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Eu doping-induced enhancement of magnetocaloric effect in manganite $La_{1.4}Ca_{1.6}Mn_2O_7$

Y. Ma [a,b], Q.Y. Dong [a,*], Y.J. Ke [b], Y.D. Wu [a], X.Q. Zhang [b], L.C. Wang [b], B.G. Shen [b], J.R. Sun [b], Z.H. Cheng [b,*]

[a] Center for Condensed Matter, Department of Physics, Capital Normal University, Beijing 100048, People's Republic of China
[b] State Key Laboratory for Magnetism, Institute of Physics, Chinese Academy of Sciences, Beijing 100190, People's Republic of China

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ABSTRACT

The structure, magnetic properties and magnetocaloric effects of perovskite manganese oxides $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ have been investigated. They undergo a first-order ferromagnetic–paramagnetic phase transition around their respective Curie temperatures (235 K and 215 K, respectively). The doping of Eu and Sr atoms enhances greatly the value of magnetization, which leads to the large magnetocaloric effect. For a field change of 0–5 T, the maximum value of magnetic entropy change is only 4.5 J/kg K for $La_{1.4}Ca_{1.6}Mn_2O_7$ compound. However, it increases to 7.1 J/kg K for $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ compound. Meanwhile, a large refrigerant capacity of 240.4 J/kg is also achieved. Large reversible magnetocaloric effect and refrigerant capacity indicate the potentiality of $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ compound as a candidate for magnetic refrigerant.

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1. Introduction

The magnetic refrigeration, based on the magnetocaloric effect (MCE), has attracted a lot of interest in recent years because of its advantages over the conventional gas compression refrigeration, particularly for higher efficiency, less energy consumption, and not using ozone-depleting or global-warming gases [1–3]. The magnetocaloric effect (MCE) is intrinsic to all magnetic materials and is due to the coupling of the magnetic sublattice with the magnetic field, which changes the magnetic part of the entropy of a solid [4]. So MCE becomes the maximum around the transition temperature of magnetocaloric materials [5]. Recently, large MCE near room temperature has been reported in many compounds with a first-order magnetic phase transition such as Mn(Fe,P)As [6], $La(Fe,Si)_{13}$ [7], MnFe(P,Si,Ge) [8] as well as $(La_{1-x}M_x)MnO_3$ (M=Na, Ag, Ca, Sr, and Ba etc.) [9–13]. However, the hysteresis loss as well as the slow kinetics inherent in these materials may reduce the actual magnetocaloric efficiency. Therefore, it is desirable to find new materials with a large reversible MCE, especially at low magnetic fields and with a wide temperature range [14].

In the past few years, some authors have investigated the MCE in $La_{1-x}Ca_xMnO_3$ compounds and found that the magnetic entropy change of $La_{1-x}Ca_xMnO_3$ is comparable to that of Gd [15,16]. These compounds exhibit large magnetic entropy change (ΔS_M) and relative cooling power (RCP) near room temperature due to the paramagnetic (PM)-ferromagnetic (FM) phase transition at the Curie temperatures T_C, justifying their potential use as magnetic refrigerants. Apart from the above-mentioned manganites, the MCE of the bilayered perovskite manganites $La_{2-2x}Ca_{1+2x}Mn_2O_7$ have also been studied extensively [17–19]. In 2002, Zhu et al. reported a large magnetic entropy change of 16.8 J/kg K for $La_{1.4}Ca_{1.6}Mn_2O_7$ for a field change of 0–5 T, which allows magnetic refrigeration at room temperature [19]. Hereafter, there are a lot of literatures to repeat this work [17,18]. Although that the samples have the same nominal compositions, but the phase transition temperature and magnetic entropy change values are completely different. In order to eliminate this doubt, we prepared $La_{1.4}Ca_{1.6}Mn_2O_7$ compound. Moreover, the substitution of Eu for La may enhance the magnetization of the compound, which is necessary to obtain large magnetocaloric effect. However, there were reports that T_C was reduced by the substitution of magnetic rare earth atom for La [20]. It was reported that the doping of Sr could shift T_C toward high temperature [18]. Therefore, in the present work, we report the magnetic properties and magnetocaloric effect of $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$.

2. Experiments

Bulk $La_{1.4}Ca_{1.6}Mn_2O_7$ sample and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ sample were prepared by the conventional solid-state reaction

* Corresponding authors. Tel.: +86 10 68902348.
E-mail addresses: dongqy@cnu.edu.cn (Q.Y. Dong), zhcheng@iphy.ac.cn (Z.H. Cheng).

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processing in air. The stoichiometric mixtures of La_2O_3, $CaCO_3$, MnO_2, Eu_2O_3, $SrCO_3$ were ground and calcined at 1000 °C for 48 h. The resulting powders were reground, pressed into pellets and then sintered at 1450 °C for 48 h. Powder X-ray diffraction with Cu Kα radiation was carried out to characterize the crystal structure of the samples. Magnetization measurements were performed on a commercial superconducting quantum interference device-vibrating sample magnetometer (SQUID-VSM) from Quantum Design.

3. Results and discussion

X-ray diffraction patterns for $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ at room temperature are shown in Fig. 1. The pattern for $La_{1.4}Ca_{1.6}Mn_2O_7$ reveals $Sr_3Ti_2O_7$-type tetragonal (*I4/mmm*) perovskite structure. The lattice parameters are determined to be $a=3.8643$ Å and $c=19.2776$ Å. The pattern for $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ can be indexed to an orthorhombic ABO_3-type perovskite structure with a space group *Pbnm*. The lattice parameters are calculated to be $a=5.4410$ Å, $b=5.4536$ Å and $c=7.6854$ Å. Meanwhile, impurity phase of CaO is determined in these two samples marked with "*" in Fig. 1. The minor doping of Eu and Sr atoms can greatly affect the formation of crystalline structure.

Fig. 2 displays the temperature (T) dependences of zero-field cooling (ZFC) and field-cooling (FC) magnetization (M) of $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ compounds under a field of 0.1 T, respectively. In the ZFC mode, the sample was cooled to 5 K before the measuring field H was switched on and the measurement was made while warming up the sample to high temperature. After finishing the ZFC M–T measurement, we followed to take the data again in the presence of the same H while cooling the sample. This was the FC mode. One can find that both compounds experience a FM–PM transition around their respective Curie temperature T_C (235 K and 215 K, defined as the minimum values of dM/dT curves). Moreover, M–T curves seem to show a small irreversible behavior in heating and cooling processes around T_C. In order to confirm it, we make detailed magnetization measurements with an interval of 0.5 K in the vicinity of T_C for these two compounds, as shown in the inset of Fig. 2. A small temperature hysteresis of ~1 K is observed.

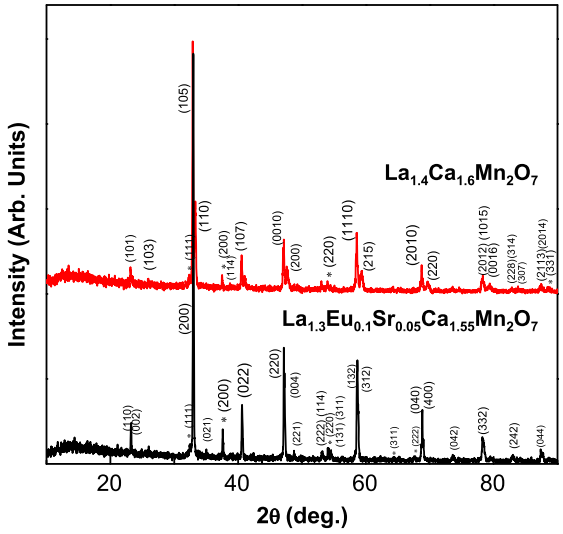

Fig. 1. X-ray diffraction patterns of $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ compounds at room temperature, marked by "*" are the impurity of CaO phase. Miller indexes are also displayed.

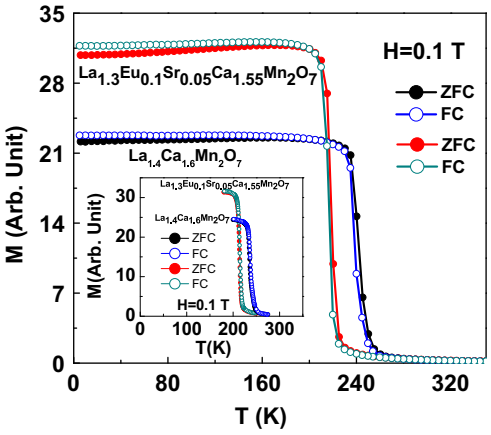

Fig. 2. Temperature dependences of ZFC and FC magnetizations of $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ under 0.1 T. The inset shows detailed ZFC and FC magnetizations versus temperature for the two compounds around T_C under 0.1 T.

The isothermal magnetization curves as a function of magnetic field for $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ compounds were measured in applied fields of up to 5 T in a wide temperature range. Fig. 3(a) and (b) shows the magnetization curves of $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ in the temperature ranges of 220–261 K and 200–240 K, respectively. One can find that they exhibit typical FM nature at temperatures lower than T_C. However, the magnetization of $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ under 5 T at 5 K reaches 83.3 Am^2/kg, which is much higher than 61.8 Am^2/kg of $La_{1.4}Ca_{1.6}Mn_2O_7$. This may result from the change of crystalline structure and the doping of magnetic atom Eu. Therefore, large MCE can be expected in $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ compound. The Arrott plots [21] around T_C for $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ compounds are shown in Fig. 3(c) and (d), respectively. According to the Banerjee criterion [22], a magnetic transition is expected to be of first-order when the negative slope or an obvious inflection point of M^2 versus M/H plot is observed. It is very clear that the Arrott plots for them indicate a characteristic of first-order phase transition.

Fig. 4 shows the magnetization isotherms measured under increasing and decreasing magnetic fields at several temperatures around T_C for the two compounds. The hysteresis losses, which are very harmful to magnetic refrigeration Ericsson cycle, are determined by calculating the area enclosed by the ascending and the descending branches of magnetization curves. The temperature dependences of hysteresis loss for $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ in the vicinity of T_C are shown in the inset of Fig. 4. One can find that they display scarcely any hysteresis loss, although the two compounds exhibit the nature of first-order phase transition. This point is very attractive for magnetic refrigeration.

The magnetic entropy change can be calculated from isothermal magnetization data by using Maxwell relation. Fig. 5 displays the values of $-\Delta S_M$ for the two samples as a function of temperature for the typical field changes, respectively. One can find that the $-\Delta S_M$ peak broadens asymmetrically toward high temperature for the two manganese oxides with the increase of the applied field. The peak values of $-\Delta S_M$ for $La_{1.4}Ca_{1.6}Mn_2O_7$ for the applied field changes of 0–1, 0–2 and 0–5 T are 2.2, 3.1 and 4.5 J/kg K, respectively. However, they are improved to 4.3, 5.6 and 7.1 J/kg K for $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ under the same fields, respectively. The enhancement of magnetization as well as the first-order phase transition is responsible for the significant improvement of ΔS_M. The values of $-\Delta S_M$ for $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ are comparable with or much large than those of many reported magnetocaloric materials with the ABO_3-type

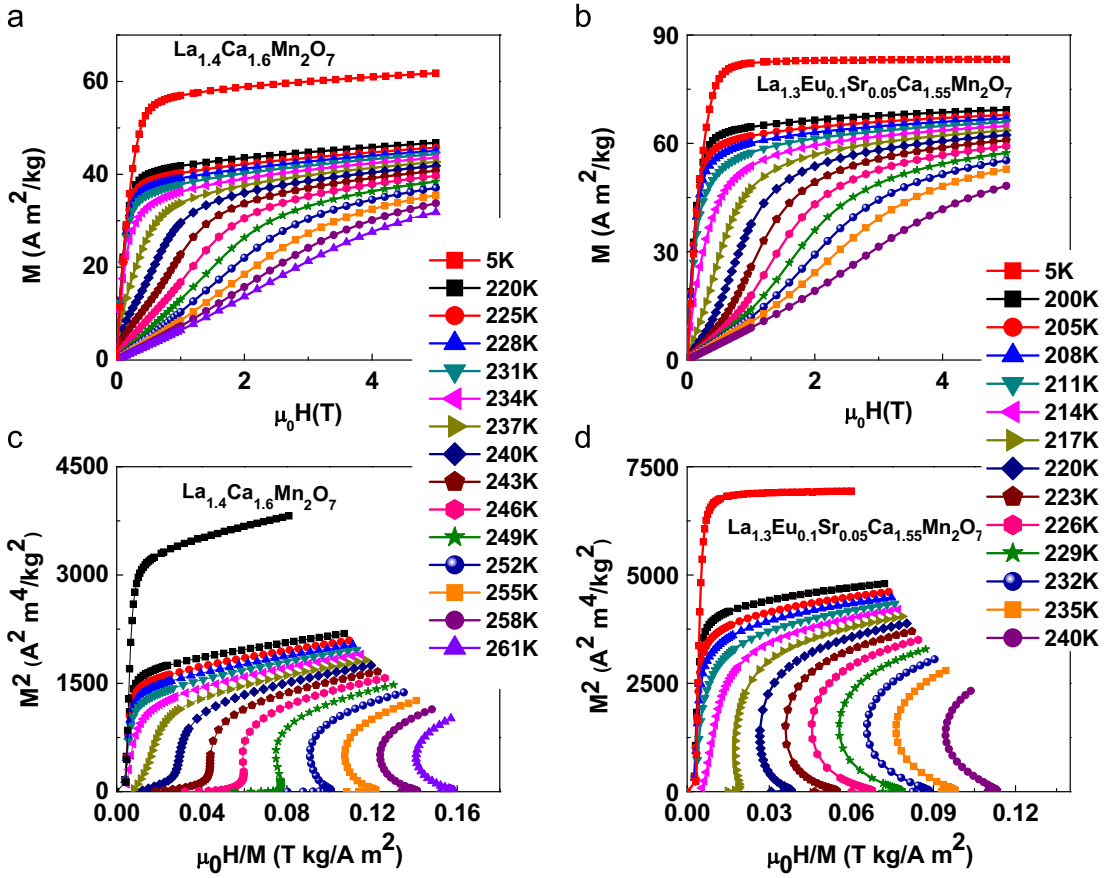

Fig. 3. Magnetic isothermals ((a) and (b)) and Arrott-plots ((c) and (d)) for $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ around T_C, respectively.

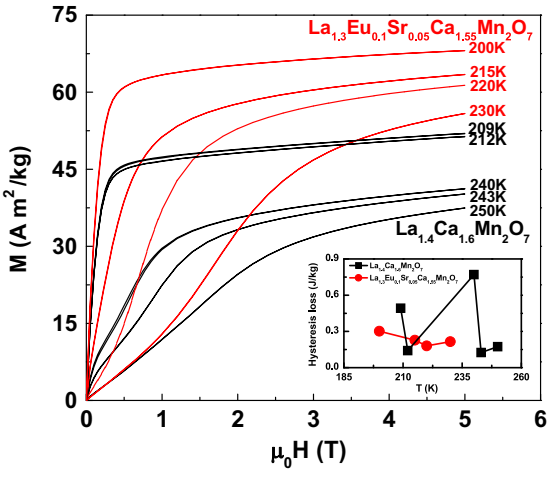

Fig. 4. Magnetization isotherms of $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ measured under increasing and decreasing fields in the vicinity of T_C. Black and red lines correspond to $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$, respectively. The inset displays the temperature dependences of hysteresis loss for the two compounds. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

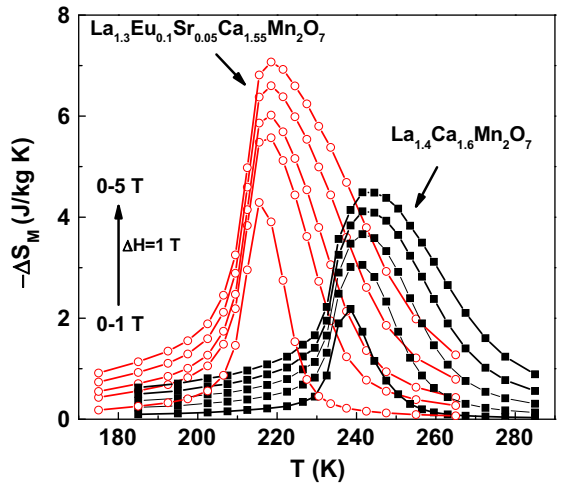

Fig. 5. Magnetic entropy change as a function of temperature for $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ under typical magnetic field changes.

perovskite structure in a similar magnetic transition temperature range under the same field change, such as $La_{0.9}Na_{0.1}MnO_3$ (1.53 J/kg K around 218 K for 0–1 T) [23], $La_{0.880}Na_{0.999}Mn_{0.977}O_3$ (1.52 J/kg K around 220 K for 0–1 T) [24], $La_{0.75}Na_{0.25}MnO_3$ (4.7 J/kg K around 224 K for 0–1.5 T) [25], $La_{0.5}Nd_{0.2}Ca_{0.3}MnO_3$ (2.31 J/kg K around 213 K for 0–1 T) [26], $La_{0.65}Nd_{0.05}Ca_{0.3}Mn_{0.9}Cr_{0.1}O_3$ (0.96 J/kg K around 218 K for 0–1 T) [27], $Pr_{0.7}Pb_{0.3}MnO_3$ (1.35 J/kg K around 225 K for 0–1.35 T) [28] and $La_{1.4}Ca_{1.6}Mn_2O_7$ (2.28 J/kg K around 215 K for 0–1 T) [18].

Besides the ΔS_M, the RCP is another important parameter that characterizes the refrigerant efficiency of the material. In the present work the value of RCP is calculated by using

$$RCP = -\Delta S_{Max} \times \delta T_{FWHM},$$

where ΔS_{Max} represents the maximum magnetic entropy change and δT_{FWHM} its full-width at half-maximum. For a field change of 0–2 T, the RCP value of $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ are 56.5 and 104.7 J/kg, respectively. They are increased to 151.8 and 240.4 J/kg for a field change of 0–5 T. Therefore, the perovskite manganite oxide $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ can be considered to

Table 1
Comparison of lattice parameters, c/a ratio, Curie temperature, and magnetic entropy change of $La_{1.4}Ca_{1.6}Mn_2O_7$ at room temperature.

Preparation technique	a (Å)	c (Å)	c/a	T_C (K)	ΔS_{max} (J/kg K) (0–2 T)	References
Sol–gel	3.8658	19.2769	4.9870	225	1.1	[20]
Solid state	3.8643	19.2776	4.9886	235	3.1	This work
Sol–gel	3.8637	19.2790	4.9893	265	4.0	[20]
Sol–gel	3.8524	19.3436	5.0212	268	4.7	[20]
Solid state	3.862	19.324	5.004	270	11.3	[22]

be a good candidate material for use as active elements in magnetic refrigeration.

$La_{1.4}Ca_{1.6}Mn_2O_7$ compound is often fabricated by the sol–gel or solid-state reaction methods [17–19]. Although many $La_{1.4}Ca_{1.6}Mn_2O_7$ compounds sintered at various temperatures exhibit the $Sr_3Ti_2O_7$-type structure, they display different lattice parameters (a and c). The change of c/a ratio means a variation of Jahn–Teller (J–T) distortion [18]. The coupling of FM ordering and J–T distortion may determine the degree of first-order phase transition, phase transition temperature and saturated magnetization. The structural parameters determined from the XRD pattern (see Fig. 1), Curie temperature, and magnetic entropy change of the present $La_{1.4}Ca_{1.6}Mn_2O_7$ compound are compared with those in literatures [17,19], as shown in Table 1. One can find that high T_C and large ΔS_M could be obtained when the c/a ratio displays an appropriate value. The c/a ratio for the present compound is 4.9886, which lies between 4.9870 and 4.9893 [17], so we obtain middle values of T_C and ΔS_M, which may be due to the intermediate level of the J–T distortion.

4. Conclusions

In summary, from the magnetization measurements it is found that both $La_{1.4}Ca_{1.6}Mn_2O_7$ and $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ compounds undergo a first-order ferromagnetic–paramagnetic phase transition around their respective Curie temperatures (235 K and 215 K, respectively). The substitutions of Eu for La and Sr for Ca for $La_{1.4}Ca_{1.6}Mn_2O_7$ induce the change of crystalline structure and the improvement of magnetization. Therefore, $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ shows large magnetocaloric effect. For a field change of 0–5 T, the peak value of ΔS_M and RCP reach 7.1 J kg^{-1} K^{-1} and 240.4 J/kg, respectively. Large ΔS_M and high RCP as well as scarcely any hysteresis loss make $La_{1.3}Eu_{0.1}Sr_{0.05}Ca_{1.55}Mn_2O_7$ compound a promising candidate for magnetic refrigeration.

Acknowledgments

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