

Review

Recent Advances of Colossal Magnetoresistance in Versatile La-Ca-Mn-O Material-Based Films

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Abstract: Hole-doped manganese oxides exhibit a gigantic negative magnetoresistance, referred to as colossal magnetoresistance (CMR), owing to the interplay between double-exchange (DE) ferromagnetic metal and charge-ordered antiferromagnetic insulator/semiconductor phases. Magnetoresistive manganites display a sharp resistivity drop at the metal–insulator transition temperature (T^{MI}). CMR effects in perovskite manganites, specifically $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ (La-Ca-Mn-O or LCMO), have been extensively investigated. This review paper provides a comprehensive introduction to the crystallographic structure, as well as the electronic and magnetic properties, of LCMO films. Furthermore, we delve into a detailed discussion of the effects of epitaxial strain induced by different substrates on LCMO films. Additionally, we review the early findings and diverse applications of LCMO thin films. Finally, we outline potential challenges and prospects for achieving superior LCMO film properties.

Keywords: La-Ca-Mn-O; thin films; manganite; magnetron sputtering; colossal magnetoresistance



Academic Editors: Lucian Petrescu and Catalin-Daniel Constantinescu

Received: 17 December 2024

Revised: 14 January 2025

Accepted: 15 January 2025

Published: 16 January 2025

Citation: Boora, N.; Ahmad, R.; Rahman, S.; Dung, N.Q.; Ahmad, A.; Alshammari, M.B.; Lee, B.-I. Recent Advances of Colossal Magnetoresistance in Versatile La-Ca-Mn-O Material-Based Films. *Magnetochemistry* **2025**, *11*, 5. <https://doi.org/10.3390/magnetochemistry11010005>

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1. Introduction

The discovery of high-temperature superconductivity rekindled interest in magnetoresistive perovskite oxides. The term ‘colossal magneto-resistance (CMR)’ has gained relevance, as it distinguishes the significant negative magnetoresistance observed in perovskite-based manganite from the giant magnetoresistance (MR) observed in transition metal systems, such as in granular or multilayer forms. The MR in manganite around the Curie temperature (T_C) was already known [1]. Searle and Wang first reported the magnetic-field dependency of resistivity in 1969 [2]. Subsequently, this phenomenon was elaborated upon in theoretical works [3–6]. The rediscovery of CMR phenomena and the intriguing magnetic-field-induced insulator–metal (I-M) or lattice–structural transitions have rekindled interest in MR within perovskite oxides. In the current context, perovskite manganites stand out as superior materials that exhibit I-M transitions or versatile electronic–lattice

structural changes when subjected to external factors, such as a magnetic field, light irradiation, electron-beam irradiation, X-ray irradiation, or current injection.

CMR perovskite oxides exhibit a distinguished phenomenon of MR, which occurs near T_C as a magnetic field induces paramagnetic–ferromagnetic (P-F) transitions, metal–insulator transitions, and lattice–structural transitions [1]. MR is the percentage change in electrical resistance under an applied external magnetic field and is calculated using Equation (1).

$$MR(T) = \frac{\rho(H, T) - \rho(0, T)}{\rho(0, T)} \quad (1)$$

where $\rho(0, T)$ and $\rho(H, T)$ represent resistivities in the absence and presence of applied magnetic fields at a fixed temperature. The resistivity at low temperatures exhibits metallic behavior in terms of magnitude and temperature dependence. As temperature increases, resistivity rises until it reaches a metal–insulator transition temperature (T^{MI}). Beyond T^{MI} , resistivity decreases. Manganite materials exhibit numerous exotic properties such as CMR, phase coexistence at T^{MI} , charge ordering, the magnetocaloric effect, multiferroicity, and half-metallicity, making them promising candidates for spintronic applications. There is a sharp decrease in resistivity near the T^{MI} . These materials demonstrate higher MR values just below room temperature (RT) ($260\text{ K} < T_C < 280\text{ K}$). Mixed-valence oxides are rich in physics related to electron–lattice interaction and electron–electron interaction. The magnetic, electrical, and structural properties of these oxides are inherently interconnected. The geometry of the MnO_6 octahedra plays a significant role in governing the remarkable physics of manganite materials.

The generated strain induces the elongation, rotation, and compression of the octahedral geometry in manganite materials, resulting in the splitting of d-orbitals. Consequently, a reconstruction of complex orbitals takes place within manganite materials by altering the electron occupancy. The double-exchange (DE) mechanism effectively explains this striking phenomenon in hole-doped manganese oxides.

The La-Ca-Mn-O (LCMO) structures, both in bulk and as thin films, are of significant importance due to their unique structural, magnetic, and electronic properties, which make them ideal for various technological applications. In bulk form, LCMO structures are essential for their CMR, metal–insulator transition, and DE mechanism, which govern their magnetic and electronic properties. These features make LCMO valuable for magnetic sensors, memory devices, and magneto-electronic applications, providing high spin polarization and tunable transport behavior critical for advanced materials research and device technologies [7–9]. To validate practical applications, high-quality epitaxial thin films of these materials are required. Additionally, tailoring their magneto-transport and electrical properties through doping and substrate modification is crucial for achieving higher MR values and T_C around or above RT. Hole-doped manganese oxides or mixed-valent manganites [$RE_{1-x}A_xMnO_3$, where RE and A represent trivalent rare earth and divalent alkaline earth elements, respectively] have been recently reviewed [7–10]. In this context, different concentrations of x result in an anti-ferromagnetic insulator phase at high and low concentrations, whereas a specific concentration centered around $x = 1/3$ leads to a ferromagnetic metallic phase [11]. Recently, CMR oxides have found applications in highly sensitive magnetic field sensors, making them excellent materials in demand for the read-heads of magnetic memory devices.

In this review, we discuss the physical origin of CMR using the DE and Jahn–Teller (J-T) distortion mechanisms. We also review various fabrication techniques for depositing La-Ca-Mn-O (LCMO) films on different substrates, revealing changes in their magneto-transport properties for potential device applications. Furthermore, we include future prospects, along with potential challenges for the development of superior LCMO films.

2. Structure, DE Mechanism, and J-T Distortion

2.1. Crystallographic Structure

Perovskite structures are exhibited in two forms: halide and oxide. Halide perovskites are mainly studied in optoelectronic and photovoltaic applications due to their wide tunable bandgap [12]. Oxide perovskites, such as LCMO and their composites, are primarily investigated for magnetic characteristics like CMR [1]. The structure of $\text{RE}_{1-x}\text{M}_x\text{MnO}_3$ manganese oxide is very similar to cubic perovskite, where large-sized trivalent rare earth metal ions and divalent ions (M) occupy the A-site with 12-fold oxygen coordination. Meanwhile, smaller-sized manganese ions in the $\text{Mn}^{3+}\text{--Mn}^{4+}$ state occupy the B-site with 6-fold coordination, located at the center of oxygen octahedra (Figure 1). The concentration of Mn ions with valencies of 3^+ and 4^+ is represented by $1 - x$ and x , respectively, in this stoichiometric oxide. The structure of perovskite oxide is determined by the tolerance factor (t), defined by Equation (2).

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)} \quad (2)$$

where t should fall within the range of $0.89 < t < 1.02$. At $t = 1$, a perfectly cubic structure forms, while perovskite exhibits orthorhombic or rhombohedral symmetry structures at low temperatures (from near zero degrees Celsius down to cryogenic temperatures (-196°C) [13]. The parameter t measures the lattice-matching of the AO and BO_2 planes. LCMO displays ferromagnetic ordering in the Mn-O layers (magnetic), which are separated by non-magnetic La (Ca)-O layers [14].

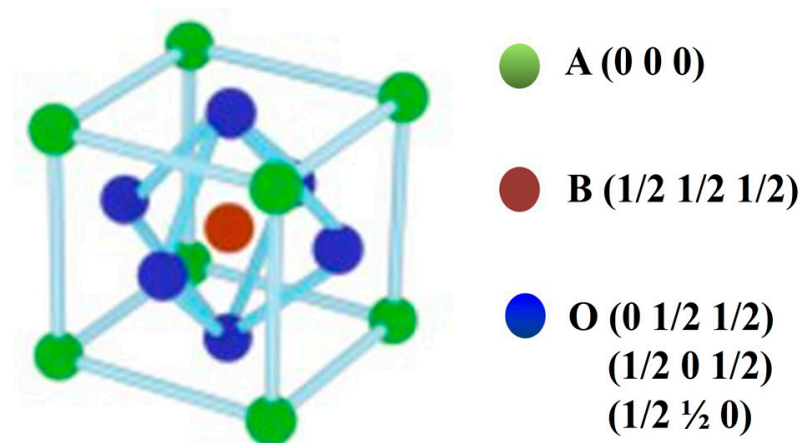


Figure 1. A schematic of the cubic perovskite structure.

The composition and crystallographic structure of La-Ca-Mn-O (LCMO) significantly influence its magnetic, electronic, and transport properties, which are essential for its use in advanced technological applications [8,9]. For example, the doping level of calcium (x in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$) determines the ratio of Mn^{3+} to Mn^{4+} ions, which directly controls the DE mechanism responsible for ferromagnetism and metallic conductivity [8]. At an optimal doping level around $x \approx 0.33$, LCMO exhibits maximum CMR and a high T_C , making it ideal for magneto-electronic devices. Variations in composition, such as substituting La with other rare-earth elements or Ca with different alkaline earth metals, allow for the tuning of properties like T_C and resistivity to meet specific design requirements. Additionally, the crystallographic structure—whether orthorhombic, tetragonal, or rhombohedral—affects the material's electron bandwidth and lattice distortions, which influence the magnetic ordering and metal–insulator transition temperature. Structural factors like the tilt and bond angle of MnO_6 octahedra play a critical role in determining the efficiency of electron

hopping and the strength of magnetic interactions [10,14]. Therefore, precise control over both composition and structure is crucial for optimizing LCMO's performance in applications such as spintronics, memory devices, and magnetic sensors.

2.2. Crystallographic Structure and 3D-Orbitals of Mn^{4+} and Mn^{3+} Ions Determining the Magnetic Properties of LCMO

In cubic perovskite, for an isolated ion, the crystal field of the 5-fold degenerate d-orbitals splits into 3 low-energy t_{2g} orbitals (d_{xy} , d_{yz} , d_{zx}) and 2 high-energy e_g orbitals ($d_{x^2-y^2}$, $d_{3z^2-r^2}$), as explained in Figures 2 and 3. In these figures, the t_{2g} electrons are localized, whereas the e_g electrons are itinerant, hence creating band energy. The correlation between t_{2g} and e_g states is elucidated by the Zener and DE mechanisms, as shown in Figures 4 and 5 [15]. The DE mechanism describes the back-and-forth movement of electrons from Mn^{3+} to oxygen atoms and from oxygen atoms to Mn^{4+} , thereby enabling conduction in these oxide materials. In the DE mechanism, the transfer of an electron from Mn^{3+} to O^{2-} and from O^{2-} to Mn^{4+} takes place, as depicted in Figure 4. The magnetic properties of LCMO are influenced by an exchange interaction between Mn^{4+} and Mn^{3+} ions. Generally, Mn^{4+} -O- Mn^{4+} interactions were observed to be anti-ferromagnetic, whereas Mn^{3+} -O- Mn^{3+} interactions were noted to be sometimes ferromagnetic and anti-ferromagnetic, and Mn^{3+} -O- Mn^{4+} interactions were reported to be ferromagnetic.

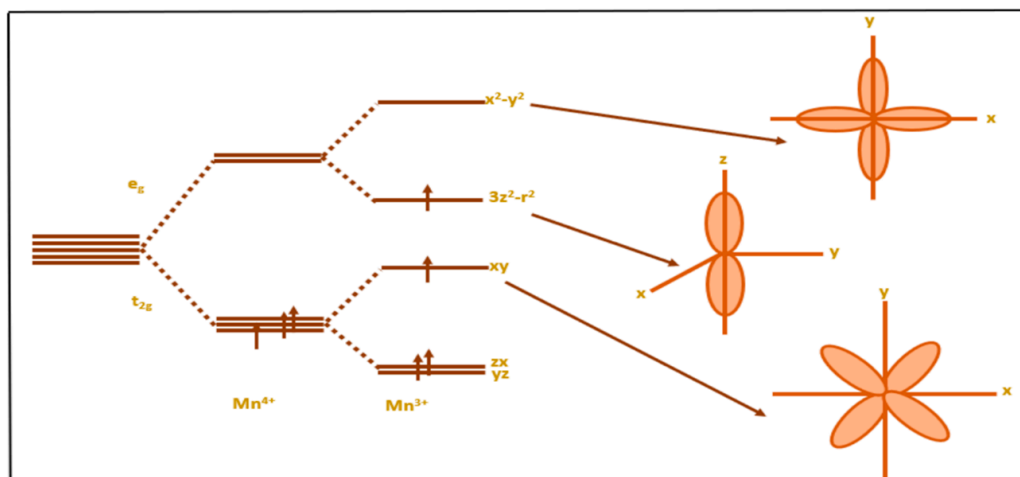


Figure 2. Orbitals and energy levels of Mn^{4+} and Mn^{3+} .

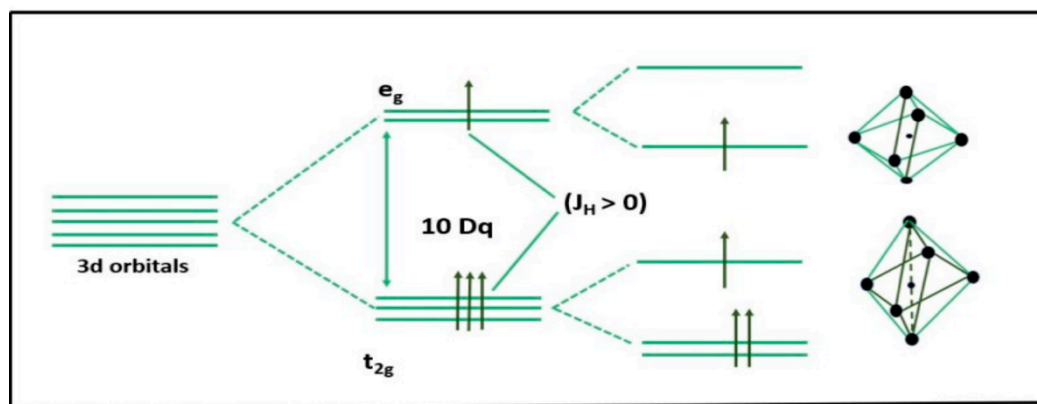


Figure 3. The crystal-field splitting of the 5-fold degenerate, split into lower t_{2g} and higher e_g levels.

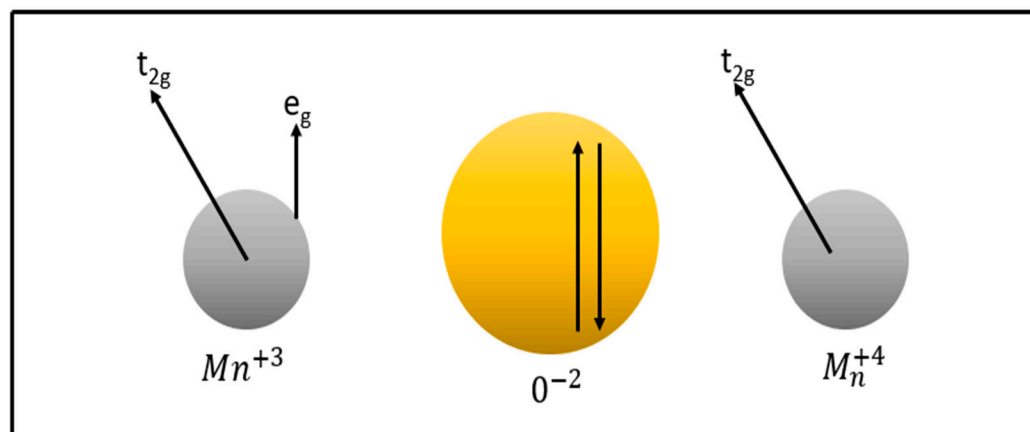


Figure 4. A schematic of the Zener pair.

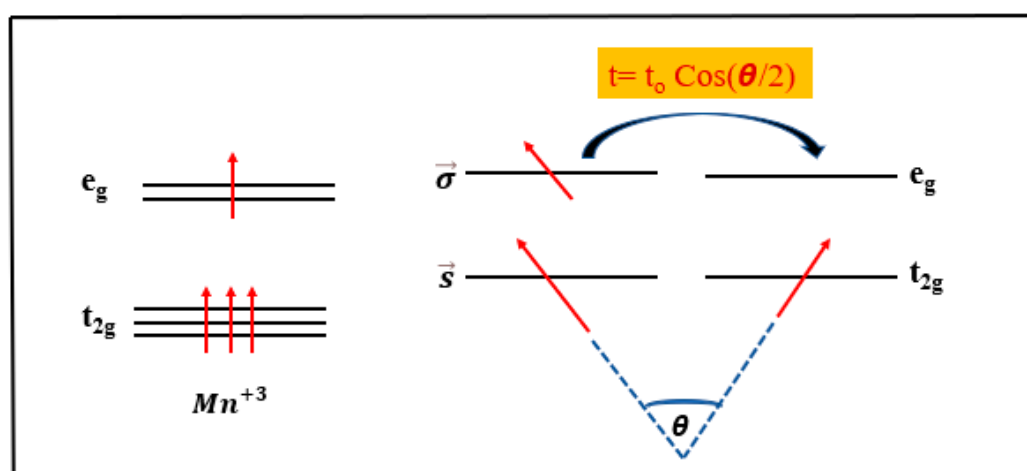


Figure 5. Schematic showing DE mechanism.

Essentially, two kinds of distortions occur in the ideal bulk perovskite structure. First, there is a rotational-like distortion in MnO_6 octahedra, which arises due to the mismatch in the averaged ionic radii r_A of A-site materials and the ionic radius r_{Mn} of manganese ions. Second, there are J-T distortions in Mn^{3+}O_6 octahedra, resulting from strong electron-phonon coupling. Lattice–substrate mismatch can also induce strain. The holes in Mn^{4+} cause DE interactions, coupling conductivity with magnetism. In contrast, the J-T distortions in Mn^{3+} ions couple the lattice and magnetism, resulting in the intimate intertwining of electronic, lattice, and magnetic degrees of freedom. The J-T coupling lifts d-orbital degeneracy and stabilizes the energy levels of the occupied d electrons by deforming the metal–ligand (Mn–O) octahedron. Mn^{3+} ions ($3d^4$) found in octahedral coordination are one example. Conduction electrons are subject to the J-T effect, which spontaneously deforms the MnO_6 octahedron. The probability of e_g electron transfer from Mn^{3+} to Mn^{4+} is calculated using the effective transfer integral, as expressed in Equation (3).

$$t = t_0 \cos(\theta/2) \quad (3)$$

where θ represents the angle between core spins. When θ is 180° between the spins, collinear ferromagnetism occurs (as shown in Figure 4). If θ deviates from 180° (as illustrated in Figure 5), at angles lower than 144° , no further exchange will occur. The maximum exchange occurs at around 174° ; beyond that point, the spins become locked, and there is no transfer between these two core spins.

Mn^{3+} possesses degenerate 3d orbitals, which, in a crystal field, split into three t_{2g} and one e_g orbital. In cases with undistorted cubic MnO_6 octahedra, when one e_g electron transfers to the Mn^{4+} site, distortion begins between the e_g orbitals. Consequently, the e_g orbitals further split into $3z^2 - r^2$ and $x^2 - y^2$, resulting in a reduction in symmetry during this hopping process. Thus, the octahedra experiences additional distortion when such hopping takes place.

The conducting electrons are responsible for conduction but are now influenced by this lattice distortion, leading to the formation of polarons. A polaron, larger than an electron, moves slowly. Consequently, the metal gradually transforms into an insulator. To inhibit polaron formation, a magnetic field is applied, initiating ferromagnetic ordering and leading to the attenuation of the insulating state.

The $\text{La}_{1-x}\text{Ca}_x\text{MnO}_{3-\delta}$ composite ($x \geq 0.5$) exhibits an orthorhombic perovskite structure, with the Pnma space group across the entire substitutional range at temperatures below 700 K. This structure closely resembles the CaMnO_3 structure. Four types of basic distortions can lead to symmetry reduction compared to the cubic perovskite:

1. Rotations of MnO_6 octahedra around the cubic [101] or [010] directions;
2. J-T distortion of octahedra;
3. Distortions arising due to the presence of electrons in the degenerate e_g orbital of the Mn^{3+} ion;
4. Shifts in A-site atoms.

In the case of CaMnO_3 , the rigid octahedra model is validated, since CaMnO_3 contains non-J-T Mn^{4+} ions. Consequently, structural distortion determines octahedra tilting. However, the substitution of La^{3+} for Ca^{2+} at room temperature generates two pairs of Mn-O bonds with varying lengths, leading to the deformation of MnO_6 octahedra [16].

A ferromagnetic metallic phase with $T_C \approx 300$ K is necessary for practical applications. According to the mean-field approximation, T_C is approximately $2x(1-x) - x^2$, and it reaches its maximum around $x = 1/3$ [1]. Hence, in perovskite oxide materials, ferromagnetic phases are typically found within a certain range of doping, particularly around $x = 1/3$. In contrast, anti-ferromagnetic (AF) phases are found in other regions. For spintronic applications, it is essential to have a ferromagnetic and metallic phase with T_C around RT. The half-metallic ferromagnetic properties of this metallic oxide's spin-polarized conduction band hold significant potential interest.

The electronic structure of LCMO has been investigated theoretically [17–20]. In the lanthanum calcium manganite series ($\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$), at a calcium content value of around $x = 0.01$, there is a transition from a canted anti-ferromagnetic state to a ferromagnetic insulator state. With further doping of calcium, this ferromagnetic insulator state changes into a ferromagnetic metallic state, which is of particular interest from an application perspective. In the specific range of $x = 0.2 - 0.5$, there is a considerable decrease in resistance, and for the nominal calcium composition at $x = 0.33$, the ferromagnetic transition reaches its maximum (as shown in Figure 6) [21]. Subsequently, it begins to diminish, influenced by another significant domain, which could be either charge-ordered or anti-ferromagnetically ordered. Thus, the system does not necessarily remain in a metallic state for an extended period. There is a critical composition that incidentally occurs at $x = 0.5$, and beyond 0.5, there continues to be some degree of magnetic exchange, albeit in the opposite direction. In other words, the system alternates between ferromagnetic and anti-ferromagnetic states and displays an unusual charge-ordered manganite state.

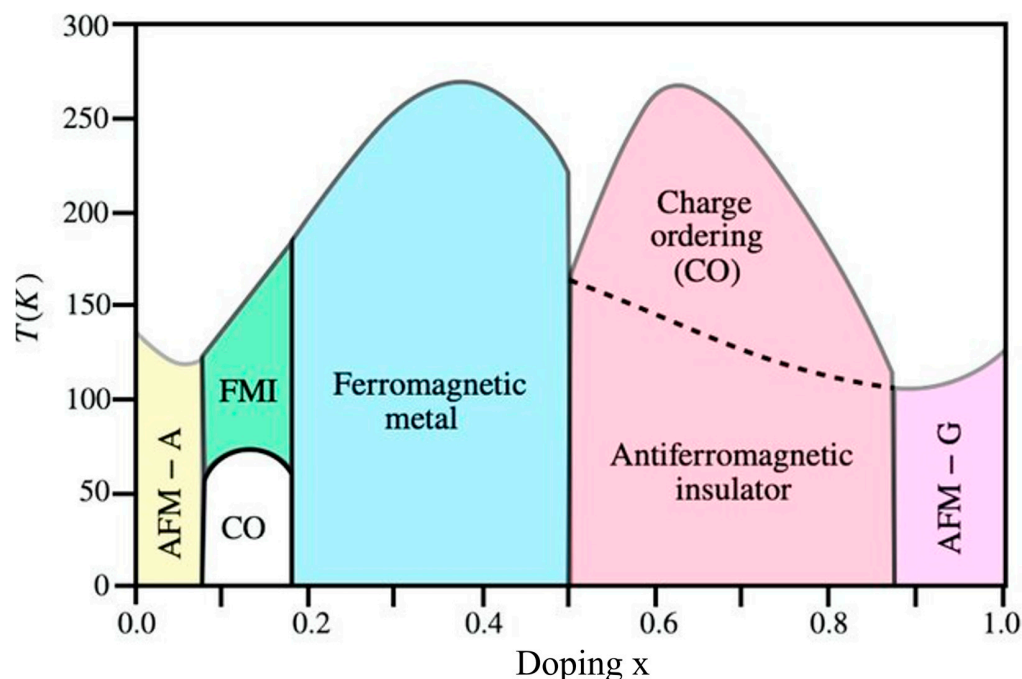


Figure 6. Shows the maximum ferromagnetic transition around $x = 0.33$. Adapted from [21], copyright 2024, Elsevier.

2.3. Electrical Transport/Resistivity

2.3.1. Insulating Region

Resistivity is a thermally activated process where electrons become excited into the conduction band due to temperature effects. In the paramagnetic phase, the resistivity of manganites exhibits a strong temperature dependence, which can be explained using various temperature-dependent resistivity [$\rho(T)$] laws stated in Equations (4)–(7) [22].

(i) Thermal activation law:

$$\rho(T) = \rho_{\infty} \exp\left(\frac{E_0}{k_B T}\right) \quad (4)$$

where a typical gap is approximately 0.1 eV, E_0 represents the activation energy, and k_B is the Boltzmann constant. Jonker and Saten measured the resistivity of $\text{LaMnO}_3\text{-AMnO}_3$ ($A = \text{Ca, Sr, Ba}$). They observed linear resistivity when plotted as $\log(\rho)$ versus $1/T$ [23].

(ii) The hopping of adiabatic polarons: this is also a causal factor for conduction in the insulator region.

$$\rho(T) \sim T \cdot \exp\left(\frac{E_0}{k_B T}\right) \quad (5)$$

The activation energy of polaron-mediated conduction is given by Equation (6) [24]:

$$\rho(T) = \rho_0 \cdot \alpha \cdot T \cdot \exp\left(\frac{E_0}{k_B T}\right) \quad (6)$$

where ρ_0 represents the residual resistivity at 0 T. In most cases, α equals 1.6, indicating non-adiabatic small polaron hopping behavior, while in some cases, α equals 1.

(iii) The Mott variable-range hopping model: suggested by researchers, this is described by Equation (7), which best explains electron transport at low temperatures in manganese oxides when electronic states near the Fermi energy are localized [25–30]:

$$\rho(T) = \rho_{\infty} \exp \left[\left(\frac{T_0}{T} \right)^{\frac{1}{4}} \right] \quad (7)$$

These laws have several physical origins:

- (a) The existence of a pseudo-gap at the Fermi level in the paramagnetic (P) phase.
- (b) Local lattice distortion accompanying the movement of charge carriers (J-T polaron).
- (c) Localization of charge carriers due to magnetic disorder.

2.3.2. Conduction Regime

In the metallic region, the resistivity is well described by Equation (8).

$$\rho = \rho_0 + aT^2 \quad (8)$$

These materials exhibit large negative resistance known as CMR, which reaches its peak around T_C . The resistivity in the paramagnetic phase increases as the temperature decreases. In contrast, the resistivity in the ferromagnetic phase decreases with decreasing temperature, and the CMR increases as the T_C decreases, at least for a given doping concentration. The relationship between magnetization and resistivity in manganite materials is described by Equation (9).

$$\frac{\rho}{\rho_0} = 1 - C(M/M_{\text{SAT}})^2 \quad (9)$$

Additionally, the correlation between magnetization and resistivity can be interpreted using the variable-range hopping model, which incorporates a decrease in the localization potential with increasing M/M_{sat} . The experimental data of LCMO thin films were well fitted to the magnetization-dependent variable-range hopping law, as calculated using Equation (10).

$$\ln(\rho/\rho_{\infty}) = \left[T_0(1 - M/M_{\text{sat}})^2/T \right]^{1/4} \quad (10)$$

2.3.3. Low-Field Magnetoresistance

Perovskite manganites exhibit a colossal MR effect around T_C when subjected to an external magnetic field of a few tesla. In contrast, MR becomes negligible at temperatures lower than the paramagnetic–ferromagnetic transition temperature, although the magnetization remains close to saturation. Polycrystalline LCMO displays a low-field MR (LFMR), which increases with decreasing temperature and the reduction in the particle size of the manganite material. Size effects play a crucial role in the transition from LCMO ($\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$) microcrystals to nanocrystals, significantly influencing their structural, magnetic, and electronic properties [31–34]. As crystal size reduces to the nanoscale, phenomena such as quantum confinement, increased surface-to-volume ratio, and enhanced surface effects become dominant. These size-induced changes can lead to shifts in Curie temperature, modifications in magnetic anisotropy, and variations in spin polarization, all of which directly impact the performance of spintronic devices [33]. A thorough understanding and precise control of these size-dependent properties are critical for optimizing LCMO-based nanomaterials for cutting-edge technological applications [35].

3. La-Ca-Mn-O Thin Films

Many applications (i.e., electronics, spintronics, and magnetic sensor technologies) require single-crystal, high-quality epitaxial thin films with excellent magneto-transport and temperature coefficient of resistance (TCR) properties at room temperature. The term

magneto-transport properties refers to the behavior of the electrical transport properties of La-Ca-Mn-O films (like electrical resistivity, conductivity, and the Hall effect) under the influence of an external magnetic field [36,37]. Understanding magneto-transport properties is crucial for exploring and harnessing the electronic, magnetic, and optical behaviors of materials [33,35]. La-Ca-Mn-O thin films can be grown using various deposition techniques, including Radiofrequency (RF) magnetron sputtering, ion beam sputtering, chemical vapor deposition (CVD), co-evaporation, pulsed laser deposition (PLD), conventional sol-gel techniques, reactive sputtering, and spin-coating methods, among others [38–49]. The RF magnetron sputtering method is preferred for fabricating multicomponent layered films on larger substrates.

Recently, it has been discovered that it is possible to modify the properties of manganites through external perturbations without altering the chemical composition of the sample. Various results have shown that the magnetic domain structure, M-I transition, MR, and T_C of LCMO thin films are related to factors that induce different strain states. Notably, different substrates can induce various types and degrees of strain. The strain state in LCMO films usually depends on the film orientation, directly influencing surface morphology, growth, and magneto-transport properties.

The epitaxial strain in LCMO films induced by the mismatch between the film and substrate lattice affects the bond angle and bond length of Mn-O-Mn and Mn-O, respectively [50,51]. Substrate-induced strain in LCMO films can alter the bond length of Mn-O-Mn and the bond angle of Mn-O-Mn through compression, elongation, or MnO_6 octahedron rotation, thereby changing the ferromagnetism of manganese oxide films [52]. In-plane tensile strain induced by the substrate causes an increase in the bond length of Mn-O-Mn and a decrease in the bond angle of Mn-O-Mn. This, in turn, enhances the interaction in electron-phonon coupling, decreasing electronic hopping amplitude, and thus suppressing ferromagnetism and reducing the T_C of LCMO thin films [53].

Yeh et al. proposed a quantitative analysis of the magneto-transport properties in manganite thin films [54,55]. They demonstrated that magneto-transport properties are determined by J-T coupling-induced lattice polaron conduction at high temperatures ($T \rightarrow T^{\text{IM}}$). This effect can be further enhanced through substrate-induced lattice strain increases. The interplay between epitaxially grown films and the substrate plays a significant role in modifying the magneto-transport properties of the films and enhancing the magnetoresistive effect. Strain can be employed to control phase separation, subsequently increasing T_C . Thicker films release strain, leading to the formation of misfit dislocations due to the substantial energy associated with epitaxial strain. The substrate induces biaxial strain in films, altering the physical properties of the epitaxially grown films. Film growth dynamics and strain release mechanisms also contribute to changes in magnetic and electrical properties.

Strains generated at the film-substrate interface can result from the following factors:

1. Dissimilarities in the film-substrate lattice spacing during epitaxial growth.
2. Differences in thermal expansion coefficients between the film and substrate.
3. Structural transformations due to additional stress in the film.

The strain induced by differences in substrate lattice parameters and manganite properties is a critical factor and plays a pivotal role in controlling the size and fraction of ferroic phases, such as the ferromagnetic metal (FMM) and charge-ordered anti-ferromagnetic (CO-AFM) insulator, that coexist due to strong coupling between lattice, spin, and orbital degrees of freedom. Strain induces changes in Mn-O bond lengths and angles, subsequently altering electronic structures and electron hopping rates. The preference for orbital occupancy strongly depends on the type of strain, whether it is tensile or compressive.

Tensile strain, by enhancing the in-plane bond length of Mn-O, favors the occupation of the energetically more favorable $d_{x^2-y^2}$ orbital. In contrast, in-plane compressive strain

promotes the out-of-plane $d_{3z^2-r^2}$ orbital. The relationship $\{t\alpha\cos(\varphi)/d^{3.5}\}$, where φ represents the angle between Mn-O-Mn and d represents the Mn-O bond length, illustrates that an increase in φ and d leads to an increase and decrease in electron hopping, respectively. Tensile strain, by increasing bond length and Mn-O-Mn bond angle, decreases the hopping integrals. In this scenario, occupied $d_{x^2-y^2}$ orbitals lead to electron localization, and tensile strain removes the FMM phase.

Conversely, if compressive strain is applied to the structure, it reduces bond length and increases bond angles in the hopping integrals. The $d_{3z^2-r^2}$ orbital becomes favorable, increasing the J-T distortion and promoting electron localization. Consequently, the FMM phase expands due to bond reduction and electron localization from the J-T effects, which compete against each other. This competition between the two states results in a metallic phase becoming more favorable. The strain has different effects on the FM and CO-AFM phases.

Tensile strain in the ferromagnetic phase increases the A-type AFM phase, while compressive strain reinforces the C-type AFM phase. In addition to the lattice mismatch between the substrate and the film, other internal factors (such as disordered strains and a dead layer) and external factors (such as thickness and deposition conditions) affect the strain behavior of LCMO thin films [56]. Previous reports have indicated that film parameters, including resistance, magnetoresistance, magnetization, CMR ratios, and T_C , depend on the preparation conditions, film thickness, and substrate used for film deposition [57]. Typically, these films are grown at high temperatures (around 600–700 °C) to achieve epitaxial growth. Research findings have demonstrated that LCMO films can be successfully grown on a variety of substrates, including magnesium oxide (MgO), lanthanum aluminate (LaAlO₃), strontium titanate (SrTiO₃), neodymium gallate (NdGaO₃), and silicon (Si).

The lattice mismatch along the strontium titanate (STO) interface is calculated as $\delta = (a_{p \text{ substrate}} - a_{p \text{ bulk}})/a_{p \text{ substrate}}$. Positive values of δ result in tensile strain, while negative values of δ correspond to compressive stresses. Substrate lattice mismatch induces deformation in the lattice, which can be analyzed through unit cell distortion [58]. The electrical properties of the grown films are dependent on the growth parameters and crystallinity. Single crystalline films with low-field MR exhibit strong ferromagnetism. Percolation theory was employed to fit the R-T curves and to understand the effect of thickness and substrate on the properties of La-Ca-Mn-O films during the transition [59,60].

For low temperatures (lower than the M-I transition ($T \ll T_C$)), the temperature dependence of the resistance can be easily understood as exhibiting metallic behavior, characterized by band electron conduction. This behavior involves the additional resistance component R_0 , electron–electron interaction (T^2), and electron–phonon interaction, which follows a T^5 dependency. Therefore, the resistance at low temperature (R_L) can be expressed using Equation (11):

$$R_L = R_0 + BT^2 + CT^5 \quad (11)$$

where A , B , and C are constants, with A representing the residual resistance of the film (R_0). The transport behavior above T_C is described using the thermally active hopping law, specifically a small polaron hopping behavior.

$$R_H = DT \cdot \exp(E_H/kT) \quad (12)$$

where E_H represents the hopping energy. Around $T \approx T_C$, both low-temperature metallic behavior and high-temperature hopping behavior contribute to the film's conductivity. The R-T relation is described by Equation (13).

$$\frac{m}{3}(R - R_L) \frac{1}{R_L + g_{\parallel} \times (R - R_L)} + \frac{2}{R_L + g_{\perp} \times (R - R_L)} + 3(1 - m) \frac{R - R_H}{R + 2 \times R_H} = 0 \quad (13)$$

where $g_{\perp} = 1/2$, $g_{\parallel} = (b^2 R_H / a^2 R) \ln[1 + (aR/bR_H)]$, and a and b represent the characteristic lengths of the polaron in directions perpendicular ($\perp$) and parallel ($\parallel$) to the current direction, respectively. The parameter $m = 1/[1 + (\exp(k \cdot (T - T_C)))]$ represents the contribution of electrons from the band at temperature T , where k is a fitting parameter. Therefore, there are only two variables: k (representing the fraction of polarons contributing to resistance) and the ratio w (indicating the shape of the polarons). The parameters $A = R_0$, B , C , D , and E were determined through fitting R - T curves in both low- and high-temperature regions. To fit the curves across the entire temperature range, the least square method was employed for R - T curve fitting to obtain the coefficients k and w .

4. Early Findings

In recent years, LCMO films have been doped to improve their properties and operating temperature. Cao et al. reported the fabrication of strontium-doped LCMO films ($\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$, where $x = 0, 0.10, 0.15, 0.25$, and 0.30) on Si substrates using the sol-gel method to enhance their T_C [61]. T_C increased monotonically from 235 K to 343 K with Sr doping. The study also reported a decrease in resistivity with Sr dopant, as Sr^{2+} ions are larger than Ca^{2+} ions. This enlargement of the Mn-O-Mn bond length enhances exchange interactions between Mn^{3+} -O- Mn^{4+} ions, resulting in a higher T_C . Mikailzade et al. fabricated thin films of $\text{La}_{0.66}\text{Ca}_{0.33}\text{MnO}_3$ and $\text{La}_{0.66}\text{Ba}_{0.33}\text{MnO}_3$ on glass substrates using the conventional sol-gel technique [62]. They investigated the thermo-magnetic properties of the grown films in zero-field-cooled (ZFC) and field-cooled (FC) regimes. The study concluded that the films exhibited supermagnetic behavior with a wide distribution of blocking temperatures, averaging around 190 K for LCMO and 200 K for LBMO films, respectively. Additionally, the calculated T_C values were different, approximately 230 K for LCMO and 270 K for LBMO. XS Wu et al. presented AFM images of LCMO films grown on different substrates with varying thicknesses [63].

To improve the performance of LCMO, various materials were used as dopants to create nanocomposites [64–74]. Lau and the group reported the synthesis of nanosized TiO_2 -doped LCMO using the conventional sol-gel technique [75]. They claimed an improvement in low-field magnetoresistance (LFMR) due to the introduction of a secondary phase in the LCMO matrix. As the content of TiO_2 increases, magnetization also increases. TiO_2 added to the LCMO film acts as an insulating barrier that affects spin disorder at the grain boundaries, facilitating LFMR. LCMO: TiO_2 nanocomposites were found to be suitable for magnetic sensors and memory devices. They also observed that the resistivity of LCMO shifts from 172 K to 176 K with an applied magnetic field of 1 T, and MR also shows a sharp increase from 0 T to 1 T, as extrinsic MR was more prominent in this region. Boora and co-workers have grown thin films of LCMO on n-type Si/ SiO_2 substrate using RF magnetron sputtering in an atmosphere with a mixture of argon and oxygen at 100-watt power and 3 millibar base pressure [76]. They examined the prepared films for MR at different applied magnetic fields (i.e., 0 T, 0.5 T, and 1.5 T). These films showed an 8.22% and 10.28% increase in MR at RT. These films can be used for bolometric applications and magnetic refrigeration. In another report, Boora et al. analyzed silver (Ag)-doped LCMO for RT applications by calculating its MR up to an applied magnetic field of 10 T at ambient temperature [77]. They reported a 10% higher MR than the pristine LCMO with a $T_C \sim 277$ K, where R - T curves showed a noticeable resistance change while applying a magnetic field.

Tselev et al. fabricated $\text{La}_{5/8}\text{Ca}_{3/8}\text{MnO}_3$ films doped with Ag on a TiO_2 -terminated SrTiO_3 substrate with the pulsed laser deposition (PLD) technique using a KrF excimer laser ($\lambda = 248$ nm) and showed Ag's influence on the LCMO surface [78]. Also, it provided a way to modify the surface properties of manganese oxides. Ag improves the electrical homogeneity in the LCMO due to the oxygenation effect after Ag_2O deposition. Microscopic analysis showed that surface doping with Ag gives mainly three types of reconstructions that depend on the spatial position. Also, on the tip state, a $\sqrt{2} \times \sqrt{2}$ $R45^\circ$ surface reconstruction was seen on the samples without substantial Ag presence. Studies revealed the modification in surface properties of LCMO after Ag addition. Awana and co-workers synthesized $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\text{:Ag}_x$ ($x = 0.00, 0.10, 0.20, 0.30$, and 0.40) composites using the conventional solid-state method and examined their structural, morphological, electrical, and magnetic properties [79]. The paramagnetic–ferromagnetic transition temperature (T_C) increased slightly after Ag addition. MR was found to be maximum near T_C , which was around 280 K. Increased MR up to 60% was observed for the higher Ag content LCMO sample under RT and 7T magnetic fields. The TCR increased significantly (up to 15%) after Ag addition, and a sharper metal–insulator transition was achieved. The improvement in T_C , TCR, and MR can be explained by improved grain size and connectivity with Ag addition in the LCMO matrix. The manganite materials can be used as magnetic switching devices.

In another report, Awana et al. followed the solid-state method to develop $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ and $\text{Ag-La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ composites and studied their optimized magneto-transport properties [80]. Sr^{2+} ions were partially substituted at the Ca^{2+} site, which controlled the T^{MI} as the divalent ion substitutions changed the Mn–O–Mn bond and governed the dopant's ionic size, tuning it to RT. Ag induced sharper transitions. The $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3$ composition resulted in a maximum TCR ($\sim 9\%/K$) and LFMR of $\sim 20\%$ and 30% at 5 kOe and 10 kOe, respectively. This material can be used for RT bolometers (with high TCR) and magnetic sensors (with high MR). Tripathi and co-workers compared the structural, morphological, and magneto-transport properties of indium (In) and Ag-doped LCMO [81]. The Ag-doped LCMO synthesized samples proved to be superior to the In-doped samples. LCMO–In doped samples showed a decreased para–ferro transition temperature and TCR with deteriorated grain morphology compared to pristine LCMO, whereas Ag-added LCMO showed positive modifications in magneto-transport properties. To act as a switching device for bolometric applications, a material must have a high TCR and should exhibit a sharp transition over a small temperature difference.

Jha et al. reported the magnetocaloric effect (MCE) in 10% Ag-doped $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ ($x = 0.0, 0.5, 0.10$) [82]. The MCE is an adiabatic temperature or isothermal magnetic entropy change in a magnetic material under an applied magnetic field. It was found that rare-earth manganite materials showed good MCE, with large magnetic moments. Hence, they can be useful in magnetic refrigeration. The $\text{La}_{0.7}\text{Ca}_{0.2}\text{Sr}_{0.1}\text{MnO}_3\text{:Ag}_{0.10}$ composition has been examined with a maximum entropy change of $7.6 \text{ J}\cdot\text{kg}^{-1}\text{K}^{-1}$ at a field change of 5T near T_C , where T_C and T^{MI} were found to be 298 K. The MR% was as high as 31% at 1T and 49% at 3T, which is remarkably good. This can be used as an active refrigerant material at RT. Gadolinium has the highest MCE due to its second-order phase transition, but it is costly, which limits its usage as a potential candidate in magnetic refrigeration. The huge magnetic entropy change in manganese oxides was due to a change in magnetization near the para–ferro transition temperature. Hence, they observed that Ag-added manganite bulk composite could be used in magnetic refrigeration.

Ramadhan et al. examined the effect of sintering on the electric properties and magnetoresistance of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ [83]. Around 34% higher MR was observed for the LCMO sample sintered at 1000°C , and 32% for LCMO at 1100°C with a 200 K and 20,000 oersted applied magnetic field. Whereas, at 280 K, LCMO at 1100°C has more MR than LCMO at

1000 °C, as LCMO at 1000 °C tends to become saturated faster. At low sintering temperatures, mostly filled shells had oxygen defects, and crystallographic imperfections became thicker and magnetically disordered, leading to an anti-ferromagnetic state. The magnetic field magnetically ordered the sample, and hence ferromagnetism suppressed the paramagnetic semiconducting state, which decreased resistivity and shifted the T^{MI} to a higher value towards RT. Zhang et al. explained this by using their proposed core-shell model [84].

Siwach and their group explored RT MR and TCR in $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Ag}_x\text{MnO}_3$ thin films (0.5 μm) grown on $\text{LaAlO}_3(100)$ substrate ($a = 3.795 \text{ \AA}$) via nebulized spray pyrolysis method [85]. The spray pyrolysis technique uses a low synthesis temperature compared to the solid-state method, which requires a high working temperature of around 1300 °C. The virgin LCMO film showed a para-ferro transition at $\sim 260 \text{ K}$ and T^{MI} at $\sim 245 \text{ K}$ because of oxygen deficiency in the grain boundary region. However, 30% Ag doping in pristine LCMO shifted the T_{C} to $\sim 315 \text{ K}$, and T^{MI} was found to be around 325 K, which was 10 K higher than T_{C} at 7T applied field. Strong irreversibility was seen in zero-field cooled magnetization curves of all grown films, and irreversibility temperature modified with Ag addition, forming clusters above T_{C} . Pristine LCMO showed a small MR value of $\sim 20\%$ and low TCR at RT, whereas for Ag-doped LCMO, there was an enhancement in MR value of $\sim 60\%$ for $x = 0.15$, which decreased to $\sim 30\%$ for pure Ag-added samples. Ag-added manganite showed a good TCR $\sim 4\%/K$ at ambient temperature. The interplay between J-T effect, DE interaction, and potential discrepancies were noticed because of RE/AE site valence fluctuations due to Ag-doping, which also enhanced the properties of LCMO. The MR dependence on the field was given by the power law, where $\text{MR} \propto H^{\alpha}$.

Kuru and coworkers presented the RT MR in barium (Ba)-doped LCMO-Ag films [86]. Epitaxial $\text{La}_{0.7}\text{Ca}_{0.2}\text{Ba}_{0.1}\text{MnO}_3$ -Ag films of different thicknesses (25 nm, 75 nm, and 150 nm) were grown on (001) and (111) STO and (001) SrLaGaO_3 (SLGO) substrates via the PLD technique using a polycrystalline ceramic target consisting of LCBMO and Ag. The most significant MR value ($\sim 75\%$) was observed on (111) STO under RT and 7 T magnetic fields. It was observed that the thickness of LCBMO films affected the T^{MI} due to epitaxial strain relaxation, with some defects in the lattice. The higher MR values at RT were well explained by first tuning the T^{MI} of bulk LCMO to RT by doping with the appropriate amount of Ba and then adding Ag to LCBMO to enhance grain connectivity, making percolation of the metallic region easier. The LCBMO was deposited on a well-suited substrate with a minimum lattice mismatch, which refined the magneto-transport properties further without degrading the RT MR properties. Due to the imposed strain by the substrate and possible structural changes, and the reconstruction of the surface or formation of vacancies, it was observed that J-T distortions were fewer in the film grown on (111) STO, and the epitaxial strain of STO on LCBMO hindered the formation of the AFM and insulating phase via dimensional changes accompanying the phase transition from AFM to FM. Also, there was a reduction in electron-phonon interaction, which enhanced the metallic behavior in LCBMO films. These optimized films can be used in sensing applications.

Zhang et al. reported the control and tunable LFMR in single-phase $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ films with vertically aligned nanostructures (VAN) using a high magnetic field on $(\text{LaAlO}_3)_{0.3}(\text{Sr}_2\text{AlTaO}_6)_{0.7}(001)$ [LSAT (001)] substrate deposited via PLD at 10T (HMF-PLD) [87]. LFMR in LCMO VAN films was modified using a high magnetic field. LCMO VAN films showed $\sim 45\%$ LFMR at 150 K and a 1 T magnetic field. LFMR larger than 25% was obtained at 127–200 K with an applied field of 1 T, which can be attributed to the enhancement in vertical interfaces and grain boundary density with the application of a high magnetic field related to the spin-polarized tunneling effect. During film deposition, a high magnetic field was applied to control the microstructure of as-grown films, which further tuned the physical properties. VAN thin film consisted of continuous planar layers

and a vertically aligned nanocolumnar layer. The continuous LCMO VAN thin-film layer was responsible for tunability in transport properties. These films can be used in magnetic head sensors to measure a wide range of temperatures.

Debnath and coworkers reported the LFM and TCR of epitaxially grown $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ films (200 nm) fabricated on (100) LaAlO_3 substrate using the PLD technique (Figure 7a) [88]. The fabricated film showed a firm out-of-plane texture. Approximately 73% and 57% MR were obtained in the a–b and c planes, respectively, at an applied field of 1.5 T (Figure 7b). The TCR value in the a–b plane was 14.2% K^{−1}, whereas along the c direction, it was recorded to be 11.5% K^{−1}. The observed T_c was 249 K, which was higher than that of bulk samples due to strain induced by the LaO substrate and non-stoichiometry in LCMO films (Figure 7c). Strain induced by the substrate affects the transfer integral of electron hopping in $\text{Mn}^{4+}\text{--O--Mn}^{3+}$, which further enhances T_c .

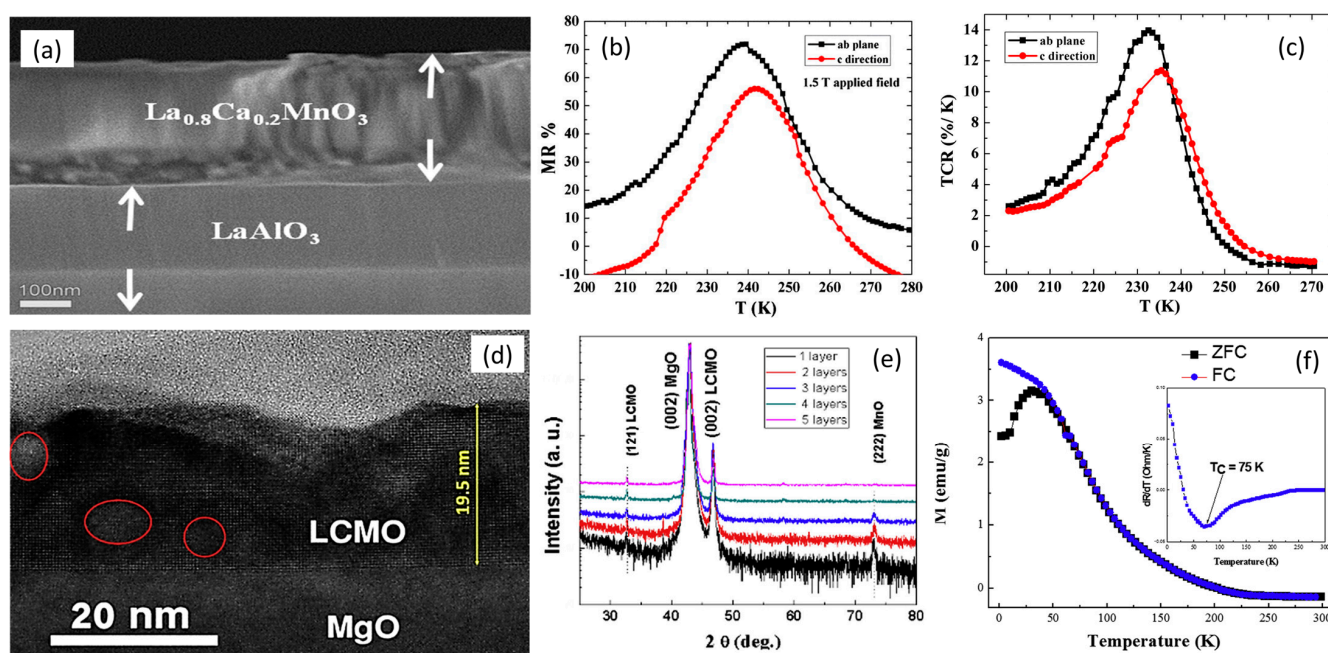


Figure 7. (a) A cross-sectional SEM image of the $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3/\text{LaAlO}_3$ film; (b) MR at an applied field of 1.5 T; (c) TCR values along the a–b plane and in the c direction [adapted from [88], copyright 2015, Elsevier]; (d) a TEM image; (e) the XRD of LCMO/MgO film; and (f) magnetization vs. temperature for LCMO film (inset shows the T_c value) [adapted from [89], copyright 2020, Elsevier].

Recently, uncooled IR detectors have been developed for both civil and military purposes, such as night-vision cameras, thermal sensors, and surveillance cameras. A bolometer is a device that uses the characteristics of a thermosensitive layer, where the thermosensitive layer changes its sheet resistance with respect to temperature. The larger the change in resistance, the higher the TCR and sensitivity. Such films can be used as IR active layers of bolometers. Also, these films exhibit a dramatic resistivity change at T_c and T^{MI} , which results in high TCR values and can be used for magnetoresistive sensing applications near RT. The maximum MR (approximately 94%) and TCR (around 14% K^{−1}) were reported, making them well-suited for novel electronic and uncooled and moderately cooled infrared imaging (bolometric) applications.

Dauodi et al. investigated the microstructure and electron transport in epitaxially grown Ca-doped La-Mn-O films on (001) MgO ($a = 4.20 \text{ \AA}$) substrate via the metal–organic deposition technique (Figure 7d) [89]. XRD data revealed a low-intensity secondary phase peak of MnO at $\sim 73.2^\circ$ along with the LCMO peak at $\sim 32.7^\circ$, confirming the successful growth of LCMO/MgO. The LCMO and MgO had a lattice mismatch difference of $\sim 8.14\%$,

which imposed a large out-of-plane compressive strain and a significant in-plane tensile strain (Figure 7e). The magneto-transport properties in LCMO nanofilms depend on the degree of strain as well as relaxation. Here, magnetization vs. temperature measurements showed a T_C of ~ 75 K (Figure 7f). This report also calculated the electrical properties using the variable-range hopping model and small polaron hopping. In perovskite oxides, it was also observed that annealing temperature plays an essential role in controlling the stoichiometry and crystallinity. The large lattice mismatch in LCMO/MgO weakens the charge carrier movement and reduces the ferromagnetic DE phenomenon. Less crystalline LCMO films showed semiconducting-like behavior over a large range of temperatures.

Yotsuya et al. examined the optical response of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films fabricated on MgO and SrTiO_3 substrates by the PLD method [90]. As-grown films showed a phase transition from para to ferro at ~ 190 K T_C with a sharp drop in resistivity. These films were used as bolometric photosensors, which showed a detectivity and noise equivalent power of $D^* = 2.7 \times 10^8 \text{ cm } \sqrt{\text{Hz W}^{-1}}$ and $\text{NEP}/\sqrt{B} = 7.4 \times 10^{-10} \text{ W } \sqrt{\text{Hz}}$, where B is the bandwidth of the amplifier and assumed to be 1 Hz. Also, the carrier density ($3 \times 10^{19} \text{ cm}^{-3}$) was calculated at 300 K using Hall effect measurements. LCMO film has an absorption edge at a 7 μm wavelength, which is correlated with the plasma frequency and was calculated using Equation (14).

$$\omega_p = \sqrt{Ne^2/m\varepsilon} \quad (14)$$

where N is charge density, e is the charge of an electron, m is the effective mass, and ε is the dielectric constant of the plasma. The charge density determined by the equation comes out to be $4.13 \times 10^{19} \text{ cm}^{-3}$, which was close to the experimental data. The temperature-resistivity dependence can be given by Equation (15).

$$R = R_0 e^{\frac{\Delta E}{kT}} \quad (15)$$

where R_0 is the fitting parameter, ΔE is the energy gap, and K is the Boltzmann constant. The absorbance vs. wavelength was also calculated in the given experiment, which showed that the thin film can work as a bolometric radiation detector. A high value of TCR gives high sensitivity. A sharp transition from para to ferro was observed at 190 K, which can be used for a superior bolometer.

Zhou et al. produced self-assembled epitaxial LCMO:NiO and LCMO:Co₃O₄ thin films on LaAlO_3 substrate using the inexpensive polymer-assisted deposition (PAD) method [91]. They reported an enhancement in LFMR by the addition of 10% NiO and 10% Co₃O₄ in virgin LCMO, from -44.6% to -59.1% and -52.7% , which is ascribed to the introduction of an insulating phase at the grain boundaries (GBs). Self-epitaxially grown thin composite films exhibited a remarkable increase in resistivity from $0.0061 \Omega \cdot \text{cm}$ to $0.59 \Omega \cdot \text{cm}$ and $1.07 \Omega \cdot \text{cm}$, along with a decrement in T^{MI} from 255 K to 180 K and 172 K for LCMO:10%-NiO and LCMO:10%-Co₃O₄ compositions. These two observations can be attributed to the insulating phase introduced at GBs, which induced barriers in electrical transportation and obstructed magnetic spin alignment at GBs. This, in turn, increased the tunneling barrier height between adjacent magnetic grains. M-T curves revealed that T_C followed the same trend as that of T^{MI} . LCMO:Co₃O₄ films have more suppressed magnetism than NiO due to their AFM properties. Solution-processed films with extraordinary properties can bring a breakthrough in hole-doped manganite materials and their growth.

5. Applications of La-Ca-Mn-O Films

Hao and colleagues reported LCMO film growth using PLD and facing target sputtering techniques on LaAlO_3 and NdGaO_3 substrates for RT bolometric applications [92]. This work described the photo response of LCMO thin films to a He-Ne laser (632.8 nm)

and incident infrared (IR) (8–14 μm) power at RT. Optical responses to both incident radiations were reduced with an increase in chopping frequency, which was consistent with the bolometric response mechanism. The optical response increased linearly with the bias current. Manganite-based bolometers can have a wide range of military and thermal imaging applications over a broad wavelength region. Also, the suggested LCMO films are an excellent material for bolometric elements, since they have a higher TCR than metals and semiconductors near RT. Therefore, the opportunity exists to utilize LCMO films as sensitive optical bolometers, which can tailor the desired working temperature, such as RT. These characteristics are highly inspiring for promising applications in an uncooled optical detector using hole-doped manganese oxides. Karuna et al. investigated the current switching behavior of LCMO and LCMO-rGO (0.1%) composites by analyzing the I - V characteristics of the nanocomposite below RT [93]. Goyal et al. revealed the potential for using thin manganite films as heat-sensitive material in uncooled or slightly cooled bolometers [94,95].

Recently, the application of LCMO thin films in magnetic sensors at RT has been under consideration. A steep change in resistance with respect to temperature and high TCR values near T^{MI} could be of interest for bolometry, as it allows for the detection of optical excitations by tuning the magnetic field. The magnetocaloric effect in Sr-doped LCMO films could be used for magnetic refrigeration [82]. Recent research has highlighted the potential of highly spin-polarized manganese oxides, which will be fascinating nanomaterials for spintronics nano-devices in the near future [96]. Their unique properties, including high Curie temperatures and strong magnetic anisotropy, make them a promising candidate for nano-device applications. Manganese oxides such as MnO , Mn_2O_3 , Mn_3O_4 , and their mixed-valent forms can exhibit significant spin polarization at the Fermi level, a critical feature for spintronic devices. These materials are essential for components like magnetic tunnel junctions, spin valves, and other devices that utilize electron spin. The large spin-polarization of charge carriers in half-metallic manganites and spin-dependent tunneling between two FM manganese oxide electrodes across an insulating barrier gives a high value of MR response [97]. Also, these materials allow for true switching operations. Hence, these materials are suitable for sensor elements of non-volatile devices, such as magnetic random-access memory (MRAM). To achieve large MR effects, planar devices that use LFMR across GBs, artificial defects, and domain walls have been proposed and are promising from an applications perspective.

The first application of the MR effect was as a field-sensitive sensor, reported by Hunt in 1971. Later, IBM introduced an MR head that could read and write bits on an MR strip, eventually turning it into the first hard disk drive in 1991. Nowadays, MR is used in a wide range of devices, from price tags and badge readers to magnetic tapes. Since the MR effect originates from the scattering of conducting electrons, it inevitably shows temperature dependence. However, its behavior is specific to the material used. LCMO also has its usefulness in magnetic cooling at around RT and low-temperature regions. Manganite materials can be used as position sensors, contactless potentiometers, sensor elements of non-volatile MRAMs, and in the patterning of MR heads at the submicron level. Synthetic antiferromagnets (S-AFMs) consisting of strongly correlated oxides have shown potential for spintronic device applications [98]. The CMR mechanism has the potential for miniaturizing electric circuits that work at a lower power. CMR research directly affects the development of new electronic and spintronic devices, including new forms of ‘non-volatile’ computer memory, such as resistive random-access memory (RRAM).

MR has great technological importance, mainly in designing magnetic memory systems (such as hard disks, magnetic sensing, and magnetic storage). CMR manganite materials have the potential for use in information storage and processing, drug delivery,

sensor fabrication, cooling technology, etc. [99,100]. In today's era, nanoscale magnetism provides detailed scientific knowledge with application potential. This includes ferrofluids, magnetic recording media, magnetic refrigeration, catalysis, bioprocessing, medical diagnostics, drug delivery systems, and miniaturized magnetic sensor applications. LCMO films that exhibit a high CMR effect can be used in CMR-B-scalar sensors [101,102]. These allow for the measurement of the absolute magnitude of the magnetic flux density during high-magnetic-field pulses. They have also been used to measure magnetic field distribution in railguns [103–105], coil guns [106], and non-destructive pulsed-field magnets [99,107]. However, in plasma science applications, it is of huge interest to have sensors that operate at cryogenic temperatures and over a wide range of magnetic field amplitudes (0.1–100 T). For example, the efficient and successful operation of the International Thermonuclear Experimental Reactor requires a reliable set of magnetic diagnostics [108,109]. Magnetic diagnostic systems can measure several parameters essential for the operation and understanding of TOKAMAK plasmas [108,109]. In particular, plasma position and shape, plasma current, and the magnetic field distribution created by superconducting magnets inside and outside the vacuum vessel of the reactor are measured using various magnetic field sensors (Rogowski coils, flux loops, Faraday rotation method) [109]. Recently, it was shown that CMR-B-scalar sensors can be used for low-temperature applications. Research has shown that LCMO films have high sensitivity towards lower memory effects, magnetic fields, and faster resistance relaxation during the measurements of pulsed magnetic fields [110,111]. The magnetoresistive phenomenon is useful in magnetic sensors, spintronic devices, spin-polarized quasi-particle injectors, uncooled IR bolometer sensors, magnetic flux concentrator transducers, and ferroelectric gates [112–116].

6. Conclusions and Future Prospects

We reviewed a detailed and systematic study of lanthanum-based manganese oxide and discussed its crystal structure, DE mechanism, and Jahn–Teller distortion. Different growth techniques have been utilized to deposit LCMO films on various substrates, and the magneto-transport properties of fabricated films were evaluated. LCMO's unique combination of electrical, magnetic, magneto-transport, and thermal properties makes it an outstanding material in advanced technology fields. The DE interaction that causes ferromagnetism in the perovskite manganites is an effective interaction that is unlike the familiar Heisenberg direct exchange interaction. Due to the fascinating properties of LCMO films, such as large CMR and high TCR, these films are used in bolometry, night-vision cameras, thermal sensors, artificial planar junctions, and magnetic refrigeration, among other applications. The resistive switching properties of LCMO are being examined by various researchers for usage in non-volatile memory devices, which could lead to faster and durable memory storage solutions. LCMO is also used in catalytic applications, such as the oxidation of hydrocarbons and reduction reactions because of its surface properties and oxygen mobility. The temperature dependence of resistivity in LCMO makes it fit for use in thermistors and other temperature-sensing devices. However, the major critical issue related to these films is their high growth temperature and the use of expensive single-crystal substrates. For practical purposes, more emphasis should be given to LFMR at RT.

To further improve the magneto-transport properties of LCMO films, researchers are using different dopant materials in LCMO films to achieve T_C near RT. Additionally, for industrial applications, the growth temperature should be decreased, the use of inexpensive single-crystal substrates should be overcome, and the film growth area should be improved. The most promising techniques for depositing magnetoresistive oxides are CVD, PLD, and sputtering, which are expensive. These issues should be resolved to reduce the manufacturing cost of magnetoresistive oxide-based devices.

Perovskite manganite have a high TCR (~10–15%) but operate around the M-I transition, which is slightly below RT and requires cooling, as with thermoelectric refrigeration. The limited working temperature range necessitates temperature stabilization of the working point and limits the dynamic range of the bolometer. Manganese oxides are low-resistance materials, making it possible to create a microbolometer with resistance that can be easily matched with the readout electronics to achieve sufficiently high voltage sensitivity. However, nanofilms are preferred to create the heat-sensitive layer in the form of a meander. Further study is required to reduce the current noise in manganite thin films.

Author Contributions: Conceptualization, N.B., R.A. and B.-I.L.; investigation, N.B. and R.A.; writing—original draft preparation, N.B. and R.A.; writing—review and editing, S.R., N.Q.D., A.A., M.B.A. and B.-I.L.; methodology, S.R.; data curation, N.Q.D. and A.A.; visualization, N.Q.D.; supervision, R.A. and B.-I.L.; project administration, M.B.A.; funding acquisition, M.B.A. and B.-I.L. All authors have read and agreed to the published version of the manuscript.

Funding: This work was supported by the Global Joint Research Program funded by the Pukyong National University (202412430001). A.A. and M.B.A. acknowledge the generous support from Prince Sattam Bin Abdulaziz University Project Number (PSAU/2025/R/1446).

Data Availability Statement: Not applicable.

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

References

1. Tokura, Y. Critical Features of Colossal Magnetoresistive Manganites. *Rep. Prog. Phys.* **2006**, *69*, 797. [\[CrossRef\]](#)
2. Searle, C.W.; Wang, S.T. Studies of the Ionic Ferromagnet (LaPb)MnO₃ III. Ferromagnetic resonance studies. *Can. J. Phys.* **1969**, *47*, 2023. [\[CrossRef\]](#)
3. Kubo, K.; Ohata, N. A Quantum Theory of Double Exchange. I. *J. Phys. Soc. Jpn.* **1972**, *33*, 21–32. [\[CrossRef\]](#)
4. Zener, C. Interaction Between the d-shells in the Transition Metals. II. Ferromagnetic Compounds of Manganese with Perovskite Structure. *Phys. Rev.* **1951**, *82*, 403. [\[CrossRef\]](#)
5. Anderson, P.W.; Hasegawa, H. Considerations on Double Exchange. *Phys. Rev.* **1955**, *100*, 675. [\[CrossRef\]](#)
6. Gennes, P.G.D. Effects of Double Exchange in Magnetic Crystals. *Phys. Rev.* **1960**, *118*, 141. [\[CrossRef\]](#)
7. Salamon, M.B.; Jaime, M. The Physics of Manganites: Structure and Transport. *Rev. Mod. Phys.* **2001**, *73*, 583. [\[CrossRef\]](#)
8. Dagotto, E.; Hotta, T.; Moreo, A. Colossal Magnetoresistant Materials: The Key Role of Phase Separation. *Phys. Rep.* **2001**, *344*, 1. [\[CrossRef\]](#)
9. Izyumov, Y.A.; Skryabin, Y.N. Double Exchange Model and the Unique Properties of the Manganites. *Phys. Usp.* **2001**, *44*, 109. [\[CrossRef\]](#)
10. Coey, J.M.D.; Viret, M.; Molnar, S.V. Mixed-valence Manganites. *Adv. Phys.* **1999**, *48*, 167. [\[CrossRef\]](#)
11. He, W.; Kong, L.; Zhao, W.; Yu, P. Atomically Thin 2D van der Waals Magnetic Materials: Fabrications, Structure, Magnetic Properties and Applications. *Coatings* **2022**, *12*, 122. [\[CrossRef\]](#)
12. Assirey, E.A.R. Perovskite Synthesis, Properties and Their Related Biochemical and Industrial Application. *Saudi Pharm. J.* **2019**, *27*, 817. [\[CrossRef\]](#)
13. Nagal, V.; Kumar, V.; Ahmad, R.; Khan, M.; Khan, Z.; Singh, K.; Furukawa, H.; Khosla, A.; Hahn, Y.B.; Hafiz, A.K. Emerging Applications of g-C₃N₄ Films in Perovskite-Based Solar Cells. *ECS J. Solid State Sci. Technol.* **2021**, *10*, 065001. [\[CrossRef\]](#)
14. Wollan, E.O.; Koehler, W.C. Neutron Diffraction Study of the Magnetic Properties of the Series of Perovskite-Type Compounds [(1-x)La_xCa]MnO₃. *Phys. Rev.* **1955**, *100*, 545. [\[CrossRef\]](#)
15. Zener, C. Interaction Between the d Shells in the Transition Metals. *Phys. Rev.* **1951**, *81*, 440. [\[CrossRef\]](#)
16. Trotsenko, V.G.; Lahmar, A.; Lyanguzov, N.V.; Marssi, M.E.; Torgashev, V.I. Phase Separation and Local Lattice Distortions Analysis of Charge-Ordered Manganese Films La_{1-x}Ca_xMnO₃ by Raman Spectroscopy. *Superlattices Microstruc.* **2019**, *127*, 100. [\[CrossRef\]](#)
17. Sathpathy, A.; Popovic, Z.S.; Vukajlovic, F.R. Electronic Structure of the Perovskite Oxides: La_{1-x}Ca_xMnO₃. *Phys. Rev. Lett.* **1996**, *76*, 960. [\[CrossRef\]](#) [\[PubMed\]](#)
18. Pickett, W.E.; Singh, D.J. Electronic Structure and Half-Metallic Transport in the La_{1-x}Ca_xMnO₃ System. *Phys. Rev. B* **1996**, *53*, 1146. [\[CrossRef\]](#) [\[PubMed\]](#)

19. Zhuang, M.; Zhang, W.; Ming, N. Spin-Disorder-Scattering-Induced Spectral-Weight Transfer and Pseudogap in Doped Perovskite LaMnO_3 . *Phys. Rev. B* **1997**, *56*, 14547. [[CrossRef](#)]
20. Sing, D.J.; Pickett, W.E. Pseudogaps, Jahn-Teller Distortions, and Magnetic Order in Manganite Perovskites. *Phys. Rev. B* **1998**, *57*, 88. [[CrossRef](#)]
21. Khomskii, D.I.; Streltsov, S.V. Magnetic oxides. In *Encyclopedia of Condensed Matter Physics*, 2nd ed.; Chakraborty, T., Ed.; Academic Press: Cambridge, MA, USA, 2024; pp. 98–111.
22. Majumder, D.D.; Karan, S. *Ceramic Nanocomposites: 2. Magnetic Properties of Ceramic Nanocomposites*; Woodhead Publishing Series in Composites Science and Engineering; Woodhead Publishing Limited: Cambridge, UK, 2013; pp. 51–91.
23. Jonke, G.H.; Santen, J.H.V. Ferromagnetic Compounds of Manganese with Perovskite Structure. *Physica* **1950**, *16*, 337. [[CrossRef](#)]
24. Ye, N.C.; Tsuei, C.C. Quasi-Two-Dimensional Phase Fluctuations in Bulk Superconducting $\text{YBa}_2\text{Cu}_3\text{O}_7$ Single Crystals. *Phys. Rev. B* **1989**, *39*, 9708.
25. Yan, S.S.; Liu, J.P.; Mei, L.M.; Tian, Y.F.; Song, H.Q.; Chen, Y.X.; Liu, G.L. Spin-Dependent Variable Range Hopping and Magnetoresistance in $\text{Ti}_{1-x}\text{Co}_x\text{O}_2$ and $\text{Zn}_{1-x}\text{Co}_x\text{O}$ Magnetic Semiconductor Films. *J. Phys. Condens. Matter* **2006**, *18*, 10469. [[CrossRef](#)] [[PubMed](#)]
26. Acevedo, M.C.; Liang, D.; Chew, K.S.; DeGrave, J.P.; Kaiser, N.S.; Jin, S. Synthesis, Characterization, and Variable Range Hopping Transport of Pyrite (FeS_2) Nanorods, Nanobelts, and Nanoplates. *ACS Nano* **2013**, *7*, 1731. [[CrossRef](#)] [[PubMed](#)]
27. Arya, V.P.; Prasad, V.; Kumar, P.A. Effect of Magnetic Field on Mott's Variable-Range Hopping Parameters in Multiwall Carbon Nanotube Mat. *J. Phys. Condens. Matter* **2012**, *24*, 245602. [[CrossRef](#)] [[PubMed](#)]
28. Liu, H.; Pourret, A.; Guyot-Sionnest, P. Mott and Efros-Shklovskii Variable Range Hopping in CdSe Quantum Dots Films. *ACS Nano* **2010**, *4*, 5211. [[CrossRef](#)]
29. Medina, E.; Kardar, M.; Rangel, R. Magnetoconductance Anisotropy and Interference Effects in Variable-Range Hopping. *Phys. Rev. B* **1996**, *53*, 7663. [[CrossRef](#)]
30. Rosenbaum, R. Crossover from Mott to Efros-Shklovskii Variable-Range-Hopping Conductivity in In_xO_y Films. *Phys. Rev. B Condens. Matter* **1991**, *44*, 3599. [[CrossRef](#)]
31. Jiang, J.; Guan, X.; Gu, X.; Han, J.; Wu, K.; Zhao, L.; Yan, Y.; Zhu, X.; Liu, X. Optimization of the Electrical Transport Properties of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ Films by Sintering Temperature Adjustment. *Ceram. Int.* **2023**, *49*, 38174. [[CrossRef](#)]
32. Wang, Z.; Liang, X.; Wang, Y.; Jiang, J.; Wang, H.; Chen, Z.; Pan, Z.; Sun, J.; Ma, J.; Jiang, X.; et al. Improved Electrical Transport Properties of $\text{La}_{0.8}\text{Ba}_{0.2}\text{MnO}_3$ Films via Suppressed Electron Scattering Behavior. *Colloids Surf. A Physicochem. Eng. Asp.* **2025**, *704*, 135566. [[CrossRef](#)]
33. Wu, K.; Guan, X.; Li, H.; Gu, X.; Yu, Z.; Jin, S.; Yu, X.; Yan, Y.; Zhao, L.; Liu, H.; et al. Enhanced Electrical Transport Properties of Polycrystalline $\text{La}_{0.67}\text{Sr}_x\text{Ca}_{0.23-x}\text{K}_{0.1}\text{MnO}_3$ Ceramics Through A-site Multielement Co-doping. *Ceram. Int.* **2023**, *49*, 1344. [[CrossRef](#)]
34. Jithin, P.; Bitla, Y.; Patidar, M.M.; Ganesan, V.; Sankaran, K.J.; Kurian, J. Enhanced Magnetoresistance and Evolution of Griffiths-Like Phase in $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ ($x = 0.4, 0.5$) Nanoparticles. *J. Nanopart. Res.* **2023**, *25*, 207. [[CrossRef](#)]
35. Wang, Z.; Jiang, J.; Gu, X.; Han, J.; Liang, X.; Wang, Y.; Chen, Z.; Wang, H.; Liu, X. Large Temperature Coefficient of Resistivity (TCR) of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ Polycrystalline Ceramics Improved by Optimizing Sintering Temperatures. *Ceram. Int.* **2024**, *50*, 10160. [[CrossRef](#)]
36. Zhang, K.; Dai, J.; Zhu, X.; Zhu, X.; Zuo, X.; Zhang, P.; Hu, L.; Lu, W.; Song, W.; Sheng, Z.; et al. Vertical $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ Nanorods Tailored by High Magnetic Field Assisted Pulsed Laser Deposition. *Sci. Rep.* **2016**, *6*, 19483. [[CrossRef](#)] [[PubMed](#)]
37. Fan, M.; Wang, H.; Misra, S.; Zhang, B.; Qi, Z.; Sun, X.; Huang, J.; Wang, H. Microstructure, Magnetic, and Magnetoresistance Properties of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3\text{:CuO}$ Nanocomposite Thin Films. *ACS Appl. Mater. Interfaces* **2018**, *10*, 5779. [[CrossRef](#)] [[PubMed](#)]
38. Omar, S.; Kulkarni, S.B. Effect of Simultaneous Substitution of Sr and Ca in LaMnO_3 Thin-Film Electrode Prepared via In Situ Sol-Gel Process. *J. Mater. Sci. Mater. Electron.* **2024**, *35*, 1542. [[CrossRef](#)]
39. Yu, X.; Jin, S.; Guan, X.; Yan, Y.; Wu, K.; Zhao, L.; Liu, X. Large Temperature Coefficient of Resistivity (TCR) of $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ Films Prepared by Spin-Coating Method. *J. Alloys Compd.* **2022**, *890*, 161788. [[CrossRef](#)]
40. Chen, X.; Tao, B.; Zhao, R.; Yang, K.; Li, Z.; Xie, T.; Zhong, Y.; Zhang, T.; Xia, Y. Efficient Preparation of the Inclined $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ Films with Excellent Light-Induced Transverse Thermoelectric Performance Based on MOCVD Process. *Vacuum* **2023**, *208*, 111695. [[CrossRef](#)]
41. Dadhich, H.; Rajyaguru, B.; Gadani, K.; Goswami, H.; Rathod, V.R.; Shrimali, V.G.; Mukherjee, S.; Asokan, K.; Shah, N.A.; Solanki, P.S. Thermionic Emission Assisted Charge Conduction Mechanisms Across $\text{LaMnO}_3/\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ Interface of Manganite Thin Film Structure. *Curr. Appl. Phys.* **2023**, *50*, 1–12. [[CrossRef](#)]
42. Wang, Z.; Jiang, J.; Liang, X.; Wang, Y.; Han, J.; Chen, Z.; Wang, H.; Pan, Z.; Sun, J.; Ma, J.; et al. Exploration of Electrical Conduction Mechanisms via Modulating Sintering Period of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ Films in Various Phase Regions. *Ceram. Int.* **2024**, *50*, 55920. [[CrossRef](#)]

43. Mohan, B.; Manral, P.; Rani, R.; Malik, V.K. Large Photoresistance and Photoinduced Magnetoresistance in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ Thin Film on Silicon Substrate. *J. Phys. D Appl. Phys.* **2025**, *58*, 055302. [\[CrossRef\]](#)
44. Rajyaguru, B.; Gohil, H.; Dadhich, H.; Gadani, K.; Shrimali, V.G.; Choudhary, R.J.; Phase, D.M.; Shah, N.A.; Solanki, P.S. Interface Based Field Effect Configuration and Charge Conduction Mechanisms for Manganite Thin Film Heterostructures. *New J. Chem.* **2023**, *47*, 13508. [\[CrossRef\]](#)
45. Guo, J.; He, B.; Han, Y.; Liu, H.; Han, J.; Ma, X.; Wang, J.; Gao, W.; Lü, W. Resurrected and Tunable Conductivity and Ferromagnetism in the Secondary Growth $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ on Transferred SrTiO_3 Membranes. *Nano Lett.* **2024**, *24*, 1114. [\[CrossRef\]](#)
46. Purnakanti, A.; Lakshmi, Y.K.; Kumar, S.; Venkatesh, R.; Reddy, M.S. Grain Boundary Modification in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ Manganites with Additives: Impact on Magneto-Transport Properties. *Appl. Phys. A* **2023**, *129*, 706. [\[CrossRef\]](#)
47. Hua, W.; Lu, L.; Shen, L.; Jin, J.; Wang, H.; Liu, M.; Ma, C.; Jia, C.L. Modulating the Transport Property of Flexible $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ Thin Film by Mechanical Bending. *Appl. Phys. Lett.* **2021**, *118*, 052404. [\[CrossRef\]](#)
48. Salas-Colera, E.; Muñoz-Noval, A.; Sebastiani-Tofano, E.; Castro, G.R.; Rubio-Zuazo, J. Tuning the Metal-Insulator Transition Temperature by the Controlled Generation of Oxygen Vacancies on $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-x}$ Epitaxial Thin Films. *J. Alloys Compd.* **2024**, *989*, 174321. [\[CrossRef\]](#)
49. Hoang, V.H.; Kim, H.J. Nonohmic Behaviors and Charge-Ordering Phenomena of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ Sandwiched by CaMnO_3 Layers. *ACS Appl. Electron. Mater.* **2024**, *6*, 6949.
50. Yan, L.; Balasubramaniam, K.R.; Wang, S.; Du, H.; Salvador, P.A. Effects of Crystallographic Orientation on the Oxygen Exchange Rate of $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ Thin Films. *Solid State Ion.* **2011**, *194*, 9. [\[CrossRef\]](#)
51. Li, S.; Wang, C.; Shen, Q.; Zhang, L. Substrate-Induced Strain Effect on Magnetic and Electrical Transport Properties of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ Thin Films with Varying Orientation. *Vacuum* **2019**, *164*, 312. [\[CrossRef\]](#)
52. Rao, R.A.; Lavric, D.; Nath, T.K.; Eom, C.B.; Wu, L.; Tsui, F. Three-Dimensional Strain States and Crystallographic Domain Structures of Epitaxial Colossal Magnetoresistive $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ Thin Films. *Appl. Phys. Lett.* **1998**, *73*, 3294. [\[CrossRef\]](#)
53. Chen, X.J.; Soltan, S.; Zhang, H.; Habermeier, H.U. Strain Effect on Electronic Transport and Ferromagnetic Transition Temperature in $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ Thin Films. *Phys. Rev. B* **2002**, *65*, 174402. [\[CrossRef\]](#)
54. Yeh, N.C.; Vasquez, R.P.; Beam, D.A.; Fu, C.C.; Huynh, J.; Beach, G. Effects of Lattice Distortion and Jahn-Teller Coupling on the Magnetoresistance of and Epitaxial Films. *J. Phys. Condens. Matter.* **1997**, *9*, 3713. [\[CrossRef\]](#)
55. Yeh, N.C.; Fu, C.C.; Wei, J.Y.T.; Vasquez, R.P.; Huynh, J.; Maurer, S.M.; Beach, G.; Beam, D.A. Effects of Lattice Distortion on the Physical Properties and Surface Morphology of Magnetoresistive Perovskite Epitaxial Films. *J. Appl. Phys.* **1997**, *81*, 5499. [\[CrossRef\]](#)
56. Zarifi, M.; Kameli, P.; Ehsani, M.H.; Ahmadvand, H.; Salamati, H. Effects of Strain on the Magnetic and Transport Properties of the Epitaxial $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ Thin Films. *J. Magn. Magn. Mater.* **2016**, *420*, 33. [\[CrossRef\]](#)
57. Koo, T.Y.; Park, S.H.; Lee, K.B.; Yeong, Y.H. Anisotropic Strains and Magnetoresistance of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$. *Appl. Phys. Lett.* **1977**, *71*, 977. [\[CrossRef\]](#)
58. Haghir-Gosnet, A.M.; Renard, J.P. CMR Manganites: Physics, Thin Films and Devices. *J. Phys. D Appl. Phys.* **2003**, *36*, R127. [\[CrossRef\]](#)
59. Jaime, M.; Lin, P.; Chun, S.H.; Salamon, M.B.; Dorsey, D.; Rubinstein, M. Coexistence of Localized and Itinerant Carriers near TC in Calcium-Doped Manganites. *Phys. Rev. B* **1999**, *60*, 1028. [\[CrossRef\]](#)
60. Verhage, M.; Minne, E.V.D.; Kiens, E.M.; Korol, L.; Spiteri, R.J.; Koster, G.; Green, R.J.; Baeumer, C.; Flipse, C.F.J. Electronic and Structural Disorder of the Epitaxial $\text{La}_{0.67}\text{Sr}_{0.33}\text{MnO}_3$ Surface. *ACS Appl. Mater. Interfaces* **2024**, *16*, 21273. [\[CrossRef\]](#)
61. Cao, D.; Zhang, Y.; Dong, W.; Yang, J.; Bai, W.; Chen, Y.; Tang, X. Structure, Magnetic and Transport Properties of $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3$ Thin Films by Sol-Gel Method. *Ceram. Int.* **2015**, *41*, 381. [\[CrossRef\]](#)
62. Mikailzade, F.; Onal, F.; Maksutoglu, M.; Zarbali, M.; Goktas, A. Structure and Magnetization of Polycrystalline $\text{La}_{0.66}\text{Ca}_{0.33}\text{MnO}_3$ and $\text{La}_{0.66}\text{Ba}_{0.33}\text{MnO}_3$ Films Prepared Using Sol-Gel Technique. *J. Supercond. Nov. Magn.* **2018**, *31*, 4141. [\[CrossRef\]](#)
63. Wu, X.S.; Cai, H.L.; Xu, J.; Tan, W.S.; Hu, A.; Jiang, S.S.; Hase, T.P.A.; Tanner, B.K.; Xiong, G. Substrate and Thickness Effects on Structure and Transport Properties of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3$ Films. *J. Appl. Phys.* **2004**, *95*, 7109. [\[CrossRef\]](#)
64. Lau, L.N.; Hon, X.T.; Wong, Y.J.; Lim, K.P.; Kamis, N.H.; Awang Kechik, M.M.; Chen, S.K.; Ibrahim, N.B.; Shabdin, M.K.; Miryala, M.; et al. Wide temperature range magnetoresistance enhancement of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$: NiO nanocomposites. *Appl. Phys. A* **2023**, *129*, 297. [\[CrossRef\]](#)
65. Boora, N.; Sharma, P.; Alam, A.; Rahman, S.; Ahmad, R.; Awana, V.P.S.; Hafiz, A.K. Impact of NiO Nano-particles on Colossal Magneto-Resistance of $\text{La}_{0.70}\text{Ca}_{0.30}\text{MnO}_3$ composite. *Mater. Lett. X* **2022**, *14*, 100147. [\[CrossRef\]](#)
66. Srivastava, P.; Singh, A.K.; Tyagi, U.P.; Singh, J.; Srivastava, A. Enhanced Magnetotransport Properties of Ag-doped $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Ag}_x\text{MnO}_3$ Polycrystalline Ceramics. *J. Electron. Mater.* **2023**, *52*, 6425. [\[CrossRef\]](#)
67. Wang, S.; Hou, R.; Tian, L.; Zhang, H.; Li, Y. Qingming Chen, Enhanced TCR and MR by Grain Boundary Modification and Phase Competition in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$: Aux ($x = 0, 0.05, 0.1, 0.15$) Composite Ceramics. *Ceram. Int.* **2024**, *50*, 2443. [\[CrossRef\]](#)

68. Dhungana, S.; Casey, J.; Neupane, D.; Pathak, A.K.; Karna, S.; Mishra, S.R. Effect of Metal-Oxide Phase on the Magnetic and Magnetocaloric Properties of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ -MO (MO=CuO, CoO, and NiO) Composite. *Magnetochemistry* **2022**, *8*, 163. [\[CrossRef\]](#)
69. Jin, F.; Wu, D.; Lu, Y.; Pan, Z.; Gu, M.; Wang, H. $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_{3-\delta}$:Ag Nanocomposite Thin Films with Large Temperature Coefficient of Resistance (TCR). *J. Mater.* **2022**, *8*, 799.
70. Venkateshwarlu, D.; Dadhich, H.; Rajyaguru, B.; Hans, S.; Ranjan, M.; Venkatesh, R.; Ganesan, V.; Solanki, P.S.; Shah, N.A. Semiconducting Nature and Magnetoresistance Behaviour of $\text{ZnO}/\text{La}_{0.3}\text{Ca}_{0.7}\text{MnO}_3/\text{SrTiO}_3$ heterostructures. *Mater. Sci. Semicond. Process.* **2021**, *136*, 106154. [\[CrossRef\]](#)
71. Adigamova, M.V.; Malyshev, I.V.; Lukiyanichuk, I.V.; Tkachenko, I.A.; Vyalii, I.E.; Egorkin, V.S. Magnetism of Al_2O_3 Matrix Containing $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ Particles. *J. Alloys Compd.* **2024**, *1004*, 175875. [\[CrossRef\]](#)
72. Kandoliya, M.; Rajyaguru, B.; Gadani, K.; Vaghela, N.; Dadhich, H.; Venkateshwarlu, D.; Joshi, A.D.; Shah, N.A.; Solanki, P.S. Electric Field Effects on Charge Conduction for LaMnO_3 Controlled $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ Manganite. *Surf. Interfaces* **2022**, *30*, 101949. [\[CrossRef\]](#)
73. Lau, L.N.; Lim, K.P.; Ngai, L.M.; Ishak, A.N.; Awang Kechik, M.M.; Chen, S.K.; Ibrahim, N.B.; Shaari, A.H. Influence of Al_2O_3 on the Low-Field Magnetoresistance of Sol-Gel Grown $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3:\text{Al}_2\text{O}_3$ Nanocomposites. *Appl. Phys. A* **2020**, *126*, 730. [\[CrossRef\]](#)
74. Lau, L.N.; Lim, K.P.; Chok, S.Y.; Ishak, A.N.; Hon, X.T.; Wong, Y.J.; Awang Kechik, M.M.; Chen, S.K.; Ibrahim, N.B.; Miryala, M.; et al. Effect of NiO Nanoparticle Addition on the Structural, Microstructural, Magnetic, Electrical, and Magneto-Transport Properties of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ Nanocomposites. *Coatings* **2021**, *11*, 835. [\[CrossRef\]](#)
75. Lau, L.N.; Pah, L.K.; Kechik, M.M.A.; Chen, S.K.; Ibrahim, N.B.; Halim, S.A.; Lai, S.Y. Structural, Magnetic and Magnetotransport Properties of Sol-Gel Synthesized $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3:\text{TiO}_2$ Nanocomposite. *Solid State Phenom.* **2020**, *307*, 9. [\[CrossRef\]](#)
76. Boora, N.; Rani, P.; Nagal, V.; Rahman, S.; Awana, V.P.S.; Hafiz, A.K. Synthesis and Characterization of LCMO Composite and Fabrication of Its Thin Films by RF Magnetron Sputtering for Room-Temperature Applications. *AIP Conf. Proc.* **2020**, *2276*, 020047.
77. Boora, N.; Ahmad, R.; Rani, P.; Maheshwari, P.K.; Khosla, A.; Bansal, S.; Awana, V.P.S.; Hafiz, A.K. Room Temperature Synthesis of Colossal Magneto-Resistance of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:\text{Ag}_{0.10}$ Composite. *ECS J. Solid State Sci. Technol.* **2021**, *10*, 027006. [\[CrossRef\]](#)
78. Tselev, A.; Vasudevan, R.K.; Kalinin, S.V.; Baddorf, A.P. Effect of Silver Doping on the Surface of $\text{La}_{5/8}\text{Ca}_{3/8}\text{MnO}_3$ Epitaxial Films. *Appl. Phys. Lett.* **2014**, *105*, 106102. [\[CrossRef\]](#)
79. Awana, V.P.S.; Tripathi, R.; Balamurugan, S.; Kishan, H.; Takayama-Muromachi, E. Magneto-Transport of High TCR (Temperature Coefficient of Resistance) $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:\text{Ag}$ Polycrystalline Composites. *Solid State Commun.* **2006**, *140*, 410. [\[CrossRef\]](#)
80. Awana, V.P.S.; Tripathi, R.; Kumar, N.; Kishan, H.; Bhalla, G.L.; Zeng, R.; Chandra, L.S.S.; Ganesan, V.; Habermeier, H.U. Magnetotransport of $\text{La}_{0.70}\text{Ca}_{0.3-x}\text{Sr}_x\text{MnO}_3(\text{Ag})$: A Potential Room Temperature Bolometer and Magnetic Sensor. *J. Appl. Phys.* **2010**, *107*, 2331. [\[CrossRef\]](#)
81. Tripathi, R.; Awana, V.P.S.; Balamurugan, S.; Kotnala, R.K.; Kishore, R.; Kishan, H.; Takayama-Muromachi, E. Inter Comparison of the Magneto Transport of $\text{La}_{2/3}\text{Ca}_{1/3}\text{MnO}_3:\text{Ag}/\text{In}$ Polycrystalline Composites. *IEEE Transactions Magn.* **2007**, *43*, 3055. [\[CrossRef\]](#)
82. Jha, R.; Singh, S.K.; Kumar, A.; Awana, V.P.S. Room Temperature Magnetic Entropy Change and Magnetoresistance in $\text{La}_{0.70}(\text{Ca}_{0.30-x}\text{Sr}_x)\text{MnO}_3:\text{Ag}$ 10% ($x = 0.0 - 0.10$). *J. Magn. Magn. Mater.* **2012**, *2853*, 2849. [\[CrossRef\]](#)
83. Ramadhan, M.R.; Kurniawan, B.; Manaf, A.; Pratama, R.; Nanto, D.; Saptari, S.A.; Imaduddin, A. Sintering Temperature Effect on Electric Transport Properties and Magnetoresistance of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$. *AIP Conf. Proc.* **2016**, *1729*, 020025.
84. Zhang, N.; Ding, W.; Zhong, W.; Xing, D.; Du, Y. Tunnel-Type Giant Magnetoresistance in the Granular Perovskite $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$. *Phys. Rev. B* **1997**, *56*, 8138. [\[CrossRef\]](#)
85. Siwach, P.K.; Awana, V.P.S.; Kishan, H.; Prasad, R.; Singh, H.K.; Balamurugan, S.; Takama-Muromachi, E.; Srivastava, O.N. Room Temperature Magneto-Resistance and Temperature Coefficient of Resistance in $\text{La}_{0.7}\text{Ca}_{0.3-x}\text{Ag}_x\text{MnO}_3$ Thin Films. *J. Appl. Phys.* **2007**, *101*, 073912. [\[CrossRef\]](#)
86. Kuru, Y.; Habermeier, H.U.; Tripathi, R.; Awana, V.P.S.; Kishan, H. Room Temperature Magnetoresistance of $\text{La}_{0.7}\text{Ca}_{0.2}\text{Ba}_{0.1}\text{MnO}_3/\text{Ag}$ Thin Films. *Phys. Status Solidi Appl.* **2010**, *207*, 1485.
87. Zhang, K.; Dai, J.; Zhu, X.; Zhu, S.; Yin, L.; Tang, X.; Sun, Y. Vertically Aligned Nanostructure Control and Tunable Low-Field Magnetoresistance in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ Single-Phase Thin Films Manipulated by a High Magnetic Field. *Appl. Phys. Lett.* **2020**, *116*, 053103. [\[CrossRef\]](#)
88. Debnath, J.C.; Strydom, A.M. Large Low Field Magneto-Resistance and Temperature Coefficient of Resistance in $\text{La}_{0.8}\text{Ca}_{0.2}\text{MnO}_3$ Epitaxial Thin Film. *J. Alloys Compd.* **2015**, *621*, 7. [\[CrossRef\]](#)
89. Daoudi, K.; El-Helali, S.; Othmen, Z.; Suleiman, B.M.; Tsuchiya, T. Microstructure and Electrical Transport Mechanisms of the Ca-doped LaMnO_3 Films Grown on MgO Substrate. *J. Materio.* **2020**, *6*, 17. [\[CrossRef\]](#)
90. Yotsuya, T.; Kusaka, T.; Kakehi, Y.; Ogawa, S. Optical Response of LaCaMnO Thin Film Prepared by Pulsed Laser Deposition. *Mater. Chem. Phys.* **1998**, *54*, 169. [\[CrossRef\]](#)

91. Zhou, M.; Li, Y.; Jeon, I.; Yi, Q.; Zhu, X.; Tang, X.; Wang, H.; Fei, L.; Sun, Y.; Deng, S.; et al. Enhancement of Low-field Magnetoresistance in Self-Assembled Epitaxial $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3\text{:NiO}$ and $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3\text{:Co}_3\text{O}_4$ Composite Films via Polymer-Assisted Deposition. *Sci. Rep.* **2016**, *6*, 26390. [[CrossRef](#)] [[PubMed](#)]
92. Hao, J.H.; Mao, X.; Chen, C.H.; Lu, D.X. Room Temperature Bolometric Applications Using Manganese Oxide Thin Films. *Int. J. Infrared Millim. Waves* **1999**, *20*, 2113. [[CrossRef](#)]
93. Kumari, K.; Kumar, A.; Thakur, A.D.; Ray, S.J. Effect of Temperature and Magnetic Field in Resistive Switching Behavior of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3\text{:rGO}$ Nano-composite. *AIP Conf. Proc.* **2020**, *2220*, 080007.
94. Rajeswari, M.; Chen, C.H.; Goyal, A.; Kwon, C.; Robson, M.C.; Ramesh, R.; Venkatesan, T. Low-Frequency Optical Response in Epitaxial Thin Films of $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ Exhibiting Colossal Magnetoresistance. *Appl. Phys. Lett.* **1996**, *68*, 3555. [[CrossRef](#)]
95. Goyal, A.; Rajeswari, M.; Shreekal, R.; Lofland, S.E.; Bhagat, S.M.; Boettcher, T.; Kwon, C.; Ramesh, R.; Venkatesan, T. Material Characteristics of Perovskite Manganese Oxide Thin Films for Bolometric Applications. *Appl. Phys. Lett.* **1997**, *71*, 2535. [[CrossRef](#)]
96. Gregg, J.F.; Petej, I.; Jouguelet, E.; Dennis, C. Spin Electronics-A Review. *J. Phys. D Appl. Phys.* **2002**, *35*, R121. [[CrossRef](#)]
97. Park, J.H.; Vescovo, E.; Kwon, H.J.; Ramesh, R.; Venkatesan, T. Direct Evidence for a Half-Metallic Ferromagnet. *Nature* **1998**, *392*, 794. [[CrossRef](#)]
98. Lan, D.; Chen, B.; Qu, L.; Zhang, K.; Xu, L.; Jin, F.; Guo, Z.; Chen, F.; Gao, G.; Wu, W. Tuning Antiferromagnetic Interlayer Exchange Coupling in $\text{La}_{0.67}\text{Ca}_{0.33}\text{MnO}_3$ -Based Synthetic Antiferromagnets. *APL Mater.* **2019**, *7*, 031119. [[CrossRef](#)]
99. Wibowo, N.A.; Juharni, J.; Sabarman, H.; Suharyadi, E. A Spin-Valve GMR Based Sensor with Magnetite@silver Core-Shell Nanoparticles as a Tag for Bovine Serum Albumin Detection. *ECS J. Solid State Sci. Technol.* **2021**, *10*, 107002. [[CrossRef](#)]
100. Rajeswari, G.; Prabavathi, N.; Prakasam, A.; Kumar, R.; Geetha, S.; Tamizhdurai, P.; AlOthman, Z.A.; Aljuwayid, A.M.; Rajaji, U. Effect of La Doping on NiCr_2O_4 Properties and Catalytic Applications toward Decolorization of 4-Nitrophenol. *ECS J. Solid State Sci. Technol.* **2022**, *11*, 026001. [[CrossRef](#)]
101. Balevicius, S.; Žurauskienė, N.; Stankevič, V.; Keršulis, S.; Plaušinitienė, V.; Abrutis, A.; Zherlitsyn, S.; Herrmannsdorfer, T.; Wosnitza, J.; Wolff-Fabris, F. Nanostructured Thin Manganite Films in Megagauss Magnetic Field. *Appl. Phys. Lett.* **2012**, *101*, 092407. [[CrossRef](#)]
102. Stankevic, T.; Medišauskas, L.; Stankevič, V.; Balevicius, S.; Žurauskienė, N.; Liebfried, O.; Schneider, M. Pulsed Magnetic Field Measurement System Based on Colossal Magnetoresistance-B-Scalar Sensors for Railgun Investigation. *Rev. Sci. Instrum.* **2014**, *85*, 044704. [[CrossRef](#)]
103. Schneider, M.; Schneider, R.; Stankevic, V.; Balevicius, S.; Zurauskienė, N. Highly Local Measurements of Strong Transient Magnetic Fields During Railgun Experiments Using CMR-Based Sensors. *IEEE Trans. Magn.* **2006**, *43*, 370. [[CrossRef](#)]
104. Schneider, M.; Liebfried, O.; Stankevic, V.; Balevicius, S.; Zurauskienė, N. Magnetic Diffusion in Railguns: Measurements Using CMR-Based Sensors. *IEEE Trans. Magn.* **2009**, *45*, 430. [[CrossRef](#)]
105. Haran, T.L.; Hoffman, R.B.; Lane, S.E. Diagnostic Capabilities for Electromagnetic Railguns. *IEEE Trans. Plasma Sci.* **2013**, *41*, 1526. [[CrossRef](#)]
106. Liebfried, O.; Löffler, M.; Schneider, M.; Balevicius, S.; Stankevic, V.; Zurauskienė, N.; Abrutis, A.; Plausinaitienė, V. B-Scalar Measurements by CMR-Based Sensors of Highly Inhomogeneous Transient Magnetic Fields. *IEEE Trans. Magn.* **2009**, *45*, 5301. [[CrossRef](#)]
107. Balevicius, S.; Žurauskienė, N.; Stankevič, V.; Herrmannsdorfer, T.; Zherlitsyn, S.; Skourski, Y.; Wolff-Fabris, F.; Wosnitza, J. CMR-B-Scalar Sensor Application for High Magnetic Field Measurement in Nondestructive Pulsed Magnets. *IEEE Trans. Magn.* **2013**, *49*, 5480. [[CrossRef](#)]
108. Degraeve, J.; Felici, F.; Buchli, J.; Neunert, M.; Tracey, B.; Carpanese, F.; Ewalds, T.; Hafner, R.; Abdolmaleki, A.; Casas, D.D.L.; et al. Magnetic Control of Tokamak Plasmas Through Deep Reinforcement Learning. *Nature* **2022**, *602*, 414. [[CrossRef](#)] [[PubMed](#)]
109. Testa, D.; Toussaint, M.; Chavan, R.; Guterl, J.; Lister, J.B.; Moret, J.M.; Perez, A.; Sanchez, F.; Schaller, B.; Tonetti, G.; et al. The Magnetic Diagnostic Set for ITER. *IEEE Trans. Plasma Sci.* **2010**, *38*, 284. [[CrossRef](#)]
110. Zhang, K.; Dai, J.; Zhu, X.; Tian, Y.; Chen, L.; Sun, Y. Vertical Strain Tuning and Perpendicular Magnetic Anisotropy in $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ Vertically Aligned Nanostructured Thin Films by the Application of High Magnetic Fields. *J. Alloys Compd.* **2021**, *888*, 161511. [[CrossRef](#)]
111. Lv, F.; Qin, Y.; Gao, Y.; Huang, F.; Tang, H.; Liu, J.; Long, L.; Yang, Y. Nonvolatile Resistive Switching in Lead-Free $\text{La}_2\text{CoMnO}_6$ -Based Memory Device. *Mater. Today Commun.* **2023**, *36*, 106454. [[CrossRef](#)]
112. Marton, L.C.; Andres, A.D.; Martínez-Lope, M.J.; Casais, M.T.; Alonso, J.A. Raman Phonons as a Probe of Disorder, Fluctuations, and Local Structure in Doped and Undoped Orthorhombic and Rhombohedral Manganites. *Phys. Rev. B* **2002**, *66*, 174303. [[CrossRef](#)]
113. Parkin, S.S. Spintronic Materials and Devices: Past, present and future! IEDM Technical Digest. *IEEE Int. Electron Devices Meet.* **2004**, *2004*, 903.
114. Mostufa, S.; Liang, S.; Chugh, V.K.; Wang, J.P.; Wuet, K. Spintronic Devices for Biomedical Applications. *NPJ Spintronics* **2024**, *2*, 26. [[CrossRef](#)]

115. Liu, Y.K.; Yin, Y.W.; Li, X.G. Colossal Magnetoresistance in Manganites and Related Prototype Devices. *Chin. Phys. B* **2013**, *22*, 087502. [[CrossRef](#)]
116. Yu, V.Z.; Malyarov, V.G. Heat-Sensitive Materials for Uncooled Microbolometer Arrays. *J. Opt. Technol.* **2001**, *68*, 939.

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