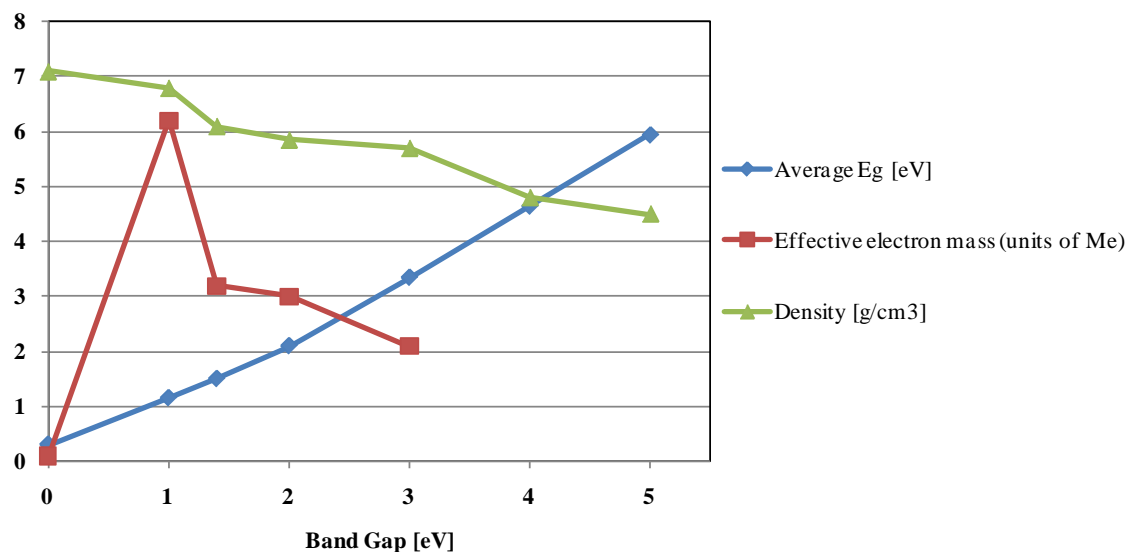


Figure 2: Analysis of the average measured semiconductor properties in the semiconductor data resource as a function of measured band gap. Properties values shown at each value of the band gap along the x-coordinate are the average values of the individual reports within the band gap (+/- 0.5 eV). Effective electron mass values are 1/10 the y-coordinate value.

The connection between band gap and density is a tendency within the bounds of specific materials chemistries, and does not represent a fundamental constraint on gamma-detection materials. This suggests exploration of material classes such as mixed-cation materials using group IA and IIA elements. We observe that this suggestion arises purely from consideration of a possible property tradeoff and the associated design rules.

The property relationship between carrier lifetime and mobility is also of interest, and currently under investigation. Because both properties have a connection to charge separation (for carrier lifetime through the defect energy), it is possible that these properties will exhibit a trade-off with an optimal charge difference between cation and anion.

Finally, we turn to some specific outcomes of our materials screening, focusing on results for II-VI and related semiconductors. Illustrative of these results are the property maps seen in Figure 4. These maps were constructed from successive application of SPRs for the target properties onto the II-VI materials candidate listing in Table 2. Normalized figures of merit were developed for each SPR based upon the target properties, and mapped across the composition series results in individualized property maps. Combined across several properties, these maps result in a composite figure of merit for candidate compounds.

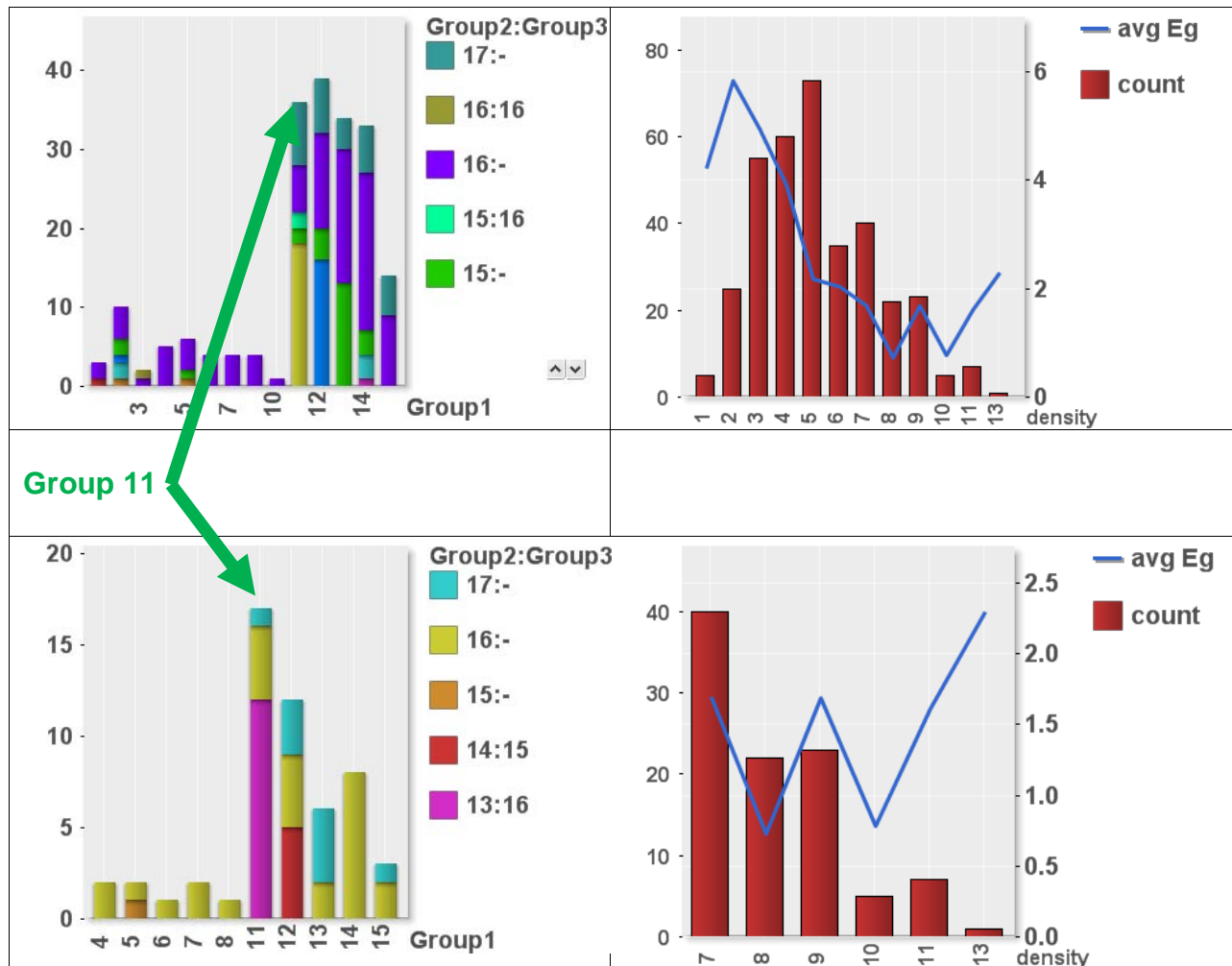


Figure 3. The relationship between band gap and density is biased due to the preponderance of measurements from the right-hand side of the periodic table. The top two figures show compositions and densities for general wide-band-gap (WBG) semiconductors (1.0-5.0 eV); the lower two figures show the compositions and densities for high-density WBG semiconductors. High density WBG semiconductors are known, but are fewer in number and more highly represented by elements outside periodic table groups 12-16 (group 11 in particular).

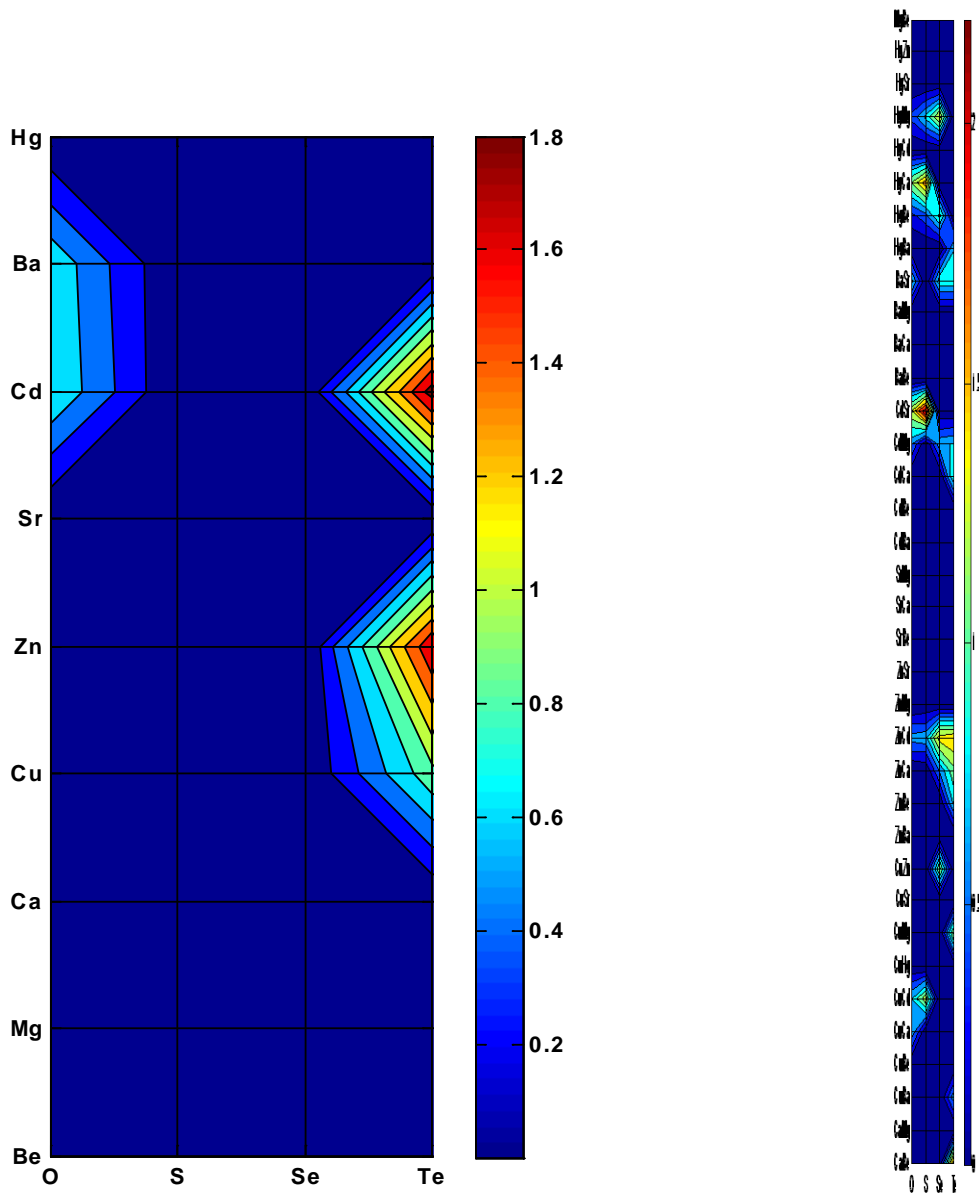


Figure 4. Composite property map illustrating screening results for II-VI materials. On the left are the property maps for binary II-VI systems. The right-hand map shows partial results for ternary II-VI systems. Figure of merit values in the range of 1.6 (see color scale) indicate potential compositions with an estimated combination of properties comparable to CZT.

Most systems for II-VI materials are eliminated by a combination of density and band gap effects. In particular, suitably-dense classic II-VI semiconductors (cation/anion from groups 12 and 14) tend to have band gaps that are *too low*. The previous discussion on band gaps and mobility suggests that introduction of more ionic cations from groups 1-11 might successfully repair the low band gap. Indeed, some transition-metal/VI materials pass these our initial screens, and should be considered for possible prototyping. It is noteworthy, but not unexpected, that CdTe and ZnTe pass the binary II-VI screen. Of note, two oxide systems (BaO and CaO) also display moderately good scores although both compositions are known to have band gaps outside the targeted property range. This situation exhibits two other characteristics of informatic downselection; property estimates have a specific range of validity (representation of related compositions for both compounds in the knowledge base was sparse, and band gaps of both compositions were outside the targeted range of the SPR) and the nature of false positives/negatives in the downselection process. Since synthetic issues creating high-quality inorganic oxide crystals are generally significant, these might not have been ultimately be prototyped. In a systematic exploration, these results would be passed on for further assessment by synthesis and crystallization experts. Secondary examination of the initial downselected candidates allows more critical assessment of these materials; and typically they fall into grouping of related materials chemistries. In general we find that fewer than 10% of the original II-VI materials set survive the initial combined screens of density, band gap, and mobility out of the original 2000+ candidate set, with a similar reduction upon the secondary examination. This offers a concrete metric of the difficulty in meeting gamma-radiation-detector design requirement.

## **CONCLUSIONS**

The process of screening a suitable set of initial materials against physically-based SPRs yields a modest percentage of materials suitable for further consideration in potential semiconducting gamma detection applications. Many of these new materials are outside the classical compositions associated with wide-band-gap semiconductors, and employ transition-metal or even group IA and IIA elements. Design rules based on SPR and candidate analysis offer an assessment of property trade-offs, and can also show why some materials classes cannot be improved by simple compositional substitutions.

Current work is incorporating additional screening properties, including carrier lifetime and thermodynamic properties. Additional screens can only decrease the number of candidates suitable for physical prototyping. However, current work suggests that one may expect to identify new material compositions with properties at least the equal of current systems, as well as a better understanding of the design options for tuning new and existing systems.

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