TOPICAL REVIEW — Magnetism, magnetic materials, and interdisciplinary research

Review of magnetocaloric effect in perovskite-type oxides*

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We survey the magnetocaloric effect in perovskite-type oxides (including doped ABO_3-type manganese oxides, $A_3B_2O_7$-type two-layered perovskite oxides, and $A_2B'B''O_6$-type ordered double-perovskite oxides). Magnetic entropy changes larger than those of gadolinium can be observed in polycrystalline $La_{1-x}Ca_xMnO_3$ and alkali-metal (Na or K) doped $La_{0.8}Ca_{0.2}MnO_3$ perovskite-type manganese oxides. The large magnetic entropy change produced by an abrupt reduction of magnetization is attributed to the anomalous thermal expansion at the Curie temperature. Considerable magnetic entropy changes can also be observed in two-layered perovskites $La_{1.6}Ca_{1.4}Mn_2O_7$ and $La_{2.5-x}K_{0.5+x}Mn_2O_{7+\delta}$ ($0 < x < 0.5$), and double-perovskite $Ba_2Fe_{1+x}Mo_{1-x}O_6$ ($0 \leq x \leq 0.3$) near their respective Curie temperatures. Compared with rare earth metals and their alloys, the perovskite-type oxides are lower in cost, and they exhibit higher chemical stability and higher electrical resistivity, which together favor lower eddy-current heating. They are potential magnetic refrigerants at high temperatures, especially near room temperature.

Keywords: perovskite-type oxides, magnetocaloric effect, magnetic entropy change, magnetic phase transition

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1. Introduction

The magnetocaloric effect (MCE) is intrinsic to all magnetic materials and is induced through the coupling of a spin system with a magnetic field. When a magnetic field is applied adiabatically to a magnetic material, the spins in the material are aligned parallel to the field. Due to the reduced magnetic entropy, the material warms up to offset the lost magnetic entropy through an increase of the lattice entropy. Upon removal of the magnetic field, the ensuing spin randomization results in a rise of the magnetic entropy and a decrease of the lattice entropy (i.e. a drop in temperature). Scientists and engineers have demonstrated that magnetic refrigeration is a viable technology and has a great potential to compete with gas-compression refrigeration.[1,2] The former shows several advantages over the latter.[3] (i) The Carnot-cycle cooling efficiency is higher (30–60% compared to 5–10%). (ii) By using solid substances, magnetic refrigerators can be compact. (iii) Magnetic refrigeration does not use ozone-depleting or global-warming gases and is therefore environment-friendly.

Historically speaking, the investigation of magnetic refrigeration has progressed from low-temperature to high-temperature operation. In 1926 and 1927, respectively, Debye[4] and Giauque[5] independently suggested the use of magnetic refrigeration to reach temperatures below those previously attainable. In 1933, Giauque and MacDougall[6] used the proposed method of adiabatic demagnetization to achieve cooling from 3.5 K to 0.5 K. In 1990, cyclic magnetic refrigerators were designed to operate in the temperature range from 1.2 K to 15 K for helium liquefaction.[7,8] In order to design magnetic refrigerators with a broader range of working temperature (especially near room temperature), a great deal of effort has been made (theoretical as well as experimental) to search for refrigerants that show a large magnetic entropy change ($|\Delta S_M|$). According to the Curie–Weiss law, ferromagnetic materials with a large effective Bohr magneton number P ($P = g[J(J+1)]^{1/2}$, where g is the g factor and J is the total angular momentum quantum number) are expected to have a large ΔS_M at the Curie temperature T_C.[9] In view of that, researchers of the previous studies mainly concentrated on intermetallic compounds and the alloys of rare earth metals with high J. In 1976, Brown observed a large MCE in Gd near room temperature.[10] Since then, Gd has been considered to be the most suitable refrigerant in room-temperature magnetic refrigeration. However, Gd is rather expensive, and its T_C cannot be adjusted readily. It is hence of interest to search for cheaper materials that exhibit better performance than that of Gd.

In recent years, significant progress has been made in this search. In 1997, a giant MCE was observed by Pecharsky and Gschneider[11,12] in $Gd_5(Si_xGe_{1-x})_4$ pseudobinary alloys, and the discovery is considered to be a milestone in the magnetic cooling field. Since then, many additional efforts have

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been made theoretically and experimentally to seek alternative materials, especially those without rare-earth elements and exhibiting a large MCE around room temperature. Hu *et al.* at the Institute of Physics, Chinese Academy of Sciences, found that the Heusler alloy Ni–Mn–Ga exhibits a large MCE around room temperature.[13,14] Furthermore, Mn–As–Sb alloys reported by Wada and Tanabe,[15] La–Fe–Co–Si alloys by Fujieda *et al.*,[16] and Mn–Fe–P–As alloys by Tegus *et al.*[17] all showed large MCEs. Nonetheless, the materials showed large thermal and field hystereses, factors considered to be unbeneficial for active magnetic refrigeration (AMR). In 1995 and 1996, anomalous thermal expansions were observed in perovskite-type ferromagnetic oxides at their Curie temperatures; some of them exhibited a sharp change of magnetization and a discontinuous volume variation at the ferromagnetic transition.[18–22] The simultaneous structural and magnetic changes at T_C could have a strong influence on the magnetic entropy change. In view of that, Guo and his coworkers of Nanjing University measured the magnetic entropy change of perovskite-type manganese oxides, and found that the compounds $La_{1-x}Ca_xMnO_3$ ($x = 0.2$, 0.33) show peak values of $|\Delta S_M|$ larger than that of Gd.[23,24] Compared with the rare earth metals and their alloys, the perovskite-type oxides exhibit a considerably smaller magnetic hysteresis, a higher chemical stability, and a higher electrical resistivity that favors a lower value of eddy-current heating. In other words, the perovskite-type oxides appear to be more suitable candidates for magnetic refrigeration at high temperature, especially near room temperature.

Perovskite-type oxides belong to a big family that includes $A_{n+1}B_nO_{3n+1}$-type perovskite compounds and $A_2B'B''O_6$-type ordered double-perovskite materials. In the former, besides ABO_3-type ($n = \infty$) oxides with three-dimensional B–O networks, there are the $A_{n+1}B_nO_{3n+1}$-type compounds that have layered perovskite structures with two-dimensional or quasi-two-dimensional B–O networks. In this article, we survey the recent progress in MCE investigations, including our contributions on doped ABO_3-type manganese oxides, $A_3B_2O_7$-type two-layered perovskite oxides, and $A_2B'B''O_6$-type ordered double-perovskite oxides.

2. Doped ABO_3-type perovskite oxides

2.1. $La_{1-x}(Ca, Sr)_xMnO_3$ oxides

Due to their unique properties such as colossal magnetoresistance,[25–28] giant piezoresistance,[29,30] and giant magnetostrictive effect,[31] perovskite manganese oxides $R_{1-x}A_xMnO_3$ (where R is a trivalent rare-earth ion such as La, Pr, Nd, or Sm, and A is a divalent ion such as Ca, Sr, Ba, or Pb) have been investigated since the 1990s. In fact, the magnetic and electric properties of these materials have been known for a long time. The pure $RMnO_3$ compounds are antiferromagnetic insulators. Upon doping with A^{2+} ions, there is a co-presence of Mn^{3+} ($t_{2g}^3e_g^1$) and Mn^{4+} (t_{2g}^3) ions. The e_g electrons can delocalize due to the strong hybridization with the oxygen 2p states, mediating the ferromagnetic interaction between localized t_{2g} spins. Arising from the competition between the antiferromagnetic superexchange and the ferromagnetic double-exchange interaction, various magnetic structures form upon the partial substitution of R by A.

Some of the perovskite manganese oxides show lattice distortions as a modification from the cubic structure. One of the plausible origins of the lattice distortion is the deformation of the MnO_6 octahedron arising from the Jahn–Teller effect (inherent to high-spin Mn^{3+} with double-degeneracy e_g orbital). Another cause of lattice deformation comes from the connecting pattern of MnO_6 octahedra in the perovskite structure, forming a rhombohedral or orthorhombic lattice. In these distorted perovskite oxides, the MnO_6 octahedra show alternating buckling. Such a lattice distortion of the perovskite in the form of ABO_3 is governed by the so-called tolerance factor t, which is defined as $t = (r_A + r_O)/\sqrt{2}(r_B + r_O)$. Here r_A, r_B, and r_O represent the average ionic radii of the elements. By definition, the tolerance factor t measures the lattice matching of the sequential AO and BO_2 planes. For $t \approx 1$, the cubic perovskite structure is realized. With a decrease of r_A or t, the lattice structure becomes rhombohedral ($0.96 < t < 1$) and then orthorhombic ($t < 0.96$), where the B–O–B bond angle is bent and deviates from 180°.

Another important feature of perovskite manganese oxides is that the compounds are reasonably appropriate for carrier doping (filling control) since the structure is robust against chemical modifications on the A site. In other words, the magnetic properties, Curie temperature, and saturation magnetization of perovskite manganese oxides are strongly doping-dependent.

Motivated by the fact that certain perovskite manganese oxides exhibit a discontinuous variation in lattice volume and a sharp change in magnetization at the ferromagnetic transition,[18–22] Du and his coworkers of Nanjing University studied the magnetic entropy change of perovskite-type manganese oxides and found that at the Curie temperature of 230 K, the peak value of $|\Delta S_M|$ in compound $La_{0.8}Ca_{0.2}MnO_3$ was 5.5 $J\cdot kg^{-1}\cdot K^{-1}$ under a field change of 0–1.5 T, which is larger than that of Gd (4.2 $J\cdot kg^{-1}\cdot K^{-1}$) under the same change of magnetic field.[23,24] The origin of the large $|\Delta S_M|$ can be attributed to a considerable variation of magnetization near T_C. The structural phase transition induced by an external magnetic field indicates that there is a considerable coupling between magnetism and the lattice. Because of the coupling effect, there are simultaneous changes in the lattice structure (in the Mn–O bond distance as well as in the Mn–O–Mn bond an-

gle) with the change of temperature. The variation in lattice volume can cause an additional change in magnetism. In other words, the abrupt change in magnetization and the large $|\Delta S_M|$ of $La_{0.8}Ca_{0.2}MnO_3$ at T_C can be associated with the extent of discontinuity in the volume change.

The Curie temperature of $La_{1-x}Ca_xMnO_3$ is below room temperature, whereas that of $La_{0.75}Sr_{0.25}MnO_3$ can be as high as 348 K, higher than room temperature.[24] To further explore the magnetic entropy change of perovskite-type manganese oxides at a T_C that is near room temperature, we controlled the Sr replacement with Ca in $La_{0.75}Sr_{0.25}MnO_3$, leading to the formation of $La_{0.75}Sr_{0.25-y}Ca_yMnO_3$ with T_C of 327 K and 283 K ($y = 0.10$ and 0.125, respectively). The successful synthesis of these materials indicates that the perovskite-type manganese oxides are potential materials for magnetic refrigeration near room temperature. The observation that a decrease in the average ionic radius of A sites decreases the T_C provides a guideline for the convenient adjustment of the Curie temperature. It is feasible to achieve a constant $|\Delta S_M|$ against a large temperature-variation span using a complex magnetic refrigerant composed of several kinds of perovskite-type manganese oxides having different T_C; these materials are suitable for the ideal Ericsson cycle.[32]

MCE in $La_{1-x}Ca_xMnO_3$ perovskite oxides has been reported. Morelli *et al.*[33] first reported the MCE of $La_{0.67}Ca_{0.33}MnO_3$ perovskite oxide film; however, the $|\Delta S_M|$ peak value obtained was not very large (for $\Delta H = 5.0$ T, $|\Delta S_M|$ reached a maximum of about 2.06 $J\cdot kg^{-1}\cdot K^{-1}$ at $T_C = 252$ K). Zhang *et al.*[34] found in $La_{0.67}Ca_{0.33}MnO_3$ a small $|\Delta S_M|$ value of 0.6 $J\cdot kg^{-1}\cdot K^{-1}$ for $\Delta H = 1.0$ T and a wide MCE peak. Lin *et al.*[35] measured the MCE of $La_{0.67}Ca_{0.33}MnO_3$ and found an adiabatic temperature change (ΔT) of 2.4 K for $\Delta H = 2.02$ T. This ΔT value was smaller than that of Gd. This discrepancy could arise from the difference in sample processing routes and/or from the difference in chemical composition.

2.2. $La_{1-x}(Na, K)_xMnO_3$ oxides

Systematic studies were conducted on ABO_3-type perovskite oxides doped with alkaline-earth metals.[23,24] However, references to magnetic and electronic properties of ABO_3-type perovskite oxides doped with alkali metals are scarce. Considering that the donor property of alkali metals is stronger than that of alkaline-earth metals, Zhong *et al.*[36–38] in 1998 investigated the structure, composition, and magnetocaloric properties of alkali-metal-doped perovskite oxides $La_{1-x}A_xMnO_{3+\delta}$ (A = Na, K; $x = 0.075$, 0.10, 0.165, 0.20), which were prepared by a sol–gel technique to obtain highly pure and homogeneous powder samples. It was found that there is no clear correlation between the doping level x and the average manganese oxidation state $\langle V_{Mn}\rangle$, in contrast to the expected monotonic linear increase with x. In fact, for all the samples studied, the average manganese oxidation state $\langle V_{Mn}\rangle$ was practically a constant, 3.32 ±0.02 for A = Na and 3.40 ± 0.04 for A = K.

Figure 1 displays the plot of Curie temperature versus average manganese oxidation state $\langle V_{Mn}\rangle$ of $La_{1-x}K_xMnO_{3+\delta}$. There is no close relationship between $\langle V_{Mn}\rangle$ and T_C, although such a relationship has been observed in alkaline-earth-doped lanthanide manganites.[23,24] Figure 2 shows the variation of T_C with the Mn−O bond distance determined by XRD analysis. One can see that T_C tends to increase with the decrease of the Mn–O distance.[38] Similar phenomena were observed in $La_{1-x}Na_xMnO_{3+\delta}$.[37] In accordance with the double-exchange interaction theory, a shorter Mn–O distance in this structure means a larger Mn–O–Mn bond angle, leading to a stronger interaction and a higher T_C.

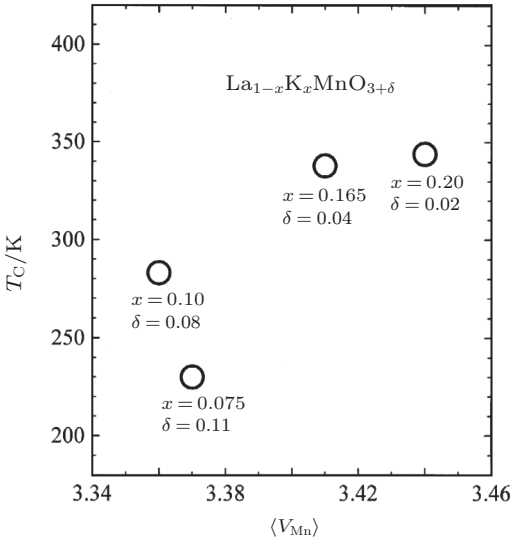


Fig. 1. Dependence of Curie temperature T_C on the average manganese oxidation state $\langle V_{Mn}\rangle$ of $La_{1-x}K_xMnO_{3+\delta}$.[38]

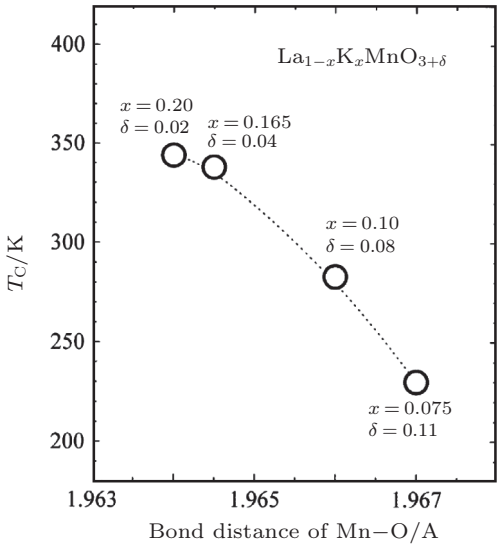


Fig. 2. Dependence of Curie temperature T_C of $La_{1-x}K_xMnO_{3+\delta}$ on Mn–O distance.[38]

MCE investigations showed that the peak temperature of $|\Delta S_M|$ can be tuned in the temperature range from 195 K to 334 K for $La_{1-x}Na_xMnO_{3+\delta}$ compounds and in the temperature range from 230 K to 334 K for $La_{1-x}K_xMnO_{3+\delta}$ compounds. These polycrystalline samples exhibit considerably smaller magnetic hystereses with coercivity below 50 Oe. The $La_{1-x}A_xMnO_{3+\delta}$ (A = Na, K) compounds show $|\Delta S_M|$ maximum values lower, and $|\Delta S_M|$ distribution curves broader than those of pure Gd. With a significant magnetic entropy change and a Curie temperature that is easily tunable, the alkali-metal-doped perovskite oxides are potential refrigerants for magnetic cooling in a wider temperature span.

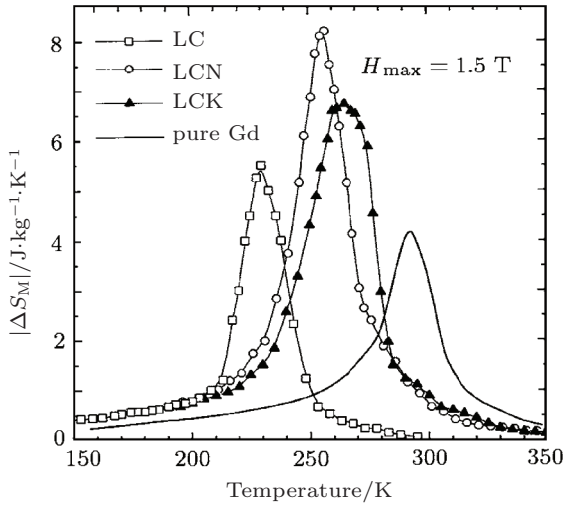


Fig. 3. Magnetic entropy change $|\Delta S_M|$ of the denoted polycrystalline samples (LC: $La_{0.802}Ca_{0.198}Mn_{1.00}O_{2.99}$, LCN: $La_{0.837}Ca_{0.098}Na_{0.038}Mn_{0.987}O_{3.00}$, and LCK: $La_{0.822}Ca_{0.096}K_{0.043}Mn_{0.974}O_{3.00}$) for a field change from 0 T to 1.5 T as a function of temperature.[40] The plain solid line represents $|\Delta S_M|$ of pure Gd metal as a reference.

In 2000, Tang *et al.* of Nanjing University observed a large MCE in Ag-doped perovskite oxides.[39] They reported that for $\Delta H = 1$ T, the peak value of $|\Delta S_M|$ is 3.4 J·kg^{-1}·K^{-1} for $La_{0.8}Ag_{0.2}MnO_3$; this value is larger than that observed in Gd (3.1 J·kg^{-1}·K^{-1}).[39] Later, Zhong *et al.* described the effect of substituting small amounts of alkali metal (Na or K) for a part of Ca in $La_{0.8}Ca_{0.2}MnO_3$ on the $|\Delta S_M|$ and T_C.[40] It was found that such a substitution resulted in a substantial shift of the T_C to a higher temperature (from 230 K to 256 K for Na substitution, and to 265 K for K substitution) as well as a sharper change in magnetization near the T_C. The lattice parameters as a function of temperature for the $La_{0.837}Ca_{0.098}Na_{0.038}Mn_{0.987}O_{3.00}$ sample clearly showed a lattice contraction below the T_C (256 K), with abrupt decreases of all lattice parameters and a volume discontinuity ($\Delta V/V = 0.24\%$). The magnetic-field-induced $|\Delta S_M|$ as determined from the isothermal magnetization measurements is shown in Fig. 3 for a field change from 0 T to 1.5 T; $|\Delta S_M|$ of pure Gd metal is also shown for comparison. It is obvious that even a small doping of Na (or K) has a significant impact on the maximum value of $|\Delta S_M|$, which is about twice as large as that of Gd in terms of the peak value, irrespective of their Curie temperatures. It is important that the addition of Na or K results not only in an increase of T_C, but also in increased $|\Delta S_M|$.

For practical applications, $|\Delta S_M|$ under a moderate field is of interest. Figure 4 shows the variation of $|\Delta S_M|$ in $La_{0.837}Ca_{0.098}Na_{0.038}Mn_{0.987}O_{3.00}$ at different temperatures as a function of the applied field. It is worth noting that under moderate fields, the $|\Delta S_M|$ of $La_{0.837}Ca_{0.098}Na_{0.038}Mn_{0.987}O_{3.00}$ at T_C (256 K) has significant values, e.g., ~ 3.5 J·kg^{-1}·K^{-1} at 0.6 T, ~ 2.5 J·kg^{-1}·K^{-1} at 0.4 T, and ~ 1.4 J·kg^{-1}·K^{-1} at 0.2 T, substantially higher than those of the other manganese perovskite oxides reported previously.

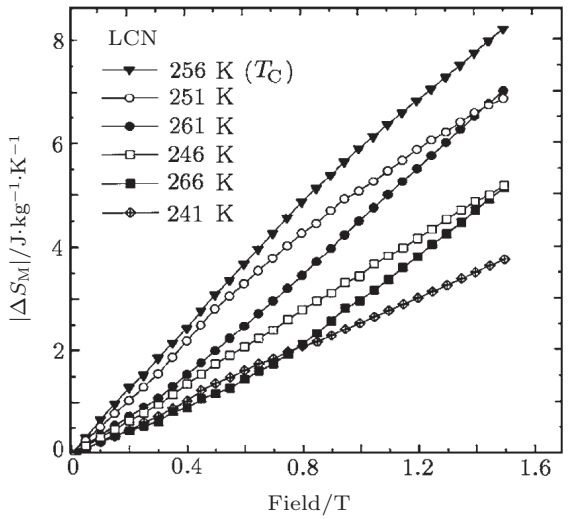


Fig. 4. Magnetic entropy change $|\Delta S_M|$ of polycrystalline $La_{0.837}Ca_{0.098}Na_{0.038}Mn_{0.987}O_{3.00}$ at different temperatures as a function of magnetic field.[40]

The origin of the larger $|\Delta S_M|$ measured in Na- or K-doped perovskite oxides (compared with the previously reported values of other compounds) can be attributed to the differences in composition and processing details. Based on the thermodynamic theory, $\Delta S_M(T,H)$ is given by

$$\Delta S_M(T,H) = \int_0^H \left(\frac{\partial M(T,H)}{\partial T}\right)_H \mathrm{d}H.$$

Larger magnetization M and $\partial M/\partial T$ (corresponding to the sharpness of the M–T curve) can give a larger $|\Delta S_M|$. Both $La_{0.837}Ca_{0.098}Na_{0.038}Mn_{0.987}O_{3.00}$ and $La_{0.822}Ca_{0.096}K_{0.043}Mn_{0.974}O_{3.00}$ compounds have structures similar to that of $La_{0.802}Ca_{0.198}Mn_{1.00}O_{2.99}$, exhibiting a first-order ferromagnetic–paramagnetic phase transition and a discontinuous variation in lattice volume at T_C. The variation in lattice volume causes an additional change in magnetism, and is beneficial to $|\Delta S_M|$ enlargement. The doping of small amounts of alkali metal results in both reduced lattice parameters and enlarged discontinuity of the lattice volume at T_C, giving rise to a sharper change in magnetization. In addition,

with the doping (in small amounts) of alkali metal, there is an increase of magnetization M. The preparation details also appear to be important for achieving $|\Delta S_M|$ enlargement. It was observed that the sharpness of the M–T curve also depends on the sample quality such as grain size and T_C homogeneity.

2.3. Effect of introducing vacancies on magnetic and magnetocaloric properties of $La_{1-x}(Ba, Ca)_xMnO_{3-\delta}$ oxides

Recent studies indicated that the double-exchange interaction between the spins of the Mn^{3+} and Mn^{4+} ions alone cannot adequately explain the magnetic behaviors observed experimentally in hole-doped perovskite-type manganese oxides. It was suggested that other effects ruled by the average A-site cationic radius,[41] the A-site cationic size mismatch,[42] and the oxygen stoichiometry[43,44] could play crucial roles in aspects such as Mn valence, charge ordering or pinning, polaron effects, and Jahn–Teller distortion.[45] In order to investigate the influence of oxygen stoichiometry on the MCE of $La_{2/3}Ba_{1/3}MnO_{3-\delta}$, Zhong *et al.*[46] annealed $La_{2/3}Ba_{1/3}MnO_3$ under different conditions at 1023–1223 K in an N_2 atmosphere and obtained a series of $La_{2/3}Ba_{1/3}MnO_{3-\delta}$ samples with $\delta = 0.00$, 0.02, 0.05, 0.08, 0.10. The results of XRD analysis showed that all $La_{2/3}Ba_{1/3}MnO_{3-\delta}$ samples have a cubic perovskite structure. As δ increases, the measured lattice parameters at room temperature increase monotonously from $a = 3.892(3)$ Å ($\delta = 0.00$) to $a = 3.909(3)$ Å ($\delta = 0.10$). With increasing oxygen deficiency, the average manganese oxidation state $\langle V_{Mn} \rangle$ calculated from electric neutrality decreases from 3.33 to 3.13, indicating that the manganese ions increase in size. The ferromagnetic ordering transition temperature T_C, defined as the temperature at which the $|dM/dT| \sim T$ curve reaches a minimum, has been determined from the M–T curves. As δ increases, the T_C decreases from 337 K ($\delta = 0.00$) to 268 K ($\delta = 0.10$). Figure 5 displays the temperature dependence of magnetization M. The magnetization was measured upon warming the $La_{2/3}Ba_{1/3}MnO_{3-\delta}$ samples in a field of 10 kOe after cooling to 100 K in zero field. As δ increases, the M at 100 K decreases gradually from 88.7 emu·g^{-1} to 78.4 emu·g^{-1}. The MCE investigation showed that the maximum $|\Delta S_M|$ is of the order of 2.77 J·kg^{-1}·K^{-1} for $La_{2/3}Ba_{1/3}MnO_{3-\delta}$ with $\delta = 0.00$ upon changing the applied field from 0 kOe to 10 kOe. As δ increases, the maximum $|\Delta S_M|$ decreases and the peak of $|\Delta S_M|$ shifts to lower temperatures.

A refrigeration technique based on MCE needs materials that show a big enough magnetic entropy change in a wide range of temperatures. This property is difficult to attain with only one material; however, it is possible if one takes an ensemble of materials that have maximum $|\Delta S_M|$ at different temperatures, such as the $La_{2/3}Ba_{1/3}MnO_{3-\delta}$ materials with different oxygen deficiencies. Shown in Fig. 6 is the calculated result of $|\Delta S_M|$ obtained in a mixture of five $La_{2/3}Ba_{1/3}MnO_{3-\delta}$ samples ($\delta = 0.00$, 0.02, 0.05, 0.08, 0.10) with equal weight percentages (20 wt.%). It is observed that the magnetic entropy change of the mixture is broadened in a wide range of temperatures (300 ± 40 K), and the maximum $|\Delta S_M|$ is observed near room temperature.

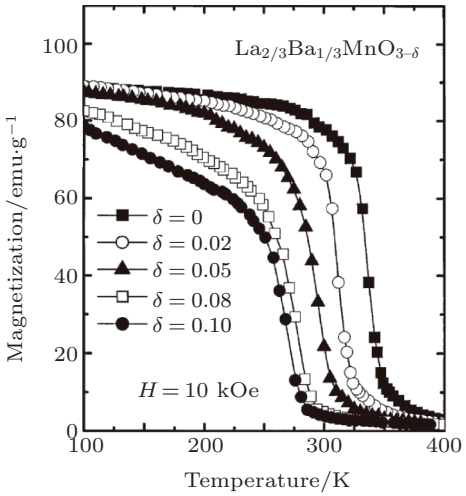


Fig. 5. Temperature dependence of magnetization (warming curves) for $La_{2/3}Ba_{1/3}MnO_{3-\delta}$ perovskite-type oxides recorded after zero-field cooling (ZFC).[46]

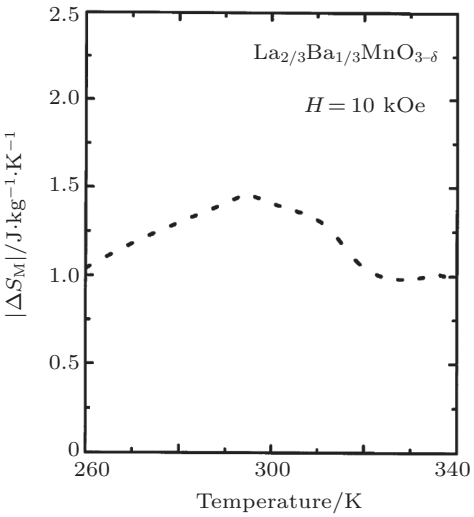


Fig. 6. Temperature dependence of magnetic entropy change (calculated) under applied field $H_{max} = 10$ kOe for the mixture of five $La_{2/3}Ba_{1/3}MnO_{3-\delta}$ samples ($\delta = 0.00$, 0.02, 0.05, 0.08, 0.10) with equal weight percentages.[46]

Hou *et al.* of Hebei Normal University also investigated the magnetic and magnetocaloric properties of $La_{0.67-x}Ca_{0.33}MnO_3$ ($x = 0$, 0.02, 0.06, 0.1) with deficient La-site vacancies.[47] They reported that the largest $|\Delta S_M|$ value is 2.78 J·kg^{-1}·K^{-1} at 277 K for $\Delta H = 1$ T in the $La_{0.65}Ca_{0.33}MnO_3$ sample. Phan *et al.* reported that for $(La_{1-x})_{0.8}Ca_{0.2}MnO_3$ ($x = 0.05$, 0.10, 0.20, 0.30) samples, increased La deficiency results in not only the enhancement of magnetocaloric properties, but also the improvement of the Curie temperature.[48,49] Similar results were observed by Chen *et al.* in manganese perovskites $La_{0.8-x}Na_{0.2}\diamondsuit_xMnO_{3+\delta}$ ($\diamondsuit$ = vacancies, $x = 0.01$–0.04).[50] The results suggest that

perovskite oxides with vacancy deficiency might well be suitable working materials for refrigerant devices near room temperature.

2.4. $Eu_{0.55}Sr_{0.45}MnO_3$ oxides

Based on the local magnetic moment model, the utmost magnetic entropy change for a material would be $\Delta S = Nk_B \ln(2J+1)$, where N is the number of spins, J is the quantum number of the spin, and k_B is the Boltzmann constant. This is the entropy released by the system when the material transforms from a completely ordered magnetic state to a disordered magnetic state. However, the experimentally detected entropy change is usually much lower than that suggested by the theory. Many factors are known to affect the entropy of materials, especially in compounds that undergo a first-order phase transition. Recently, the short-range magnetic order (SRMO) in the paramagnetic (PM) state was found to be yet another factor affecting the magnetic entropy. An initial analysis revealed that the presence of sizable ferromagnetic (FM) clusters in the PM state prevents a complete release of the magnetic entropy, and as a result suppresses the entropy change associated with the PM–FM transition. Sun and Shen's group at the Institute of Physics, Chinese Academy of Sciences studied the effects of SRMO on the magnetic entropy change in perovskite oxide $Eu_{0.55}Sr_{0.45}MnO_3$. The compound shows a field-sensitive magnetic behavior. They reported an ideal first-order phase transition that results in a great magnetization drop/jump.[51–53]

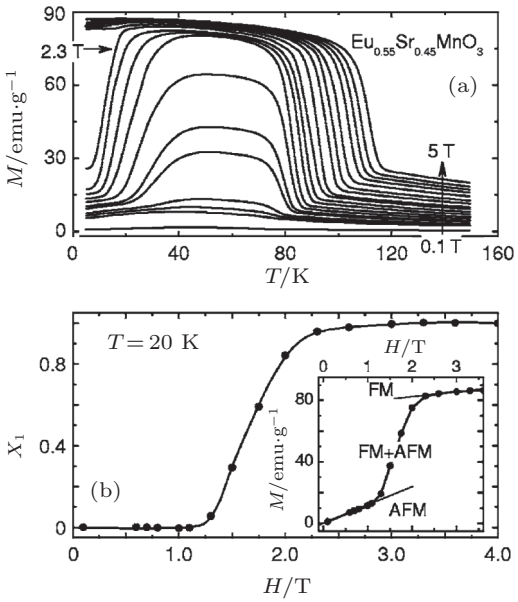


Fig. 7. (a) Thermal magnetization of $Eu_{0.55}Sr_{0.45}MnO_3$ measured under different magnetic fields, and (b) the proportion of the FM phase (X_1) as a function of magnetic field at a selected temperature of 20 K; inset shows the corresponding isothermal magnetization curve.[52]

Figure 7(a) shows the temperature-dependent magnetization of $Eu_{0.55}Sr_{0.45}MnO_3$ measured under fields between 0.1 T and 5 T. Two magnetic processes take place sequentially with the decrease of temperature. The first one is a PM to FM transition at a high temperature, and the second one is an FM to antiferromagnetic (AFM) transition at a low temperature. In the intermediate ranges of temperature and magnetic field, FM and AFM phases coexist. It is obvious that the proportion of each phase, which can be calculated based on the magnetization isotherms, is a function of the external field. Figure 7(b) displays the variation of FM population with magnetic field at 20 K. The compound is AFM below 1 T, and transitions to FM when the applied field exceeds $\sim$ 1.2 T. The fully FM polarized state is obtained above $\sim$ 2.25 T.

The maximum entropy change in $Eu_{0.55}Sr_{0.45}MnO_3$ determined by heat capacity is only $\sim$7 J·kg^{-1}·K^{-1}, much smaller than the theoretical expectation ($\Delta S = Nk_B \ln(2J+1) \sim 55$ J·kg^{-1}·K^{-1}). Jia *et al.*[51] have suggested that the presence of SRMO greatly depresses the magnetic entropy of the paramagnetic phase; thus there is a change of entropy at the field-induced transition from PM to FM phase. This result suggests a promising perspective: it is possible that the experimentally detected entropy change is only a small fraction of the total value held by the material, and if one could find a way to prevent or destroy the short-range order, the magnetic entropy change would be greatly enhanced.

In addition, it should be noted that if two or more phases coexist in the compound, the applicability of the Maxwell relation should be checked carefully, as the relation is derived for a homogeneous system in an equilibrium state. Liu *et al.*[52] have pointed out that calorimetric data should be used to estimate the entropy change in phase-separated compounds (such as $Eu_{0.55}Sr_{0.45}MnO_3$) and that significant errors could be introduced in the use of the Maxwell relation when the proportions of coexisting phases are subject to modification by an external field.

3. Doped $A_3B_2O_7$-type two-layered perovskite oxides

The $A_3B_2O_7$-type perovskite manganese oxides have a natural layered structure. Investigations[54–59] indicate that a reduction in dimensionality of the Mn–O–Mn networks leads to several intriguing changes in the features of ferromagnetic manganate perovskites, including enhanced magnetoresistance effects, unconventional magnetostriction, and anisotropic transport of charge carriers. Moreover, the layered systems exhibit a variety of ferromagnetic and antiferromagnetic states, such as paramagnetic insulating (PI), antiferromagnetic metallic (AFM), ferromagnetic metallic (FM), canted antiferromagnetic (CAF), antiferromagnetic insulating (AFI), and charge-ordered (CO) states.[60–65]

Figure 8 shows a schematic view of ABO_3-type and $A_3B_2O_7$-type perovskite compounds. The ABO_3-type manganese compound consists of perovskite units with three-dimensional Mn–O networks. In contrast, the $A_3B_2O_7$-type

two-layered manganese oxide exhibits two-dimensional Mn–O networks and contains double-perovskite layers interleaved with *A*–O layers. In other words, Mn–O–Mn bonds in the *c*-axis direction are separated from one another by the *A*–O layers. Among the structural consequences of the transition of an ABO_3-type perovskite to an $A_3B_2O_7$-type manganite are the introduction of a two-dimensional character and a reduction from 6 to 5 in the number of nearest-neighbor Mn cations around each transition-metal site. This is expected to produce anisotropic exchange interactions (specifically, the intra-layer exchange interaction that works within perovskite MnO_2 bilayers) and interlayer exchange interactions that act between the perovskite MnO_2 bilayers. The former is due to the double-exchange interaction, and is perhaps much stronger than the latter.

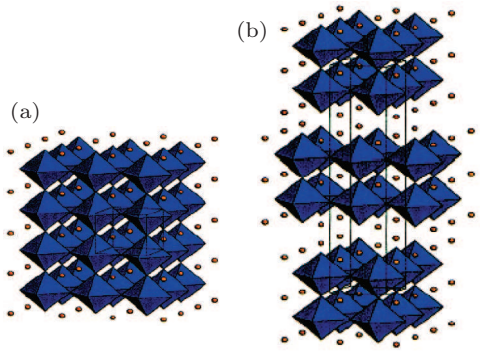


Fig. 8. Schematic view of (a) ABO_3-type and (b) $A_3B_2O_7$-type perovskite compounds. Small points denote *A* ions; octahedra denote BO_6 units: an oxygen ion occupies each vertex of an octahedron, and *B* ions are omitted for simplicity.

Zhong *et al.*[66,67] synthesized polycrystalline layered-perovskite $La_{2.5-x}K_{0.5+x}Mn_2O_{7+\delta}$ ($0 < x < 0.5$) by a modified sol–gel method, and observed that these layered manganites have a metal–insulator transition temperature (T_ρ) far (100 K) below the magnetic transition temperature T_C. They assumed that the layered perovskite $La_{2.5-x}K_{0.5+x}Mn_2O_{7+\delta}$ exhibits two types of ferromagnetic orderings caused by anisotropic carrier transport and exchange interaction. The electrical properties of the samples are dominated by a less conductive transport along the *c* direction, which is due to a weaker exchange interaction. By contrast, the magnetic transitions of the materials are governed by a strong in-plane exchange interaction. Thus, T_ρ is observed to be far below T_C. The maximum $|\Delta S_M|$ is of the order of 1.4 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ for $La_{2.5-x}K_{0.5+x}Mn_2O_{7+\delta}$ with $x = 0.35$ under a 1 T applied magnetic field.[66] Due to the anisotropy exchange interaction existing in two-layered manganites, the T_C of $La_{2.5-x}K_{0.5+x}Mn_2O_{7+\delta}$ is reduced by 30 K to 90 K as compared to that of $La_{1-x}K_xMnO_{3+\delta}$,[38] consequently causing a shift of $|\Delta S_M|$ peak to lower temperatures. The fact that the maximum of $|\Delta S_M|$ is restricted to a narrow temperature range around T_C (far above T_ρ) seems to indicate that the origin of $|\Delta S_M|$ in $La_{2.5-x}K_{0.5+x}Mn_2O_{7+\delta}$ can be largely attributed to the intra-layer exchange interaction.

Zhou *et al.*[68] compared the magnetocaloric properties of $La_{1.6}Ca_{1.4}Mn_2O_7$ and $La_{0.8}Ca_{0.2}MnO_3$ (the ratio of Mn^{+3} to Mn^{+4} is the same for $La_{1.6}Ca_{1.4}Mn_2O_7$ and $La_{0.8}Ca_{0.2}MnO_3$). At the temperatures of 166 K and 230 K, which are slightly lower than their respective Curie temperatures, the $|\Delta S_M|$ peak values are 3.8 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ and 5.3 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ for $La_{1.6}Ca_{1.4}Mn_2O_7$ and $La_{0.8}Ca_{0.2}MnO_3$, respectively, under a 1.5 T applied magnetic field (see Fig. 9). Clearly, the $|\Delta S_M|$ of two-layered perovskite oxide $La_{1.6}Ca_{1.4}Mn_2O_7$ is comparable to that of Gd, smaller but broader than that of $La_{0.8}Ca_{0.2}MnO_3$. Zhu *et al.*[69] found a large $|\Delta S_M|$ of 17 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ at 270 K under a 5.0 T applied magnetic field in the $La_{1.4}Ca_{1.6}Mn_2O_7$ compound. This value of $|\Delta S_M|$ is much larger than that of Gd ($\sim$10.2 $J{\cdot}kg^{-1}{\cdot}K^{-1}$, $\Delta H = 5.0$ T). These results indicate that these materials could be used as magnetic refrigerants below room temperature.

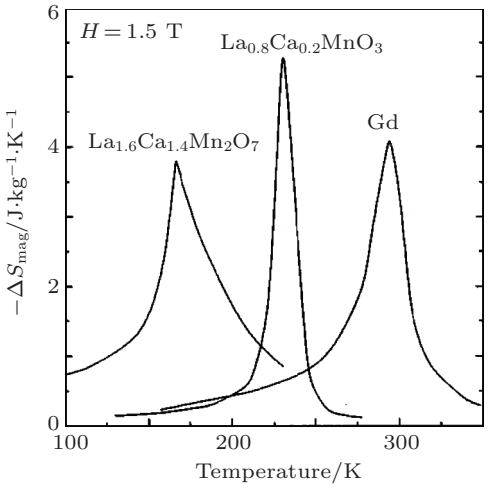


Fig. 9. Temperature dependence of $|\Delta S_M|$ in $La_{1.6}Ca_{1.4}Mn_2O_7$, $La_{0.8}Ca_{0.2}MnO_3$, and Gd under an applied field of 1.5 T.[68]

4. $A_2B'B''O_6$-type ordered double-perovskite oxides

Oxides of the $A_2B'B''O_6$ type tend to adopt the perovskite structure in which *A* is a large cation capable of 12-fold coordination with oxygen, while B' and B'' are smaller cations suitable for octahedral coordination. If the difference in charge between B' and B'' cations is large, these ions assume an ordered arrangement in the perovskite lattice.[70] With regard to magnetic properties, the double-perovskite compounds can be divided into two categories: ferromagnets (or ferrimagnets) and antiferromagnets. The former includes A_2FeMoO_6,[71–74] A_2FeReO_6,[75–77] A_2CrReO_6,[78,79] A_2CrWO_6,[80] (where *A* = Ca, Sr, Ba), etc.; the latter includes Sr_2FeWO_6,[81] Sr_2MnMoO_6,[82] Sr_2CoWO_6,[83] Sr_2YRuO_6,[84] etc. Among the multitudinous members of the family of double perovskites, the Fe-based compounds A_2FeMoO_6 (*A*= Sr, Ba, Ca)

have attracted much attention. This is particularly so with the magnetically ordered Sr_2FeMoO_6, which shows a low-field colossal magnetoresistance that remains significant up to room temperature.[71] In A_2FeMoO_6 compounds, the B positions of the perovskite structure are occupied alternately by Fe and Mo atoms in such a way that each FeO_6 octahedron is corner-linked to six MoO_6 octahedra and vice versa. It has been suggested that these compounds consist of Fe^{3+} ($3d^5$, S = 5/2) and Mo^{5+} ($4d^1$, S = 1/2) ions alternating along the cubic axes. The Fe and Mo sublattices are ferromagnetically coupled within each sublattice, while the two sublattices are supposed to be antiferromagnetically coupled to give rise to an $S = 2$ state. The results of Mössbauer spectroscopy, X-ray absorption, and X-ray magnetic circular dichroism studies[85,86] have demonstrated the antiferromagnetic coupling of ferromagnetic Fe and Mo sublattices below their Curie temperatures, and revealed the presence of mixed oxidation states for Fe (2+/3+) and Mo (5+/6+) ions. Recent studies[87,88] have demonstrated that an increase in the size of A-site ions results in an increase in the fractional amount of Fe^{2+}/Mo^{6+} pairs in the material. As such, the majority of Fe/Mo pairs would have oxidation states close to Fe^{3+}/Mo^{5+} in Sr_2FeMoO_6 and close to Fe^{2+}/Mo^{6+} in Ba_2FeMoO_6.

Since 2004, Zhong *et al.*[89–93] have conducted systematic studies of the structural, magnetic, and electrical properties of double-perovskite A_2FeMoO_6 (A = Sr, Ba). Generally, the synthesis route most commonly employed for the A_2FeMoO_6 phase is the conventional solid-state reaction method that involves the firing of mechanically mixed powder precursors in a flow of H_2/Ar or H_2/N_2 gas at 900–1200 °C. The drawback of this method is that a sample with a high degree of Fe/Mo order is not easily obtainable due to the partial evaporation of constituent metals during the long heating periods. The samples prepared by this method are mostly in the form of isotropic grains of micrometer size. A modified wet-chemical method was introduced to prepare high-aspect-ratio "bulrush-like" double-perovskite oxides. It should be noted that in order to guarantee a precise sample composition, the conditions for thermal treatment must be monitored carefully. Too high a temperature and/or too long a sintering time result in an unsatisfactory composition of the samples, partly due to the evaporation of the molybdenum oxide.

Figure 10(a) shows the TEM image of Ba_2FeMoO_6. One can see that these materials show bulrush-like rods, 2 m in length and 100–150 nm in diameter. Figure 10(b) displays the saturation magnetic moment per formula unit (M_S) obtained in a commercial superconducting quantum interference device (SQUID) magnetometer at $T = 5$ K and in an applied magnetic field of up to 5 T. The M_S values are $3.78\mu_B$ and $3.59\mu_B$ for Ba_2FeMoO_6 and $Ba_2Fe_{1.1}Mo_{0.9}O_6$, respectively. The M_S values obtained for Ba_2FeMoO_6 are smaller than the predicted $4\mu_B$. The difference between ideal and actual materials could be a result of a distinct discrepancy in antisite defect concentration. As suggested before,[94–96] since the sub-lattice Fe and Mo are antiferromagnetically arranged, each antisite defect contributes to a certain decrease in M_S of the sample. The M_S values of $Ba_2Fe_{1.1}Mo_{0.9}O_6$ are smaller than those of Ba_2FeMoO_6. It is believed that the magnetization is a result of Fe–O–Fe and Fe–O–Mo super-exchange interactions. Compared to the Ba_2FeMoO_6 case, more Mo sites in $Ba_2Fe_{1.1}Mo_{0.9}O_6$ are occupied by Fe^{3+} ions, and if an Fe^{3+} ($S = 5/2$) ion at an Mo site is surrounded by Fe^{3+} ions, its magnetic moment tends to be anti-parallel to those of the surrounding Fe^{3+} ions, hence causing a decrease in the net magnetization.[97]

Two approaches were used to measure the Curie temperature of the bulrush-like Ba_2FeMoO_6 sample: (i) linear extrapolation of $M(T)$ to zero magnetization and (ii) Arrott plots. The temperature dependence of the normalized magnetization for the bulrush-like Ba_2FeMoO_6 sample in a low field (1 kOe) and the T_C derived by extrapolation are shown in Fig. 10(c). The Arrott plots for the same sample are shown in Fig. 10(d). In the Arrott plots, the T_C value is given by the isotherm that displays a linear M^2 versus H/M variation (indicated by the dashed line). The Curie temperatures determined by the two different methods are 349 K and 341 K, respectively. It should be noted that the Arrott plots display a linear behavior above T_C, indicating a second-order phase transition.

In the MCE investigation of double-perovskite $Ba_2Fe_{1+x}Mo_{1-x}O_6$ ($0 \le x \le 0.3$), it was observed that the Curie temperatures are almost constant (ca. 340 K) for all the compositions explored. Many factors can affect the T_C of double-perovskite materials.[98–101] For $Ba_2Fe_{1+x}Mo_{1-x}O_6$ ($0 \le x \le 0.3$) we examined, a substitution of Mo^{5+} by Fe^{3+} cannot satisfy the charge neutrality without changing the Mo valence, providing that Fe remains in the trivalent state. A simple consideration shows that Fe can remain in the trivalent state for $0 \le x \le 0.3$ with Mo continuously changing its valence from Mo^{5+} (for $x = 0$) to $Mo^{5.86+}$ (for $x = 0.3$). Considering an idealized fully ordered structure with Fe and Mo alternating along the three cubic axes, all Fe ions substituting for Mo beyond $x = 0$ must necessarily give rise to Fe–O–Fe–O–Fe sequences. A strong superexchange interaction between Fe–O–Fe bonds should enhance the ferromagnetic coupling among the Fe ions in the same sublattice, and hence increase the T_C. On the other hand, the decreasing number of the itinerant electrons (1-3x) should lower the T_C.[102] As a result of these two opposing influences, the T_C remains roughly constant across the range of compositions.

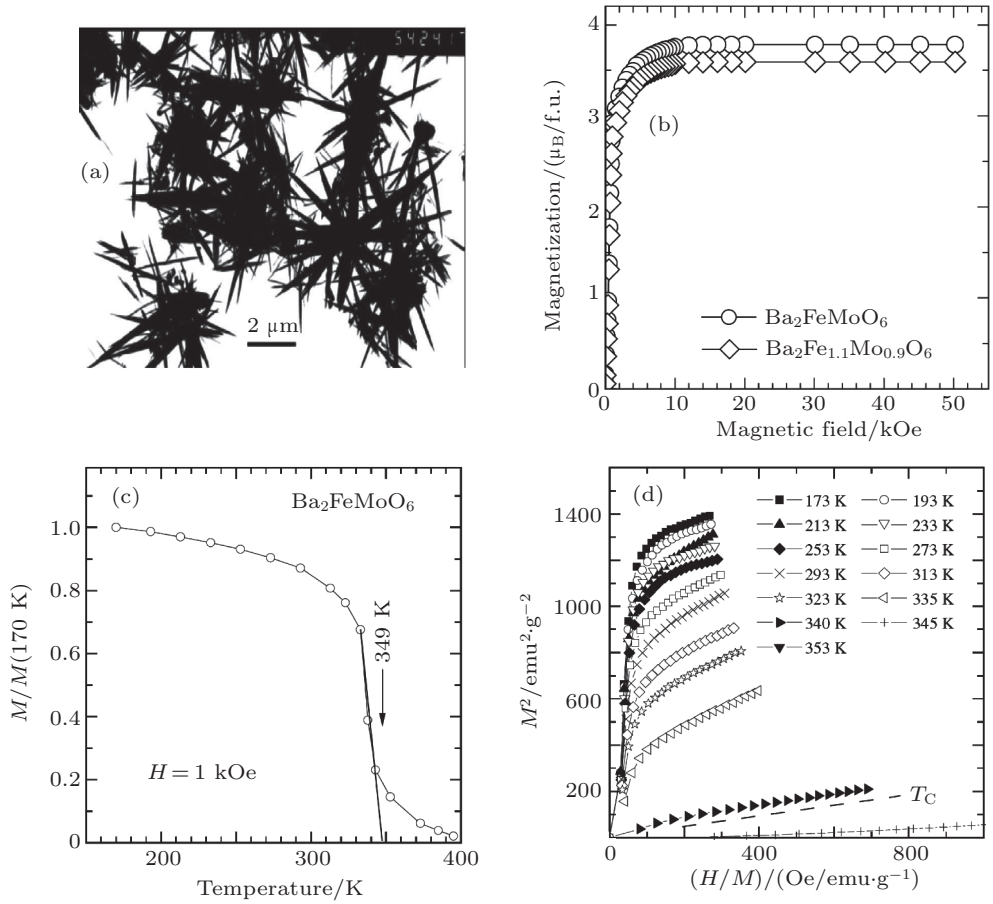


Fig. 10. (a) TEM image of Ba_2FeMoO_6.[89] (b) Magnetization of double-perovskite samples as a function of applied field at 5 K.[93] (c) Temperature dependence of normalized magnetization, $M/M(170\ \mathrm{K})$, for Ba_2FeMoO_6.[92] (d) Arrott plots for Ba_2FeMoO_6 sample.[89]

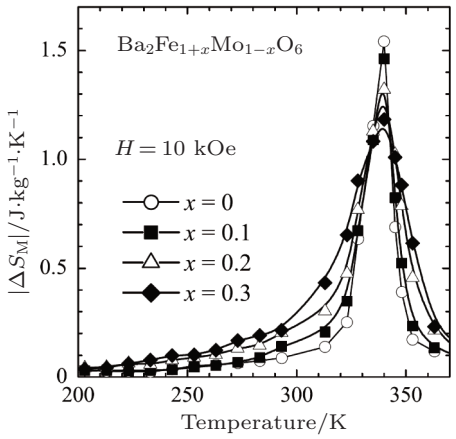


Fig. 11. Temperature dependence of magnetic entropy change ($|\Delta S_M|$) in applied field $\Delta H = 1.0$ T for $Ba_2Fe_{1+x}Mo_{1-x}O_6$.[89]

$Ba_2Fe_{1+x}Mo_{1-x}O_6$ exhibits a small magnetic hysteresis with coercivity below 40 Oe. Figure 11 shows the temperature dependence of $|\Delta S_M|$ observed in $Ba_2Fe_{1+x}Mo_{1-x}O_6$ under an applied field of 10 kOe. The maximum $|\Delta S_M|$ is of the order of 1.54 $J{\cdot}kg^{-1}{\cdot}K^{-1}$ at $x = 0$. As x increases, the maximum $|\Delta S_M|$ value decreases and the $|\Delta S_M|$ peak broadens. Since the $Ba_2Fe_{1+x}Mo_{1-x}O_6$ ($0 \le x \le 0.3$) samples exhibit an almost constant T_C, the position of the $|\Delta S_M|$ peak is restricted to the same narrow temperature range around 340 K (higher than room temperature). In an attempt to shift T_C toward room temperature, Kim *et al.*[103] partially replaced the Ba^{2+} of Ba_2FeMoO_6 with K^+, and found that the magnetic transition temperature decreases with increasing K^+ doping at a rate of 5.6 K/(mol% of K). This result is of interest for designing double-perovskite oxides as magnetic refrigerants that work near room temperature.

5. Summary

Perovskite-type oxides generally are promising candidates for active magnetic refrigeration, because they show large MCEs that are comparable to those of Gd. Moreover, compared to Gd and other candidate materials, the perovskite-type oxides are more convenient to prepare, and they exhibit higher chemical stability as well as higher resistivity, both of which are favorable for lowering eddy-current heating. In addition, the perovskite-type oxides possess much smaller thermal and field hystereses than the alloys that exhibit first-order phase transitions. The MCE peak temperature can be easily tuned in a wide temperature range from 100 K to 375 K, suitable for active magnetic refrigeration at various temperatures. This class of active magnetic materials is the cheapest among the known magnetic refrigerants, and should be considered as

promising candidates in future magnetic refrigeration technology.

The two disadvantages of perovskite oxides are as follows: 1) their $|\Delta S_M|$ values are not very large compared with some alloy materials; and 2) their adiabatic temperature change is not very large due to their relatively high heat capacity. We believe that the perovskite oxides with both superior MCE under a low field (< 2 T) and large adiabatic temperature change will be the choice for future magnetic refrigeration technology.

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