



# Research Progress of Doped Manganite Materials in Magnetic Refrigeration

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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.

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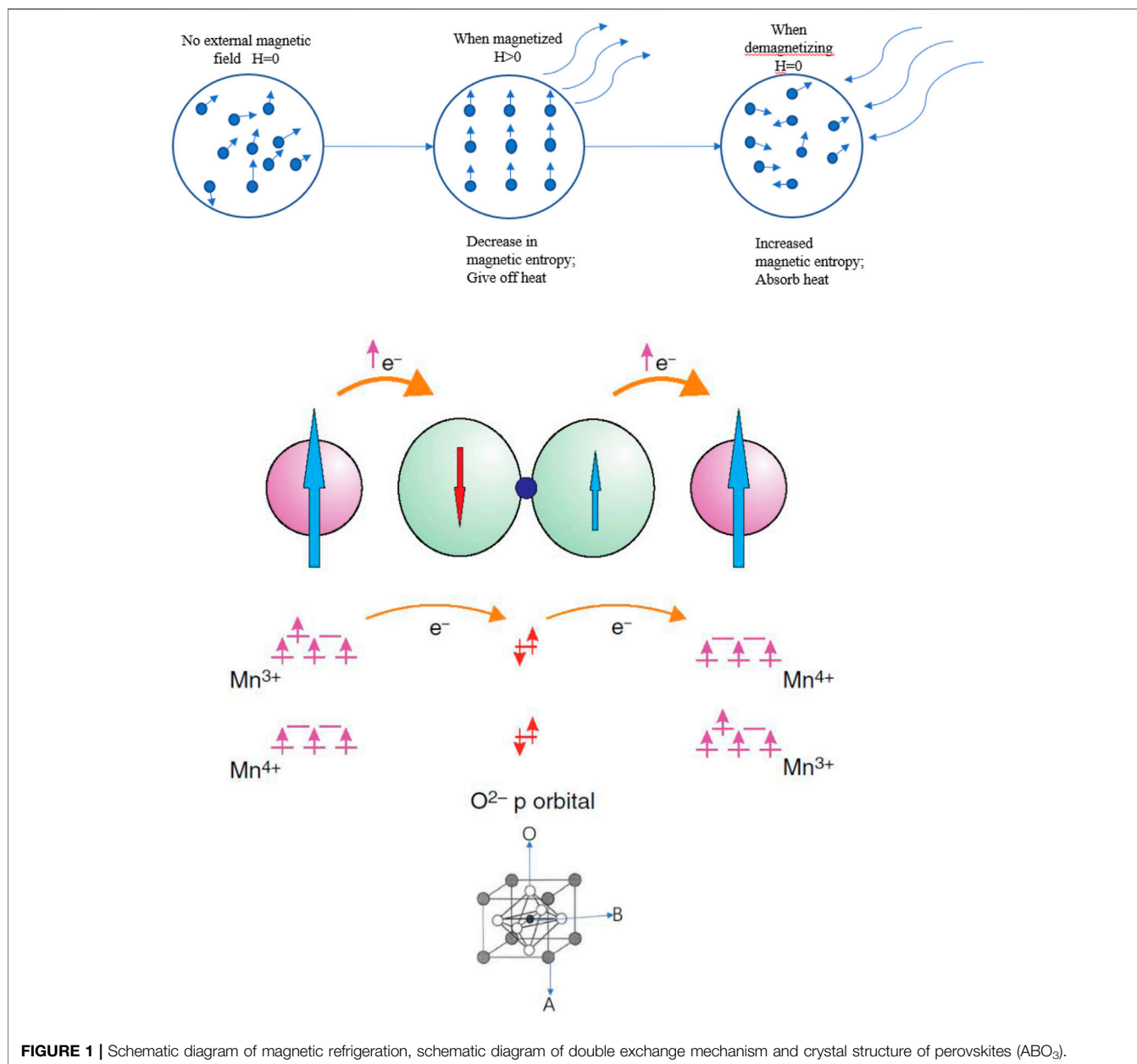
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## INTRODUCTION

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 T<sub>c</sub> 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 RE<sub>1-x</sub>AE<sub>x</sub>MnO<sub>3</sub>, 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 ABO<sub>3</sub>. The ideal ABO<sub>3</sub> 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 O<sup>2-</sup> 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 ABO<sub>3</sub> 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 are 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; Sffir 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

**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)
La <sub>0.9</sub> Na <sub>0.1</sub> MnO <sub>3</sub> (Wei et al., 1998)	1.00	1.53	218
La <sub>0.925</sub> Na <sub>0.075</sub> MnO <sub>3</sub> (Wei et al., 1998)	1.00	1.32	195
La <sub>0.835</sub> Na <sub>0.165</sub> MnO <sub>3</sub> (Wei et al., 1998)	1.00	2.11	342
La <sub>0.80</sub> Na <sub>0.20</sub> MnO <sub>3</sub> (Wei et al., 1998)	1.00	1.96	334
La <sub>0.65</sub> Sr <sub>0.35</sub> MnO <sub>3</sub> (Phan et al., 2003)	1.00	2.12	305
La <sub>0.67</sub> Sr <sub>0.33</sub> MnO <sub>3</sub> (Morelli et al., 1996)	5.00	1.69	348
La <sub>0.75</sub> Sr <sub>0.25</sub> MnO <sub>3</sub> (Guo et al., 1998)	1.50	1.50	340
La <sub>0.80</sub> Sr <sub>0.20</sub> MnO <sub>3</sub> (Szewczyk et al., 2005)	7.00	7.90	305
La <sub>0.815</sub> Sr <sub>0.185</sub> MnO <sub>3</sub> (Szewczyk et al., 2005)	7.00	7.10	280
La <sub>0.865</sub> Sr <sub>0.135</sub> MnO <sub>3</sub> (Szewczyk et al., 2005)	7.00	4.40	200
La <sub>0.88</sub> Sr <sub>0.120</sub> MnO <sub>3</sub> (Szewczyk et al., 2005)	7.00	6.00	152
La <sub>0.84</sub> Sr <sub>0.16</sub> MnO <sub>3</sub> (Szewczyk et al., 2000)	5.00	5.85	244
La <sub>0.845</sub> Sr <sub>0.155</sub> MnO <sub>3</sub> (Phan et al., 2004)	1.35	1.72	310
La <sub>0.845</sub> Sr <sub>0.155</sub> MnO <sub>3</sub> (Szewczyk et al., 2003)	7.00	6.60	234
La <sub>0.87</sub> Sr <sub>0.13</sub> MnO <sub>3</sub> (Szewczyk et al., 2003)	5.00	5.80	197
La <sub>2/3</sub> Sr <sub>1/3</sub> MnO <sub>3</sub> (Mira et al., 2002)	1.00	1.50	370
La <sub>0.80</sub> Ag <sub>0.20</sub> MnO <sub>3</sub> (Hien and Thuy, 2002)	1.00	2.40	300
La <sub>0.78</sub> Ag <sub>0.22</sub> MnO <sub>3</sub> (Szewczyk et al., 2003)	1.00	2.90	306
La <sub>0.75</sub> Ag <sub>0.25</sub> MnO <sub>3</sub> (Hien and Thuy, 2002)	1.00	1.52	306
La <sub>0.70</sub> Ag <sub>0.30</sub> MnO <sub>3</sub> (Hien and Thuy, 2002)	1.00	1.35	306
La <sub>0.95</sub> Ag <sub>0.05</sub> MnO <sub>3</sub> (Hien and Thuy, 2002)	1.00	1.10	214
La <sub>0.80</sub> Ca <sub>0.20</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	1.50	5.50	230
La <sub>0.75</sub> Ca <sub>0.25</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	1.50	4.70	224
La <sub>0.70</sub> Ca <sub>0.30</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	1.00	1.38	256
La <sub>0.54</sub> Ca <sub>0.32</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	0.90	2.90	272
La <sub>0.55</sub> Ca <sub>0.45</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	1.50	1.90	238
La <sub>2/3</sub> Ca <sub>1/3</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	3.00	6.40	267
La <sub>0.67</sub> Ca <sub>0.33</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	1.50	4.30	260
La <sub>0.60</sub> Ca <sub>0.40</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	3.00	5.00	263
La <sub>0.5</sub> Cd <sub>0.5</sub> MnO <sub>3</sub> (Dhahri et al., 2009)	1.00	2.33	268
La <sub>0.7</sub> Ba <sub>0.30</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	1.00	1.60	336
La <sub>0.67</sub> Ba <sub>0.33</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	5.00	1.48	292
La <sub>2/3</sub> Ba <sub>1/3</sub> MnO <sub>3</sub> (Phan and Yu, 2007)	1.00	2.70	337
La <sub>0.9</sub> K <sub>0.1</sub> MnO <sub>3</sub> (Yu, 2003)	1.50	1.50	283
NdSrMnO <sub>3</sub> (Al-Yahmadi et al., 2002)	5.00	1.61	81.5
NdSrMnO <sub>3</sub> (Chandra et al., 2015)	5.00	2.60	75
Nd <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub> (Al-Yahmadi et al., 2002)	9.00	4.73	127
Nd <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub> (Al-Yahmadi et al., 2002)	5.00	2.78	127
Nd <sub>0.6</sub> Sr <sub>0.4</sub> MnO <sub>3</sub> (Al-Yahmadi et al., 2002)	3.00	4.87	256
Nd <sub>0.4</sub> Sr <sub>0.6</sub> MnO <sub>3</sub> (Al-Yahmadi et al., 2002)	9.00	1.80	220.5
Nd <sub>0.67</sub> Sr <sub>0.33</sub> MnO <sub>3</sub> (Fkhar et al., 2020)	1.00	3.12	257.5
Nd <sub>0.55</sub> Sr <sub>0.45</sub> MnO <sub>3</sub> (Xu et al., 2016)	3.00	3.12	274
Nd <sub>0.55</sub> Sr <sub>0.45</sub> MnO <sub>3</sub> (Xu et al., 2016)	1.00	1.42	-

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<sub>c</sub>) and maximum magnetic entropy ( $\Delta S_M^{\max}$ ).

Based on the selected substrate RaMnO<sub>3</sub> (Ra=La, Nd, Pr, Sm, such as LaMnO<sub>3</sub>), 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-, 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<sub>3</sub>. Zhong et al. (1998), Zhong et al. (1999), Das and Dey (2007) studied La<sub>1-x</sub>Na<sub>x</sub>MnO<sub>3</sub> (0 < x < 0.15) and La<sub>1-x</sub>K<sub>x</sub>MnO<sub>3</sub> (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<sup>+</sup>, K<sup>+</sup> doping amount. It's T<sub>c</sub> also rises, when the K doping amount x = 0.2, its  $\Delta S_M$  becomes 2.2 J/(kg K), and its T<sub>c</sub> also rises to 350 K. While Li<sup>+</sup> doping will decrease Magnetic change and T<sub>c</sub> 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 T<sub>c</sub>, and there is often an extreme value, which should be related to the effect of doping on Mn<sup>3+</sup>/Mn<sup>4+</sup> 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<sub>3</sub>. McBride et al. (2016), Demin and Koroleva (2004) and others have carried out research on the A-site Sr<sup>2+</sup> doping of LaMnO<sub>3</sub>. They believe that the A-site doping of Sr<sup>2+</sup> with a slightly larger radius than La<sup>3+</sup> will cause the lattice structure to deviate from the ideal cubic structure, thereby producing Mn-O The bond length and Mn<sup>3+</sup>-O<sup>2-</sup>-Mn<sup>4+</sup> bond angle changes, the overlap of electron orbits increases the DE and the MCE. With the increase of Sr<sup>2+</sup> content, the magnetic entropy change of La<sub>1-x</sub>Sr<sub>x</sub>MnO<sub>3</sub> (0.1 < x < 0.3) increases, and T<sub>c</sub> also increases,  $\Delta S_M^{\max} = 1.7$  J/(kg K), and T<sub>c</sub> is about 350–360 K. Bohigas et al. (2000), Sun et al. (2000) studied the change of the MCE of La<sub>0.6</sub>Ca<sub>0.4</sub>MnO<sub>3</sub>. Under the same magnetic field change condition, with the increase of Ca<sup>2+</sup> doping, the material  $\Delta S_M$  first increased and then decreased. Hussain et al. (2016) studied the MCE of La<sub>0.6</sub>Ba<sub>0.4</sub>MnO<sub>3</sub> and revealed that the MCE first increased and then decreased with the increase of Ba<sup>2+</sup> doping. When the doping amount exceeds 0.3, both the  $\Delta S_M$  and the T<sub>c</sub> 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<sup>3+</sup>/Mn<sup>4+</sup> distribution period is affected and the DE is weakened.

When multi-ion doping, the effect of doping behavior on the magnetocaloric properties and T<sub>c</sub> of perovskite manganite is more complicated. One study found that La<sub>0.65</sub>Sr<sub>0.35</sub>MnO<sub>3</sub> (Phan et al., 2003) with an applied magnetic field of 1 T has T<sub>c</sub> = 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<sub>0.65</sub>Sr<sub>0.35</sub>MnO<sub>3</sub> 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 T<sub>c</sub> 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<sub>3</sub>, the Mn<sup>4+</sup> will substitute the Mn<sup>3+</sup>, when the Alkaline earth metal ions access to this system. Moreover, the ratio of Mn<sup>3+</sup>/Mn<sup>4+</sup> is considered changed along with the content of doping ions. Linh et al. (2017) studied the  $\Delta S_M$  change and the T<sub>c</sub> of La<sub>0.7</sub>Ca<sub>0.3-x</sub>A<sub>x</sub>MnO<sub>3</sub> and

found that the  $T_c$  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  $(La_{0.5}Pr_{0.5})_{0.6}Ba_{0.4}MnO_3$  material and found that with the doping of Pr, the  $\Delta S_M$  of the material will increase to a certain extent, but the  $T_c$  will be reduced Temperature. 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  $T_c$  will 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  $Pr_{1-x}Sr_xMnO_3$  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,  $T_c$  gradually decreases, and the Neel temperature (critical temperature of antiferromagnetic-paramagnetic transition) increases with the two transitions when 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  $Pr_{1-x}Sr_xMnO_3$ . Bingham (Caballero-flores et al., 2014) found that  $Pr_{0.5}Sr_{0.5}MnO_3$  has a significant anomalous MCE. When the external magnetic field is 5 T,  $\Delta S_M = 6.8$  J/(kg K). Biswas et al. (2014) found that the charge ordering degree of  $Pr_{0.5}Sr_{0.5}MnO_3$  is very closely related to the size of the particles and has no effect on the  $T_c$  and DE.

## B-Site Doping

To maintain the balance of the valence state after doping, A-site doping indirectly changes the ratio and content of  $Mn^{3+}/Mn^{4+}$ , changes the structure of the perovskite manganite, and affects its DE and rich physical properties (magnetic, electrical, etc.). As  $Mn^{3+}-O^{2-}-Mn^{4+}$  is the basis of DE, the magnetic properties of  $ABO_3$  perovskite structures are usually produced based on B-site ions; thus, B-site doping directly affects the ratio of  $Mn^{3+}/Mn^{4+}$ . At the same time, other magnetic ions introduced by doping increase the abundance and complexity of the DE between B-site ions. Therefore, a small amount of doping is performed at the B-site to change the  $T_c$  and increase the magnetic moment of the site to increase the  $\Delta S_M$ .

B-site can be doped with transition metals (Ni, V, Fe, Co, Cr, Cu). Kong (2018) doped Ni and V at the B site for  $La_{0.65}Sr_{0.35}MnO_3$ . When doped with Ni, the  $T_c$  decreased significantly with the doping content, which moved below room temperature. When the B site was doped with V,  $T_c$  showed an increasing trend, but the  $\Delta S_M$  was relatively low (Kong, 2018). The  $La_{0.67}Pb_{0.33}Mn_{1-x}Co_xO_3$  ( $0.15 \leq x \leq 0.3$ ) material studied by N. Dhahri (Abdoul et al., 2019), with the increase of Co ion content, the  $\Delta S_M$  of the material has been increased to 3.1 J/(kg K), but it caused the  $T_c$  to drop drastically to about 250 K. Phan (Phan and Yu, 2007) found that when the

external magnetic field of  $La_{0.67}Sr_{0.33}Mn_{0.9}Cr_{0.1}O_3$  is 5T, its  $T_c = 328$  K is higher than room temperature, and  $\Delta S_M = 5$  J/(kg K). Lu (Lu et al., 2006) found that when Mo trace elements are doped in  $LaMnO_3$ , they replace the Mn sites to produce  $Mn^{2+}$ , which result in the DE of  $Mn^{2+}-O^{2-}-Mn^{3+}$  and exhibits ferromagnetism.

Studies have found that after perovskite manganese oxide is doped at the B site and is placed under an external magnetic field, the  $T_c$  and  $\Delta S_M$  changes are much lower than those after A-site doping. This is because the magnetic nature of perovskite manganese oxides and the MCE are primarily by DE, which are based on the movement of external electrons outside in  $Mn^{3+}-O^{2-}-Mn^{4+}$ .

The main reasons why the doping effect of the B site is lower than that of the A site are as follows. 1) Changes in  $T_c$  depend directly on the DE, and mixed interactions occur after the B site is doped with ions. At greater doping contents and, after the doping ions replace the Mn sites, the DE between  $Mn^{3+}-O^{2-}-Mn^{4+}$  decreases due to the increased super-exchange between doping and the surrounding ions, which causes the  $T_c$  to decrease. 2) After the B -sites are doped, the doping ions replace one of the  $Mn^{3+}-O^{2-}-Mn^{4+}$  ions in the double exchange, such as Co ions. The diverse spin electronic states and complex valence states of Co ions produce complex DE. Thus, Co doping is considered to as a partial replacement of Mn ions for DE. When Co ions replace Mn, antiferromagnetic super exchange channels ( $Co^{3+}-O^{2-}-Mn^{4+}$ ,  $Co^{2+}-O^{2-}-Co^{4+}$ ) and ferromagnetic double exchange channels ( $Mn^{3+}-O^{2-}-Mn^{4+}$ ,  $Co^{3+}-O^{2-}-Co^{4+}$ ) form in the system (Ghosh et al., 1999). Thus, antiferromagnetic double exchange interactions and ferromagnetic double exchange interactions coexist. As antiferromagnetic and ferromagnetic exchanges coexist, as the doped Co ions content increases and the long-range ferromagnetic order of the sample is replaced with ferromagnetic cluster behaviors (Chainani et al., 1992). This result in spin magnetic moment direction. The deviation and chaotic magnetic moment of the spin result in an overall decreased magnetic moment and  $\Delta S_M$ .

During ion doping modification, more consideration should be given to doping at the A site of the perovskite manganese oxide to indirectly change the proportion of manganese ions to affect the crystal structure and physical properties of the perovskite manganese oxide.

## Vacancy Doping

The crystal structure of perovskite manganese oxides can be changed through doping. Thus, research has been conducted to determine the impact of vacancy doping. Holes are divided into two categories: oxygen and elements. However, the generation of oxygen holes reduces DE of the material, while the  $T_c$  and  $\Delta S_M$  of the material decrease (Xu). In element holes, researchers have discovered the giant magnetoresistance effect and giant MCE in  $La_{0.9}MnO_3$  (Patra et al., 2009).

The  $T_c$  of the  $La_{0.925-x}MnO_3$  prepared by Xu (Xu) decreased with  $x$ .  $La_{0.925-x}MnO_3$  was also affected by the decreased  $T_c$  due to the ionic radius of the A site and the increased  $Mn^{4+}$  content, which led to an increased  $T_c$ . the large  $La_{0.925-x}MnO_3$  ion vacancy concentration causes significant lattice distortion, and a smaller A-site ion radius is the main factor controlling the decrease in  $T_c$ .

$\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  has a high magnetic entropy change and a relatively low  $T_c$ , which can be increased by doping.  $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$  replaces  $\text{La}^{3+}$  with  $\text{Ca}^{2+}$ . To balance the valence,  $\text{Mn}^{4+}$  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  $\text{La}_{0.65-x}\text{Ca}_{0.35}\text{MnO}_3$  ( $0 \leq x \leq 0.15$ ). The experimental results show that as the  $\text{La}^{3+}$  vacancy concentration increases, the ion radius and the mismatch factor change. The  $T_c$  of  $\text{La}_{0.65-x}\text{Ca}_{0.35}\text{MnO}_3$  also gradually increases. When the external magnetic field is 0–5 T,  $\Delta S_M = 1.17 \text{ J}/(\text{kg K})$ . This is because there are four electrons in the outermost layer of  $\text{Mn}^{3+}$ , of which three are in the  $t_{2g}$  localized state and the other is 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  $\text{Mn}^{3+}$  ions gradually decreases, the number of  $\text{Mn}^{4+}$  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  $\text{La}_{1-x}\text{MnO}_3$ . The study found that the  $T_c$  of  $\text{La}_{0.93}\text{MnO}_3$  and  $\text{La}_{0.97}\text{MnO}_3$  were 170 and 118 K, respectively, and the  $\text{Mn}^{4+}$  content was 21 and 9%. Brion believed that when  $x$  mol of  $\text{La}^{3+}$  is replaced with a vacancy,  $3x$  mol of  $\text{Mn}^{3+}$  is converted into  $\text{Mn}^{4+}$ . Walha et al. (2009) found that  $\text{Mn}^{4+}$  increased with the vacancy concentration. However, Sankar (Joy et al., 2002) prepared  $\text{La}_{1-x}\text{MnO}_3$  using the solid-phase method, which indicated that  $T_c$  increased with the vacancy concentration but  $\text{Mn}^{4+}$  decreased. There are different experimental results for  $\text{Mn}^{4+}$  with changes in the vacancy concentration, which manifest in the A site of perovskite manganese oxide. A small amount of AE or RE with a large ion radius can be added when synthesizing samples. To generate cation vacancies, it is first ignored that there are more B-site ions than A-site ions, which can enter A-sites. Tang et al. (2007) researched and proposed the  $\text{A}_{1-x}\text{BO}_{3-\delta}$  model

based on the minimum energy principle and the crystal defects in thermal equilibrium theory. In the model, the A-site gap is larger than the B-site gap. Ions on the lattice points are generated in high-temperature heat-treated samples. The 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  $\text{Mn}^{3+}/\text{Mn}^{4+}$  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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