Combinatorial Analysis Methodologies for Accelerated Research: The Case of Chalcogenide Thin-Film Photovoltaic Technologies

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One of the fastest ways for the discovery, understanding, development, and further optimization of new complex materials is the application of combinatorial analysis methodologies, which have already shown impressive results for different organic and inorganic materials, leading to the fast development of different scientific fields and industrial applications. However, in the case of thinfilm materials for optoelectronic devices and, in particular, for second-generation photovoltaic (PV) devices, the application of combinatorial analysis is still quite uncommon with a desultory rather than systematic application. The present review discusses the main constraints for the application of combinatorial analysis to thin-film materials with a focus on chalcogenide compounds and different strategies to overcome them. Special attention is paid to the requirements for the preparation of graded thin films, characterization, and analysis of the results, providing different hints for the implementation of high-quality combinatorial analysis. Finally, an overview of the currently published results in the field of chalcogenide thin-film PV technologies is presented, showing the relevance of the combinatorial approach for boosting the development not only of this promising PV technology, but also of other optoelectronic devices based on complex materials and multilayered structures.

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1. Introduction

Energy is among the main product demanded in modern society. Its production and consumption is swiftly growing and, being still mainly based on the combustion of fossil fuels, this makes a significant contribution to the greenhouse effect.^[1] To reduce greenhouse gas emissions and mitigate climate change effects, a transition from traditional energy sources to cleaner and efficient energy systems is strongly required. Solar energy is clearly one of the renewable energy sources that can take significant part in this transition, providing daily energy that is 10 000 times higher than the energy needed on the Earth. Photovoltaic (PV) technologies which directly convert solar light into electricity is leading this race for our sustainable future.^[2] Among the different PV technologies, the one based on crystalline silicon (known as first-generation PV) clearly dominates the market.^[3] However, its application is limited by the brittleness

and the relatively high weight of the modules, which compromise the development of advanced PV integration concepts. This has given interest to the development of thin-film solar technologies also known as second-generation PV, which has promised to reduce the cost of manufacturing PV modules by lowering the materials consumption.^[2] In addition, thin-film PV employs a wide range of different absorber materials, substrates, and deposition techniques, and has a much higher technological flexibility, which opens the way for wider and innovative applications such as building-integrated PV, transport-integrated PV, space flight, wearables, or Internet of things, among others.^[4]

Chalcogenide compounds are promising candidates as absorber materials in thin-film solar cells, and some of them not only show the promising efficiency values, but have already reached the mass production state. In between them is the family of CdTe absorbers which allowed to reach a 22.1% record cell energy conversion efficiency. CdTe technology has the highest global market share compared with all thin-film PV industrial technologies.^[3,5] The family of chalcopyrite Cu(In,Ga)(S,Se)₂ (CIGSSe) absorbers has allowed to achieve record cell efficiencies up to 23.35% and, despite having a lower market share, offer



high versatility in terms of commercial PV applications.^[3,6] A 13% efficiency has been reached in the solar cells based on the family of kesterite Cu₂ZnSn(S,Se)₄ (CZTSSe) absorbers, which offer the same versatility as chalcopyrites but avoid the use of critical raw materials.^[5] Finally, the rediscovered family of quasy-1D absorbers, mainly Sb₂(S,Se)₃, has already shown promising values of the device performance exciding 10% efficiency and offers a single-phase structure.^[7] Despite the advantages of chalcogenides and the promising efficiencies achieved at cell level, the study of these materials has to be continued for further performance improvement and device optimization. Optimization of these technologies will open very interesting perspectives for the development of next-generation advanced PV integration concepts, contributing to further decentralization of the energy production process.

Material development has been traditionally carried out by means of different experiments consisting of synthesizing samples and testing them one by one. This method produces high-quality materials, but it is slow and very time-consuming for exploring modern advanced materials that are often alloys involving three or more elemental components, whose properties are frequently modified by the adjustment of several factors such as the crystal-linity, the mesostructure, or the layering schemes.^[8–10] In consequence, the time that elapses between the laboratory discovery of new materials and their first practical use in the market is typically between 10 and 20 years.^[10,11] To reduce this time, alternative materials science methodologies that enable the study of a high amount of materials in a shorter period of time have to be applied.

Combinatorial (or high-throughput) material analysis consists of the synthesis of a sample that contains a large array of diverse materials. This so-called "library" sample is studied by rapid, sensitive, and spatially localized measurements employing different characterization techniques. Finally, the obtained massive dataset that covers the physical and/or chemical properties of various materials is analyzed to identify a family of "lead" materials with a desired property. Thanks to the simultaneous synthesis of different materials and their rapid characterization, the combinatorial approach results in a screening, discovery, and optimization of materials in less time and with a higher throughput.^[8,10,12–15]

A variation of conventional combinatorial approaches that is based on the synthesis of one sample containing an array of diverse materials can be the synthesis of a sample, showing controlled slight gradual change of a given property. This allows the achievement of a large number of samples, allowing to ensure the statistical validity of the performed study.^[16] As in the conventional combinatorial approach, this high number of samples is studied by different characterization techniques that allow rapid measurements. In this case, the analysis of the massive dataset provides trends of the impacts of different physicochemical properties on the materials that would not be identified with the use of a low statistical set of data, thus enabling finer material optimization that otherwise would be impossible.

The origin of the combinatorial analysis is found in the decade of 1960, when Merrifield developed the stepwise addition of protected amino acids to a growing peptide chain.^[17] In 1970, Hanak questioned the efficiency of studying one composition at a time and introduced a new approach consisting of synthesizing,

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analyzing, testing, and evaluating large parts of multicomponent systems in single steps.^[18] This concept was commercially applied in the pharmaceutical industry for drug discovery in the decade of 1990,^[19–21] while combinatorial thin film synthesis was developed by Xiang et al. in 1995.^[22] Since then, the combinatorial approach has been applied in many fields such as catalysts,^[14,23–28] amor-

phous bulk materials,^[29,30] luminescent materials,^[31–33] functional materials,^[34,35] shape memory alloys,^[36,37] sensing materials,^[38,39] biomaterials,^[40] organic coatings,^[41,42] inorganic materials,^[15] electronic materials,^[43] and ferromagnetic materials.^[44,45] Despite its wide expansion, combinatorial analysis has been

subjected to some criticisms. For example, the unintentional but inevitable variation of other parameters when changing the parameter that is the focus of the study may produce doubts about whether the obtained results are due to the parameter varied intentionally or to the ones varied unintentionally. However, this issue can be resolved using a great number of characterization techniques that, after analyzing the obtained data, allow to identify the impact of the different varied parameters.^[46] Another problem of the combinatorial analysis is that the process conditions when synthesizing a library sample are different than the conditions when synthesizing a material for its intended application, but this can be sorted out by taking into account that combinatorial analysis provides the knowledge of the tendency of the impact of one property on the device performance rather than an exact value of that physical property. Combinatorial approach also requires a higher investment in the initial equipment, but it becomes less expensive in the long term. A final critical point is that this methodology may not be useful when studying properties that are highly structure sensitive. Due to these issues combinatorial analysis has to be complemented with traditional experiments.^[12,14]

Even taking into account the mentioned critical points, the combinatorial analysis is a fast and cheap method that can help to optimize PV materials and improve the energy conversion efficiency of the solar cells. There exist general experimental designs for synthesizing combinatorial thin-film solar cells,^[47–49] and the combinatorial approach has been extensively employed for optimizing oxide materials including Cu₂O,^[50] In₂O₃:ZnO:SnO₂,^[51] (Zn,Mg)O,^[52,53] ZnO,^[54] ZnO–SnO₂,^[55] TiO₂–Cu₂O,^[56] ZnO–SnO₂–TiO₂,^[57] TiO₂/Co₃O₄/MoO₃,^[58] and SnO₂–TiO₂–WO₃,^[59] which can play different roles inside the solar cells such as absorber material, contacts, buffer layers, and window layers. Combinatorial studies have also been reported on nitride^[60,61] and perovskite solar cell absorbers.^[62,63] Focusing on chalcogenide thin-film solar cells, there are few literature reports on the use of the combinatorial approach; however, taking into account its benefits, the interest in the combinatorial analysis in this field should be significantly increased.

In this frame, this work aims to provide a roadmap for applying combinatorial analysis for the accelerated research of chalcogenide absorber materials. The work includes: 1) a critical review of the requirements for optimal synthesis and characterization techniques when performing combinatorial experiments; 2) a review of the possible approaches for suitable processing of the obtained massive set of data; and 3) a review of the stateof-art combinatorial analysis applied on chalcogenide-based thin-film PV technologies.



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2. Practical Considerations for the Optimal Implementation of Combinatorial Analysis Methodologies: A Case Study of Thin-Film Chalcogenides

2.1. Preparation of Combinatorial Samples

The predominant methods for synthesizing thin-film combinatorial samples are the physical vapor deposition (PVD) techniques, including sputtering deposition, thermal evaporation, pulsed laser deposition (PLD), and molecular beam epitaxy.^[35,64–66] The advantage of PVD techniques regarding combinatorial synthesis is that it offers high control for synthesizing samples with compositional gradients.^[64] Chemical methods (CMs), including chemical vapor deposition (CVD), chemical bath deposition (CBD), ultrasonic spray coating, and dip coating, have been also applied for producing thin-film combinatorial samples.^[64-68] CM techniques offer the advantage of producing samples with less epitaxial stress and less strain due to lattice mismatch with the substrate, and they also allow achieving excellent coverage on nonflat substrates. However, despite these advantages, the higher degree of control of the compositional gradient that can be achieved with PVD techniques makes them the preferred strategy for synthesizing thin-film combinatorial samples.^[64] Focusing on chalcogenidebased solar cells, synthesized by combinatorial methods, there exist several works reporting the employment of sputtering,^[69–79] a lower amount of articles report the use of thermal evaporation^[80-83] and CBD,^[66,84,85] and there are also reports describing the use of sprav coating,^[68,86] PLD,^[87] and CVD.^[88] The experimental setups required for adapting both PVD and CM techniques for the deposition of combinatorial samples are discussed in a review by McGinn.^[65]

Independent of the deposition techniques, there are two main strategies for creating thin-film combinatorial samples. The first one consists of producing discrete, individual libraries inside the same substrate, as shown in **Figure 1**a, by means of physical masks that cover defined regions in a particular deposition step.^[22] Alternatively, discrete libraries can also be achieved by means of photolithography, which consists of depositing the thin-film material on a substrate coated with a patterned photoresist and, then, removing the photoresist with a chemical etching procedure.^[33] Each sample of the produced discrete

library has a particular well-defined value of a given layer property, so the library location and the property are directly correlated. This strategy produces different homogeneous samples with well-defined preparation conditions, but it requires a complex masking system, resulting in quite high time consumption for the preparation of hundreds of samples, and it only allows to tune the deposition conditions in a small range and/or with fixed steps of changes defined by the system configurations.^[9,10,47,89]

The second strategy consists of creating a gradient library where the physical or chemical property varies continuously all over the surface of the sample, as shown in Figure 1b.^[90,91] This is achieved by introducing an "inhomogeneity factor." The latter can be divided by mechanical (like masks, inclinations, distance, absence of rotation, etc.) and ambient (like temperature or pressure inhomogeneity) factors and can be applied during the deposition process or after the deposition process, using postdeposition treatment (PDT). In some cases, application of an inhomogeneity factor is as easy as to stop the substrate rotation during deposition, which is widely used in case of sputtering of coevaporation, where the geometry of the targets and substrate holder determines the presence of a natural gradient in one or more constituent elements (Figure 2a). However, more advanced methods can also be applied, when a specific mask and/or shutters are applied at different deposition stages to form a gradient in a combinatorial sample (Figure 2b). Gradient in the temperature of the substrate during the CVD process is an example of atmosphere inhomogeneity factors, that can provide a smooth gradient of composition (e.g., see Figure 2c with Sn/S ratio gradient determined by the variation of temperature).^[92] Finally, most of the inhomogeneity factors are applied directly during thin-film deposition, however, the possibility of performing an inhomogeneous PDT of a homogeneous sample can be also an option to create a combinatorial sample. This can be a chalcogenation step of the metallic precursor stack or a rechalcogenation process of the final thin film in a furnace and can result in a gradient of the chalcogens or chalcogen composition ratios.

The gradient library approach results in hundreds of samples in a natural way, the preparation time is comparable with the one of standard sample deposition, and it allows fine tuning of the required property. However, it produces inhomogeneous samples with uncertainties in the preparation conditions.^[9,10,47,89] In thinfilm systems, it is easier to produce a gradient library than a



Figure 1. a) Example of a discrete library. Reproduced with permission.^[22] Copyright 1995, The American Association for the Advancement of Science. b) Schematic layout of a gradient library.

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Figure 2. a) Schematic illustration of gradient preparation by different sources geometries. b) Schematic illustration of gradient preparation by applying masks: a continuous movement of the shutter mask leads to a linear thickness variation; a stepwise movement of the shutter mask results in a step gradient. c) Scheme presenting the chemical vapor transport method resulting in a lateral gradient in the composition of α -SnS samples, and photo of the obtained combinatorial sample. Reproduced with permission.^[92] Copyright 2020, Elsevier.

discrete one and, in general, the advantages and disadvantages of each method allow to select the most proper one for a specific study.^[65]

It is worth noticing that a conventional combinatorial approach involves usually the gradual variation of the chemical composition of a deposited layer.^[93] Even more, in the case of gradient library, the obtained sample is usually called as continuous compositional spread.^[43] However, for the thin-film technology and for thin-film PV devices, this can be extended to a variety of other properties that are also important for the performance of the final devices. For instance, gradual variations of doping, intrinsic or extrinsic, in bare thin films^[16,66,94,95] or gradual variations of the thickness of a specific layer in a thin-film solar cell^[66,72,84,87,96] can be an efficient way for the further materials/device improvement and can be included as a relatively novel approach in combinatorial analysis.

Finally, it has to be taken into account that, for a proper combinatorial experiment, the synthesis of the combinatorial sample has to be carefully designed in advance, employing theoretical guidance, materials database assistance, and empirical knowledge. After the synthesis and study of the combinatorial sample, new samples have to be synthesized, narrowing the variation of the studied property according to its identified optimal values.^[8] As one of the hints in samples preparation, it is proposed to combine both presented strategies for synthesizing combinatorial thin-film samples. In the first stage, a gradient library with a large variation of the studied parameter can be synthesized for mainly fundamental materials study and evaluation of the optimal range of focused materials property. In the second stage, a discrete library with a narrowed parameter variation can be used for the finer process optimization. In this way, a first combinatorial sample will provide a full picture of the influence of specific materials property on the devices performance and will allow to strongly limit the samples for the second stage that is designed for the fine optimization of the synthesis process.

2.2. Characterization Techniques for Combinatorial Analysis

Over the years of implementation of the combinatorial approach for the research of thin films, a variety of different techniques have been employed to provide the most complete analysis of graded samples. In the case of thin-film chalcogenides PV technologies, these have been mainly limited to some conventional techniques that provide information about the main physicochemical properties of these materials, including X-ray fluorescence (XRF),^[73,75,84,94] energy-dispersive X-ray spectroscopy (EDS),^[66,74,86,97] X-ray diffraction (XRD),^[73,78,81,94] optical spectroscopy,^[78,84,97,98] and photoluminescence (PL) spectroscopy (see **Figure 3**).^[72,81,86,99] In the last years strong





Figure 3. Characterization techniques and their application requirements for the combinatorial analysis.

attention has also been given to Raman spectroscopy,^[73,74,86,95] which has shown high potential for the detection and control of secondary phase formation, crystalline quality, structural/compositional polymorphs, etc.^[100] Evaluation of these techniques results in several requirements that should be taken into account for combinatorial analysis. 1) Nondestructive: As the sample has to be measured by several techniques with no modifications of its properties between one measurement and the next one, it is important to give preference to the use of nondestructive techniques. 2) Fast measurements: As there are a high number of samples to be characterized, the employed technique has to allow short-time measurements, or, at least, the measurement time should not exceed the relevance of the results that provide the used technique. 3) Automatized mappings: In parallel to the measurement's time limitations, it is essential to have the possibility to implement automated mapping measurement procedures; these allow not only to perform the measurement without the need for the permanent presence of a researcher, but also to align the measurement points used in the different techniques for better results correlation. 4) Combined techniques: Combining several techniques in parallel measurements can greatly decrease the total measuring time; however, this option is barely realized in commercial available systems, and these are rather customized solutions (e.g., see another study^[16]). 5) Spatial resolution should be high enough to resolve significant property variations in a graded sample. 6) "Macrotechniques:" Techniques that allow to measure the part of a sample that is representative for a selected unit cell size in a combinatorial sample; this is a special requirement applied in case of the thin-film combinatorial sample made as gradient library.

The techniques already indicated deal with the determination of physicochemical properties strongly relevant for the in-depth materials analysis. However, in the case of PV devices, these measurements have to be correlated with the determination of the optoelectronic properties of test cell devices, which are mainly based in current density-voltage (J-V) measurements performed under well-controlled illumination conditions.^[72,78,96,101] Combination of the analysis of different techniques with optoelectronic data provides valuable information about the impact of the variation of the selected layer property on the performance of the devices, determining the optimal range of the graded property.^[16,69,72,77,94] In this context, the last hint in the requirements of selection of measurement techniques with a macrospot while measuring a gradient library becomes more evident. Indeed, to perform reliable optoelectronic characterization, the combinatorial gradient library sample should be divided into separated unit cells, which in the case of thin-film PV technologies is usually made by mechanical or laser scribing. This implies several conditions to the cell size, which on one hand cannot be too small, in order to avoid shading of a significant part of the cell by the contact points and, on the other hand, should be small enough in order not to have significant variation of the graded property inside the cell. This, however, does not totally exclude the presence of possible inhomogeneities inside the cell, and additional techniques, applied for the study of structural, compositional, optical, or other properties, should be representative for the selected unit cell size, and not to focus on possible microscopic variations. This can be illustrated in the recent study^[102] on nongraded high-efficiency kesterite-based solar cells, which identifies the presence of in-homogeneities in the composition and defects concentration between different grains of the kesterite polycrystalline absorber as one of the limiting factors for this technology. Taking into account that in a combinatorial sample the gradient is intentionally made, the expected inhomogeneities even between close-spaced grains could be significant. Thus a "microtechnique", when the measurement spot is comparable or smaller with the grain size (e.g., micro-Raman, nano-XRF, EDS, etc.), cannot provide representative results for a cell device with sizes of few square millimeters, unless tens of measurements are done for each cell and the results are averaged, which significantly increase the total measurement time of a combinatorial sample. On the other hand, "macrotechniques" (like macro-Raman, XRF, XRD, etc.) for which the measurement spot is big enough to provide the average information from tens or hundreds of gains will lead to more representative results for a cell that can be correlated with the optoelectronic properties with higher reliability. Here it is also important to notice the limitations in spatial resolution of some of the techniques, for instance, XRD, for which the measurement spot for a thin-film sample should be in order of 1 cm², which usually exceeds the size of a unit cell.^[103,104] Under these conditions, a combination with other techniques that allow to preselect few regions of interest can be a strategy for the correct application of XRD.^[105]

Finally, for an advanced combinatorial analysis, a combination of several techniques that provide different relevant results that still can be correlated one to the other is the best strategy for performing both fundamental materials study and device characterization, leading to the full picture of the physicochemical and/or optoelectronic parameters and providing the fast progress in knowledge mining and technologies development.

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2.3. Correlation and Computational Approaches in Data Analysis

Analyzing the massive amount of data generated by combinatorial experiments is a challenge that can be addressed by two main approaches. The first one is the correlation approach, which is based on searching correlations among the data to obtain information about the properties and physicochemical processes in the materials, the main parameters that limit the device performance and quantitative device performance results. The second one is the computational approach, which consists of applying artificial intelligence (AI) or machine learning (ML) algorithms to recognize patterns among the different data and predict an outcome from an input data.

The first of the approaches in data analysis, the correlation one, is the most widely used conventional method and is mainly based on defining the relevant correlations between the variation of the measured physicochemical properties with the graded parameter of the combinatorial sample. For several techniques, in order to extract the correct data related to the variation of the physicochemical property, several data pretreatment steps are required. For instance, in case of Raman spectroscopy, the full width at the half maximum of the peaks has to be extracted to define the variations in the crystalline quality of the samples. Similarly, in the case of photoluminescence spectra, the changes in the intensity of the bands have to be determined as they can be associated with changes in the nonradiative recombination processes.^[16,106-109] All these pretreatments can be easily performed by applying several existing software solutions, although in most cases this has to be done only in manual mode which significantly increases the data pretreatment and treatment process times. Taking this into account, in the case of spectroscopic techniques (as Raman and PL), the group from IREC has developed a Python package spectrapepper, which includes several useful functions allowing to treat big amount of data in an easy and fast way.^[110] For other techniques similar packages can be found or need to be developed with the participation of the experienced researchers in the field, as automation seems to be the most logic evolution in the research data treatment in the nearest future.

After performing the data pretreatment and selecting the most relevant features in the obtained results, the correlation analysis is followed by an actual correlation procedure. This can be performed by simply comparing different extracted parameters plotted in 2D graphs or 2D mappings. However, this simple approach is limited only to the case of analysis of few parameters, and for a denser analysis of a combinatorial sample with the application of several techniques, the amount of extracted parameters increases up to dozens. In this case a well-known statistical correlation can be applied, for example, different correlation coefficients like Pearson,^[111] which simply defines the existence of linear correlations between two given parameters, or like Rank,^[112] which analyzes the existence of more complex correlations between two parameters. However, in cases of PV devices the dependencies are more complex and multiple properties have to be taken into account to define which of them is more relevant and at which ranges of values of the graded parameter. In this case more complex 3D graphs can be plotted, where a third dimension is introduced as color or size of the dots (e.g., see

Figure 4). The use of Combinograms has also been proposed for the data correlation of complex cases including multiple varied parameters.^[113] Although significant effort is required in order to build a well-structured Combinogram and its presentation is not always straightforward, this approach is well suited to the degree of complexity involved in the combinatorial analysis of thin-film solar cells. In these kinds of samples, the gradient in one parameter influences several relevant materials properties (i.e., composition gradient can influence the formation of different secondary phases and the mechanisms of formation of the defects in main phase).^[46,74,76,77,81,100,114,115] In addition, the photovoltaic conversion efficiency depends on a high amount of parameters that are varied in a combinatorial sample. Thus application of Combinograms for the data analysis and presentation can be a key for the combinatorial analysis of thin-film PV devices. In the recent years, some software tools have been developed to help researchers in performing combinatorial analysis and correct results presentations, which is the case of the aforementioned spectrapepper^[110] and the COMBIgor^[116] software packages.

On the other hand, computational ways in data treatment based on AI or more specifically ML algorithms are becoming more widely used in the analysis of research data. However, this approach is still quite rare in combinatorial analysis methodologies. The main reason for this is likely related to the type of data that is obtained as result of the analysis. In this analysis each set of parameters obtained for a measurement point, cell, or separated sample in a discrete library is slightly different, because of the gradual change of the desired property. This makes complex to select a big set of well-defined data for algorithm training, which finally strongly limits the possibility to apply ML for the patterns identification. A potential way to solve this problem is the application of dimension reduction algorithms, as reported in another study.^[69] In this work thin-film solar cells based on Cu₂ZnGeSe₄ absorber with a [Zn]/[Ge] compositional graded ratio was analyzed. The authors proposed to select several classification groups which included some ranges of target parameters (efficiency, open-circuit voltage, and [Zn]/[Ge] ratio). In all cases good training scores were obtained using Raman spectra measured under different excitation wavelengths. Although, a clear overfitting of the classification group was also observed, leading to not very high test scores (especially in the case of the efficiency and Voc targets), the authors showed the applicability of the dimension reduction ML algorithms for the combinatorial analysis of thin-film PV devices. Moreover, combining the computational results with the conventional correlation approach allowed authors to assign the calculated discriminants to a physical parameter that was identified as the main parameter which controls the efficiency of the solar cells (see Figure 5).

Finally, even if there are already automated or semiautomated solutions for performing the experimental measurements involved in the combinatorial analysis, which allows to simplify the measurement process and strongly decrease the time spent by the researcher for combinatorial analysis, in the case of the data treatment and results evaluation, the automatic or semiautomatic approaches are still far to be well developed. The full development of such approaches constitutes one of the main challenges that might compromise the further development and massive implementation of the combinatorial analysis methodologies.

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Figure 4. Left: Correlation plots of a) J_{sc} , b) V_{oc} , c) FF, and d) efficiency versus CIGSe absorber thickness in glass/Mo/CIGSe/CdS/ZnO/AZO solar cells. The color of the bubbles correspond to CIGSe thickness and the size of the bubbles is scaled according to the thickness of the CdS buffer layer or the Ga content in the CIGSe absorber. Adapted with permission.^[117] Copyright 2014, IEEE. Right: Dependence of optoelectronic properties (a) efficiency, b) short-circuit current, c) open circuit voltage, and d) fill factor of $Cu_2ZnGeSe_4$ (CZGSe)-based solar cells versus the relative integrated intensity of the CZGSe Raman band at 176 cm⁻¹. The color scale corresponds to the [Zn]/[Ge] ratio in the CZGSe absorber. Reproduced with permission.^[69] Copyright 2021, Royal Society of Chemistry.

3. Combinatorial Analysis of Chalcogenide-Based Thin-Film PV Technologies

3.1. CdTe Family

Being composed of two elements, CdTe offers low possibilities for varying its composition in a combinatorial sample. Thus, the main focus in the combinatorial analysis of these PV device is the analysis of variations of other CdTe absorber layer properties or the properties of the other layers present in the device architecture. A combinatorial CdTe sample with different absorber thicknesses from 0.75 up to 1.5 μ m was synthetized in another study^[87] by PLD in a single substrate (**Figure 6**). The combination of different techniques has allowed the authors to conclude that the CdTe grain size depends on the layer thickness and the layer thickness had no influence on crystalline orientation. In this study, the thinnest layer produced the devices with highest energy conversion efficiency due to the reduced charge recombination in the bulk of the CdTe absorber layer related to the decreased number of grain boundaries. Kartopu

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Figure 5. a) Relative integrated intensity of the CZGSe Raman peak at 176 cm⁻¹ plotted against discriminant D1c and b) efficiency of the solar cells plotted against discriminant D2c of the [Zn]/[Ge] ratio LDA classification target. Reproduced with permission.^[69] Copyright 2021, Royal Society of Chemistry. The explanation of the dotted oval line can be found in the main text.^[69]



Figure 6. Schematic drawing of the samples made with varying CdTe thickness. Reproduced with permission.^[87] Copyright 2016, Hindawi Publishing Corporation.

et al. also studied the solid solution of (Cd,Zn)Te synthesized by combinatorial metalorganic CVD in order to evaluate the possibility to apply these layers as top cell absorbers in tandem devices.^[88] The obtained samples were characterized by several techniques allowing to establish the main morphological, optical, electrical, and electronic properties of the (Cd,Zn)Te solid solutions, defining the main issues that limit the device efficiency while increasing the Zn content and proposing possible solutions in order to overcome these issues.

A study of alternative window layers for CdTe-based solar cells has also been reported by Treharne et al.^[70] In this study, solar cell devices with structure $ZnO/Cd_{(1-x)}Zn_xS/CdTe/CdTe:As$ were fabricated on a $45 \times 90 \text{ mm}^2$ substrate of SnO₂:F varying the [Zn]/[Cd] ratio between 0.0 and 0.8. Despite the limited number of techniques that were applied for the sample characterization (only composition, thickness, and optoelectronic properties were analyzed), this study allowed the authors to show the existence of a direct correlation between the solar cells efficiency and the [Zn]/[Cd] compositional ratio in the $Cd_{(1-x)}Zn_xS$ layer and define the optimal composition of this window layer (Figure 7). Moreover, the authors also concluded that, thanks to the combinatorial analysis, the scatter in the data was significantly reduced by eliminating the drifts in the run-torun deposition conditions that would have been encountered in the analysis of a multisample set. This supports the relevance of this approach for thin-films PV devices' research.

3.2. Chalcopyrite Family

The Cu(In,Ga)(S,Se)₂ (CIGSSe) family of compounds offer higher versatility for composition tuning, since both the ratio of cationic and anionic elements can be modified. In consequence, there are a higher amount of works reported in the literature performing combinatorial analysis of these compounds in the case of CdTe-based solar cells. All these works can be divided in three categories: 1) intrinsic gradient of the chalcopyrite absorber layer by changing chemical composition and/or the thickness of the layer; 2) extrinsic gradient of the absorber by doping or passivation strategies; and 3) gradient of buffer layers in chalcopyrite-based solar cells.

In the first case of intrinsically graded properties of the absorber layer, several strategies have been used for the synthesis of the combinatorial samples. A first strategy involves the use of coevaporation processes with different elemental targets,^[80,117,118] and in these cases the gradients were naturally obtained due to the geometrical configuration of the targets. Another strategy involves the use of sputtering systems, and this includes the use of CuInSe₂ and CuGaSe₂ targets,^[73] as well as more complex processes based in a more advanced Intermolecular Tempus'" P-30 High Productivity Combinatorial (HPC) sputtering tool that allows the simultaneous use of four different targets for co- and/or sequential sputtering of Cu, In, and Ga with systematically controlled lateral gradients in composition and thickness within one substrate.^[72] Independent of the used deposition techniques, in all the works, the gradient library was obtained, leading to tens or hundreds of different unit cells. The analysis of the data has allowed determining the dependence of the physicochemical properties of the different layers in the device structure on the offstoichiometric chemical composition and/or the thickness of the absorber layer. These includes the results of Marko et al.,^[80] who studied the influence of a Cu compositional gradient in wide-bandgap CIGSe solar cells (with increased Ga content \approx 0.55) and showed that for these kinds of





Figure 7. Left: Profile of Zn/(Cd+Zn) compositional ratio across cosputtered $Cd_{(1-x)}Zn_xS$ -graded film. The black contour lines show the variation in thickness profile as determined using spectroscopic ellipsometry. Right: Efficiency map of completed solar cells having a $Cd_{(1-x)}Zn_xS$ window layer. Fully black areas represent cells with efficiencies below 8%. The dotted line indicates the locations of cells for which detailed *J*–*V* and EQE analysis was performed. Adapted with permission.^[70] Copyright 2014, IEEE.



Figure 8. PL intensity plotted in log scale versus efficiency of CIGSe-based solar cells. Reproduced with permission.^[72] Copyright 2012, IEEE.

absorbers higher efficiency is achieved with compositions close to stoichiometry, in contrast with standard CIGSe devices where Cu-poor conditions are more favorable.^[80] Also, a recent work of Guc et al. performed on a Ga-free chalcopyrite combinatorial sample with a strong [Cu]/([Cu] + [In]) gradient (from \approx 0.4 up to \approx 1.0) has allowed to analyze the strong dependence of the defects present at the surface region of the Cu-poor absorbers on layer composition, identifying the presence of a novel "defective chalcopyrite" phase, which had a significant influence on device efficiency.^[104] Moreover, some of these works showed the high potential of several nondestructive techniques like PL (**Figure 8**) and spectral ellipsometry (Figure 4 left) for the

monitoring of the quality of absorbers allowing to predict the potential efficiency of the final devices from measurements performed at the early-deposition stages of the absorber layers, making the first steps toward the implementation of zero-defect production^[119] and Industry $4.0^{[120]}$ concepts in PV industrial technologies.

In the second case of extrinsically graded properties of the absorber layer, a study of the extrinsic doping of CIGSe absorbers with Sb has been reported by Yan et al., [66] who applied combinatorial CBD to obtain discrete libraries with varying Sb doping from 0 to 19.04%. Characterization of the obtained samples by several techniques (EDS, SEM, XPS, and XRD) showed that the Sb concentration increased the CIGSe grain size and decreased the layer resistivity and allowed to propose a model for the CIGSe growth promoted by a quasiliquid Sb₂Se₃ phase. On the other hand, one of the main driving forces in the achievement of high-efficiency CIGSe-based solar cells is related to the doping of the absorber with alkali elements.^[3,6] Eid et al.^[94] studied the impact of the addition of NaF addition in CIGSe absorbers by varying the thickness of the deposited NaF layer from 10 to 30 nm in combinatorial samples synthesized with different stoichiometry. More than 6000 solar cells were fabricated to ensure the statistical significance of the results, which showed that NaF addition reduces the Ga content and increases the grain size at the CIGSe surface, and that depending on the absorber composition slightly different concentrations of Na result in highest device efficiency. More recently, a study of the influence of RbF PDT performing a high statistical analysis has been reported by Fonoll-Rubio et al.^[16] Strictly speaking this work cannot be directly considered as a combinatorial analysis, as only samples with four different PDT temperatures were analyzed. However, this work can be considered as the second step with a discrete

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Figure 9. Left: 3D plot for the fine monitoring and prediction of V_{oc} value based on Raman and PL data obtained in a combinatorial experiment regarding CIGSe solar cells. Right: comparison of the V_{oc} predictive power for two different criteria with either separated Raman or PL data or a combination of both. Reproduced with permission.^[16] Copyright 2014, John Wiley and Sons.

library, for which only a limited variation of the selected parameter is required. The high statistics employed in this work (>100 cells studied for each PDT temperature) has allowed to identify the origin of the beneficial influence of the RbF-PDT on the absorber surface. These results also allowed to develop a methodology for predicting the open-circuit voltage (V_{oc}) of the CIGSe solar cells devices from the analysis of the Raman and PL data, as shown in **Figure 9**.

Finally, a combinatorial study of different buffer layers has also been reported in other studies.^[84,85] In these cases the combinatorial CBD was applied for optimizing the thickness of the CdS buffer layer^[84] and the composition of alternative (Cd,Zn)S buffer layers^[85] for CIGSe-based solar cells, determining the optimal deposition conditions and layer properties and identifying the main limitations of these processes in terms of final device efficiency.

3.3. Kesterite Family

Similarly to the above-discussed CIGSSe chalcopyrites, the kesterite-type compounds are multicomponent complex materials that are also well suited for combinatorial analysis. As in the case of chalcopyrites, reported studies include the analysis of the gradient of either intrinsic and extrinsic absorber layer properties, as well as changes in the properties of other layers in the solar cell device structure.

The family of kesterite-type compounds includes a very wide range of different materials consisting of different cations and anions.^[100] However, the main focus in the combinatorial analysis is centered on the Cu₂ZnSnS₄ (CZTS) and Cu₂ZnSnS₄ (CZTSe) compounds and their solid solutions (CZTSSe). This is related to the main achievements in the efficiency of kesteritebased devices.^[121,122] The first studies describing the gradient of intrinsic properties of the CZTS and CZTSe compounds were focused on combinatorial samples with varied cation ratios. This includes a series of works of the group of Teeter et al., who synthesized pure sulfide CZTS samples with compositional gradient by combinatorial coevaporation. Based on the detailed compositional and structural characterization of the samples, a schematic

phase diagram for the thin-film CZTS system has been constructed.^[81,99,123] These studies were completed with those achieved from combinatorial samples cosputtered from the binary sulfides, which allowed to correlate the composition of the absorber layer and the solar cells efficiency directly with the crystalline quality of the grains, the mechanical stress, and the composition and morphology of the surface region of the absorbers.^[101] Finally, Scragg et al. reported different studies investigating composition-spread CZTS samples made by cosputtering of binary sulfides with subsequent annealing in order to determine the single-phase region, the effect of the composition, and prospects for defect engineering.^[74,103,115] Combined EDS and Raman measurements determined the existence of a variable CZTS single-phase region size that depends on the partial pressures of SnS and S₂ during the sputtering processes, as shown in Figure 10, confirming a theoretical model that was reported in the same work. According to the analyzed data, the typical CZTS synthesis strategies are not capable of accessing the full range of the CZTS single-phase region as the required partial pressure of S₂ is too large. This indicates that the understanding of CZTS defect chemistry from the experimental studies is still incomplete and that there is still room for a further tuning of the defect properties for improved solar cell performances.^[74] It has also been found that the CZTS composition has no influence on the critical temperature of the order-disorder transition, but the [Cu]/[Sn] composition ratio strongly affects its activation energy, which means that tuning the cation composition could allow reducing the Cu-Zn cation disorder.[115]

The CZTSe-based combinatorial samples have been mainly investigated by the group of Perez-Rodriguez, who deposited the samples by sequential sputtering of a metal stack and a subsequent selenization process.^[75–77] The combined characterization of the samples by XRF, Raman spectroscopy, and J-V characteristic has allowed to propose the cationic [Cu]/[Sn] ratio as a more suitable predictor of the device performance than the previously used [Cu]/([Zn] + [Sn]) and [Zn]/[Sn] ratios, identifying the optimal cation compositional ratios.^[75] In addition to the materials study, combinatorial analysis of the CZTSe samples allowed to develop nondestructive methodologies based on

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Figure 10. Thin-film phase diagrams defined from combinatorial samples prepared using a) high S partial pressure and b) high S and SnS partial pressures. Apparent secondary-phase boundaries for each obtained phase are plotted with dashed lines. Italic numbers show the number of phases in each region bounded by the white lines (CZTS is in all regions), and the single-phase region is marked (*). Reproduced with permission.^[74] Copyright 2014, American Chemical Society.

Raman spectroscopy for the assessment of point defects present in the absorbers (**Figure 11**) and for the evaluation of the optoelectronic parameters of the final solar cell devices.^[76,77]

On the other hand, the works of Collord and Hillhouse have been mainly focused in the analysis of CZTSSe solid solutions using the combinatorial samples made by spraying of prepared solution inks.^[68,86,124] These works allowed to observe the existence of a direct correlation of the quasi-Fermi-level splitting extracted from the analysis of the absolute photoluminescence spectra with the $V_{\rm oc}$ of the final devices.^[68] In addition, these authors also performed a detailed investigation of the influence of different extrinsic doping processes to the device performance by the analysis of combinatorial samples with different dopants (Cd, Fe, Li, Na, K, Rb). These results allowed to observe a clear detrimental effect of Fe, while Cd has a neutral effect of the Cd, and alkali impurities have a beneficial effect that is mainly observed in the solar cells fill factor due to the improvement of the shunt resistance.^[68,124]

A combinatorial analysis has also been reported in a previous $study^{[125]}$ for the study of the [Ge]/([Ge] + [Sn]) composition ratio in Cu₂Zn(Sn,Ge)(S,Se)₄ solid solutions. According to this analysis, a slight substitution of Sn by Ge can be beneficial for the device performance, and in general a relatively high performance can be kept up to [Ge]/([Ge] + [Sn]) = 0.5, which allows a significant absorber bandgap tuning.^[125] Recently, a combinatorial Cu₂ZnGeSe₄ sample made by sequential sputtering process with varying [Zn]/[Ge] composition was also studied by Raman spectroscopy, XRF, and *I-V* curves analysis.^[69] The correlation approach in the data analysis performed in this work has allowed to established the off-stoichiometric limits of formation of the pure CZGSe phase. In addition, V_{Cu} point defects inside the CZGSe structure extracted from Raman spectra have a strong influence on the final device efficiency (see Figure 4 right). This was also proved by combining the results of the correlations analysis with the results obtained using ML methodology (Figure 5), showing the high potential in applying this computational approach to the analysis of combinatorial samples.^[69]

Finally, Zakytaev et al. also studied combinatorial CZTSe and CZTS solar cells synthesized with a graded thickness of the buffer layer, using either conventional CdS buffer layers and alternative In_2S_3 buffer layers, respectively.^[78,84] The CdS layer was deposited by CBD leading to a discrete library, and the In_2S_3 layer was deposited by sputtering leading to a gradient library. In both cases, the optimal thickness of the buffer layer was defined, and the analysis of the samples showed the possibility to replace the Cd-containing buffers without degrading the device efficiency.

3.4. Quasi-1D Family

Recently, special attention in the thin-film PV research community is being given to the quasi-1D materials that have been proposed as the basis of a new generation of solar cells.^[126-129] One of the leading materials in this family is the Sb-based chalcogenides that have already shown promising solar cell efficiency values.^[121,122] Similar to CdTe, the binary structure of the Sb_2S_3 and Sb₂Se₃ compounds limits the possibility to perform combinatorial studies based on the gradient of intrinsic layer properties. In principle there is only one work dealing with combinatorial analysis of the Sb₂(S,Se)₃ solid solution.^[82] In this work, the thin films were deposited by the close-space dualplane-source evaporation method and a continuous composition spread $Sb_2(Se_xS_{1-x})_3$ library was obtained. An advanced analysis of the compositional, structural, morphological, and optical properties allowed authors to analyze the evolution of all of these properties with the anions ratio. Additionally, the analysis of the optoelectronic properties of the complete devices allowed to establish an optimal anion ratio, leading to devices with the highest efficiency (Figure 12). The differences in the



(a) 0.70

0.65

0.60

0.55

0.50

(c) 0.70

0.65

0.60

0.55

0.50

A[176]/(A[196]+A[176])

Zn/Sn

1.8

1.7

16 5

13

2

1.8

1 1

A [176]/(A [196]+A [176])





A-Type

[Zn_{cu}+V_{cu}]

0.70

0.65 0.60

0.55

0.50

1.3

performance of the devices synthesized with different absorber compositions have been related to their different quantum yield and defect states. Thus the Se-rich devices show the presence of shallow defects, while heavily S-rich devices show only the presence of relatively deep defects.

The other combinatorial analysis works reported in Sb₂Se₃based thin film solar cells deal with the grading of the lavers which form the heterojunction with the Sb₂Se₃ absorber layer. Chen et al. studied TiO_2/Sb_2Se_3 solar cells with a TiO_2 thickness gradient and a postannealing temperature gradient of this layer.^[96] The combinatorial approach allowed these authors to define the optimal thickness and postannealing conditions. In a different work, Siol et al. obtained an orthogonal gradient of the substrate temperature and the ZnS layer thickness in a sample with Sb₂Se₃/ZnS heterojunction, which was characterized by in situ XPS.^[79] The experiment allowed to construct a schematic band diagram of the Sb₂Se₃/ZnS heterointerface with a large conduction band offset and an interface reaction. According to these results, ZnS is not suitable as buffer layer for Sb₂Se₃-based solar cells. The authors state that their developed combinatorial method could be applied to other material systems, enabling a more accurate picture of the electronic processes across potential device interfaces, which is crucial for tailoring heterointerfaces where different deposition conditions influence the device performance.^[79]

A-Type [Zn_{cu}+V_{cu}]

3.5. Other Chalcogenide Compounds

In addition to the development of the headliners in the chalcogenide thin-film technologies discussed in the previous sections, there are also few additional chalcogenide compounds with a relevant potential for PV applications. This includes materials that are constituted by nontoxic and environmentally friendly elements or materials that have some attractive preparation conditions. In this field, it is interesting to point out the significant contributions of the Zakutayev's group, which has reported several combinatorial studies over the years involving $CuSbS_{2},^{[71,98,130]}$ $CuSbSe_{2},^{[131,132]}$ $Cu_{2}SnS_{3},^{[95,98,133]}$ (Cu,Zn) S,^[134] and Ba-Cu-S.^[135] An advanced and detailed analysis of the deposited combinatorial samples allowed the authors to define the main physicochemical properties of these materials and to establish their optimal values for the synthesis of solar cell devices

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Figure 12. A) PV conversion efficiency mapping of a solar cell array from a continuous composition spread Sb₂(S,Se)₃ film. B) Evolution of efficiencies with Se content. C) V_{oc} and J_{sc} evolution with Se content. D) J-V curves and E) EQE spectra of representative compositions of Se-rich (x = 0.68) and S-rich (x = 0.14) devices. Reproduced with permission.^[82] Copyright 2018, John Wiley and Sons.

depending on the further applications (top/bottom cells in tandem devices, semitransparent devices, devices with low processing temperature, etc.). Even though for most of the materials the efficiency of the PV devices was quite low, the detailed screening of various chalcogenide compounds performed by Zakutayev et al. has allowed to significantly increase our knowledge about possible materials for thin-film solar cells application, while the presented fundamental analysis of the materials provides insights for their implementation in other relevant technologies.

Another group, who has been recently also strongly involved in the combinatorial analysis of chalcogenide materials suitable for thin-film solar cells is the group of Perez-Rodriguez. During the last years the group reported the investigation of CuIn₂Se₃- ZnSe,^[136] Cu–Sn–S,^[137] and Sn–S^[92] systems. The first system appeared as an extension of classical chalcopyrite compounds with a reduced amount of scarce elements. The previous analysis of this system was focused on the use of different ratios of ZnSe component in the solid solution. More recently, Ref. [136] has clearly shown the influence of the Cu content in this complex system and the possibility to perform defect engineering in these materials, which finally has a decisive impact on the performance of the devices. On the other hand, the main limitations found in the Cu–Sn–S and Sn–S systems are related to their high structural and compositional polymorphism (e.g., see **Figure 13**). This was studied by means of XRD and Raman scattering analysis allowing to define not only clear ranges of compositions

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Figure 13. Optical images and the compositional phase distribution on the surface of the Cu–Sn–S-graded samples measured by Raman spectroscopy. Here the red color corresponds to Cu_2SnS_3 , blue to Cu_3SnS_4 , and green to Cu_4SnS_4 . Numbers in the top indicate the average [Cu]/[Sn] ratio in the corresponding area. Reproduced with permission.^[137] Copyright 2020, Elsevier.

where different polymorphs dominate, but also to propose easy and robust ways to identify the presence of different polymorphs.

4. Conclusion

In conclusion, combinatorial analysis constitutes a powerful approach for the accelerated materials research. In terms of the combinatorial sample synthesis, the optimal strategy is to combine a gradient library at the first stage for the fundamental materials study and, at the second stage, a discrete library for the process optimization can be implemented. In terms of the characterization of combinatorial samples, combining different techniques using a macroscopic spot will provide a full picture of a combinatorial sample; such characterization techniques should be nondestructive, fast, and compatible with automated mapping approaches. Once the massive set of data has been obtained from the measurements, automation of the data pretreatment facilitates fast data processing. Then, two main strategies exist for the data analysis. First, the correlation approach that is based on finding correlations between the different data. This is a powerful approach that can provide relevant information about the properties and physicochemical processes in the materials and devices, the main parameters that limit device performance, and quantitative results. The second strategy is the analysis based on ML algorithms, which can provide a tool for the materials properties or device performance prediction. A combination of correlation and ML approaches can provide additional details about the main parameters that influence the device performance. Finally, several important steps in combinatorial analysis of chalcogenide-based thin-film solar cells have been already done, as follows from the variety of studies presented in this review. The results achieved in the wide range of combinatorial research studies performed in the different chalcogenide thin films confirm that the combinatorial approach constitutes a powerful tool for: 1) the basic materials study, providing relevant information about the evolution of different properties with the graded parameter; 2) the basic device analysis, allowing to define the optimal ranges of different properties where the highest efficiency can be obtained; and 3) the advanced analysis of the materials and devices, leading to the evaluation of the main factors that limit the device efficiency. Moreover, in the framework of the performed combinatorial analysis many authors proposed not only new solutions for this specific approach (samples deposition, characterization, or data analysis), but also proposed novel methodologies for fast materials evaluation, which are compatible with the industrial process monitoring, contributing also to the development of Industry 4.0 concepts, which can be the main driving force in the increase of production of PV devices.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords

chalcogenides, combinatorial analyses, correlation analyses, discrete libraries, gradient libraries, machine learning, thin-film photovoltaics

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