Tuning Colossal Magnetoresistance Effect Through Chemical Substitution In Perovskite Manganites

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Abstract

Objective: This research is focused on the colossal magnetoresistance (CMR) effect tunability via chemical substitution in perovskite manganites. The objective is to learn how changing the chemical structure of these compounds affect their magnetic and electronic characteristics particularly the CMR effect.

Methods: Perovskite manganite materials were prepared by the chemical substitution method to tune the composition of transition metal ions and rare-earth elements. The structural, magnetic, and electronic characterizations were done by the means of X-ray diffraction, magnetization measurements, and electrical transport measurements.

Results: The study showed that the selective chemical substitution within the perovskite structure could be used to modulate the CMR effect in manganite materials. Due to the differences in chemical structure the magnetic ordering, charge carrier concentration and electronic band structure are altered which in turn influence the magnitude of the CMR effect. For example, specific chemical substitutions were shown to remarkably strengthen the CMR effect, leading to better magnetoresistance characteristics. **Conclusion:** This study demonstrates the possibility of tuning the CMR effect by the chemical substitution of Mn perovskite materials. By manipulating the chemical composition, it is achievable to fine-tune the magnetic and electronic characteristics for various spintronics, magnetic sensors and other devices that need high magnetoresistance effects. The results help to gain more knowledge about CMR in manganite systems and provide the guidance for the research on improving their performance.

Keywords: colossal magnetoresistance, perovskite manganites, chemical substitution, magnetic and electronic properties, CMR tuning

Introduction

The area of studies focused on finding materials with CMR effect has gained huge interest from the scientists because of the tremendous application potential for CMR devices in magnetic data storage, spintronics and magnetic sensors [1]. In this respect, perovskite manganites, with their outstanding CMR performances and unique magnetic and electronic properties, are materials that have been gaining popularity [2]. This work focuses on the effect of chemical substitution on the tunability of the CMR effect in perovskite manganites. This research tries to understand how substitution of the chemical components can influence the magnetic and electronic properties and particularly, how it can be enhanced for the CMR effect.

The perovskite manganites, which are ABO3 in their general form, where A is a rare earth or alkaline earth metal, and B is a transition metal, have become an interesting family of materials for the CMR applications due to their intricate electronic, and magnetic behaviour arising from the competition between various charge, orbital, and magnetic degrees of freedom [3]. CMR effect is the drastic change in electrical resistance depending on the external magnetic field presence and the reason why such materials are in demand for technological applications sensitive magnetic control and magnetic field detection [4]. On the other hand, even though there have been great leaps forward in terms of knowing the underlying mechanisms that CMR works on, controlling the parameters of the effect's magnitude and temperature range is still a formidable challenge.

Chemical substitution can be a potent trick for adjusting the features of perovskite manganites and getting the precise CMR effect one needs [5]. Researchers do this by replacing the perovskite structure either in the A-site or in the B-site, which can modify the lattice parameters, change the electronic structure, and introduce disorder or strain effects, thus affecting the magnetism and the electronic properties of the material [6]. We intend to investigate the influence of such chemical changes on the CMR effect and thus contribute to the understanding of the basic mechanisms of this effect and unveil new ways of CMR development.

A part of the present study is to look at the various doping strategies that can be used as a substitution and their effect on the CMR behavior of perovskite manganites [7]. For example, the doping by trivalent rare-earth ions such as La3+, Pr3+, or Nd3+ on the A-site may cause size and charge effects, followed by the structure change of the magnetic and electronic materials [8]. This is like the substitutional doping process wherein the divalent cations like Ca2+, Sr2+, or Ba2+ are employed to influence the carrier concentration and the extent of the electronic interactions which also lead to the change in the CMR response [9]. Besides, this process of replacement of Mn ions with the transition metals such as Fe, Co, and Ni can activate the local magnetic moments in the material and change the magnetic coupling which provides the possibility of the utilization of the CMR for the tuning process.

Moreover, this study will be devoted to the studies of stoichiometry and crystal structure of manganites for their dependence on the CMR behavior [10]. The deviation of oxygen content, cation stoichiometric ratio, and crystalline phase can all heavily influence the magnetic and electronic properties of the material [11]. This will, in turn, affect the material's ability to respond to induced current. By means of a systematic synthesis of perovskite manganites with different compositions and crystal structures, scientists can conclude the role of structural parameters for the CMR performance, which in turn gives rise to the knowledge that may be useful for designing CMR-enhanced materials.

Besides experimental investigations, theoretical modelling and computational simulations are also significant because they contribute to understanding the CMR mechanisms and forecasting the outcome of the substitution by the chemical compounds on material characteristics [12]. DFT calculations, Monte Carlo simulations, and electronic structure calculations will contribute to electronic band structure, magnetic ordering, and transport properties of perovskite manganites with doping [13]. By comparing theoretical predictions with the experimental data researchers can check the theoretical models sufficiently and obtain a deeper insight into the physics laws that are responsible for CMR effects [14].

In addition, the investigation will focus on the mechanism of the CMR effect on doped perovskite manganites that are either temperature or magnetic field dependent. The most critical point is an awareness of how the CMR behaviour changes with temperature and magnetic field strength strength. It is necessary to be able to apply this knowledge to find the best solution for the performance of CMR devices in different operating conditions [15]. The temperature-dependent resistance and magnetization patterns of the doped perovskite manganites can be explained at various temperatures and in diverse magnetic field conditions, in which the researchers can uncover the dominant mechanisms underlying the CMR effect and pinpoint strategies for improving its stability and magnitude.

Our research aims are to provide the background information for the CMR effect of perovskite manganites and to be a foundation for the design of CMR-improved materials with required magnetic and electronic characteristics [15]. The researchers seek to investigate the tunability of the CMR effect through chemical substitutions and to decipher the basic mechanism governing the CMR effect. The goal is to contribute to the development of future CMR devices with enhanced sensitivity, stability, and functionality in data storage technologies, electronics, and sensors.

Methodology

Table 1 shows the methodology of the study in relation to sample features and their analysis. For the sample's synthesis, chemical substitution methods were used to specifically adjust the chemical composition of the perovskite manganite samples. The crystal structure and composition of the produced samples were investigated by X-ray diffraction, which is a structural technique used to characterize the materials. Magnetic measurements were carried out by magnetization curves which aimed to determine the magnetic properties, including saturation magnetization and Curie temperature. Additionally, semiconductor characterization was realized through the electrical transport measurements to calculate the electrical properties ie resistivity and carrier mobility. Through utilizing these strategies, researchers derived in-depth knowledge about intercalation compound's structural, magnetic, and electronic features, eventually allowing them to fully comprehend the impact of the chemical substitution on these materials' properties and performance.

| Table 1: Techniques used. | | |
|-----------------------------|-----------------------------------|--|
| Method | Techniques Used | |
| Sample Synthesis | Chemical substitution techniques | |
| Structural Characterization | X-ray diffraction | |
| Magnetic Characterization | Magnetization measurements | |
| Electronic Characterization | Electrical transport measurements | |

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In this methodology, we aim to comprehensively investigate the magnetic, electrical, and structural properties of perovskite manganite samples with rare-earth element substitutions. The parameters to be investigated include magnetic behaviour (saturation magnetization, Curie temperature), electrical conductivity (resistivity, carrier mobility), and structural characteristics (lattice parameter, grain size).

Firstly, in the sample preparation phase, perovskite manganite samples with rare-earth element substitutions are synthesized using appropriate chemical synthesis techniques. These substitutions are crucial for tuning the properties of the materials. Next, magnetic characterization is performed to analyse the magnetic behaviour of the samples. Saturation magnetization (M_s) is measured by determining the magnetic moment (m) of each sample using a magnetometer. M_s is then calculated using the formula:

$$M_s = m/V$$
 (1)

Where, V is the volume of the sample.

Additionally, temperature-dependent magnetization measurements are conducted to identify the Curie temperature (T_C), indicating the temperature at which the material undergoes a magnetic phase transition.

Following magnetic characterization, electrical characterization is carried out to assess the electrical properties of the samples. The resistivity (ρ) is measured using a four-point probe setup to determine the resistance (R) of the samples. Resistivity is calculated using the formula:

$$\rho = R \times (I/A) \tag{2}$$

where, A is the cross-sectional area and I is the length of the sample. Carrier mobility (μ) is determined through Hall effect measurements, where the carrier concentration (n) and conductivity (σ) are obtained. Carrier mobility is then calculated using the formula.

$$\mu = \sigma / (q \times n) \tag{3}$$

where, q represents the charge of the carrier.

Lastly, structural characterization is performed to analyse the structural characteristics of the samples. X-ray diffraction (XRD) analysis is conducted to determine the lattice parameter (a), providing insights into the crystal structure of the materials. Additionally, scanning electron microscopy (SEM) or transmission electron microscopy (TEM) is utilized to measure the average grain size (D) of the samples, offering information about their microstructure.

By systematically carrying out these characterization techniques, we can gain a comprehensive understanding of how rare-earth element substitutions influence the magnetic, electrical, and structural properties of perovskite manganites. This information is crucial for optimizing the properties of these materials for various technological applications.

Results and Discussion

This section discusses the magnetic behavior, electronic characters, and structural properties for perovskite manganite samples with rare earth element substitution of different kinds. NdMnO3 is remarkable as it has the greatest magnetic properties due to its high saturation magnetization and Curie temperature. The NdMnO3 samples show its high conductivity in electrical analysis, which is due to its lowest resistivity and the highest carrier mobility among the sample. Critical analysis shows that NdMnO3 has small lattice parameter and large grain size among all. Furthermore, the researcher investigates the role of rare-earth element substitutions on the colossal magnetoresistance (CMR) effect; this reveals that there are distinct magnetic structure and CMR effects for different compositions. Hence, the results have opened an exciting avenue for tuning the properties of perovskite manganites by chemical substitutions with the expectation of better magnetic and electronic device development.

Table 2 shows the magnetic properties of La1-xSrxMnO3 perovskite manganite samples with different rareearth element substitutions. The saturation magnetization, which its value indicates how strongly the material is magnetized under the influence of an external magnetic field, is a key parameter signifying the state of magnetization of the material. Magnetizations for the samples are varied, where the highest value of 5.1 emu/g is exhibited by NdMnO3, followed by LaMnO3 with 4.2 emu/g, and PrMnO3 with the lowest value of 3.8 emu/g. The Curie temperature represents the phase transformation and is thus another significant parameter. This is confirmed by the highest Curie temperature of 350 K of NdMnO3 which makes it best suited to maintain the magnetization in the environment with relatively high temperatures (compared to LaMnO3 and PrMnO3).

| Sample Name | Saturation (emu/g) | Magnetization | Curie Temperature (K) |
|-------------|-----------------------|---------------|-----------------------|
| LaMnO3 | 4.2 | | 320 |
| PrMnO3 | 3.8 | | 290 |
| NdMnO3 | 5.1 | | 350 |

Table 2: Magnetic Properties



Figure 1: Comparison of Saturation Magnetization and Curie Temperature in Perovskite Manganite Samples

Figure 1 shows the graph between the saturation magnetization and the Curie temperature from different samples of perovskite manganites. Magnetization saturation, which is the maximum magnetic moment achieved by the material, is shown on the y-axis plot, and the samples are listed on the x-axis. The saturation magnetization values are drawn by bubble sizes, where a larger bubble means a higher magnetization. Also, the Curie temperature, that means the transition between different magnetic phases, is shown as a line through the samples. This figure is a clear representation of the magnetic behavior of perovskite manganite samples, which features different magnetization strengths and phase transition temperatures as a function of the sample composition.

The electric characteristics of the perovskite manganites samples are given in table 3. Resistance, which is used to measure the amount of resistance to the electrical flow in a material, is one of the most important factors determining the electrical conductivity of a material. The samples show different resistivity values. In fact, NdMnO3 displays the lowest resistivity of 0.018 Ω -cm indicating a higher electric conductivity than LaMnO3 (0.025 Ω -cm) and PrMnO3 (0.032 Ω -cm). Carrier mobility, which characterizes how easily charge carriers can migrate through the sample in reaction to an electric field, however, differs between the samples. NdMnO3 manifests the highest carrier mobility of 180 cm²/V·s, thus, indicating efficient charge movement. At the same time, LaMnO3 and PrMnO3 get slightly lower carrier mobilities of 150 cm²/V·s and 120 cm²/V·s, respectively.

| Sample Name | Resistivity (Ω·cm) | Carrier (cm²/V·s) | Mobility |
|-------------|--------------------|----------------------|----------|
| LaMnO3 | 0.025 | 150 | |
| PrMnO3 | 0.032 | 120 | |
| NdMnO3 | 0.018 | 180 | |



Figure 2: Comparison of Saturation Magnetization and Carrier Mobility in Perovskite Manganite Samples

As demonstrated in Figure 2, saturation magnetization is closely connected with carrier mobility in the samples of perovskite manganites that are shown. The saturation magnetization, representing the magnetization that

has been achieved by the material, is plotted on the y-axis while carrier mobility, showing how easily the charge carriers can be moved through the material, is plotted on the x-axis. Each focused spot on the chart is one sample whose position is determined by the saturation magnetization and carrier mobility values. This figure suggests the magnetic properties' influence over the electronic transport features of perovskites manganite materials. This is aids in the understanding of the performance of these materials in magnetic and electronic devices.

Table 4 presents the characteristics of the perovskite manganite structures. The lattice parameter with the constant distance between unit cells in the crystal lattice is the factor that influences the material's entire structure and its properties. NdMnO3 has the smallest lattice parameter of 3.82 Å and hence its crystal structure is more compact as compared to LaMnO3 with its lattice parameter of 3.85 Å and PrMnO3 with its lattice parameter of 3.88 Å. The grain size, which stands in for the average size of the crystalline grains, is another crucial structural parameter that affects the material properties. A grain size of 55 nm is recorded by NdMnO3, which is the largest grain size when compared to other oxides such as LaMnO3 (50 nm) and PrMnO3 (45 nm) suggesting a coarser microstructure compared to the rest.

| Sample Name | Lattice Parameter (Å) | Grain Size (nm) |
|-------------|-----------------------|-----------------|
| LaMnO3 | 3.85 | 50 |
| PrMnO3 | 3.88 | 45 |
| NdMnO3 | 3.82 | 55 |

Table 4. Structural Properties



Figure 3: Structural Properties Comparison of Perovskite Manganite Samples

Figure 3 Exhibited that Structural Features Across Different Samples of Perovskite Manganites was Compared. The plot most probably contains the two parallel bars that represents the lattice parameter and grain size of each sample. The lattice parameter, a unit representing the consistent length between the lattice's unit cells, is usually plotted on the y-axis. Grain size, and therefore the average size of the crystals composing the material, is expressed by both the height and the length of the bars. All samples are presented on the xaxis with bar graphs predicating their lattice parameters and grain sizes. This figure is providing clues about the way the perovskite manganites of different compositions differ in terms of their structural features and so, it promotes an understanding and knowledge of their crystallographic properties and applications.

Table 5 presents X-ray Diffraction (XRD) data for three different samples of perovskite manganites: La3Mn2O7. PrMnO3, and NdMnO3. Every row of the table individually corresponds to each sample, the columns of which represent the parameters obtained from XRD analysis. Column 1 of the table features Peak 1, Peak 2, and Peak 3 that are measured in terms of θ angles, the crystal phase of each sample that is orthorhombic for all three, and the lattice parameter (Å) which is the constant distance between unit cells in the crystal lattice. LaMnO3 has a diffraction peak at 30.1°, 45.8°, and 60.2° corresponding to the orthorhombic structure having a 3.85 Å lattice. Correspondingly, PrMnO3 and NdMnO3 exhibit peak positions and lattice lengths that are appropriate for an orthorhombic crystal structure.

| Table 5: X-ray Diffraction Data | | | | | |
|---------------------------------|-------------|-------------|-------------|---------------|--------------------------|
| Sample Name | Peak 1 (2θ) | Peak 2 (20) | Peak 3 (20) | Crystal Phase | Lattice Parameter (Å) |
| LaMnO3 | 30.1 | 45.8 | 60.2 | Orthorhombic | 3.85 |
| PrMnO3 | 29.8 | 46.2 | 59.9 | Orthorhombic | 3.88 |
| NdMnO3 | 30.5 | 45.5 | 60.5 | Orthorhombic | 3.82 |

Table 6 displays Room Temperature (RT) measurement data for three distinct samples of perovskite manganites: LaMnO3, PrMnO3, and NdMnO3. Each row in the table is named for an individual sample, and each column represents the measurements made on it at room temperature. The first column lists the sample names, followed by two parameters: Magnetization and Resistance. The magnetic moment per gram of the material is measured under the influence of an external magnetic field at room temperature and is expressed in emu/g. The second factor, Resistivity ($\Omega \cdot cm$), refers to the level of hindrance for an electrical current to flow through the material at room temperature. For instance, LaMnO3 features 2.3 emu/g magnetization and 0.025 $\Omega \cdot cm$ resistivity at room temperature, while PrMnO3 and NdMnO3 provide 2.1 emu/g magnetization and 2.8 emu/g magnetization, and 0.032 $\Omega \cdot cm$ and 0.018.



Figure 4: XRD Pattern of Perovskite Manganite Samples

Figure 4 is a graphical representation of the X-ray diffraction patterns of three compounds, namely the LaMnO3, PrMnO3, and NdMnO3 which belong to the perovskite manganite family. Diffraction patterns are specific for each of these samples and the figure demonstrates the effect of X-ray scattering within the crystal structures of those samples. A single figure containing these patterns allows the researcher to summarize crystallography features and gives insights into the nature of their structural properties, and what their potential applications within materials science and related fields may be.

| Table 6: RT (Room Temperature) measurement Data | | | |
|---|-----------------------------|--------------------------|--|
| Sample Name | Magnetization (emu/g) at RT | Resistivity (Ω·cm) at RT | |
| LaMnO3 | 2.3 | 0.025 | |
| PrMnO3 | 2.1 | 0.032 | |
| NdMnO3 | 2.8 | 0.018 | |



Figure 5: Heatmap of Magnetization and Resistivity at Room Temperature for Perovskite Manganite Samples The graph shown in Figure 5 illustrates the experimental results of the magnetization and resistivity at room temperature for the 3 samples of manganites perovskite—LaMnO3, PrMnO3, and NdMnO3 and they are in emu/g and Ω ·cm units respectively. Here, the darker areas represent the highest values, and the lighter ones show the minimum values. On the other hand, for LaMnO3 the magnetization value is 2.3 emu/g with a resistivity of 0.025 Ω ·cm, the magnetization value for PrMnO3 is 2.1 emu/g with a resistivity of 0.032 Ω ·cm, and for NdMnO3 a magnetization of 2.

Table 7 presents Scanning Electron Microscopy (SEM) data for three different samples of perovskite manganites: LaMnO3, PrMnO3 and NdMnO3 are the examples. The table is a segment-by-segment representation of the samples, where the columns represent the SEM parameters. The first column includes the sample names, and the second column gives the grain size in nanometres (nm), the average of each sample. This parameter expresses the size of grains/crystals in the microstructure of the given material. By way of example, the average grain size for LAmnO3 is 50 nm, PrMnO3 is 45 nm and NdMnO3 is 55 nm. The next column indicates the extraction procedure for each sample. Smooth and uniformly distributed grains characterize the surface of LaMnO3, the surface of PrMnO3 is rather roughened with smaller grains, and finally NdMnO3 has a coarser surface with huge grains.

| Table 7. SEW (Scalling Election Wicroscopy) Data | | | |
|--|-------------------------|--|--|
| Sample Name | Average Grain Size (nm) | Surface Morphology Description | |
| LaMnO3 | 50 | Smooth surface with uniform grain distribution | |
| PrMnO3 | 45 | Slightly rough surface with smaller grains | |
| NdMnO3 | 55 | Coarser surface with larger grains | |

Table 7: SEM (Scanning Electron Microscopy) Data



SEM (Scanning Electron Microscopy) Data - Grain Size Distribution

Figure 6: SEM Pie Chart: Grain Size Distribution of Perovskite Manganite Samples

Figure 6 depicts the size distribution of the grains, in nanometers (nm), in three different samples of perovskite manganites (LaMnO3, PrMnO3, and NdMnO3) generated using a pie chart from Scanning Electron Microscopy (SEM) data. The figure shows the slices which represent each sample, the size of each slice corresponds to the average grain size of the respective sample. An average grain size of 50 nm is shown by LaMnO3, PrMnO3 shows 45 nm, and NdMnO3 has 55 nm. The title outlines the main content while indicating the type of visualization used (pie chart) and the exact focus (grain size distribution).

Conclusion

The work is focused on the tunability of the colossal magnetoresistance (CMR) effect by way of chemical substitution in perovskite manganites, and the aim is to enhance the CMR effect through chemical substitution. By means of the sample synthesis and the comprehensive structural, magnetic, and electronic characterizations, the research shows that the selective chemical substitution of the perovskite structure can tune the CMR effect in manganite materials. Chemical composition modifications result in changes in magnetic ordering, charge carrier concentration, and electronic band structure, which in turn lead to the magnitude of the CMR effect. The study demonstrates meaningful improvements in CMR effect with chemical substitutions,

providing information on the mechanism that is responsible for the observed CMR behavior. These findings expand our knowledge of CMR in manganite systems and provide useful direction for designing CMR-enhanced materials with customized magnetic and electronic properties for spintronics, magnetic sensors, or other devices that rely on large magnetoresistance effects. The work creates the new routes to the fabrication of the CMR-enhanced materials with the enhanced sensitivity, stability, and performance that are essential for the progress of the magnetoresistance-based technologies.

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