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# Electronic and structural properties of single-crystal Jahn–Teller active $Co_{1+x}Mn_{2-x}O_4$ thin films

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#### Abstract

Recent investigations on spinel CoMn<sub>2</sub>O<sub>4</sub> have shown its potential for applications in water splitting and fuel cell technologies as it exhibits strong catalytic behavior through oxygen reduction reactivity. To further understand this material, we report for the first time the synthesis of single-crystalline  $Co_{1+x}Mn_{2-x}O_4$  thin films using molecular beam epitaxy. By varying sample composition, we establish links between cation stoichiometry and material properties using *in-situ* x-ray photoelectron spectroscopy, x-ray diffraction, scanning transmission electron microscopy, x-ray absorption spectroscopy, and spectroscopic ellipsometry. Our results indicate that excess Co ions occupy tetrahedral interstitial sites at lower excess Co stoichiometries, and become substitutional for octahedrally-coordinated Mn at higher Co levels. We compare these results with density functional theory models of stoichiometric  $CoMn_2O_4$  to understand how the Jahn–Teller distortion and hybridization in Mn–O bonds impact the ability to hole dope the material with excess Co. The findings provide important insights into  $CoMn_2O_4$  and related spinel oxides that are promising candidates for inexpensive oxygen reduction reaction catalysts.

Keywords: CoMn<sub>2</sub>O<sub>4</sub>, molecular beam epitaxy, x-ray photoelectron spectroscopy, x-ray absorption spectroscopy, density functional theory

**S** Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

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#### 1. Introduction

The development of materials for alternative clean energy sources is central to much of condensed matter research today. Catalytic reactivity for the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) is an important property for technologies such as electrolyzers, metal–air batteries and fuel cells [1–7]. To date, expensive metals such as platinum dominate this field of research, having shown great promise in both ORR and OER [1, 3, 8, 9]. However, economic considerations demand cheaper materials that offer comparable performance to platinum. Oxygen catalysis systems comprised of inexpensive materials such as transition metal oxides stand as alternatives to platinum. Spinel oxides containing earth-abundant elements such as cobalt, iron, manganese and nickel are particularly promising in this regard [1, 10-12].

Indeed, the Co–Mn spinel system with end members  $CoMn_2O_4$  (CMO) and  $MnCo_2O_4$  (MCO) exhibits ORR properties on par with platinum [1, 11, 13, 14], making it promising for efficient and affordable catalysis technologies as well as energy storage [15–18]. While CMO has been synthesized and studied in nanoparticle and nanocrystalline forms [1, 4, 12, 15–19], characterization reports on CMO thin films are limited to island growth on lattice-mismatched SrTiO<sub>3</sub> substrates [20]. Coherent single crystal epitaxial films provide opportunities to tune properties through strain and to characterize fundamental material properties in the absence of grain boundary effects.

Normal spinels are described by the formula  $AB_2O_4$  where cation A generally possesses a 2+ formal charge in a tetrahedral site and cation B possesses a 3+ formal charge in an octahedral site. While most spinels possess a face-centered cubic Bravais lattice structure (space group $Fd\bar{3}m$ ), the Jahn–Teller (JT) interaction can induce a body-centered tetragonal lattice (space group  $I4_1/amd$ ). This produces a  $45^\circ$  in-plane rotation of the *a* and *b* axes from the conventional cubic lattice. Such is the case with CMO [1, 16–19, 21–23], where crystal-field splitting breaks the cubic symmetry [4, 22–25]. Specifically, the JT-active Mn<sup>3+</sup> ions in CMO break the degeneracy of partially-filled electronic d-orbital states [26, 27]. This leads to elongation of the c-axis parameter through octahedral distortion, as illustrated in Figure 1(a).

In contrast to the normal spinel structure, the inverse spinel structure has all the A cations and half of the B cations octahedrally coordinated, leaving all tetrahedral sites to be occupied by B cations. The cations of a spinel have preferred coordinations in which the material's overall energy is lowest which causes a spinel to trend toward either normal or inverse. The structure type a spinel material adopts depends on cation formal charges and crystal field splitting effects [14, 28, 29]. Excessive growth temperatures can incite spinels to adopt intermediate structures between normal and inverse by increasing the probability of cation coordination defects. The general formula  $(A_{1-\lambda}B_{\lambda})^{Th}[A_{\lambda/2}B_{2-\lambda}]_2^{Oh}O_4$  is able to describe all possible cases, with cations in parentheses representing tetrahedral occupation and cations in brackets representing octahedral occupation. In the case of an ideal normal-type or inverse-type structure, the degree of inversion

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 $(\lambda)$  takes on values of 0 or 1, respectively. CMO of an ideal 1:2 cation ratio exhibits a normal spinel structure [19, 21, 30, 31], as do the binary spinels  $Co_3O_4$  [28, 31] and  $Mn_3O_4$  [28, 31]. This means that ideal CMO should be comprised of tetrahedral Co<sup>2+</sup> and octahedral Mn<sup>3+</sup> cations. MCO has been reported to trend toward an inverse spinel [32-35] in which all the Mn and half the Co are octahedrally coordinated, while the remaining Co are tetrahedrally coordinated. MCO has also been reported as having a cubic structure rather than tetragonal [32], suggesting the absence of any JT effect. Additionally, the MCO spinel, rather than possessing the typical 2+ and 3+ cation valences, may instead possess Mn<sup>4+</sup> and Co<sup>2+</sup> cations, owing to the instability of tetrahedrally coordinated  $Co^{3+}$  brought on by unpaired eg orbitals. However, literature on the subject is mixed, with some groups reporting Mn<sup>4+</sup> character [35, 36] and others only  $Mn^{3+}$  [33]. While  $AB_2O_4$  is the ideal spinel formula, a material with non-standard spinel stoichiometry of the form  $A_{1+x}B_{2-x}O_4$  is often expected to form a solid solution between end-members, though phase segregation and other structural defects have been reported in some cases.

Here, we focus on understanding the Co-Mn spinel material system through synthesis of epitaxial single crystal CMO thin films grown using molecular beam epitaxy (MBE), a method that allows for precise control of sample stoichiometry and produces uniform single crystal films. This is among the few works that study CMO from a single crystal thin film perspective [37]. We grew  $Co_{1+x}Mn_{2-x}O_4$  films that vary in stoichiometry from ideal to increased cobalt, and studied them using characterization techniques to identify patterns between stoichiometry and material properties. We determine structural and electronic properties of CMO that are contested or unreported in literature such as cation valence states through x-ray photoelectron spectroscopy and cation-oxygen bond lengths from x-ray absorption spectroscopy. We also present electronic structure calculations for models of CMO through use of density-functional theory

#### 2. Methods

The present work involves synthesis and characterization of epitaxial thin film samples of CMO with different metal stoichiometries, grown using MBE (Mantis Deposition). All samples were grown on (001) MgAl<sub>2</sub>O<sub>4</sub> (MAO) spinel substrates due to its isostructural template and small in-plane lattice mismatch with CMO. MAO's conventional in-plane parameter is 8.083 Å (MTI Corporation), while CMO's primitive inplane parameter has been reported as 5.716 Å [1], which is equivalent to a conventional parameter of 8.144 Å after a  $45^{\circ}$ in-plane rotation. This produces a lattice mismatch of  $\sim 0.8\%$ so that CMO experiences minor epitaxial strain. MAO substrates were sonicated in acetone and isopropyl alcohol for 5 min each before being loaded into the MBE chamber. Co and Mn metals were deposited concurrently during film growth and effusion cell temperatures were kept constant, with deposition rates calibrated pre-growth using a quartz-crystal microbalance. The sample stage temperature was controlled by employing an infrared ceramic heating source and measured via thermocouple on the stage, producing an overestimation



**Figure 1.** (a) Crystallographic model of  $CoMn_2O_4$ , where Co tetrahedra and Mn octahedra are shaded blue and orange, respectively; (b) RHEED image of CMO film after growth; (c) and (d) cross-sectional STEM bright-field (STEM-BF) (c) and STEM-EDS map (d) of representative sample showing smooth MAO/CMO interface and homogeneous CMO film (red-Al K, green-Mn K, blue-Co K, magenta-Pt M edges); (e) Out-of-plane XRD of the four  $Co_{1+x}Mn_{2-x}O_4$  films.

(~50 °C-100 °C) relative to the substrate surface temperature. All samples were grown at 500 °C temperature setpoints and subsequently cooled to ambient temperature over ~30 min. Atomic oxygen was introduced into the growth chamber by a radio-frequency plasma source with 300 W RF power. Oxygen plasma pressure was maintained at ~ $2.0 \times 10^{-5}$  Torr during growth and decreased to ~ $2.9 \times 10^{-6}$  Torr during cooldown of the sample stage.

Reflection high-energy electron diffraction (RHEED) was used to monitor the growth process. Preliminary growths showed that lengthy exposure to RHEED adversely affected CMO films, forming a streak visible to the naked eye along the line the RHEED electrons were incident upon. To minimize this effect, use of RHEED was limited to quick bursts for image acquisition during and after sample growth (<2 s every 1-2 min). After cooling, samples were analyzed using x-ray photoelectron spectroscopy (XPS, PHI 5400 refurbished by RBD Instruments). The XPS system was connected to the MBE system by a vacuum transfer line that prevents surface contamination. A monochromatic Al  $K\alpha$  x-ray source was used for all samples. An electron pass energy of 17.9 eV and a scanning step size of 0.05 eV was used during measurements. An electron emission neutralizer compensated for sample charging during data acquisition. Spectra were shifted to place their O 1s metal-oxygen bond peaks to 530.0 eV binding energy (S1) to compensate for the effect of the neutralizer as it artificially lowers the measured binding energy due to a small negative charge induced/accumulated on the surface.

Atomic force microscopy (AFM) images were acquired using a Park XE7 AFM in non-contact mode. Rutherford backscattering (RBS) data was collected through helium ion bombardment using a 6HDS-2 tandem, National Electrostatics Corporation Pelletron, with 2 sources for ions, an alphatross (rf source for production of He<sup>+</sup>) and source of negative ions by cesium sputtering (SNICS source). X-ray diffraction/reflectivity (XRD/XRR)  $\theta$ -2 $\theta$  patterns were collected using a Rigaku SmartLab diffractometer with the incident beam (Cu  $K\alpha$ ) filtered using a parabolic mirror and two-bounce Ge(220) monochromator. Both x-ray absorption near edge spectroscopy (XANES) and extended x-ray absorption fine structure (EXAFS) were performed at the advanced photon source at sector-20 BM in fluorescence mode for both in-plane (parallel) and out-of-plane (perpendicular) polarized x-rays at the Co and Mn K edges. Spectroscopic ellipsometry (SE) measurements were performed using a rotating analyzer based instrument with a compensator (V-VASE; J A Woollam Co., Inc.) over the spectral range from 0.4 to 5.8 eV. Data were fit to a general oscillator model after fixing the film thickness to specified values (S2) to extract values for the refractive index, n, and extinction coefficient, k. The absorption coefficient, a, was calculated from the extinction coefficient as  $a = \alpha$ ,  $p = \pi$ ,  $l = \lambda$ , where *l* is the incident wavelength.

Film morphology and composition were also analyzed using aberration-corrected scanning transmission electron microscopy (STEM). STEM samples were prepared using a standard lift out process on a FEI Helios DualBeam 660 focused ion beam microscope, with initial cuts performed at 30 kV and final thinning 2 kV ion milling energy. STEM-BF, high-angle annular dark field (STEM-HAADF), and mediumangle annular dark field (STEM-MAADF) images were collected on a probe-corrected JEOL GrandARM-300F microscope operating at 300 kV, with a convergence semi-angle of 29.7 mrad and a collection angle of 72-495 mrad for the STEM-HAADF and 47-144 mrad for the STEM-MAADF, respectively. Energy-dispersive x-ray spectroscopy (STEM-EDS) maps were collected using a dual JEOL Centurio detector setup, with a 1 Å probe size,  $\sim 237$  pA probe current, 10  $\mu$ s px<sup>-1</sup> dwell time, and ~5 min total acquisition time. The electronic properties of CMO were analyzed via density functional theory (DFT) using a pseudo-hybrid Hubbard

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**Table 1.** c-lattice parameters of CMO samples calculated from(004) peaks of XRD data.

$Co_{1+x}Mn_{2-x}O_4$ sample	<i>c</i> -lattice parameter (Å)		
x = 0.04	9.19(1)		
x = 0.14	9.24(1)		
x = 0.23	9.16(1)		
x = 0.24	9.15(1)		

density functional (ACBN0) [38], where exchange-correlation energy is parameterized by spin-polarized generalized gradient approximation functionals [39]. Here, tetragonal unit cells were fully relaxed when accounting for different magnetic states. Moreover the Brillouin zone is sampled using an  $8 \times 8 \times 6$  Monkhorst-Pack mesh. The calculations employ PAW pseudopotentials [40] for the description of the atomic cores with cutoff energies of 50 Ry and 325 Ry for the Kohn–Sham wave functions and densities, respectively. All calculations are carried out using the quantum espresso software suite [41].

#### 3. Results and discussion

For each of the  $Co_{1+x}Mn_{2-x}O_4$  samples, the cation ratios were determined via RBS (fits found in supplemental information, S3). This study focuses on four samples comprising nearly ideal CMO (x = 0.04) and Co rich cases (with x up to 0.24). AFM images reveal extremely smooth films with root-meansquare roughness of less than 0.15 nm (S4). RHEED patterns of the films match those of their MAO spinel substrates with slight streaking, owing to the small lattice mismatch between film and substrate and the smooth layer-by-layer growth (Figures 1(b), S5). Moreover, the unchanging diffraction patterns obtained with RHEED throughout the growth process show that the films are single-crystalline. STEM-BF and EDS maps (Figures 1(c) and (d), S6) confirm that the film exhibits excellent compositional uniformity, without phase separation or defects, and that it possesses a sharp interface with the substrate. XRD of the samples aligns with a tetragonal crystal structure (Figure 1(d)) and confirm that they are all single-phase, with finite thickness fringes indicating a smooth surface and interface. Reciprocal space maps show that the CMO films are epitaxially strained to the MAO substrate and share the same a and b-lattice parameters (direct space map in supplemental information, S9). Calculation of the *c*-lattice parameter from the films' (004) Bragg reflections gives the values found in Table 1. All are reasonably close to values reported in literature (c = 9.252 Å [1], c = 9.095 Å [42]) and vary with stoichiometry. Epitaxial strain should only have a small effect on these parameters ( $\sim 0.8\%$  lattice mismatch). As will be explained later, we believe the increase in lattice parameter from x = 0.04 to x = 0.14 is due to excess Co filling interstitial sites as  $Co^{2+}$  tetrahedra, thereby expanding the crystal along the c direction. The decrease in lattice parameter beyond the x = 0.14 level could be attributed to excess Co replacing the JT-active Mn<sup>3+</sup> octahedra with Co<sup>2+</sup> octahedra.

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**Figure 2.** XPS data of (a) Co 2*p*; (b) Mn 2*p*; and (c) Mn 3*s* peaks for several samples.

XPS data for Co 2p, Mn 2p and Mn 3s are shown in Figure 2 with peak information found in Table 2. Despite changes in stoichiometry, overlapping spectra for various samples of both the Co 2p and Mn 2p spectra show that their peak shapes are nearly identical when normalized, with  $2p_{1/2}$  and  $2p_{3/2}$  peaks at the same location. All Co 2p spectra possess a satellite peak on the high binding energy side of the Co  $2p_{3/2}$  peak that is characteristic of the Co<sup>2+</sup> valence state [44]. The Mn 2s and Co L<sub>3</sub>M<sub>23</sub>M<sub>45</sub> Auger regions overlap with Co 2p and

**Table 2.** XPS Co and Mn  $2p_{3/2}$  peak positions and Mn 3*s* multiplet separation values with valence state references [43].

	Peak pos	sition (eV)	Separation	
Stoichiometry	Co 2 <i>p</i> <sub>3/2</sub>	Mn 2p <sub>3/2</sub>	Mn 3s (eV)	<b>Mn<sup>2+</sup> Ref:</b> 5.68 eV
<i>x</i> = 0.04	781.7(1)	641.9(1)	_	<b>Mn<sup>3+</sup> ref:</b> 5.26 eV
x = 0.14	781.7(1)	642.0(1)	5.2(2)	
x = 0.23	781.6(1)	641.8(1)	5.2(2)	<b>Mn<sup>4+</sup> ref:</b> 4.53 eV
x = 0.24	781.8(1)	642.0(1)	5.2(2)	

contribute to a feature on the low binding energy side of each Co  $2p_{3/2}$  peak located from about 778 eV to 770 eV. All Mn 2p spectra suggest a Mn<sup>3+</sup> valence state due to the absence of an isolated satellite peak between the Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$ peaks (Figure 2(b)), although delineation between  $Mn^{3+}$  and Mn<sup>4+</sup> can be challenging for this region [44]. The binding energy separation between the multiplet peaks of Mn 3s can also be used to more readily identify Mn valence [43]. Fits to the Mn 3s peak for all CMO samples agree well with a 3+ formal charge (Figure 2(c), Table 2). The XPS data indicate that the CMO samples have identical cation valences despite changes in cation stoichiometry. Introducing excess Co would be expected to produce either a Co<sup>3+</sup> ion on an octahedral site or charge transfer to yield a Co<sup>2+</sup> and Mn<sup>4+</sup> octahedral pair [11, 45], which could lead to a hole on the Mn site. However, XPS shows static Co<sup>2+</sup> and Mn<sup>3+</sup> valence states with increasing Co. Excess Co remains as  $Co^{2+}$  regardless of whether it is tetrahedral or octahedrally coordinated.

To better understand the structural and chemical effects of substituting Co for Mn in the system, we performed XANES and EXAFS measurements on the x = 0.04 and x = 0.14samples. Co and Mn K-edge XANES data of two CMO samples are shown in Figures 3(a) and (b). Since our RHEED and XRD data show single-crystalline films, polarizationdependent measurements follow selection rules for different transitions from the Mn and Co 1s states. The line shape differences-linear dichroism-between the in-plane and outof-plane polarizations are due to the tetragonal structure asymmetry of CMO from the JT effect, with the Mn region showing particularly large dichroism. To our knowledge, there have been no previous reports of polarization-dependent K-edge measurement on single-crystals of either CMO or related JT-active Mn<sub>3</sub>O<sub>4</sub>. Pre-edge peaks (labeled 'B') at  $\sim$ 6540 eV are consistent with predictions for JT-distorted Mn<sup>3+</sup> in Mn<sub>2</sub>O<sub>3</sub> and MnOOH [46]. All Mn K-edge data also show a large pre-edge feature at  $\sim$ 6550 eV (labeled 'C') to the left of the usual K-edge peak location (labeled 'D'). We could find no report of such a feature in polarized Mn K edge XANES, including theoretical models of many different Mn minerals [46]. Tetragonal LaSrMnO<sub>4</sub> with Mn<sup>3+</sup> valence exhibits polarization-dependent dichroism, but no 'double peak' feature like we observe here [47]. The feature is most reminiscent of polarization-dependent effects in tetragonal ferroelectric titanates, including PbTiO<sub>3</sub> and BaTiO<sub>3</sub> [48]. We tentatively attribute this feature to degeneracy breaking of the unoccupied Mn 4p states due to the JT distortion such that Mn  $4p_z$  states accessible with perpendicularly-polarized x-rays lie at lower energy than the  $4p_x$  and  $4p_y$  orbitals. The inplane measurements on both films are similar to what has been observed in NiMn<sub>2</sub>O<sub>4</sub> inverse spinel films with a primarily Mn<sup>3+</sup> valence [49].

As is the case with the XPS data, changes in sample stoichiometry had minimal effect on the XANES spectra. This suggests that there are no significant changes in the chemical coordination or electronic valence due to varying stoichiometry, at least up to the x = 0.14 excess Co threshold. The Co<sup>2+</sup> and Mn<sup>3+</sup> cation valences determined in XPS are also supported by inspecting XANES. Cation K-edges shifted toward higher photon energies indicate a higher cation valence state, and the in-plane-polarized Co and Mn K-edges of CMO are close to those of CoO (Co<sup>2+</sup>) and  $Mn_2O_3$  (Mn<sup>3+</sup>) oxide [50, 51], respectively. The Co K-edges of both samples exhibit relatively large pre-edge peaks at ~7708 eV (labeled 'A'). Tetrahedral symmetry enhances the hybridization of cation-oxygen bonds, increasing the prevalence of 4p/3d hybridization in unoccupied orbitals, which permits dipole transitions that contribute to pre-edge intensity. In the case of the normal spinel CMO, the lack of inversion symmetry in tetrahedra promotes hybridization of cation-oxygen bonds [52]. This pre-edge peak is seen in Co K-edges of  $Zn_{1-x}Co_xO$  in which Co atoms are also tetrahedrally coordinated [50, 53]. The peak intensity for each polarization on both samples is consistent with 100% tetrahedral coordination when compared to  $Zn_{1-x}Co_xO$  data. These results between samples suggests that the additional Co for the x = 0.14 sample remains in tetrahedral coordination. This leads to the idea that Co interstitials cause the c-lattice parameter to increase between x = 0.04 to x = 0.14.

From fits to the EXAFS data (S8), we calculate the nearestneighbor Co-O and Mn-O bond lengths for both the in-plane and out-of-plane polarizations (Table 3). There are no appreciable differences between the two stoichiometries, indicating that introducing excess Co into CMO hardly affects bond lengths. There is no significant variation in the Co-O bond lengths between the two polarizations, which would follow from a nearly undistorted tetrahedral coordination of the Co atoms. We see no evidence of Co occupation in octahedral sites in the lattice. As would be expected from the JT distortion of Mn<sup>3+</sup>, out-of-plane Mn–O bond lengths are larger than in-plane ones. The EXAFS bond lengths are compared to the combined Shannon crystal radii of the cation-oxygen bond [54] and the structure results from XRD on powder CMO [55]. The Co–O combination is consistent with bond lengths from EXAFS, while the Mn-O combination lies between the in-plane and out-of-plane bond lengths from EXAFS. This



**Figure 3.** (a) Co *K* and (b) Mn *K* edge XANES for in-plane (parallel) and out-of-plane (perpendicular) polarizations; (c) Co and (d) Mn EXAFS extracted from XANES data in (a) and (b). Insets show pre-edge peak close-ups for both Co and Mn XANES extracted from XANES data in (a) and (b). Insets show pre-edge peak close-ups for both Co and Mn XANES.

indicates that the octahedra experiences not only elongation along the *c*-lattice parameter, but also in-plane compression. The Mn–O bond lengths we report from EXAFS are also similar to those reported in LaSrMnO<sub>4</sub>, which were 1.90(1) Å in-plane and 2.27(3) Å out-of-plane [47]. We note that the bond lengths may be affected slightly by the epitaxial strain between substrate and film, which would induce a slight in-plane reduction and out-of-plane expansion of the bond lengths.

To better understand the electronic properties of stoichiometric CMO, we employed DFT + U models with different spin configurations, ranging from ferromagnetic systems ( $M_{\rm FM} = 12\mu_{\rm B}$  per formula unit) to antiferromagnetic ( $M_{\rm AFM} = 0$ ). CMO is known to be ferrimagnetic at lower temperatures and exhibits paramagnetism at room temperature [19, 55, 56]. While several features were similar across the different magnetic phases/structures (e.g. an indirect band gap for both spin populations), our description focuses predominately on the low-temperature ferrimagnetic phase  $(M = 3\mu_{\rm B})$ , in which Mn atoms alternate between spin-up and spin-down, while Co atom spins are all parallel, to approximate the electronic structure. The in-plane lattice parameter found from first principles is 8.18 Å while the *c*-lattice parameter (c = 9.35 Å) presents in reasonable agreement with that obtained from XRD data. Figure 4 shows the projected density of states (DOS) and band structure of the ferrimagnetic case. An indirect band gap of approximately 0.8 eV is observed for the ferrimagnetic case. Band gaps ranged from approximately 0.5 eV (in the AFM case) up to approximately 0.8 eV in the ferrimagnetic model. The valence band in all cases arises as a result of the hybridization of the  $3d_{z^2}$ -orbitals of Mn or Co, and O-*p* bands as observed in Figure 4(b). The conduction band, in contrast, is formed by contributions from Mn-3 $d_{x^2-y^2}$ , O- $p_x$ and  $O-p_{y}$ . Orbital-projected band diagrams for the Co d bands are shown in the supplemental information (S9).

Figure 5 shows the dielectric (Figure 5(a)) and optical absorption (Figure 5(b)) of the CMO samples derived from fits

**Table 3.** Co–O and Mn–O nearest neighbor bond lengths from EXAFS fits, as well as the combined crystal radii [54] and XRD results of powder CMO [55] for reference.

0 1	In-plane (Å)		Out-of-plane (Å)		Crystal radii (Å)		XRD reference (Å)	
Sample	Co-O	Mn–O	Co-O	Mn–O	Co-O	Mn–O	Со-О	1.967
x = 0.04 x = 0.14	1.97(1) 1.97(2)	1.91(2) 1.91(2)	1.96(1) 1.96(1)	2.22(1) 2.23(1)	1.96	2.02	Mn–O, In Mn–O, out	1.965 2.227



**Figure 4.** Electronic properties for the ferrimagnetic system  $(M = 3\mu_B)$  (a) Spin-polarized projected density of states indicating contributions from Mn (blue), Co (green) and O (red) localized atomic orbitals. Spin polarized band structure for spin majority (left) and minority (right) denoting contributions from: (b) Mn  $d_{z^2}$  (blue) and O  $p_z$  (red); (c) Mn  $d_{x^2-y^2}$  (blue), O  $p_x$  and O  $p_y$  (red). The Fermi energy is placed at the valence band edge.

to the SE data. All samples show similar absorption behavior regardless of stoichiometry differences, implying similarities in optical band gaps and electronic structure. Absorption features are located at similar photon energies, with no additional peaks appearing due to either free carriers (Drude response [57]) or optical transitions from different cation site occupancy. Two clear absorption peaks (inset to Figure 5(b)) are centered around 0.8 eV and 1.9 eV, respectively. Figure 5(c) shows the XPS valence spectrum of a CMO sample.

In relating experiment to theory, we qualitatively compare the ellipsometry data to the DFT + U model of the ferrimagnetic case. The two absorption peaks likely represent transitions within the minority spin DOS, while the rise in intensity at higher energy represents allowed oxygen 2p to cation 3dtransitions. The peak at 0.8 eV can be paired with the model's transition from the hybridized Mn  $3d_{z^2}$ –O  $p_z$  valence band to the unoccupied Mn  $3d_{x^2-y^2}$ –O  $p_{x/y}$  conduction band. Meanwhile, the peak at 1.9 eV can be paired with the transition from the Co-dominated minority valence band density around -0.8 eV to Co states in the conduction band. The narrow nature of these two optical transitions observed suggests that the Co and Mn *d* states may be more localized than the DFT model indicates. The strongest peak at  $\sim$ 3 eV binding energy likely corresponds to the large Co majority spin intensity at -2 eV in Figure 4(a).

Our spectroscopic characterization results indicate that CMO exhibits little change in properties with increases in Co concentration from stoichiometric CoMn<sub>2</sub>O<sub>4</sub>. However, XRD shows the c-lattice parameter to increase from ideal  $Co_{1+x}Mn_{2-x}O_4$  at x = 0.04 to x = 0.14, and then decrease with higher Co content at x = 0.23 and x = 0.24. XPS and XANES show static cation valences of Co<sup>2+</sup> and Mn<sup>3+</sup> despite changes in stoichiometry. This suggests that point defects induced during growth may drive changes in the system to preserve the Co<sup>2+</sup> and Mn<sup>3+</sup> formal charges instead of forming either an octahedrally-coordinated Co<sup>3+</sup> ion or charge transfer to produce octahedral Co<sup>2+</sup> and Mn<sup>4+</sup>. XANES and EXAFS indicate that additional  $Co^{2+}$  ions are tetrahedrally coordinated at least up to x = 0.14, even though all tetrahedral lattice sites are filled. Co-O bond lengths from EXAFS remain almost unaffected by increased Co concentration, whereas octahedrally coordinated Co<sup>2+</sup> should show variation since it is thought to be JT-active [27, 28]. We believe that tetrahedral Co interstitials cause this c-lattice parameter increase with increasing Co from x = 0.04 to x = 0.14.

For additional  $Co^{2+}$  to remain tetrahedrally coordinated in the crystal, two types of point defects to consider are  $Co^{2+}$ interstitials and Mn<sup>3+</sup> vacancies. An interstitial Co<sup>2+</sup> requires Co–O bond lengths of  $\sim 1.96$  Å in tetrahedral coordination, as seen from EXAFS. For this, there are 48 sites per conventional unit cell that are available depending on the tilting and bond angles of their surrounding polyhedral. In the case of no oxygen defects, charge balancing dictates that for every three  $Co^{2+}$ interstitials there must be two Mn<sup>3+</sup> vacancies. Oxygen vacancies and interstitials should also be considered, but they are unlikely if we assume cation coordination is unchanged. There are no sites for oxygen interstitials that would leave Co or Mn coordination unaffected. Oxygen vacancies would change Co coordination since every lattice oxygen contributes to the tetrahedral geometry of existing  $Co^{2+}$ . Interestingly, we see no evidence of degradation in RHEED patterns with increasing Co concentration, so the crystal is seemingly tolerant of such point defects.



**Figure 5.** (a) SE data for various x values showing index of refraction *n* and extinction coefficient *k*. (b) Absorption coefficient for all 4 samples; (c) valence band XPS data for x = 0.14.

XRD shows the *c*-lattice parameter to decrease from x = 0.14 to x = 0.24 which would not follow from tetrahedral Co interstitials. It is more likely that in this higher-Co regime, excess Co<sup>2+</sup> replaces Mn<sup>3+</sup> in octahedral sites, although we lack XANES/EXAFS data for samples with greater Co, x = 0.23 and x = 0.24. With less JT-active Mn<sup>3+</sup> octahedra, the *c*-lattice parameter would decrease. Tetrahedral Co interstitials could still be present in the higher-Co samples, but it seems there is a threshold between x = 0.14 and x = 0.23 in which cation substitution takes place.

While our films are single-crystalline as determined through RHEED and XRD, MCO nanoparticles have been seen to phase segregate into CMO and  $Co_3O_4$  spinel [12]. It is possible that at our MBE growth conditions, there is a high-Co threshold in which extra Co would spill over to create Co<sub>3</sub>O<sub>4</sub> after filling available interstitial sites in CMO. There could also be a range of differing growth conditions in which this phase-segregation occurs with a low likelihood of Co interstitials forming. In particular, higher oxygen reactivity may encourage this phase-segregation by allowing excess Co to form Co<sub>3</sub>O<sub>4</sub> rather than filling interstitial sites in CMO. There could also be a range of differing growth conditions in which any excess Co would lead to increased cation valences either by forming Co<sup>3+</sup> or transferring charge to form Mn<sup>4+</sup>. This should also be more likely at greater oxygen reactivities and might allow for a seamless transition from CMO to MCO without encouraging Co interstitials or phase segregation. Indeed, cation interstitials in CMO decreased as oxygen reactivity during growth increased [58]. Since MCO is predominately an inverse-type spinel [29, 35-37], a transition from CMO to MCO would see Mn remain in octahedral coordination and some Co turn to octahedral coordination. Since MCO has a cubic structure [32], it should be the case that there are no JT-active Mn<sup>3+</sup> octahedra that cause distortion. This suggests that the cation valences of single-crystal MCO would be Mn<sup>4+</sup> and  $\mathrm{Co}^{2+}$  as opposed to  $\mathrm{Mn}^{2+}$  and  $\mathrm{Co}^{3+}$ , and that a seamless transition from CMO to MCO would see an increase in Mn valence rather than Co valence. In the case of an increasing Mn valence, the c-lattice parameter would be expected to decrease since it is octahedrally coordinated Mn<sup>3+</sup> that favors JT distortion. In fact, the JT distortion may be a significant driving force preventing the formation of Mn<sup>4+</sup> states, as this ionic configuration would be energetically unfavorable in the tetragonal structure.

#### 4. Conclusion

In this study we demonstrated the first growth of single crystal  $Co_{1+x}Mn_{2-x}O_4$  spinel thin films with stoichiometries that range from ideal to increased Co. The structural and electronic properties of the samples were analyzed using an array of techniques that include in-situ XPS, XRD, STEM, XANES, EXAFS and SE. Co and Mn cations show consistent 2+ and 3+ valences across all stoichiometries. Additional Co causes Co and Mn cations to remain tetrahedrally and octahedrally coordinated, respectively, up to x = 0.14, then causes Mn to be substituted by Co in octahedral sites up to x = 0.24. All samples exhibit similar optical absorption behavior and cation-oxygen bond lengths. The fact that the electronic properties of these materials are barely affected by the replacement of Mn<sup>3+</sup> with Co<sup>2+</sup> may be attributed to the introduction of Co interstitials and Mn vacancies. This suggests that CMO's impressive ORR catalytic properties [1, 11, 13, 14] would be evident with various Co<sup>2+</sup>/Mn<sup>3+</sup> stoichiometries, potentially making it more stable under electrochemical conditions. It is possible that there is a high-Co threshold or differing set of growth conditions in which extra Co may form a secondary phase of Co<sub>3</sub>O<sub>4</sub> as seen with MnCo<sub>2</sub>O<sub>4</sub> [12], or lead to a smooth transition from CoMn<sub>2</sub>O<sub>4</sub> to single crystal MnCo<sub>2</sub>O<sub>4</sub>.

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