Magnetism and large reversible room-temperature magnetocaloric properties of antiperovskite compounds $ZnC_{1-x}N_xFe_{3-2x}Mn_{2x}$ ($0 \leqslant x \leqslant 1$)

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ABSTRACT

In this paper we report the effects of Mn substitution on the structural and magnetic properties of $ZnCFe_{3-y}Mn_y$ ($0 \leqslant y \leqslant 1$). It is found that with increasing the doping level y the increased lattice constant, enhanced Curie temperature (T_C), and decreased saturated magnetization (M_S) are obtained. However, the enhancement of T_C (>380 K) in $ZnCFe_{3-y}Mn_y$ is not suitable to explore room-temperature magnetocaloric material. Therefore, we carry out a dual doping by N and Mn on C and Fe sites of $ZnCFe_3$, respectively. As a result, with increasing x the lattice parameter increases while the T_C and M_S decrease gradually for $ZnC_{1-x}N_xFe_{3-2x}Mn_{2x}$ ($0 \leqslant x \leqslant 1$). In particular, for $ZnC_{0.5}N_{0.5}Fe_2Mn$ ($x = 0.5$) the T_C (~302 K) is tuned just at the room temperature. Correspondingly, around the T_C of $ZnC_{0.5}N_{0.5}Fe_2Mn$ the magnetocaloric effect is considerably large with a magnetic entropy change of 2.86 J/kg K ($\Delta H = 4.5$ T) as well as a relative cooling power (RCP) of 220 J/kg ($\Delta H = 4.5$ T). Given the considerably large RCP, inexpensive and innoxious raw materials, and suitable operating temperature, $ZnC_{0.5}N_{0.5}Fe_2Mn$ is suggested to be a promising candidate for room-temperature magnetic refrigeration.

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1. Introduction

Magnetic refrigerant technology based on the magnetocaloric effect (MCE) has attracted much attention because of its energy-efficient and environment-friendly features compared with the traditional gas-compression refrigeration technology. In particular, over the past decades room-temperature magnetic refrigeration has been extensively investigated experimentally and theoretically [1–3]. Generally, the giant MCE is considered to be related to a first-order magnetic transition due to the large and/or sharp changes in magnetizations between the two adjacent magnetic phases. However, the practical application of MCE around a first-order magnetic phase transition is quite restricted because of the existence of the relevant hysteresis under magnetization/demagnetization processes, which makes the magnetic refrigeration less efficient [3–5]. Moreover, most of the promising magnetic refrigerant materials contain expensive rare-earth elements (e.g. La, Gd, Tb, Dy, Er) and/or poisonous chemical elements (e.g. As) such as Gd, $Gd_5(SiGe)_4$, $La(Fe,Si)_{13}$, $LaMnO_3$, $RECo_2(RE = Tb, Dy, Er)$, MnAs [6–12]. Therefore, for actual industrial applicability, high refrigerant capability, innoxious and low-cost raw materials and

reversible room-temperature magnetic transition are becoming significant factors for refrigerant materials.

Lately, Fe-based antiperovskite compounds $AXFe_3$ (A = Al, Ga, Sn, Zn, Ni, Pd, Pt, etc.; X = C, N) have been paid considerable attention due to their interesting physical and mechanical properties, such as zero temperature coefficient of resistance [13], MCE [13,14], and high elastic modulus [15,16]. As a typical Fe-based antiperovskite compound, $ZnCFe_3$ has been investigated for several decades, which is a ferromagnetic (FM) material and undergoes a second-order magnetic transition to paramagnetic (PM) phase around 368 K as reported previously [17]. Very lately, the influences of carbon content on the structural, magnetic and electrical/thermal transport properties of ZnC_xFe_3 have been studied [14]. For the parent compound $ZnCFe_3$, the MCE is reversible and considerable large. However, the Curie temperature T_C (~358 K) is higher than room temperature, which restricts an actual industrial application [14]. As reported previously, the magnetic transition temperature can be tuned by chemical doping on A site of $AXFe_3$, such as in $Ga_xSn_{1-x}CFe_3$ [13] and $Zn_xSn_{1-x}CFe_3$ [18]. Moreover, the magnetic transition can also be adjusted by doping on Mn site in Mn-based antiperovskite compounds [19,20]. Similarly, we investigate the effects of Mn substitution on the structural and magnetic properties of $ZnCFe_{3-y}Mn_y$ ($0 \leqslant y \leqslant 1$). Our results indicate that the lattice constant and T_C increase while the saturated magnetization decreases gradually with increasing y. The increasing T_C (>380 K) is not suitable for us to explore the room-temperature magnetocaloric

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material. As reported by Fruchart and Bertaut, in $ZnNMn_3$ there is a magnetic transition from antiferromagnetism (AFM) to PM near 185 K [21]. In order to decrease the value of T_C, we carry out a dual doping by using N and Mn on C and Fe sites of $ZnCFe_3$, respectively. As a result, the lattice constant increases while the T_C and saturated magnetization decrease with increasing x in $ZnC_{1-x}N_xFe_{3-2x}Mn_{2x}$ ($0 \leqslant x \leqslant 1$). It is worth noting that, for $ZnC_{0.5}N_{0.5}FeMn_2$, the value of T_C is tuned around 300 K and the maximal magnetic entropy change and RCP value can reach 2.86 J/kg K and 220 J/kg with the magnetic field change $\Delta H = 4.5$ T, respectively, and these values are comparable with the typical MCE materials with a second-order magnetic transition. Considering the considerable large RCP, inexpensive and innoxious raw materials, and suitable T_C, $ZnC_{0.5}N_{0.5}FeMn_2$ is suggested to be a promising candidate for room-temperature magnetic refrigeration.

2. Experimental details

Polycrystalline samples $ZnCFe_{3-y}Mn_y$ ($0 \leqslant y \leqslant 3$) and $ZnC_{1-x}N_xFe_{3-2x}Mn_{2x}$ ($0 \leqslant x \leqslant 1$) were prepared by solid-state reaction in vacuum using the powders of Zn, Mn, C, Mn_2N and Fe [13,14,18]. The detailed experimental processes were reported in Ref. [13]. The X-ray powder diffraction (XRD) were obtained at room temperature using an X-ray diffractometer with Cu Kα radiation (PHILIPS, $\lambda = 0.15406$ nm) to determine the crystal structure and phase purity. Magnetic measurements were performed on a Quantum Design superconducting quantum interference device magnetometer (SQUID5T).

3. Results and discussion

Fig. 1a shows the room-temperature XRD patterns for the samples $ZnCFe_{3-y}Mn_y$ ($y = 0, 0.2, 0.3, 0.4, 0.5, 1.0, 1.5, 2.0, 2.5,$ and 3.0). Obviously, all the samples are single-phase with a cubic structure (Space group: $Pm\overline{3}m$). According to the dash line in Fig. 1a, the peak of (2 2 0) moves to low angle with increasing y, meaning the lattice constant increases with increasing doping level y. The XRD patterns of all samples were refined by a standard Rietveld technique. As shown in Fig. 1b, the refined lattice parameter increases with increasing y, which is consistent with the shift of peak (2 2 0) to low angle as shown in Fig. 1a. The expansion of
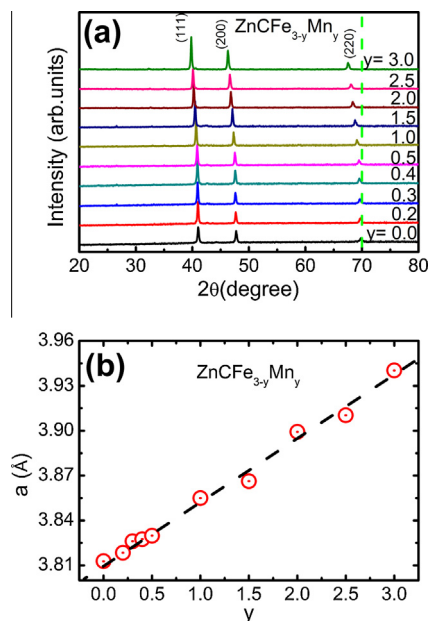
lattice is attributed to the larger atom radius of Mn compared with Fe. In order to investigate the change of T_C and magnetic ground state of $ZnCFe_{3-y}Mn_y$, temperature dependent magnetization $M(T)$ curves at 0.01 T under zero-field-cooled (ZFC) between 5 and 380 K and the isothermal $M(H)$ curves at 5 K are measured and plotted in Fig. 2a and b, respectively. Apparently, for the samples with $y = 1, 2,$ and 3 the $M(T)$ curves measured up to 380 K do not show a sharp FM–PM transition as reported in $ZnCFe_3$ ($y = 0$) previously [14,17]. For $y = 3$, around 230 K there is a magnetic transition from FM to ferrimagnetic (FIM) phase, which is consistent with previous work [21]. As shown in the Fig. 2b, the ground states for $ZnCFe_{3-y}Mn_y$ are FM (for $y = 0, 1,$ and 2) or FIM (for $y = 3$). In a word, with the doping level y increasing the T_C increases beyond the temperature of 380 K, which is much higher than room temperature. Therefore, in order to decrease the T_C a dual doping by N and Mn was carried out.

Fig. 3a shows the room-temperature XRD patterns for the samples $ZnC_{1-x}N_xFe_{3-2x}Mn_{2x}$ ($x = 0, 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8, 0.9,$ and 1.0). All the samples are single-phase with a cubic antiperovskite structure (Space group: $Pm\overline{3}m$). As shown in Fig. 3b, the enlargements of XRD pattern near the peak (1 1 1) for all the samples are plotted and the central position of peak (1 1 1) shifts to low angle with increasing Mn_2N. The Rietveld refinements of XRD patterns are carried out for all the samples $ZnC_{1-x}N_xFe_{3-2x}Mn_{2x}$ ($0 \leqslant x \leqslant 1$). As shown in Fig. 3c, the refined lattice parameter increases with increasing x, which is consistent with the shift of peak (1 1 1) to low angle as shown in Fig. 3b. Considering the lattice constants of $ZnCFe_3$ (0.381 nm) [7] and $ZnNMn_3$ (0.390 nm) [20], the expansion of lattice constant with increasing x can be easily understood.

Fig. 4a presents temperature dependent magnetization $M(T)/M(5$ K$)$ curves for $ZnC_{1-x}N_xFe_{3-2x}Mn_{2x}$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9,$ and 1.0) at 0.01 T under ZFC process. Obviously, each $M(T)$ curve exhibits a FM–PM transition as reported in $ZnCFe_3$ [14]. The T_C (determined by the minimal value of dM/dT, shown in Fig. 4b) is presented in Fig. 4d, where the value of T_C decreases with increasing x. In order to investigate the magnetic ground state of $ZnC_{1-x}N_xFe_{3-2x}Mn_{2x}$ ($x = 0, 0.1, 0.3, 0.5, 0.7, 0.9,$ and 1.0), the

Fig. 1. (a) Room-temperature XRD patterns for $ZnCFe_{3-y}Mn_y$ ($0 \leqslant y \leqslant 3$). The green dash line is guide to the eye; (b) lattice parameter as a function of y for $ZnCFe_{3-y}Mn_y$ ($0 \leqslant y \leqslant 3$). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
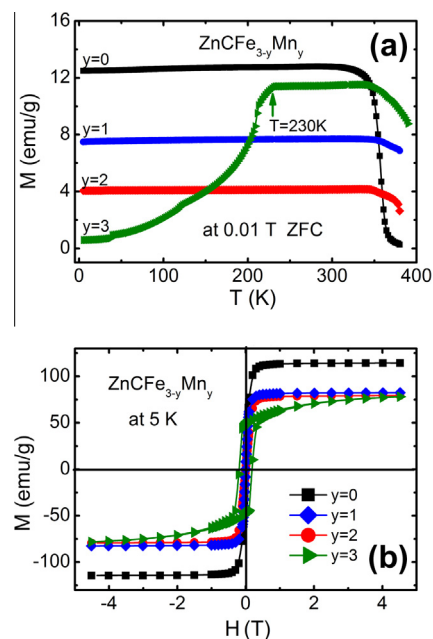

Fig. 2. (a) Temperature dependent magnetization $M(T)$ curves under ZFC process at 0.01 T for $ZnCFe_{3-y}Mn_y$ ($y = 0, 1, 2, 3$); (b) magnetic field dependence of magnetization $M(H)$ curves for $ZnCFe_{3-y}Mn_y$ ($y = 0, 1, 2, 3$) at 5 K.