



Article Synthesis and Band Gap Characterization of High-Entropy Ceramic Powders

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Abstract: This manuscript presents a comprehensive exploration of the band gap structure of $(CoCrFeNiMn)_3O_4$ powders through a series of experimental investigations. The combined use of optical techniques and X-ray photoelectron spectroscopy in this study leads to a comprehensive characterization of the band gap structure in $(CoCrFeNiMn)_3O_4$ powders. The findings contribute to the understanding of this material's electronic properties and pave the way for potential applications in electronic and optical devices.

Keywords: high-entropy materials; (CoCrFeNiMn)₃O₄; band gap structure; absorption features; chemical composition

1. Introduction

High-entropy ceramic powders are characterized by the incorporation of a greater number of elements in diverse proportions, giving rise to a structurally intricate and disordered arrangement [1]. The distinctive amalgamation of these elements holds the potential to yield properties that surpass those attainable with traditional ceramics, thereby presenting novel prospects for applications across diverse scientific domains [2].

Investigations into high-entropy oxides (HEOs) are currently in their nascent phase, with researchers actively investigating diverse combinations of constituent elements and employing various processing techniques to enhance the properties of these materials [3]. The envisaged applications for these ceramics span critical sectors such as aerospace, electronics, and energy storage, where the demand for advanced materials with meticulously engineered properties is particularly pronounced [4–6].

Crystal structure formation has been reported before [7–10], but the chemical states of the individual elements have not been reported yet. The exploration of high-entropy alloys has given rise to an innovative materials design concept [11–14].

HEO composites display bandgaps ranging from 1.91 to 3.0 eV, along with valence and conduction bands suitable for facilitating water splitting [15]. Their heightened photocatalytic activity can be primarily attributed to the increased accessibility of active sites, promoting the generation of radicals responsible for the degradation of pollutants [16]. The materials demonstrate successful hydrogen production through both photocatalytic water splitting and electrocatalysis [17,18].

Advancing our comprehension of the synergistic properties inherent in high-entropy materials involves demonstrating that the band gap transcends a simple average of the end members. A notable shift in the energy levels of transition metals is observed within highentropy spinel oxide, signifying a fundamental change. The synthesis methods employed can introduce variability in the band gap due to the distinct oxidation states of the cations.



Citation: Dallaev, R.; Spusta, T.; Allaham, M.M.; Spotz, Z.; Sobola, D. Synthesis and Band Gap Characterization of High-Entropy Ceramic Powders. *Crystals* **2024**, *14*, 295. https://doi.org/10.3390/ cryst14040295

Academic Editor: Maria Gazda

Received: 22 December 2023 Revised: 25 February 2024 Accepted: 21 March 2024 Published: 22 March 2024



Copyright: © 2024 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). This topic's importance lies in the prediction of HEO applications based on band gap values. This manuscript consists of a description of the synthesis procedure and composition characterizations for confirmation of phase purity. The following presentation of chemical states at different temperatures helps us to understand electronic structure changes. Finally, band gap calculations are provided for a demonstration of the electronic structure of the synthesized materials.

This manuscript presents a groundbreaking exploration of the band gap characteristics of $(CoCrFeNiMn)_3O_4$ powders, an intricate mixed-metal oxide, employing a combination of optical and spectroscopic techniques. To our knowledge, this study marks the inaugural attempt to define the band gap and chemical states of the individual elements within this specific material.

2. Materials and Methods

The examined samples were prepared from precursor powders using a solid-state reaction. Firstly, the following precursor oxides, with their corresponding purity in brackets, were weighed to create an equimolar structure of (CoCrFeNiMn)₃O₄ in the final product: Co_3O_4 (99.7%, Thermo Fisher Scientific, Waltham, MA, USA), Cr_2O_3 (99.0%, Erb Lachema, Brno, Czech Republic), Fe₂O₃ (99.0%, Thermo Fisher Scientific, USA), NiO (99.0%, Thermo Fisher Scientific, USA), and MnO (99.0%, Sigma Aldrich, St. Louis, MO, USA).

The mixture of oxides was milled with 5 mm zirconia balls in ethanol in a planetary mill (Fritsch Pulverisette 6, Idar-Oberstein, Germany) at 300 RPM for 60 min to improve the homogeneity of the mixture.

After milling, the mixture was dried, crushed, and filtered with a 100 μ m mesh (CCC0). Several batches were prepared for calcination in an air atmosphere using the following regimes: temperatures of 850 (CCC850), 900 (CCC900), and 950 °C (CCC950) for 12 h and 5 °C/min heating and cooling rates [10].

Calcinated/reacted powders were again crushed and filtered with a 56 μ m mesh. These powder batches were subjected to an X-ray diffraction (XRD) analysis using a Rigaku Smart Lab 3 kW X-ray powder diffractometer and a scanning electron microscopy with energy-dispersive X-ray (SEM-EDX) analysis using a high-resolution FEI Verios 460 L scanning electron microscope to clarify whether the calcination was sufficient to produce the desired high-entropy ceramic structure.

The chemical composition of the samples was investigated using an AXIS SupraTM X-ray photoelectron spectrometer (XPS) from Kratos Analytical Ltd., Manchester, UK. Data acquisition was performed at an emission current of 15 mA, utilizing a resolution of 80 with a step of 1 eV for wide spectra and a resolution of 20 with a step of 0.1 eV for element spectra. All spectra were calibrated using the C1s peak to 284.6 eV.

The band gap of the prepared powders was examined using a JASCO V-770 UV/VIS spectrometer. The powders were packed inside a special 16 mm-diameter holder for powders, and the holder was attached to a 60 mm integrating sphere to collect the reflectance spectra relative to a specular reflectance reference sample with an angle of incidence of \sim 5°.

3. Results and Discussion

The XRD data obtained from the samples prior to annealing indicated the presence of various oxide phases, confirming the expected mixed composition. Upon subjecting the samples to an elevated temperature of 900 °C, the XRD results revealed a noteworthy transformation, showcasing the emergence of a distinct pure spinel phase, as illustrated in Figure 1. This observation aligns with the anticipated changes in crystal structure and composition during the annealing process, providing valuable insights into the thermal behavior and phase transitions of the samples.



Figure 1. XRD spectra of the samples before and after calcination.

The combined SEM and EDX analysis (Figure 2) enables a comprehensive assessment of how the microstructure and elemental composition of the samples respond to different annealing temperatures. The EDX analysis complements the SEM observations by offering elemental information. The EDX analysis provides comprehensive information about the elemental composition and distribution.



Figure 2. SEM and EDX images of samples (**a**) annealed at 850 °C; (**b**) annealed at 900 °C; (**c**) annealed at 950 °C.

There is an increase in the oxygen content according to an evaluation of atomic percentages from survey spectra (Figure 3, Table 1). The most significant difference could be found in nickel and manganese contents after calcination.



Figure 3. XPS survey spectra of samples annealed at 850 °C, annealed at 900 °C and annealed at 950 °C before calcination.

Peak Name	At%, No Calcination	At%, 850 °C	At%, 900 °C	At%, 950 °C
O1s	65	75.17	83.05	78.92
Ni2p	5.06	1.37	1.75	1.8
Mn2p	15.56	6.86	1.12	3.41
Cr2p	3.80	4.67	3.74	3.64
Co2p	6.23	4.65	6.07	6.58
Fe2p	4.35	7.27	4.26	5.63

Table 1. Evaluation of sample composition from survey XPS spectra.

It is known that cations in different oxidation states are present during the crystallization of oxides into high-entropy composites. The oxidation state of Ni decreases with the increase in temperature. This was evaluated using peak deconvolution in CasaXPS software (version 2.3.23, Kratos Analytical Ltd., Manchester, UK) using a Gaussian–Lorentzian line shape and a Shirley background. Nickel tends to create stable complexes when it is in the +2 oxidation state. The high-resolution spectra of Ni at different calcination states are presented in Figure 4 at different temperatures. Moreover, the rate of increase in Ni²⁺ content as a function of the calcination temperature is presented in Table 2. The notable changes in the Ni satellite peak in the ceramic, high-entropy composite are likely due to the complex interactions and structural changes that occur when nickel is part of a complex system, as shown in Figure 4.





Table 2.	Evaluation	of com	ponent ratio	using in	ndividual	peak area	s for Ni2p.
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Peak Name	%, No Calcination	%, 850 °C	%, 900 °C	%, 950 °C
$Ni^{2+} 2p_{3/2}$	17.18	26.78	29.08	39.82
$Ni^{3+} 2p_{3/2}$	52.40	43.92	39.11	37.00
Ni sat $2p_{3/2}$	30.42	29.30	31.80	23.17

The increase in the Mn^{4+} oxidation state in the powder means that it forms two bonds with oxygen atoms, forming manganese (IV) oxide. This state is linked to stable oxygen-containing compounds of manganese. However, a continuous decrease in Mn^{2+} as a function of the calcination temperature can be observed in Figure 5 and Table 3.





Table 3. Evaluation of component ratio using individual peak areas for Mn2p.

Peak Name	%, No Calcination	%, 850 °C	%, 900 °C	%, 950 °C
$Mn^{2+} 2p_{3/2}$	38.94	35.88	24.77	22.80
$Mn^{4+} 2p_{3/2}$	31.29	35.58	46.88	49.70
Mn 2p _{3/2}	29.78	28.55	28.35	27.50

A JASCO V-770 UV/VIS spectrometer was used to study the prepared powders [12,13]. The tested range was 200–1200 nm, and the Kubelka–Munk equation was used to measure the corresponding absorption coefficient parameter F as follows [14]:

$$F = \frac{\left(1 - R\right)^2}{2R} \tag{1}$$

After obtaining *F* for all the samples, Tauc and Urbach plots were used to measure the allowed direct and allowed indirect energy gaps, along with the Urbach tailing energies for the tested powders [19,20]. Tauc plots have the form of $(\alpha hv)^n$ vs. hv, where n = 2 when measuring the allowed direct energy gap, n = 1/2 when measuring the allowed indirect energy gap, n = 1/2 when measuring the allowed indirect energy gap. The energy gap is extracted from a Tauc plot from the *x*-axis value of the interception point of the extension of the straight-line part of the plot and the plot baseline. Moreover, Urbach plots have the form of $\ln(\alpha)$ vs. hv, where the slope of the straight-line part is used to obtain the Urbach tailing energy ($E_{\rm U} = 1/{\rm Slope}$).

Studying the Urbach energy is important because it is related to important factors. The first factor is the change in the conductivity of the powder structure as a function of the density of states at different calcination temperatures. The narrower the energy gap at a lower density of states, the higher the possibility of creating an exciton, increasing the conductivity of the powder. The second factor is studying the phonon–electron interaction, $E_{e-\gamma} = E_U/K_B \hat{T}$ (all the energies are measured in eV; K_B is the Stephan Boltzmann constant and \hat{T} is the absolute temperature of the powder). At room temperature, $K_B \hat{T} = 0.0257$ eV,



Figure 6. Three graphs to present the (**a**) allowed direct Tauc plot, (**b**) allowed indirect Tauc plot, and (**c**) Urbach plot for the four tested samples.

Table 4. Evaluation of the allowed direct and allowed indirect energy gaps along with the Urbach tailing energy and the electron–phonon interaction strength. The results were obtained by analyzing the Figure 5.

Sample	E ^{dir} (eV)	E ^{indir} (eV)	E _U (eV)	$E_{e-\gamma}$
CCC0	1.441	1.320	0.331	12.88
CCC850	1.272	1.121	0.444	17.28
CCC900	1.213	1.112	0.466	18.13
CCC950	1.166	1.105	0.525	20.43

The results show a decrease in the energy gap value when increasing the calcination temperature, where the reported values for the energy gap were 1.441 eV for the reference sample (with no calcination CCCA), 1.272 eV for the sampled calcinated at 850 °C (CCCA-850), 1.213 eV for the sample calcinated at 900 °C (CCCA-900), and 1.166 for the sample calcinated at 950 °C (CCCA-950). Moreover, the results show an increase in the Urbach tailing energies in the range 0.331–0.525 eV, which can be caused by the reduction in scattering events caused by the electron–phonon interactions after the calcination process. Figure 7 presents the changes in the energy band structure in both the linear momentum and density of state spaces.

which yields $E_{e-\gamma} = E_U/0.0257$. Figure 6 shows the Tauc plots (Figure 6a,b) for the four tested samples along with the Urbach plot (Figure 6a). The analysis results are summarized in Table 4.



Figure 7. Energy band gap diagrams as function of the electron momentum (*k*-space) and density of states for the four tested samples.

The fundamental electronic characteristic known as the band gap pertains to the energy difference between a material's valence and conduction bands. The nature and extent of this band gap exert a profound influence on the electrical and optical behaviors exhibited by the substance. Consequently, a nuanced comprehension and deliberate manipulation of the band gap are imperative for the customization of materials tailored to specific applications, spanning the domain from semiconductors to optoelectronic devices.

Additionally, the electronic structure and reactivity of a material are markedly influenced by the chemical states of its constituent elements. While conventional methods have yielded valuable insights into material compositions, our manuscript pioneers an investigation into the chemical states of cobalt (Co), chromium (Cr), iron (Fe), nickel (Ni), and manganese (Mn) within (CoCrFeNiMn)₃O₄ powders. This meticulous exploration, facilitated by X-ray photoelectron spectroscopy, not only affirms the samples' composition but also reveals the chemical environments and oxidation states characterizing each individual element.

4. Conclusions

Optical techniques were employed to characterize the band gap properties of the samples. The optical analyses provided insights into the electronic transitions and absorption features, shedding light on the fundamental optical properties of the material. The obtained results showed that energy gap values were affected by calcination temperatures, where the energy gap values were decreased by increasing the temperatures, as reported earlier in Table 4.

To complement these studies, X-ray photoelectron spectroscopy was conducted to confirm the composition of the samples and to ascertain the chemical states of the individual elements within the $(CoCrFeNiMn)_3O_4$ powders. This spectroscopic technique allowed for a precise determination of the elemental composition, aiding in the validation of the experimental results and providing valuable information on the chemical environments of the constituent elements.

Our research findings indicate that the band gaps of HEOs are influenced by changes in the oxidation states of the two cations. Subsequent investigations will explore how the band gap varies with defect states and crystallite size. This exploration is crucial as these materials hold potential not only for photocatalysis but also for visible-light-harvesting applications.

Author Contributions: Conceptualization, M.M.A. and D.S.; methodology, M.M.A., T.S. and Z.S.; software, D.S.; validation, R.D., T.S. and M.M.A.; formal analysis, R.D.; investigation, M.M.A. and Z.S.; resources, T.S. and R.D.; data curation, M.M.A.; writing—original draft preparation, T.S., M.M.A. and D.S.; writing—review and editing, R.D.; visualization, M.M.A.; supervision, D.S.; project administration, T.S.; funding acquisition, R.D. and T.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Czech Science Foundation project, grant number 23-06856S.

Data Availability Statement: The data are available upon request.

Acknowledgments: The CzechNanoLab project LM2023051, funded by MEYS CR, is gratefully acknowledged for the financial support of measurements/sample fabrication at the CEITEC Nano Research Infrastructure.

Conflicts of Interest: The authors declare no conflicts of interest.

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