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## Magnetic properties and room-temperature magnetocaloric effect in the doped antiperovskite compounds $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$ ( $0 \leq x \leq 0.15$ )

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## ABSTRACT

We report the effects of Al doping on the structure, magnetic properties, and magnetocaloric effect of antiperovskite compounds  $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$  ( $0 \leq x \leq 0.15$ ). Partial substitutions of Al for Ga enhance the Curie temperature (from 250 K for  $x=0.0$  to 312 K for  $x=0.15$ ) and the saturation magnetization. On increasing the doping level  $x$ , the maximum values of the magnetic entropy change ( $-\Delta S_M$ ) decreases while the temperature span of  $-\Delta S_M$  vs.  $T$  plot broadens. Furthermore, the relative cooling power (RCP) is also studied. For 20 kOe, the RCP value tends to saturate at a high doping level (for  $x=0.12$ , 119 J/kg at 296 K). However, at 45 kOe, the RCP value increases quickly with increasing  $x$  (for  $x=0.15$ , 293 J/kg at 312 K). Considering the relatively large RCP and inexpensive raw materials,  $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$  may be alternative candidates 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 potential advantages such as environment-friendly and energy-efficient compared with the traditional vapor-cycle refrigeration technology. Particularly, room-temperature magnetic refrigeration has been paid more and more attention owing to its potential actual applications [1,2]. Generally, the giant-MCE (GMCE) usually appears in those materials with a first-order magnetic transition [3–5]. Although the maximal magnetic entropy changes ( $-\Delta S_M$ ) of these GMCE materials are larger than those of materials around second-order transitions (such as Gd), the large magnetic and/or thermal hysteresis being disadvantages of the first-order transition make the magnetic refrigeration inefficient [6,7]. Therefore, for actual industrial applicability, high refrigerant capability, innocuity, low-cost production, and room temperature are becoming significant objectives for magnetic refrigerant materials.

Recently, the Mn-based antiperovskite structural compounds  $\text{AXMn}_3$  (A, main group elements; X, carbon or nitrogen) have attracted considerable attention due to their interesting properties [8–18]. Heretofore, many functionality characteristics such

as magnetoresistance (MR) [8–10], MCE [11–13], and giant negative thermal expansion (NTE) have been discovered and widely investigated experimentally and theoretically [14–16]. As a typical antiperovskite compound,  $\text{GaCMn}_3$ , displaying intriguing magnetic structures and magnetic transitions, has been studied for several decades [8,10,11,17]. In  $\text{GaCMn}_3$ , there exist four different magnetic phases: namely, the paramagnetic (PM) phase, ferromagnetic (FM) phase, ferromagnetic intermediate (FI) phase, and antiferromagnetic (AFM) phase with decreasing the temperature [8,17]. Around the first-order AFM–FI phase transition, close correlations among lattice, spin, and charge has been observed and no structure transition appears with discontinuous volume shrinkage of 0.46% with increasing the temperature. Recently, much work has been carried out on the MCE of  $\text{GaCMn}_3$ -based antiperovskite compounds around the AFM–FI transition since its discovery [11–13]. In the parent compound  $\text{GaCMn}_3$ , MCE displays a plateau-like temperature dependence with a large entropy change  $-\Delta S_M$  (15 J/kg K under 20 kOe) around the AFM–FI transition [11]. Meanwhile, the MCE in  $\text{GaCMn}_3$  is much sensitive to chemical composition: the replacement of Co or Ni for Mn atom broadens the working temperature spans without significant loss of  $-\Delta S_M$  [13,18]. However, rare report has been focused on the MCE of the second-order FM–PM transition in  $\text{GaCMn}_3$ . According to the previous investigations, the physical properties of  $\text{GaCMn}_3$  could be effectively manipulated by the magnetic field, pressure, and chemical doping [19–23]. The A site-doping effect (A=Al, Zn, Sn, etc.) on the magnetic transitions of  $\text{GaCMn}_3$  has also been studied in

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detail [19]. However, the MCEs of these related compounds are still unknown to date. The investigations of MCE in related compounds may be much meaningful and helpful to understand the MCE of this system.

In this work, we mainly studied the Al-doping effects on the structural, magnetic properties and MCE of  $\text{GaMn}_3$ . On increasing the doping level  $x$ , both the Curie temperature  $T_C$  (from 250 K for  $x=0$  to 312 K for  $x=0.15$ ) and the saturated magnetizations gradually increase simultaneously. Meanwhile, the maximum values of  $-\Delta S_M$  are decreased while the temperature spans of  $-\Delta S_M$  vs.  $T$  plot broaden, resulting in the gradual enhancement of the relative cooling power (RCP) as functions of magnetic fields and/or doping level  $x$ . Considering the advantages such as no hysteresis loss, close to room temperature, and low-cost raw materials, the serial antiperovskite compounds  $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$  may be potential candidates for room-temperature magnetic refrigerant materials.

## 2. Experimental details

Polycrystalline samples  $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$  ( $x=0, 0.05, 0.07, 0.12, \text{ and } 0.15$ ) were prepared directly from Ga pieces (4 N), powders of Al (3 N), graphite (3 N), and Mn (4 N) as reported previously [12,18]. The starting materials were mixed in the desired proportions, sealed in evacuated quartz tubes and then heated at 1023–1148 K for 7–8 days. After quenched to room temperature, the products were pulverized, mixed, and annealed again under the same condition in order to obtain the homogeneous samples. X-ray diffraction (XRD) measurements on powder samples were performed around 300 K using Cu  $K\alpha$  radiation (PHILIPS,  $\lambda=0.15406$  nm) to identify the phase purity and the crystal structure of the samples. Magnetic measurements were carried out on a Quantum Design superconducting quantum interference device (5T-SQUID) magnetometer ( $1.8 \text{ K} \leq T \leq 400 \text{ K}$ ,  $0 \leq H \leq 50 \text{ kOe}$ ).

## 3. Results and discussion

Fig. 1 presents the powder XRD patterns of  $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$  ( $0 \leq x \leq 0.15$ ) around room temperature. All the samples are single phase with standard cubic antiperovskite structure (space group  $Pm\bar{3}m$ ) except for a small amount of excess carbon. As

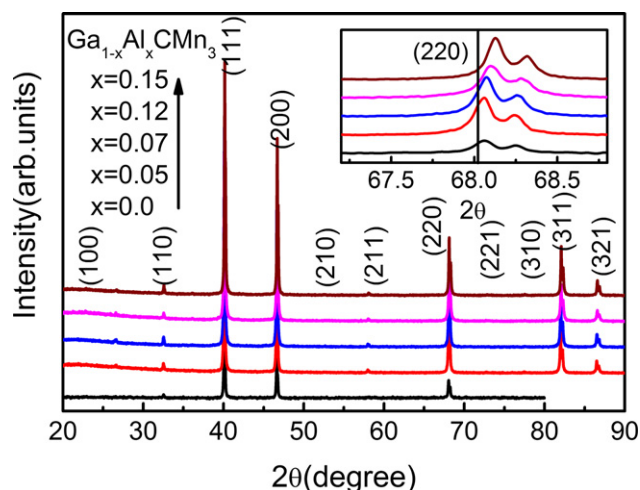


Fig. 1. (a) Room-temperature powder XRD patterns of  $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$  ( $x=0, 0.05, 0.07, 0.12, \text{ and } 0.15$ ). Inset shows the enlargement of XRD peak (2 2 0) for all the samples.

illustrated in the inset of Fig. 1, the enlargement of XRD (2 2 0) peak is plotted for all the samples. Apparently, the central positions of peak shift toward higher angles with increasing Al content, indicates that the lattice constant ( $a$ ) generally shrink with increasing Al content. The refined lattice parameters using the standard Rietveld techniques [24] almost linearly decrease with the increasing Al content, which is consistent with the results of Fig. 1 (see Fig. 3(a)).

Fig. 2 displays the temperature dependent magnetization curve  $M(T)$  of  $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$  at 100 Oe under the field-cooled cooling (FCC) and field-cooled warming (FCW) processes. For each sample, a ferromagnetic (FM)-paramagnetic (PM) phase transition could be clearly observed with increasing the temperature, consistent with previous reports [8,11]. The Curie temperatures  $T_C$  (defined as the temperature with a maximum  $|dM/dT|$  in the  $M(T)$  curve) are about 250, 258, 281, 296, and 312 K for  $x=0, 0.05, 0.07, 0.12, \text{ and } 0.15$ , respectively (see Fig. 3(a)). Meanwhile, no evident hysteresis exists between  $M_{\text{FCC}}$  and  $M_{\text{FCW}}$ , indicating a second-order magnetic transition for all the Al-doped compounds  $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$  [6, 12, 17]. All these results are basically consistent with the previous investigations [19–23].

Fig. 3(b) shows the isotherm magnetization curves  $M(H)$  of  $\text{Ga}_{1-x}\text{Al}_x\text{CMn}_3$  around 200 K (well located at FM phase for each sample). For each curve, the magnetization increases sharply at low fields and then tends to be saturated when  $H$  exceeds 10 kOe. As shown in the inset of Fig. 3(a), the magnetizations at 40 kOe (almost saturated for each sample) increases with increasing the Al content, which is consistent with the evolution of  $T_C$  (see Fig. 2 or Fig. 3(a)). According to previous reports, the pressure could affect the magnetic properties (including magnetizations, magnetic phase transition temperatures, etc.) of  $\text{GaMn}_3$  by altering the distances or magnetic interaction of Mn–Mn sites [19–23]. However, there are large discrepancies between the element doping and the pressure effect in A-site doped  $\text{GaMn}_3$ -based compounds. Previous studies suggested that the doping effect may change the electronic state except for the simple lattice effect [20]. Considering that Al atom is smaller than Mn, the replacement of Al for Ga atom could be seen as positive chemical pressure effect. Based on the previous investigations, the lattice shrinkage may result in the increase of the density of states at the Fermi level  $N(E_F)$  in  $\text{GaMn}_3$ , leading to the increase of magnetizations based on the predictions of the Stoner model [25]. Simultaneously, the lattice shrinkage also enhances the magnetic

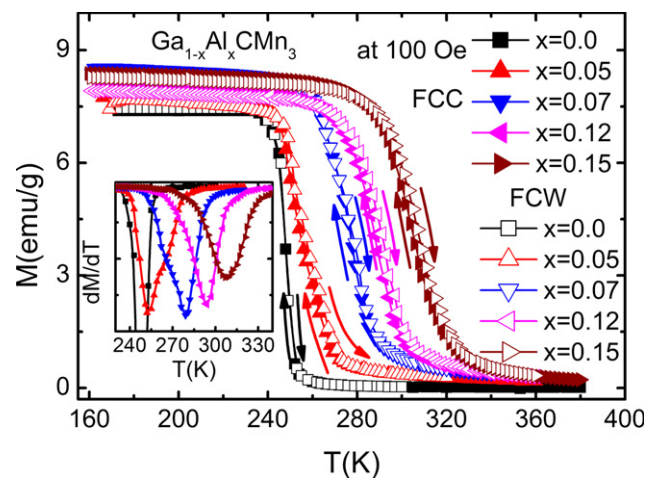


Fig. 2. Temperature dependent magnetization curve  $M(T)$  under FCC and FCW processes at a magnetic field of 100 Oe from 150 to 380 K. The arrows indicate the direction of temperature circle. Inset shows the plot of  $dM/dT$  vs.  $T$  for all the samples.

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