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Influence of Cobalt Incorporation on the Structural Evolution and Optical Band Gap of Spray-Pyrolyzed Mn_3O_4 Thin Films

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Abstract: Mn_3O_4 thin films are valuable materials for gas sensors, optoelectronic and energy storage devices, where intended doping provides a means to optimize their structural and optical characteristics. In this work, the effect of 5 at.% cobalt doping concentration in Mn_3O_4 thin films synthesized via spray pyrolysis is studied. Both undoped and Co-doped films were deposited on glass substrates at 400 °C. The 20 mL precursor solution was sprayed at a 2 mL/min flow rate under an air pressure of 30 psi, producing uniform nanocrystalline layers. Structural properties were analyzed using X-ray diffraction (XRD), while optical properties were assessed using UV–Visible spectroscopy. The absence of any extra peaks in the XRD pattern indicated the phase-pure formation of Mn_3O_4in both samples. Introduction of Cobalt resulted in a slight reduction in lattice parameters, which confirmed successful doping within the Mn_3O_4 structure. However, an increase in crystallite size upon doping indicated enhanced grain growth. Results of UV–Vis spectroscopy showed a minor decrement in bandgap energy from 2.58 eV for pure Mn_3O_4 to 2.34 eV for the 5% Co-doped film. Consequently, cobalt doping altered the electronic structure. Thus, the results show that spray pyrolysis is an effective route for the synthesis of high-quality Mn_3O_4 thin films with optimizable properties.

Keywords: *Co-Doped Mn_3O_4, Hausmannite Thin Films, Spray Pyrolysis, Lattice Contraction, Bandgap Narrowing, XRD Microstructure, Manganese Oxide.*

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I. INTRODUCTION

Transition metal oxides show fascinating electronic structures and strong lattice-charge-spin coupling, which enables various applications in energy, storage, sensing, optoelectronics and catalysis(Biradar et al., 2025; Raj et al., 2009; Sahoo et al., 2024). Particularly, manganese oxides have attracted interest due to their earth abundance, environmental compatibility and mixed oxidation states (Mn^{2+}/Mn^{3+}), facilitating tunable redox chemistry and charge transport(Biradar et al., 2025; Raj et al., 2009). Hausmannite Mn_3O_4 forms a tetragonal spinel structure, which enables Mn^{3+} ions at octahedral sites and Mn^{2+} ions at tetrahedral sites(Raj et al., 2009). This creates a mixed-valence system with semiconducting properties suitable for sensors and optoelectronics. Here, cation replacement at Mn sublattices signifies an effective strategy to organize band configuration, crystal structure and the defect chemistry of Mn_3O_4(Ibrahim & Hammoodi, 2025; Najim et al., 2018; Rossi et al., 2024). Specifically, the incorporation of cobalt ions into the spinel lattice is particularly advantageous, as the substitution of Mn cations with Co facilitates localized electronic modifications that enhance charge transport and catalytic performance(Zhou et al., 2023).

To tune the optical absorption, transmittance, and energy band gap, transition metal dopants can be used as they modify lattice parameters and alter the Mn^{2+}/Mn^{3+} ratio(Rossi et al., 2024). Being a transition metal with an ionic radius of 0.745 Å for Co^{2+} and 0.545 Å for Co^{3+}, cobalt allows isovalent substitution in the spinel structure(Petit et al., 2023). Additionally, the redox reactions of Co^{2+}/Co^{3+} induce lattice strain and oxygen vacancies, making cobalt an ideal dopant. These structural modifications significantly influence the crystallinity and internal stress of the host lattice, ultimately defining the material's suitability for high-performance electrochemical applications(Dahamni et al., 2021).

To deposit the uniform nanocrystalline Mn_3O_4 thin films, the spray pyrolysis is an effective technique as it is cost-effective, scalable and provides parameter control(Raj et al., 2009). Although Li- and Ba-doped Mn_3O_4 films via spray

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pyrolysis, as well as Co-doping by sol-gel and SILAR methods, are well-documented, the systematic studies on the correlation of result of XRD structural evolution, like peak shifting and microstrain, to UV-Vis optical properties of spray-pyrolyzed Co-doped Mn_3O_4 thin films are limited(Bayram et al., 2019).

This study addresses this gap through the synthesis, structural and optical characterization of cobalt-doped Mn_3O_4 thin films. The results show how the cobalt incorporation in the Hausmannite structure shifts the peaks and changes the microstrain, along with the correlation of these changes with optical bandgap modification(Amara et al., 2016; Bayram et al., 2019).

II. EXPERIMENTAL DETAILS

Pure and cobalt-doped Mn_3O_4 thin films were spray pyrolysed on pre-cleaned glass substrates. To prepare a precursor solution with 0.1M concentration, analytical-grade $MnCl_2·4H_2O$ and $CoCl_2·6H_2O$ were used as precursors and double-distilled water was used to dissolve them. As a first step, a 0.1M Mn precursor solution was prepared by dissolving $MnCl_2·4H_2O$ and magnetically stirring until the solution was homogeneous. Later, cobalt was introduced by adding apt volume of 0.1M $CoCl_2·6H_2O$ into the Mn solution to get a cobalt content of 5 at.% with respect to total cations. The molar concentration was kept constant by adjusting the volume of 20 mL of the final solution.

Commercial microscope glass slides were used as substrates and were first washed with Labolene, then rinsed thoroughly with tap water and then with double-distilled water. Subsequently, slides were immersed in chromic acid solution for surface etching. Then slides were repeatedly rinsed with double-distilled water and air-dried. To facilitate high-quality deposition, substrates were pre-cleaned with acetone and ethanol to remove organic residues, a fundamental requirement for the spray pyrolysis route employed in this study (Biradar et al., 2025). The substrates were mounted on the holder and kept at 400 ± 5 °C. The deposition was carried out using compressed air as the carrier gas. The nozzle to substrate distance was fixed at 28 cm, and precursor solutions were sprayed at a rate of 2mL/min, with carrier gas pressure at 30 psi. The entire solution was sprayed in 10 minutes; then the substrates were allowed to cool down naturally to room temperature.

To assess the crystallinity, phase-purity and microstructural evolution, the structural characterization of pure and Co-doped Mn_3O_4 thin films, X-ray diffraction (XRD) was carried out(Biradar et al., 2025; Said et al., 2017). XRD patterns were recorded using Cu Kα radiation of wavelength λ = 1.5406 Å, scanning 2θ = 20–80° with the step size = 0.02°(Biradar et al., 2025). Phase identification was found to match JCPDS24-0734 (Hausmannite Mn3O₄). To calculate the crystallite size Debye-Scherrer equation is used, where D is the average crystallite size, λ is the X-ray radiation wavelength (1.5406 Å), θ is Bragg's angle of diffraction, k(0.9) is the shape factor, and β is the full-width at half-maximum.

UV-Visible spectroscopy was employed to study optical properties over the range of 200–1000 nm. To compute the absorption coefficient, the following equation was used, where T is transmittance, film thickness d is derived from the weight difference. Then the direct band gap E_g was derived from the Tauc plot, i.e., vs hν and by extrapolating the linear absorption edge(Biradar et al., 2025; Vignesh et al., 2021).

III. RESULTS AND DISCUSSION

The pure and 5% Co-doped Mn_3O_4 thin film XRD pattern shows the formation of exclusive tetragonal Hausmannite and no secondary cobalt oxide phases. The primary diffraction peak confirms a preferred crystal orientation, aligning with the expected structural characteristics of spray-pyrolyzed Mn_3O_4 thin films (Raj et al., 2009; Said et al., 2017). Peak shifts indicate the lattice contraction upon 5% at. Co doping: a major shift of ~ (Saranya et al., 2022) 0.1–0.2° to higher 2θ, which further reduces the lattice parameters from a = 5.754 Å → 5.7236 Å and c = 9.4361 Å → 9.4042 Å. Additionally, the unit cell volume decreased from V = 312.51 Å³ to 308.08 Å³ upon doping as a result of the The substitution of Mn^{3+} (VI; 0.645 Å) by Co^{3+} (VI; 0.545 Å) at the octahedral B-site provides the principal contribution to the lattice contraction observed upon doping, while partial replacement of Mn^{2+} (IV; 0.66 Å) at the tetrahedral A-site by Co^{2+} (VI; 0.745 Å) accounts for the slight increase in local microstrai(Petit et al., 2023; Zhang et al., 2021).

The increase in crystallite size D shows the microstructural evolution; Debye-Scherrer analysis of the peaks suggests that Co alters the grain growth. Concurrently, the decrease in dislocation density and strain upon doping suggests Co stabilizes the Hausmannite structure by releasing the mismatch stresses(Saranya et al., 2022).

Table 1: Crystallite Size, Dislocation Density, Strain, Lattice Parameters and Volume of Pure and Co-doped Mn_3O_4 thin Films.

Samples	D (Crystallite Size) (nm)	Dislocation Density (10^{16} lines. nm^{-1})	Strain	Lattice Parameters		Volume (Å³)
				a=b (Å)	C (Å)	
Pure Mn_3O_4	13.2278	0.1442	0.0171	5.7548	9.4361	312.5116
5% Co doped	17.7675	0.0578	0.0067	5.7236	9.4042	308.0805

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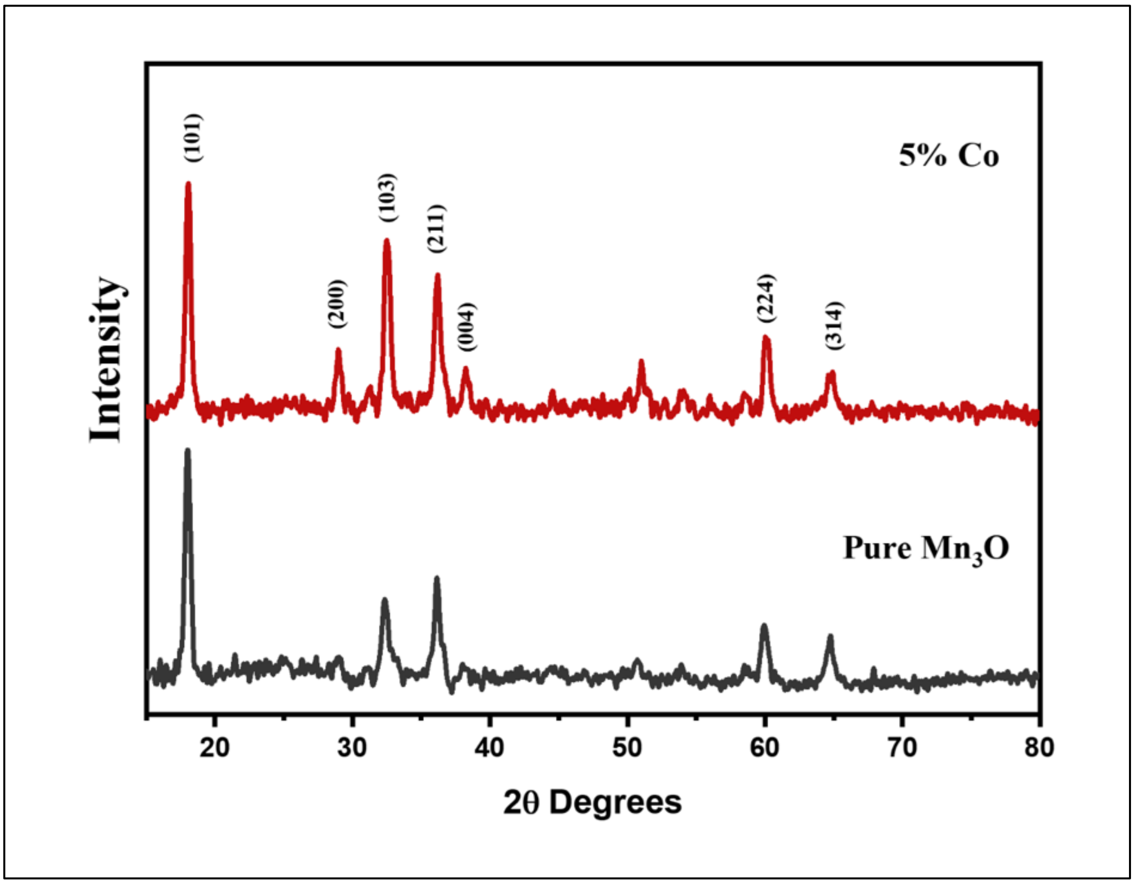

Fig. 1: X-Ray Diffraction Pattern of Pure and 5% Co-Doped Mn_3O_4 thin Films

In pure Mn_3O_4, lattice contraction typically widens the band gap by strengthening Mn–O covalency. In our Co-doped films, however, the band gap narrows from 2.58 to 2.34 eV. This reversal is may be a associated with one of the three mechanisms reported for Co-doped Mn_3O_4: (i) sp–d exchange between Co^{2+}/Co^{3+} 3d states and the host Mn 4s/4p states, (ii) the formation of oxygen vacancies to compensate for charge imbalance when Co^{2+} substitutes Mn^{3+}, and (iii) defect-assisted Urbach tailing that extends sub-band-gap absorption(Rossi et al., 2024).

Despite the decrease in dislocation density and strain, the Co introduces vacancies for oxygen, which form defects that narrow the optical band gap(Rossi et al., 2024). Consequently, the absorption edge exhibits a red shift, which is consistent with the literature, where Co doping in small quantities has contributed to narrowing the Mn_3O_4 band gap despite lattice contraction(Rossi et al., 2024; Saranya et al., 2022). Thus, Co doping in Mn_3O_4 is ideal for optoelectronics as it provides versatility for band-gap optimization(Rossi et al., 2024).

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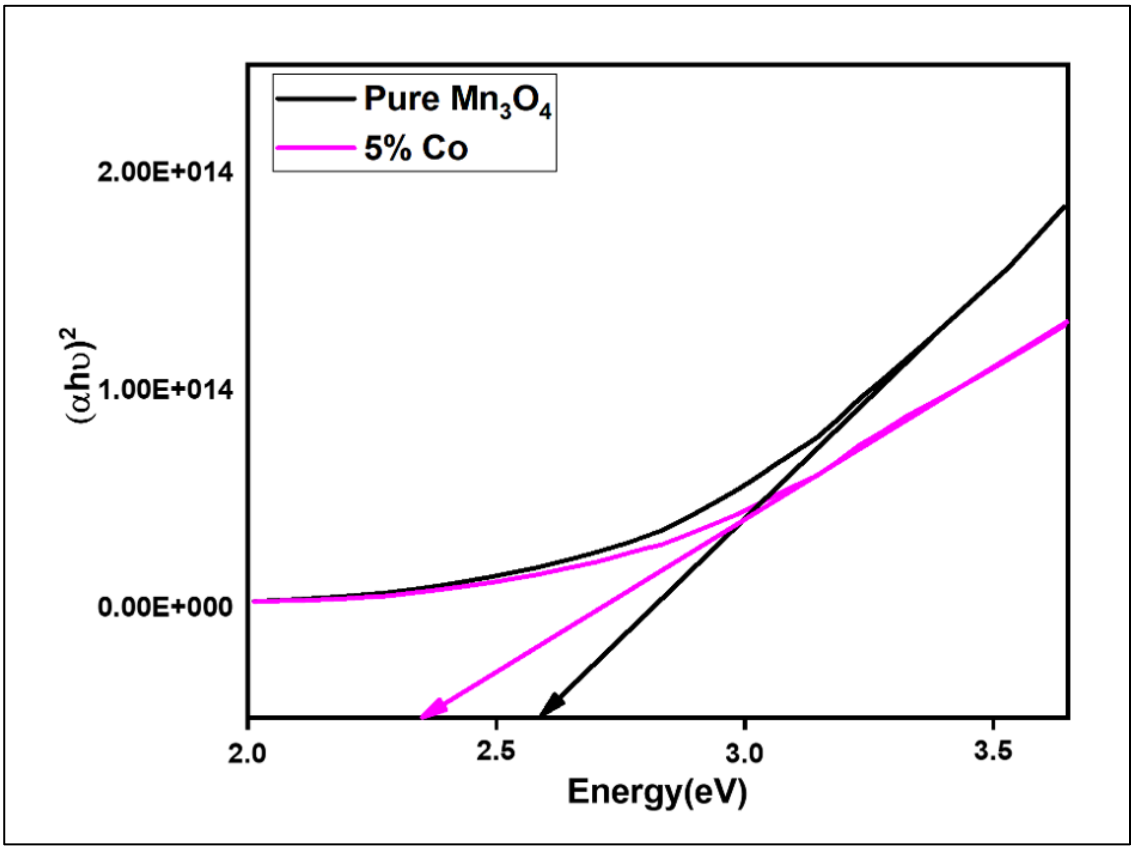

Fig. 2: Energy Band Gap Curve of Pure and 5% Co-Doped Mn_3O_4 thin Films

IV. CONCLUSION

Pure and 5 at.% Co-doped Mn_3O_4 thin films were successfully deposited on glass substrates by spray pyrolysis at 400 °C. X-ray diffraction confirmed phase-pure formation of the tetragonal Hausmannite structure (JCPDS 24-0734, space group $I4_1/amd$) in both films, with no detectable Co_3O_4 or CoO peaks (Ji et al., 2020). Cobalt doping produced measurable lattice contraction: the *a* parameter decreased from 5.7548 to 5.7236 Å and the *c* parameter from 9.4361 to 9.4042 Å, lowering the unit cell volume from 312.51 to 308.08 Å³. This contraction is consistent with the Shannon-radius mismatch between VI Mn^{3+} (0.645 Å) and the smaller VI Co^{3+} (0.545 Å) at the octahedral B-sites. Debye–Scherrer analysis gave an average crystallite size that rose from 13.23 nm in the undoped film to 17.77 nm after Co incorporation, accompanied by a fall in dislocation density ($1.44 \times 10^{15} \rightarrow 5.78 \times 10^{14}$ lines nm^{-2}) and in lattice microstrain ($0.0171 \rightarrow 0.0067$), a trend that has also been reported for Co-doped Mn_3O_4 prepared by jet-nebulizer spray pyrolysis. UV–Visible spectroscopy showed the direct band gap narrowing from 2.58 eV for the undoped film to 2.34 eV after Co incorporation. Although lattice contraction alone would be expected to widen the gap through stronger Mn–O covalency, the observed narrowing is in line with sp–d exchange between Co 3d and Mn 4s/4p states and with oxygen-vacancy formation, both of which dominate over the band-widening effect in Co-substituted oxide thin films(Rossi et al., 2024). Taken together, the data indicate that 5 at.% cobalt enters the Hausmannite lattice without breaking the spinel framework, and the resulting films are useful candidates for optoelectronic and gas-sensing devices.

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DECLARATION OF GENERATIVE AI AND AI-ASSISTED TECHNOLOGIES IN THE MANUSCRIPT PREPARATION PROCESS

Perplexity AI was used only for English grammar polishing of the Introduction, Conclusion, and Acknowledgement sections, and for a subscript and JCPDS-card consistency check. No AI tool helped plan the experiments, run the spray pyrolysis depositions, interpret the XRD patterns, fit the Tauc plots, or arrive at any of the conclusions reported here. Every suggestion was reviewed and edited by me line by line, and I take full responsibility for the content of this manuscript.

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REFERENCES

[1]. Amara, M. A., Larbi, T., Labidi, A., Karyaoui, M., Ouni, B., & Amlouk, M. (2016). Microstructural, optical and ethanol sensing properties of sprayed Li-doped Mn3O4 thin films. *Materials Research Bulletin*. https://doi.org/10.1016/j.materresbull.2015.11.042

[2]. Bayram, O., İgman, E., Guney, H., & Simsek, O. (2019). The role of cobalt doping on the optical and structural properties of Mn3O4 nanostructured thin films obtained by SILAR technique. *Superlattices and Microstructures*. https://doi.org/https://doi.org/10.1016/j.spmi.2019.01.025

[3]. Biradar, P., Nade, A., Dukare, S., & Chaudhari, V. (2025). Optimized Spray Pyrolysis Route for Mn_3O_4 Thin Film Synthesis. *International Journal of Research Publication and Reviews*. https://doi.org/10.55248/gengpi.6.1025.3618

[4]. Dahamni, M. A., Ghamnia, M., Naceri, S. E., Fauquet, C., Tonneau, D., Pireaux, J. J., & Bouadi, A. (2021). Spray pyrolysis synthesis of pure and mg-doped manganese oxide thin films. *Coatings*. https://doi.org/10.3390/coatings11050598

[5]. Ibrahim, A. Y., & Hammoodi, F. G. (2025). Structural and Optical Properties of Mn3O4:NiO Nanostructure Thin Films Prepared by Chemical Spray Pyrolysis Method. *Journal of Nanostructures*, *15*(1), 229–238. https://doi.org/10.22052/JNS.2025.01.022

[6]. Ji, J., Wan, H., Zhang, B., Wang, C., Gan, Y., Tan, Q., Wang, N., Yao, J., Zheng, Z., Liang, P., Zhang, J., Wang, H., Wang, H., Li, T., Wang, Y., Chao, D., Wang, H., & Wang, H. (2020). *Co2+/3+/4+-Regulated Electron State of Mn-O for Superb Aqueous Zinc-Manganese Oxide Batteries*. https://doi.org/10.1002/aenm.202003203

[7]. Najim, A. A., Darwoysh, H. H., Dawood, Y. Z., Hazaa, S. Q., & Salih, A. T. (2018). Structural, Topography, and Optical Properties of Ba-Doped Mn3O4 Thin Films for Ammonia Gas Sensing Application. *Physica Status Solidi (A) Applications and Materials Science*. https://doi.org/10.1002/pssa.201800379

[8]. Petit, S., Decarreau, A., Grégoire, B., & Ferrage, E. (2023). Generalized relationships between the ionic radii of octahedral cations and the b crystallographic parameter of clays and related minerals. *Clay Minerals*, *58*(2), 143–194. https://doi.org/10.1180/clm.2023.20

[9]. Raj, A. M. E., Victoria, S. G., Jothy, V. B., Ravidhas, C., Wollschläger, J., Suendorf, M., Neumann, M., Jayachandran, M., & Sanjeeviraja, C. (2009). XRD and XPS characterization of mixed valence Mn3O4 hausmannite thin films prepared by chemical spray pyrolysis technique. *Applied Surface Science*, *256*(9), 2920–2926. https://doi.org/10.1016/j.apsusc.2009.11.051

[10]. Rossi, Z., Ghannam, H., Brioual, B., Ullah, S., Zanouni, M., Diani, M., Aouni, A., & Addou, M. (2024). Effect of Cobalt Doping on The Structural, Linear and Nonlinear Optical Parameters of Manganese Oxide Thin Layers. *Crystal Research and Technology*. https://doi.org/https://doi.org/10.1002/crat.202300235

[11]. Sahoo, S., Wickramathilaka, K. Y., Njeri, E., Silva, D., & Suib, S. L. (2024). A review on transition metal oxides in catalysis. *Frontiers in Chemistry*, *12*, 1374878–1374878. https://doi.org/10.3389/fchem.2024.1374878

[12]. Said, L. B., Inoubli, A., Bouricha, B., & Amlouk, M. (2017). High Zr doping effects on the microstructural and optical properties of Mn3 O4 thin films along with ethanol sensing. *Spectrochimica Acta - Part A: Molecular and Biomolecular Spectroscopy*. https://doi.org/10.1016/j.saa.2016.08.014

[13]. Saranya, S., Sethupathi, N., & Mahalingam, P. (2022). EFFECT OF COBALT DOPING AND ANNEALING ON PROPERTIES OF MANGANESE OXIDE THIN FILMS PREPARED USING JET NEBULIZER SPRAY PYROLYSIS TECHNIQUE. *Rasayan Journal of Chemistry*. https://doi.org/10.31788/RJC.2022.1547009

[14]. Vignesh, R., Sivakumar, R., & Sanjeeviraja, C. (2021). A detailed analysis on optical parameters of spinel structured Mn3O4 thin films deposited by nebulized spray pyrolysis technique. *Optical Materials*. https://doi.org/10.1016/j.optmat.2020.110580

[15]. Zhang, S., Li, H., Wu, Z., Post, J. E., Lanson, B., Elzinga, E. J., Liu, Y., Li, H., Hong, M., Liu, F., & Yin, H. (2021). Effects of Co doping on the structure and physicochemical properties of hausmannite (Mn3O4) and its transformation during aging. *Chemical Geology*, *582*, 120448–120448. https://doi.org/10.1016/j.chemgeo.2021.120448

[16]. Zhou, Y., Guan, P., Chen, F., Feng, Z., Jia, H., Liang, T., Li, M., Wan, T., Tian, R., Han, Z., & Chu, D. (2023). Engineering work functions of cobalt-doped manganese oxide based electrocatalysts for highly efficient oxygen evolution reaction. *Journal of Colloid and Interface Science*, *642*, 23–28. https://doi.org/10.1016/j.jcis.2023.03.129