Research Progress of Doped Manganite Materials in Magnetic Refrigeration

Zhuojia Xie¹, Zhengguang Zou¹,²*, Bangrong He¹, Lilin Liu¹ and Zheng Mao¹

¹College of Materials Science and Engineering, Guilin University of Technology, Guilin, China, ²Collaborative Innovation Center for Exploration of Hidden Nonferrous Metal Deposits and Development of New Materials, Guilin University of Technology, Guilin, China

Magnetic refrigeration technology is a new, green, high-efficiency approach. It has attracted increasing attention from researchers and has a strong competitiveness over traditional refrigeration methods. With the continuous development of social lives, magnetic refrigeration technology must have important application prospects. This article briefly describes the basic principles. The focus is on the introduction and summary of research on perovskite manganite doping in magnetic refrigeration. Finally, the outlook and summary of magnetic refrigeration technology are presented.

Keywords: magnetic refrigeration, green, high efficiency, perovskite manganite, doping

INTRODUCTION

Magnetic refrigeration is a green and safe technology (Shen et al., 2021). Compared with gas compression refrigeration technologies, the gas compression refrigeration cycle can generally only reach 5–10% of the Carnot cycle, while magnetic refrigeration can reach 30–60% (Liu, 2009). Magnetic refrigeration is a technology that uses the magnetocaloric effect (MCE) of magnetic materials. MCE is unique as it changes the magnetic entropy of the material through variations in the external magnetic field. This is accompanied by the process of heat absorption and release in the material. This principle is illustrated in Figure 1 (Bao and Zhang, 2004).

There are many kinds of refrigeration materials. In 1976, Brown (1976) was the first to use Gd for magnetic refrigeration. Gd metals have a giant MCE, but their purity requirements are high and the price is too high for refrigeration. At the beginning of the 21st century, Wada et al. (2003) discovered a large MCE in the compound MnAs. Although MnAs as an Mn-based compound, has a good MCE, As is toxic. The perovskite manganese oxides have a wide range of Tc adjustments, easy preparation and synthesis, low cost, strong chemical stability, and high MCE. Therefore, many researchers have a strong interest in perovskite manganite in refrigeration.

The molecular formula of Perovskite manganite is RE₁₋ₓAEₓMnO₃, where RE is a rare earth element and AE is an alkaline earth element. RE and AE constitute the A position of the Perovskite manganite structure, and Mn constitutes the B position, so the general formula is generally written as ABO₃. The ideal ABO₃ has a cubic structure, in which the A-site ion is located at the apex of the cubic unit cell, the B-site ion is located at the body center of the cubic unit cell, and O²⁻ is located at the face center of the cubic unit cell. The tolerance factor (t) proposed by Goldschmidt is usually used to describe the stability of perovskite manganite structure (Goldschmidt, 1926; Siwach et al., 2008). In fact, the ABO₃ crystal will undergo lattice distortion, forming an orthogonal (t < 0.96) or rhombic (0.96 < t < 1) structure.
DIFFERENT WAYS OF DOPING

Ion doping can be divided into three categories: A-site, B-site, and vacancy doping. Ion doping produces three changes in perovskite manganite: 1) Change in ion valence, 2) Change in ion size, and 3) change in its crystal structure. The essential source of the magnetic properties for perovskite manganite is the double exchange effect (DE) of Mn$^{3+}$-O$^{2-}$-Mn$^{4+}$. It is believed part of the trivalent RE in perovskite manganite is replaced by low-valent AE and part of Mn$^{3+}$ will be changed to Mn$^{4+}$. The $e_g$ orbit becomes an empty state and uses O$^{2-}$ as a bridge between the two manganese ions of the two valence states to form DE (Zener, 1951; Anderson and Hasegawa, 1955). The principle of DE is shown in Figure 1. To better adjust the MCE and temperature of the magnetic phase transition, scientists have focused primarily on doping rare earth elements or AE to replace the A and B sites of perovskite manganite (CosKun et al., 2016; Ghosh and Ghatak, 2016; Sfifir et al., 2017).

A-Site Doping

At the A site, the wide variety of doped elements give differing magnetic moments, valence states, and ionic radii. This generates a mixed valence state of Mn$^{3+}$ and Mn$^{4+}$, which makes it possible to pass the DE at low temperatures and produce ferromagnetism. At the same time, the average ionic radius of the A-site ions, crystal structure, and magnetic moment of the molecules change. This affects the DE and MCE of the material while producing a

![FIGURE 1 | Schematic diagram of magnetic refrigeration, schematic diagram of double exchange mechanism and crystal structure of perovskites (ABO$_3$).](image-url)
TABLE 1 | Curie temperature and magnetic entropy change of perovskite materials substituted with different elements.

| Perovskite manganite | $H$ (T) | $\Delta S_M$ (J/kg K) | $T$ (°C) |
|---------------------|---------|----------------------|---------|
| La0.9Sr0.1MnO3 (Wei et al., 1998) | 1.00 | 1.50 | 218 |
| La0.8Sr0.2MnO3 (Wei et al., 1998) | 1.00 | 1.32 | 195 |
| La0.8Sr0.2MnO3 (Wei et al., 1998) | 1.00 | 2.11 | 342 |
| La0.7Sr0.3MnO3 (Wei et al., 1998) | 1.00 | 1.96 | 334 |
| La0.6Sr0.4MnO3 (Phan et al., 2003) | 1.00 | 2.12 | 305 |
| La0.6Sr0.4MnO3 (Mori et al., 1998) | 5.00 | 1.69 | 348 |
| La0.6Sr0.4MnO3 (Gou et al., 1998) | 1.50 | 1.50 | 340 |
| La0.6Sr0.4MnO3 (Szweczyk et al., 2003) | 7.00 | 7.10 | 280 |
| La0.6Sr1.15MnO3 (Szweczyk et al., 2005) | 7.00 | 4.40 | 200 |
| La0.6Sr1.15MnO3 (Szweczyk et al., 2005) | 7.00 | 6.00 | 152 |
| La0.6Sr1.15MnO3 (Szweczyk et al., 2005) | 5.00 | 5.85 | 244 |
| La0.6Sr1.15MnO3 (Phan et al., 2004) | 1.35 | 1.72 | 310 |
| La0.6Sr1.15MnO3 (Szweczyk et al., 2005) | 7.00 | 6.60 | 234 |
| La0.6Sr1.15MnO3 (Szweczyk et al., 2003) | 5.00 | 5.80 | 197 |

wealth of magnetic order phenomena, such as the charge order, orbit order, and mutual coupling. After A-site doping, the internal DE and molecular magnetic moment of the material strongly influence the Curie temperature ($T_c$) and maximum magnetic entropy ($\Delta S_{M_{\text{max}}}$).

Based on the selected substrate RaMnO$_3$ (Ra=La, Nd, Pr, Sm, such as LaMnO$_3$), has been found to have better magnetocaloric properties in the room temperature range (Phan and Yu, 2007; Sun et al., 2017), especially in low and medium magnetic fields, which has a larger magnetic entropy change than that of Gd and GdSiGe alloy phases.

The types of ion doping can be divided into single-ion, multi-ion doping. Single-ion doping generally uses Na, Sr, Ag, Ca, Cd, Ba, and K plasmas at the A site, as shown in Table 1. The study found that under the same valence state, different doping ion radii have different effects on the structure and magneto-caloric properties of LaMnO$_3$. Zhong et al. (1998), Zhong et al. (1999), Das and Dey (2007) studied La$_{1-x}$Na$_x$MnO$_3$ ($0 < x < 0.15$) and La$_{1-x}$K$_x$MnO$_3$ ($0 < x < 0.2$) materials, they found that under the conditions of the same magnetic field changes, $\Delta S_M$ of the material increases with the increase of Na$^+$, K$^+$ doping amount. Its Tc also rises, when the K doping amount $x = 0.2$, its $\Delta S_M$ becomes $2.2 J/(kg K)$, and its Tc also rises to $350 K$. While Li$^+$ doping will decrease Magnetic change and Tc of perovskite manganite (Ghosh and Ghatak, 2016). It can be concluded that the A-site doping of low-valence ions significantly affects the magnetic entropy change and Tc, and there is often an extreme value, which should be related to the effect of doping on Mn$^{3+}$/Mn$^{4+}$ in the material system.

At the same time, the study found that the addition of alkaline earth metal or alkali metal ions that are lower in value than La in the A site has a significant change in the performance of LaMnO$_3$. Mcbride et al. (2016), Demin and Koroleva (2004) and others have carried out research on the A-site Sr$^{2+}$ doping of LaMnO$_3$. They believe that the A-site doping of Sr$^{2+}$ with a slightly larger radius than La$^{3+}$ will cause the lattice structure to deviate from the ideal cubic structure, thereby producing Mn-O bond length and Mn$^{3+}$/Mn$^{4+}$ bond angle changes, the overlap of electron orbitals increases the DE and the MCE. With the increase of Sr$^{2+}$ content, the magnetic entropy change of La$_{1-x}$Sr$_x$MnO$_3$ ($0 < x < 0.3$) increases, and Tc also increases, $\Delta S_{M_{\text{max}}} = 1.7 J/(kg K)$, and Tc is about 350–360 K. Bohigas et al. (2000), Sun et al. (2000) studied the change of the MCE of La$_{0.6}$Ca$_{0.4}$MnO$_3$. Under the same magnetic field change condition, with the increase of Ca$^{2+}$ doping, the material $\Delta S_M$ first increased and then decreased. Hussain et al. (2016) studied the MCE of La$_{0.6}$Ba$_{0.4}$MnO$_3$ and revealed that the MCE first increased and then decreased with the increase of Ba$^{2+}$ doping. When the doping amount exceeds 0.3, both the $\Delta S_M$ and the Tc are reduced. The performance of the material is also related to the influence of the size of the doped ions on the symmetry of the crystal structure of the material, which is related to the effect of the Jahn-Teller effect on the performance of the material. When the size of the doped ions is too large or too small, the lattice distortion is intense, the Mn$^{3+}$/ Mn$^{4+}$ distribution period is affected and the DE is weakened.

When multi-ion doping, the effect of doping behavior on the magnetocaloric properties and Tc of perovskite manganite is more complicated. One study found that La$_{0.65}$Sr$_{0.35}$MnO$_3$ (Phan et al., 2003) with an applied magnetic field of 1 T has Tc = 305 K, which is close to room temperature. The $\Delta S_M$ becomes 2.12 J/(kg K) and RCP = 106 J/kg, therefore researchers usually utilize La$_{0.65}$Sr$_{0.35}$MnO$_3$ for further ion doping research. For example, Kong (Kong and Zou, 2018) doped Gd and Na at the A site. It is found that the Tc of multi-ion doping gradually decreases to around room temperature with the increase of the doping amount of Gd and Na ions. The DE has a close relationship with the doping content. On the basis of LaMnO$_3$, the Mn$^{3+}$ will substitute the Mn$^{3+}$, when the Alkaline earth metal ions access to this system. Moreover, the ratio of Mn$^{3+}$/Mn$^{4+}$ is considered changed along with the content of doping ions. Linh et al. (2017) studied the $\Delta S_M$ change and the Tc of La$_{0.7}$Ca$_{0.3}$MnO$_3$ and...
found that the Tc of the material gradually rises with the increase of Sr and Ba ion doping during multi-ion doping, but it will reduce the $\Delta S_M$ of the material. Duc, Nguyen Thi My (Duc et al., 2019) studied the La$_{0.65}$Sr$_{0.35}$MnO$_3$ material and found that with the doping of Pr, the $\Delta S_M$ of the material will increase to a certain extent, but the Tc will be reduced. When the ions doped at the A site changed the ratio of Mn$^{3+}$/Mn$^{4+}$ for the matrix material and the average ion radius of the A site, which led to change in the mismatch factor. The DE was reduced, and the Tc dropped to a certain extent.

In the study of magnetic refrigeration, Dagotto divided perovskite manganite into wide-, medium- and small-bandwidth types based on the bandwidth of the DE (Dagotto et al., 2001). La$_{0.65}$Sr$_{0.35}$MnO$_3$ material belongs to the wide-bandwidth type, and another important perovskite manganite of Pr$_{1-x}$Sr$_x$MnO$_3$ belongs to the small-bandwidth type. The ferromagnetic-antiferromagnetic and paramagnetic-ferromagnetic transitions appear in the magnetic phase diagram simultaneously for $x$ between 0.5 and 0.55 (Pollert et al., 2002). In this T range, as the Sr content at the A site increases, Tc gradually decreases, and the Neel temperature (critical temperature of antiferromagnetic-paramagnetic transition) increases with the two transitions reaching a certain value (Martin et al., 1999). This shows that Sr$^{2+}$ doping at the A site causes changes in the ratio of Mn ions, which affects the DE and phase change of the material. Since the 21st century, researchers have performed increasing studies on Pr$_{1-x}$Sr$_x$MnO$_3$. DE and phase change of the material. Since the 21st century, researchers have performed increasing studies on Pr$_{1-x}$Sr$_x$MnO$_3$. DE and phase change of the material. Since the 21st century, researchers have performed increasing studies on Pr$_{1-x}$Sr$_x$MnO$_3$. DE and phase change of the material. Since the 21st century, researchers have performed increasing studies on Pr$_{1-x}$Sr$_x$MnO$_3$. DE and phase change of the material. Since the 21st century, researchers have performed increasing studies on Pr$_{1-x}$Sr$_x$MnO$_3$. DE and phase change of the material. Since the 21st century, researchers have performed increasing studies on Pr$_{1-x}$Sr$_x$MnO$_3$. DE and phase change of the material. Since the 21st century, researchers have performed increasing studies on Pr$_{1-x}$Sr$_x$MnO$_3$. DE and phase change of the material. 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La$_{1-x}$Ca$_x$MnO$_3$ has a high magnetic entropy change and a relatively low $T_c$, which can be increased by doping. La$_{1-x}$Ca$_x$MnO$_3$ replaces La$^{3+}$ with Ca$^{2+}$. To balance the valence, Mn$^{3+}$ needs to be produced, which further modifies the magnetization and $T_c$ of the material. Changes in the valence state of Mn ions can alter the magnetic properties of the material from ferromagnetic to paramagnetic. There are two energy levels for Mn ions. The principle of the lowest energy, high energies into two orbitals, which causes crystal lattice distortion. This system has therefore become a refrigeration material that is widely studied by scientific researchers. He (He, 2019) used the sol-gel method to prepare La$_{0.65-x}$Ca$_{0.35}$MnO$_3$ (0 ≤ $x$ ≤ 0.15). The experimental results show that as the La$^{3+}$ vacancy concentration increases, the ion radius and the mismatch factor change. The $T_c$ of La$_{0.65-x}$Ca$_{0.35}$MnO$_3$ also gradually increases. When the external magnetic field is 0–5 T, $\Delta S_M = 1.17$ J/(kg K). This is because there are four electrons in the outermost layer of Mn$^{3+}$, of which three are in the $t_{2g}$ localized state and the other is in the in the patrol state and is hybridized with the 2p orbital of the O ion to form a covalent bond. With the increased vacancy concentration, the number of Mn$^{3+}$ ions gradually decreases, the number of Mn$^{4+}$ gradually increases, and the concentration of the patrol state into vacancies increases. Thus, the DE of the material increases, and the $T_c$ becomes larger.

Brion (Brion et al., 1999) used the solid phase method to prepare La$_{1-x}$MnO$_3$. The study found that the $T_c$ of La$_{0.93}$MnO$_3$ and La$_{0.99}$MnO$_3$ were 170 and 118 K, respectively, and the Mn$^{4+}$ content was 21% and 9%. Brion believed that when $x$ mol of La$^{3+}$ is replaced with a vacancy, 3x mol of Mn$^{3+}$ is converted into Mn$^{4+}$. Wallha et al. (2009) found that Mn$^{4+}$ increased with the vacancy concentration. However, Sankar (Joy et al., 2002) prepared La$_{1-x}$MnO$_3$ using the solid-phase method, which indicated that $T_c$ increased with the vacancy concentration but Mn$^{4+}$ decreased. There are different experimental results for Mn$^{3+}$ with changes in the vacancy concentration, which manifest in the A site of perovskite manganese oxide. A small amount of AE or RE replaces with a vacancy, 3x mol of Mn$^{3+}$ is converted into Mn$^{4+}$. There is a two-orbital state, which is large gaps are violent thermal movement results in the migration of vacancy defects, and large gaps are first occupied by ions. The lack of A-site ions is compensated by B-site ions (such as Mn). Therefore, vacancies in the sample appear in the A site instead of the B site.

**SUMMARY AND OUTLOOK**

This paper introduces the basic principles of magnetic refrigeration. In particular, the relationship between the doping content and properties of perovskite manganese oxide materials is introduced in detail, provide reference value for the future study. In the 21st century, important breakthroughs have been made in the research and development of magnetic refrigeration materials. However, there are still many problems that need to be studied and solved. From the current research results, when Mn$^{3+}$/Mn$^{4+}$ is close to 2:1, the double exchange effect of the materials reaches the strongest, but the internal mechanism is still unclear. In addition, the performance of the materials is also related to the size of the doped ions on the symmetry of the crystal structure, and then the Jahn-Teller effect affects the performance of the material.

Magnetic refrigeration has a good application market at room temperature, such as air conditioners. In some research fields, refrigeration materials need to be light weight and have a wide range of temperatures for refrigeration, but current magnetic refrigeration materials cannot meet the requirements. Hence, research of magnetic refrigeration has good development and application prospects.

**AUTHOR CONTRIBUTIONS**

ZX: Conceptualization, Data curation, Writing original draft.
BH: Syntax modification. ZZ, ZM, and LL: Supervision.

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