

Structural Diagnosis of Nanostructured Cadmium Manganite Thin Films Prepared by DC Reactive Sputtering

Nicola Gallinari ¹, Hammad A. Humud ^{1,2}, Mauro J. Lovato ¹

¹ Department of Metallurgy and Materials Engineering, Faculty of Engineering, University of Malta, Msida, MALTA

² Department of Physics, College of Science, University of Sfax, Sfax, TUNISIA

Abstract

In this work, an attempt to prepare cadmium manganite (CdMn_2O_4) nanostructures is presented. These nanostructures were prepared by reactive magnetron co-sputtering technique. The cadmium and manganese targets were mounted in a geometrical configuration allowing to achieve the stoichiometry of the prepared compound. The effect of $\text{Ar}:\text{O}_2$ mixing ratio on the structural characteristics of the prepared nanostructures was introduced. The growth of crystal planes in the prepared samples could be reasonably controlled by tuning the operation parameters and preparation conditions. The structural characterization showed that the prepared nanostructures were highly pure.

Keywords: Cadmium manganite; Nanostructures; Magnetron sputtering; Reactive sputtering

Received: 23 February 2025; **Revised:** 03 April 2025; **Accepted:** 17 April 2025; **Published:** 1 July 2025

1. Introduction

Cadmium manganite (CdMnO_3) nanostructures have garnered significant attention in recent years due to their unique structural, electronic, and magnetic properties, which make them promising candidates for applications in spintronics, catalysis, and energy storage devices [1-3]. The DC reactive magnetron co-sputtering technique is a versatile and efficient method for synthesizing high-quality CdMnO_3 nanostructures with controlled composition and morphology. This technique involves the simultaneous sputtering of cadmium (Cd) and manganese (Mn) targets in a reactive oxygen (O_2) environment, enabling the formation of cadmium manganite thin films or nanostructures with precise stoichiometry and structural uniformity [4-6].

One of the key structural characteristics of CdMnO_3 nanostructures prepared by this method is their crystallinity [7]. The perovskite-like structure is a common feature of manganite compounds. The perovskite structure of CdMnO_3 is characterized by a cubic or orthorhombic unit cell, depending on the synthesis conditions and post-deposition treatments [8,9]. The crystallite size usually ranges from a few nanometers to tens of nanometers, indicating the formation of nanocrystalline domains [10,11]. The high crystallinity of these nanostructures is crucial for their functional properties, as defects and grain boundaries can significantly impact their electronic and magnetic behavior [12,13].

Recently, the research interests in cadmium manganite (CdMn_2O_4) have increased due to the effectiveness of this material in the fabrication of supercapacitors and Li-ion batteries [14]. As well, this material was successfully used as an electrode material in electrochemical sensors of NO_x gases [15]. The CdMn_2O_4 nanostructures such as nanoparticles and nanofibers exhibit much better properties in such applications because of the drastic increase in surface-to-volume ratio [16]. Spinel cadmium manganite is described as a multifunctional material as the quantity and chemical identity of the Cd^{2+} ions can be tuned to obtain a wide range of properties [17]. The replacement of Mn^{2+} ions on the tetrahedral sites by Cd^{2+} ions mostly cause a large tetragonal distortion as a result of the Jahn-Teller effect [18]. The bulk CdMn_2O_4 is prepared by the solid state reaction method as the CdO and Mn_2O_3 powders are mixed and sintered at high temperatures ($\sim 900^\circ\text{C}$) [19], while the CdMn_2O_4 nanostructures are mainly synthesized by electrospinning technique [20]. In both cases, the synthesized structures include compounds other than CdMn_2O_4 . These nanostructures prepared by DC reactive magnetron co-sputtering exhibit excellent crystallinity, controlled morphology, and tunable defect density, making them highly suitable for a wide range of applications [21-24]. The ability to precisely control the structural characteristics of these materials through synthesis parameters underscores the versatility and potential of this fabrication technique [25,26].

In this work, highly-pure CdMn_2O_4 nanostructures were synthesized by reactive magnetron co-sputtering technique and the effect of mixing ratio on their structural properties was introduced.

2. Experimental Part

A dc sputtering system was used to prepare CdMn_2O_4 thin films on glass substrates. Two highly-pure targets of Cd and Mn were mounted on the cathode to perform the co-sputtering process. The dimensions of targets were determined in light of the surface binding energies of both materials (2.92 eV for Mn and 1.16 eV for Cd) and the stoichiometry of the required compound. The diameters of Mn and Cd targets were 80 and 15mm, respectively. This configuration can ensure the stoichiometric reaction of Mn and Cd with oxygen atoms available in the discharge volume. A magnetron of 450G flux density was attached to the backside of the Mn target at the cathode to confine the ions near the target surface and hence increase the collisional ionization.

The mixing ratio of argon and oxygen in the gas mixture can be precisely controlled by premixing these gases in a mixer before pumped into the discharge chamber. The total gas pressure reached 0.1 mbar. The cathode was cooled down to 4 °C in order to prevent the ion-induced secondary electron emission, while the anode was left to heat up to about 150 °C in order to induce the reaction between CdO and Mn_2O_3 particles and form the required compound (CdMn_2O_4). More details of the preparation conditions can be found elsewhere [27-30]. The nanopowders were extracted from thin film samples by conjunctional freezing-assisted ultrasonic extraction method [31-33].

The structural characteristics of the prepared thin films were determined by x-ray diffraction (XRD) and the Fourier-transform infrared (FTIR) spectroscopy.

3. Results and Discussion

Figure (1) shows the simulated XRD pattern of the CdMn_2O_4 samples prepared in this work. Figure (1a) shows the XRD pattern of the sample prepared using gas mixture of 1:1 and deposition time of one hour. All peaks belonging to the polycrystalline structure of CdMn_2O_4 are observed while no other peaks belonging to both CdO and Mn_2O_3 are seen in this pattern [34]. This initially highlights the structural purity of the prepared samples. Further tuning of the operation parameters and preparation conditions may lead to suppress some peaks and allow fewer number of crystal planes to grow. Using gas mixture of 2:1 and after 30 min of deposition, about half the number of peaks were suppressed as shown in Fig. (1b) and marked with the asterisk in table (1) as the amount of oxygen in the reaction volume was decreased as well as the time required for growth of more crystal planes. Table (1) shows the structural parameters of the prepared samples.

Figure (2) shows the FTIR spectrum of the CdMn_2O_4 samples prepared at different conditions in this work. As shown in Fig. (2a), three bands are observed at 451, 650 and 1304 cm^{-1} , which ascribed to the stretching vibrations of metal-oxygen (Mn-O, Cd-O and O-M-O) bonds [35-37]. No other bands are observed and this confirms the structural purity of the prepared samples. The two featured bands of metal-oxygen bond were seen in the sample prepared using gas mixture of 2:1 and deposition time of 30 min, while the band ascribed to the stretching vibration of O-M-O disappeared. Instead, a band around 1590 cm^{-1} , which is ascribed to the vibration of O-H bond in water molecules, was seen. This may be attributed to the possible adsorption of water by the prepared sample.

Table (1) Structural parameters of the prepared samples determined from XRD results

2 θ (deg.)	FWHM (deg.)	d_{hkl} (Å)	Crystallite size (nm)	(hkl)
28.147	0.303	3.519	27.02	(112)
30.951	0.562	3.525	14.66	(200)
31.026	0.519	2.375	15.88	(103)
35.852	0.692	3.525	12.06	(211)
48.357	0.173	3.518	50.32	(204)*
49.014	0.433	3.520	20.16	(105)*
53.167	0.649	3.502	13.68	(312)*
55.069	0.369	3.525	24.27	(303)*
58.297	0.512	3.757	17.76	(321)*
58.792	0.593	2.510	15.37	(224)
64.28	0.673	3.522	13.94	(400)*

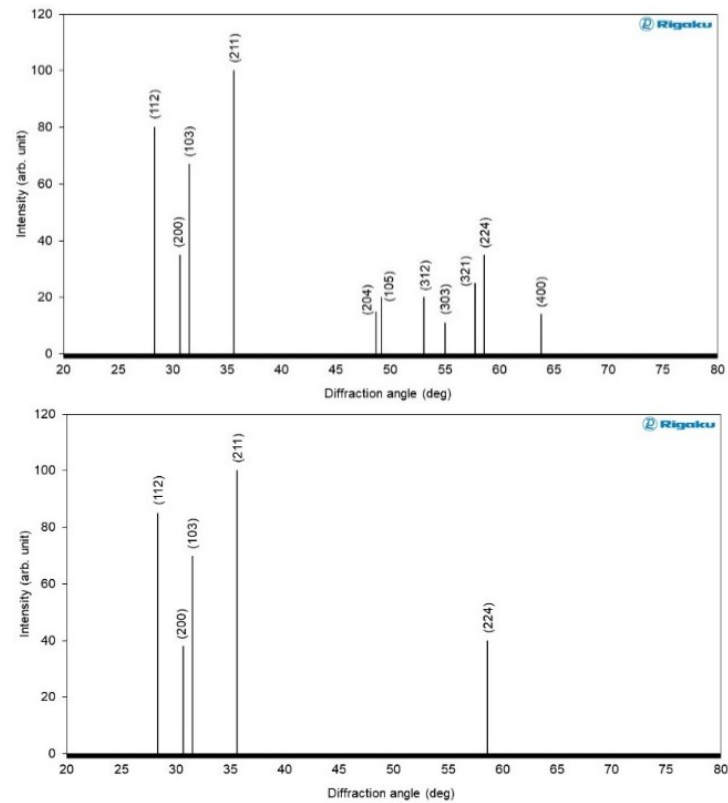


Fig. (1) Simulated XRD patterns of the CdMn_2O_4 samples prepared in this work using Ar: O_2 mixing ratio of 1:1 and deposition time of 60 min (upper) and 2:1 and 30 min (lower)

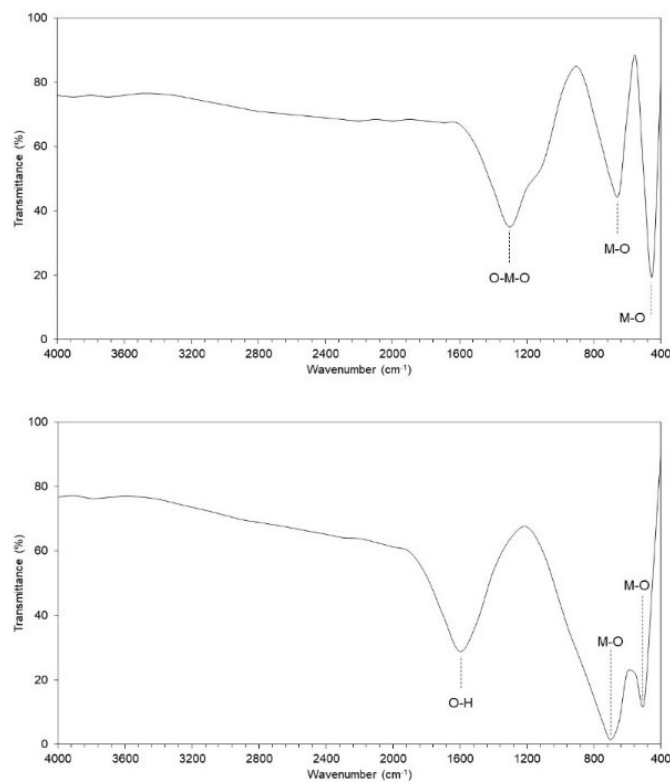


Fig. (2) FTIR spectra of the CdMn_2O_4 samples prepared in this work using Ar: O_2 mixing ratio of 1:1 and deposition time of 60 min (upper) and 2:1 and 30 min (lower)

4. Conclusion

In concluding remarks, an attempt to prepare CdMn_2O_4 nanostructures by reactive magnetron co-sputtering technique. A new geometrical configuration was used for co-sputtering process depending on the dimensions of Cd and Mn targets with respect to each other. The mixing ratio of argon and oxygen was found very effective on the structural characteristics of the prepared nanostructures, those were highly pure as no elements other than cadmium, manganese and oxygen were found in the final sample. The growth of crystal planes in the prepared samples can be controlled by tuning the operation parameters and preparation conditions, especially gas mixing ratio and deposition time.

References

- [1] N. Miura et al., Solid State Ionics, 86–88(Pt 2) (1996) 1069-1073.
- [2] J. Bhagwan et al., J. Alloys Comp., 703 (2017) 86-95.
- [3] J. Bhagwan and J.I. Han, Ceram. Int., 50(14) (2024) 26086-26096.
- [4] H.-J. Kim et al., Mater. Lett., 210 (2018) 143-147.
- [5] X. Hao et al., Sens. Actuators B: Chem., 302 (2020) 127206.
- [6] C.B. Azzoni et al., Solid State Commun., 119(10–11) (2001) 591-595.
- [7] J.D. Hem and C.J. Lind, Geochimica Cosmochimica Acta, 55(9) (1991) 2435-2451.
- [8] M. Ramstedt et al., J. Colloid Interface Sci., 285(2) (2005) 493-501.
- [9] E.V. Vladimirova, B.V. Slobodin, and L.L. Surat, Russian J. Inorg. Chem., 45(10) (2000) 1594-1597.
- [10] J.P. Araújo et al., J. Magnet. Magnet. Mater., 226-230 (Pt1) (2001) 797-799.
- [11] V. Gupta, B. Raina, and K.K. Bamzai, J. Mater. Sci.: Mater. Electron., 29(11) (2018) 8947-8957.
- [12] O.A. Hammadi, Proc. IMechE, Part N, J. Nanomater. Nanoeng. Nanosys., 232(4) (2018) 135-140.
- [13] A.P.B. Sinha, N.R. Sanjaya, and A.B. Biswas, New Cryst. Struct., 109(1-6) (1957) 410-421.
- [14] V. Gupta et al., Integ. Ferroelectr., 185(1) (2017) 165-175.
- [15] L. Bochatay, P. Persson, and S. Sjöberg, J. Colloid Interface Sci., 229(2) (2000) 584-592.
- [16] G.G. Robbrecht and C.M. Henriët-Iserentant, phys. stat. sol. (b), 41(1) (1970) K43-K46.
- [17] O.A. Hammadi, Plasmonics, 15(6) (2020) 1747-1754.
- [18] P. Ghigna, G. Flor and G. Spinolo, J. Solid State Chem., 149(2) (2000) 252-255.
- [19] I.O. Troyanchuk, H. Szymczak and N.V. Kasper, phys. stat. sol. (a), 157(1) (1996) 159-166.
- [20] J. Deng and H.J. Quah, Int. J. Nanotechnol., 21(4-5) (2024) 324-338.
- [21] N. Ishigaki et al., Thin Solid Films, 686 (2019) 137433.
- [22] S.E. Nunes, L.C. Matte, and C.R. Da Cunha, Mater. Res. Exp., 6(9) (2019) 095905.
- [23] P.H.M.A. Hedei, Z. Hassan, and H.J. Quah, Int. J. Nanotechnol., 19(2-5) (2022) 211-222.
- [24] P.H.M.A. Hedei, Z. Hassan, and H.J. Quah, Appl. Surf. Sci., 550 (2021) 149340.
- [25] H.R. Moazami et al., J. Solid State Electrochem., 24 (2020) 1231-1238.
- [26] J. Bhagwan et al., J. Alloys Compd., 703 (2017) 86-95.
- [27] S.K. Dey, Phys. Lett., 22(4) (1966) 375-377.
- [28] G.N.P. Oliveira et al., J. Appl. Phys., 116(22) (2014) 223907.
- [29] O.A. Hammadi, M.K. Khalaf and F.J. Kadhim, Opt. Quantum Electron., 47(12) (2015) 3805-3813.
- [30] E.A. Al-Oubidy and F.J. Al-Maliki, Iraqi J. Appl. Phys., 14(4) (2018) 19-23.
- [31] F.J. Al-Maliki, O.A. Hammadi and E.A. Al-Oubidy, Iraqi J. Sci., 60 (Special Issue) (2019) 91-98.
- [32] F.J. Al-Maliki and E.A. Al-Oubidy, Physica B: Cond. Matter, 555 (2019) 18-20.
- [33] O.A. Hammadi, Iraqi J. Appl. Phys., 15(4) (2019) 23-28.
- [34] Standard X-Ray Diffraction Powder Patterns, Section 10, National Bureau of Standards, Monograph 25 (1972) p. 16.
- [35] N.N. Greenwood and E.J.F. Ross, "Index of Vibrational Spectra of Inorganic and Organometallic Compounds", vol. I, Butterworth Group (London, 1960), p. 326, 328.
- [36] N.N. Greenwood and E.J.F. Ross, "Index of Vibrational Spectra of Inorganic and Organometallic Compounds", vol. II, Butterworth Group (London, 1963), p. 457.
- [37] N.N. Greenwood and E.J.F. Ross, "Index of Vibrational Spectra of Inorganic and Organometallic Compounds", vol. III, Butterworth Group (London, 1966), p. 800, 1078.