



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

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Changwon Suh, Kwiseon Kim, Joseph J. Berry, Jinsuk Lee, and Wesley B. Jones

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

Changwon Suh, Kwiseon Kim, Joseph J. Berry, Jinsuk Lee, and Wesley B. Jones

National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401, U.S.A.

## 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  $Cu_2O$  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  $ABO_2$  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 $ABO_2$ 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  $Ad^{10}$  to those of  $O2p$  [9, 10].

### Database of $ABO_2$ compounds

The search space includes selection of elements for multinary metal oxides with possible structures such as delafossites ( $ABO_2$ ) 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  $ABO_2$  compounds (i.e.  $A^{VI}B_{1/2}^{VI}B_{1/2}^{VI}O_2^{VI}$ ,  $A^{IV}B_{1/2}^{IV}B_{1/2}^{IV}O_2^{IV}$ ,  $A^{VIII}B_{1/2}^{IV}B_{1/2}^{IV}O_2^{VI}$ , and  $A^{II}B_{1/2}^{VI}B_{1/2}^{VI}O_2^{IV}$ ) and the delafossites in  $ABO_2$  compounds include  $AB_{1/2}^{3+}B_{1/2}^{3+}O_2$ ,  $AB_{1/2}^{2+}B_{1/2}^{4+}O_2$ ,  $AB_{2/3}^{2+}B_{1/3}^{5+}O_2$ , and  $A(B^{3+}, B''^{3+})O_2$ . Note that B site cation is marked with  $B_1$  and  $B_2$  to effectively include all the complex delafossites into the database. The order of  $B_1$  and  $B_2$  is not critical because we include all the mutations such that  $B_1=B_{2/3}^{2+}$  and  $B_2=B_{1/3}^{5+}$  as well as  $B_1=B_{1/3}^{5+}$  and  $B_2=B_{2/3}^{2+}$  in  $AB_{2/3}^{2+}B_{1/3}^{5+}$ , for example. 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].

### Figure-of-merit of $ABO_2$ 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 multi-dimensional 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**

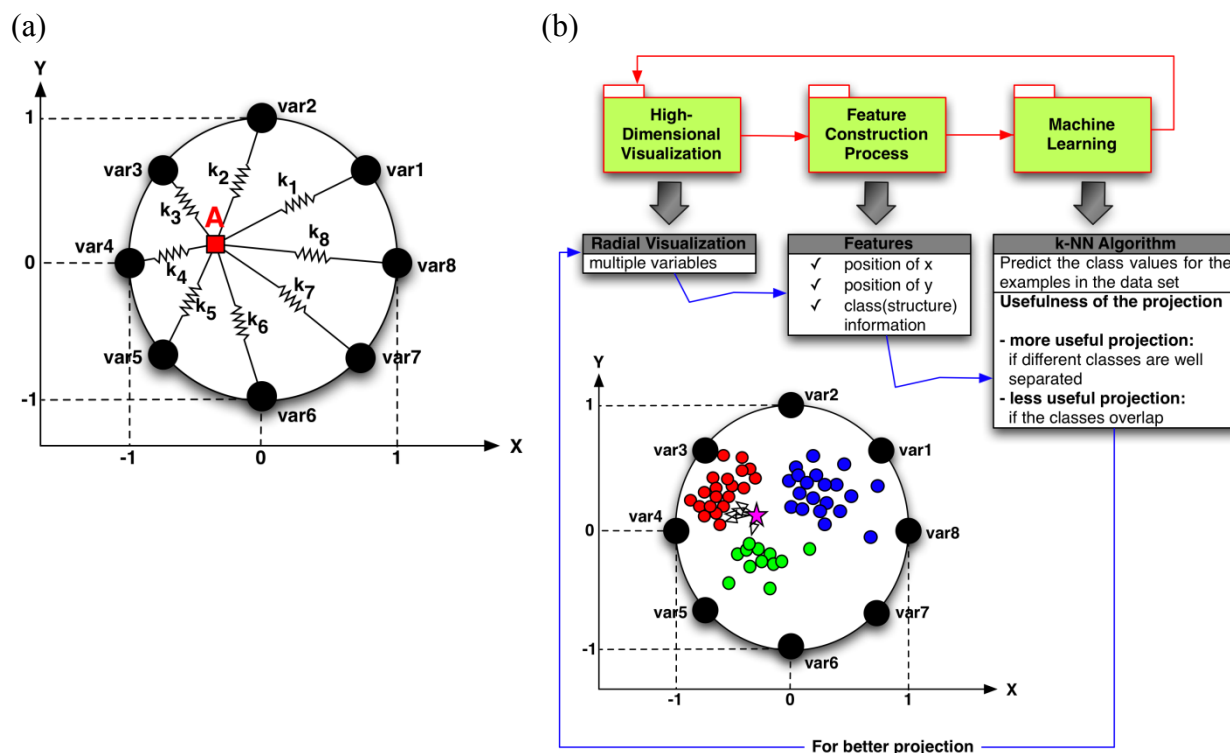
As a high-dimensional visualization tool, we utilize a radial visualization in a way that the multiple variables are equally laid out on the circumference of the circle (Figure 1(a)). This visualization uses the concept of Hooke's law such that a data point for a sample sits in a circle and it is connected 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**

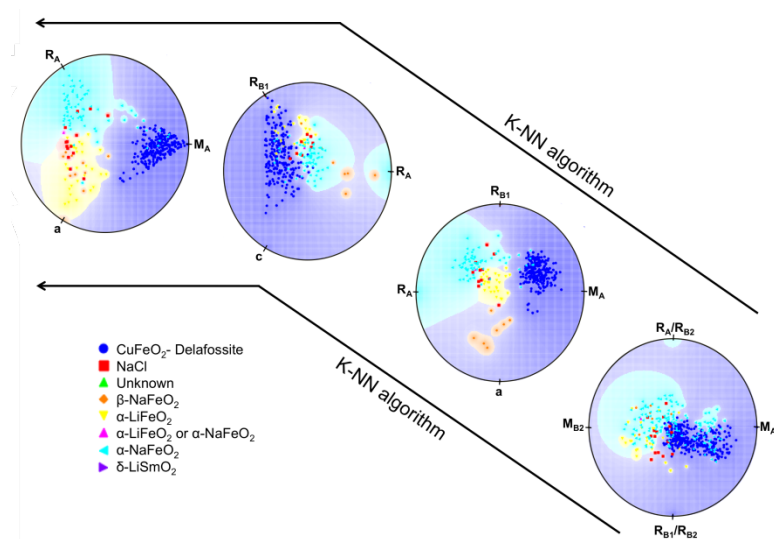
While the advantage of radial visualization over any other dimension reduction techniques such as PCA is the direct use of original data sets, the display of radial visualization highly depends on the layout of the variables. Moreover, when we show  $I$  variables of total  $M$  variables, the possible projections of  $I$  variables are  $M!/((M-I)!I!)$  and each selection of  $I$  variables produce different radial projections of  $(I-1)!/2$  [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  $ABO_3$  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  $M_A$ . Most known delafossite TCO are Cu- and Ag-based which have relatively high Mendeleev numbers of 72 and 71, respectively. It should be noted that it is always possible to unexpectedly uncover the roles of any structural factors with this approach.

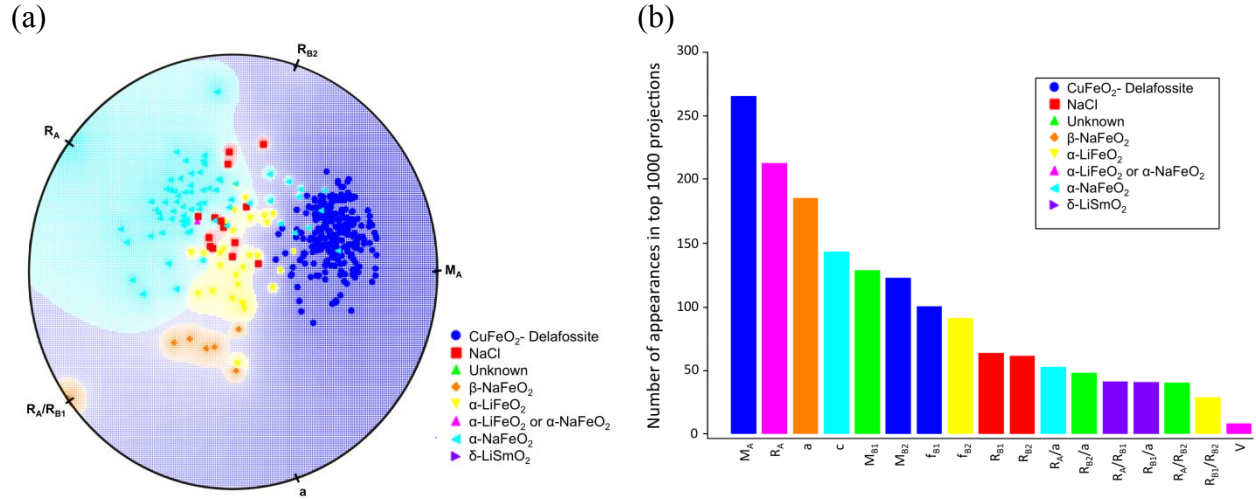


**Figure 1.** (a) A schematic of radial visualization for representing a point having 8 variables. (b) A procedure for finding interesting projections via k-NN algorithm in radial visualization. Note that the structure type of each sample (ex. marked with star-shaped) is assigned in a given order of variables for radial visualization. Here, when  $k=5$ , the four nearest neighbors are class of “red”, while one is class of “green”. Therefore, the star-marked sample is assigned as “red” class.



The ratio of ionic radii in A and B site ( $R_A/R_B$ ) can be a good classifier to discriminate  $\alpha$ - $NaFeO_2$  from  $CuFeO_2$  delafossites. The reason is that in Figure 3(b) the structure of  $\alpha$ - $NaFeO_2$  has high values of  $R_A/R_B$  while the structure of  $CuFeO_2$  delafossites has low values. Note that

this relationship is known as a result of painful crystallochemical analysis of the structure with the criterion of  $R_A/R_B > 1$  [36].



**Figure 3.** (a) An example of radial visualization-derived multivariate ABO<sub>2</sub> structure map. (b) Variable rankings of ABO<sub>2</sub> in terms of number of appearances in top 1000 radial projections.

The radial visualization can also provide variable ranking in a given data. For example, Figure 3(b) shows the number of appearances in top 1000 projections for each variable. From this, we identify that the main classifiers (i.e. variables to classify these structures) in a given ABO<sub>2</sub> formula are  $M_a$ ,  $R_a$ ,  $a$ ,  $c$  etc. From the color of the figure, delafossites are more related to Pettifor's Mendeleev sequence numbers defined in literature [1], which were also confirmed in Figure 3(a).

## CONCLUSIONS

Our approaches have shown the value of high-visualization techniques and machine learning algorithms such as radial visualization and k-NN for developing multivariate structure maps of ABO<sub>2</sub> compounds, including delafossites. Our study can be applied any kinds of dataset. Apart from the visualization of search space in terms of structure mapping, we can also unravel complex structure-processing-property relationships of materials using the demonstrated concepts in the field of materials informatics by including structural factors, processing conditions, and properties. These relationships are useful to suggest hypothetical delafossites for p-type TCO applications. We are currently developing various physicochemical parameters for better multivariate TCO structure maps.

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