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Synthesis and characterization of antiperovskite nitrides $GaNCr_{3-x}Mn_x$

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ABSTRACT

The effects of Mn-doping on the crystal structure, magnetic and electrical/thermal transport properties of $GaNCr_{3-x}Mn_x$ ($0 \le x \le 1.5$) have been investigated systematically. As a result, the lattice constant and the residual resistivity increase, while the residual resistivity ratio, electron thermal conductivity, and room-temperature carrier concentration decrease with increasing Mn-doping level. The ground state of parent compound $GaNCr_3$ is nonmagnetic, interestingly, the ferrimagnetism and antiferromagnetism are observed in Mn-doped samples $GaNCr_{3-x}Mn_x$. Correspondingly, around the antiferromagnetic transition of $GaNCr_{3-x}Mn_x$ the correlation effect is studied. Furthermore, the analysis of thermal conductivity data suggests that the electron thermal conductivity plays a major role in total thermal conductivity of $GaNCr_3$ at low temperatures, while the phonon thermal conductivity is dominant for Mn-doped $GaNCr_3$ in the whole temperature of 5–330 K. The positive values of Seebeck coefficient and Hall coefficient indicate that the nature of charge carrier is hole-type in $GaNCr_{3-x}Mn_x$.

1. Introduction

Since the first antiperovskite superconductor $MgCNi_3$ was reported in 2001 [1], the antiperovskite structural compounds AXM_3 (A=Ga, Al, Sn, Zn, Cu, In, Ge, etc.; X=C, N; M=Mn, Fe, Ni, etc.) have been studied extensively in the last decade and plenty of interesting physical properties and potential functionalities such as superconductivity [2–4], strong electron–electron correlation [5,6], magnetic frustration [7], giant magnetoresistance [8–10], magnetocaloric effect [11–13], negative thermal expansion [14–16], magnetostriction [17], and nearly zero temperature coefficient of resistivity have been observed [18–20]. Especially, recent investigations of AXM_3 are mainly focused on the Mn-, Fe-, and Ni-based antiperovskite compounds [1–20].

Up to now, there is still no detailed experimental research on Cr-based antiperovskite compounds ($AXCr_3$) except for a few theoretical reports [21–23]. For example, in 2007, the Cr-based antiperovskite nitrides $GaNCr_3$ and $RhNCr_3$ were suggested as potential candidates for $MgCNi_3$-like superconductor by using the Korringa–Kohn–Rostoker method [23]. Furthermore, Shao et al. investigated the Cr-based antiperovskite carbides $AlCCr_3$ and $GaCCr_3$ based on the density functional theory and found that the band structures of above-mentioned samples were very similar to the superconducting $MgCNi_3$, suggesting a possible superconductive behavior in $AlCCr_3$ and $GaCCr_3$ [22]. Hitherto, there is no report about successful synthesis of $AlCCr_3$ and $GaCCr_3$ [24]. Although we have tried to synthesize, however, the *MAX* phase compounds Cr_2AC (A=Al, Ga) [25,26] and surplus Cr were obtained instead of antiperovskite carbides $AlCCr_3$ and $GaCCr_3$. Subsequently, we focus on the synthesis of antiperovskite nitrides $GaNCr_3$ and $RhNCr_3$. As to the synthesis of $RhNCr_3$, no experimental research has been reported so far. More than a decade ago, the antiperovskite $GaNCr_3$ phase was obtained but accompanied by some impurities such as GaN, Ga_3Cr, and Cr_2GaN [27,28]. Furthermore, the physical properties of $GaNCr_3$ are poorly known except for the low-temperature specific heat reported previously [29].

Based on the investigations of Mn- and Fe-based antiperovskite compounds AXM_3 (M=Mn, Fe; X=C, N), the chemical doping at M site can effectively manipulate the basic physical properties [10,30–32]. For instance, in $GaCMn_{3-x}Ni_x$, $SnCMn_{3-x}Fe_x$, $CuNMn_{3-x}Co_x$, and $GaCFe_{3-x}Cr_x$, the chemical doping can affect the magnetic and electrical properties and so on [10,30–32]. Meanwhile, $GaNMn_3$ has been extensively investigated in last several decades and abundant physical properties were reported [33–35]. Therefore, the Mn-doping is expected to influence the physical properties of Cr-based antiperovskite compounds $GaNCr_{3-x}Mn_x$.

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In this work, high-quality polycrystalline samples for antiperovskite nitrides $GaNCr_{3-x}Mn_x$ ($0 \le x \le 1.5$) were synthesized and their structural, magnetic, electrical/thermal transport properties were reported. With increasing the Mn-doping level x, the lattice increases monotonously and, correspondingly, the magnetic, electrical/thermal transport properties display an interesting and regular behavior. In addition, no superconductivity was detected above 2 K in any samples investigated.

2. Experimental details

Polycrystalline samples of $GaNCr_{3-x}Mn_x$ ($x=0$, 0.1, 0.3, 0.5, 1.0, and 1.5) were prepared by the direct solid-state reaction [27,28]. Powders of Ga (5N, Alfa-Aesar), Mn (4N, Alfa-Aesar), Cr (3N, Alfa-Aesar), and self-made CrN were mixed in the desired proportions, pressed into pellets (at a pressure of 25 Mpa), sealed in evacuated quartz tubes ($\sim 10^{-3}$ Pa) and then annealed at 973–1073 K for about 7 days. After quenching the tubes to room temperature, the products were pulverized, mixed, pressed into pellets, and annealed again at 1073–1173 K for about 8 days in order to obtain the homogeneous samples. X-ray powder diffraction (XRD) was performed using a Philips X′pert PRO X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda=0.15406$ nm) at room temperature. Magnetic measurements were performed on a Quantum Design superconducting quantum interference device magnetometer (SQUID-5T). The electrical/thermal transport properties were measured on a Quantum Design physical property measurement system (PPMS-9T). The electrical transport measurements were carried out by a four-prode method to eliminate contact resistance. The measurement of specific heat was performed by a heat-pulse relaxation method on PPMS-9T. The Hall coefficient (R_H) was measured by an AC method at room temperature by reversing the direction of a magntic field of 5T on PPMS-9T.

3. Results and discussion

3.1. Structural properties

Fig. 1(a) shows the Rietveld refinement of the room-temperature powder XRD pattern of $GaNCr_3$. All the diffraction peaks could be indexed to the cubic antiperovskite structure (space group: $Pm3m$). The related fitting parameters values (such as χ^2, R_p and R_{wp}) are considerable low as presented, suggesting a good antiperovskite nitride $GaNCr_3$ is obtained. Fig. 1(b) displays the sketch map of the crystal structure for $GaNCr_3$. The refined lattice parameter (a) obtained by using the Rietveld refinement technique is 0.3879 nm, which matches well with the previous report (~0.3876 nm) [24]. Fig. 1(c) reveals the room-temperature XRD patterns for $GaNCr_{3-x}Mn_x$ ($0 \le x \le 1.5$). Obviously, all the samples are single phase with a cubic antiperovskite structure. The Rietveld refinements were performed for all the samples and the detailed refined lattice parameters of $GaNCr_{3-x}Mn_x$ ($x=0$, 0.5, 1.0, and 1.5) are listed in Table 1. As shown in Fig. 1(d), the refined lattice constant increases with increasing x. These results can be easily understood, when considering the lattice parameters of $GaNCr_3$ (~0.3876 nm) and $GaNMn_3$ (~0.3903 nm) [24,35].

3.2. Magnetic properties

Our experimental results reveal that $GaNCr_3$ is nonmagnetic, which is consistent with the previous report [23]. Fig. 2(a)–(c) shows the temperature dependent magnetization $M(T)$ curves for the selected samples $GaNCr_{3-x}Mn_x$ with $x=0.5$, 1.0, and 1.5 at a magnetic field of 1 kOe under both zero-field-cooled (*ZFC*) and field-cooled (*FC*) processes between 5 and 380 K, respectively. As shown in Fig. 2(a), with the increase of temperature, an abrupt decrease of magnetization appears around 42 K, meaning the occurrence of a

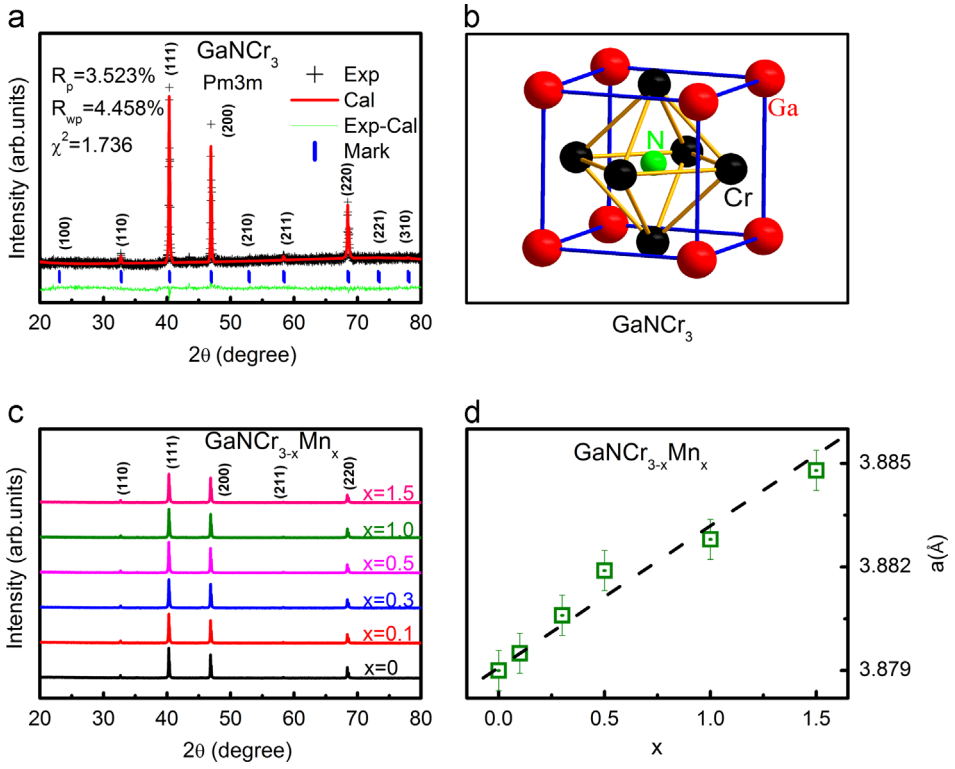

Fig. 1. (a) The Rietveld refined powder XRD patterns for $GaNCr_3$, the vertical marks (vertical lines) indicate the position of Bragg peaks, and the solid line (thin solid line) at the bottom corresponding to the difference between observed and calculated intensities; (b) the crystal structure of $GaNCr_3$; (c) room-temperature X-ray powder diffraction for all the samples $GaNCr_{3-x}Mn_x$ ($0 \le x \le 1.5$); (d) the refined lattice constant a as a function of doping level x; the dashed line is guide to the eyes.