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Magnetic field-induced metamagnetism and magnetocaloric effect in double perovskites Re_2CoMnO_6 (Re=Sm, Dy)

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HIGHLIGHTS

- External filed-induced metamagnetism is observed in Re_2CoMnO_6 (Re=Sm, Dy) ceramics.
- Two types of magnetic transition are observed.
- The metamagnetism is closely related to the rare-earth ions.

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ABSTRACT

Double perovskites Re_2CoMnO_6 (Re=Sm, Dy) have been synthesized by a solid-state reaction method. Magnetic field-induced metamagnetic behavior is observed in the samples below the ferromagnetic Curie temperature (T_C), which are respectively 123 K and 88 K in Sm_2CoMnO_6 and Dy_2CoMnO_6. The origin of this effect is attributed to the competition between the nearest-neighbor ferromagnetic super-exchange interaction (Co^{2+}-Mn^{4+}) and the next nearest-neighbor antiferromagnetic exchange interaction (Co^{2+}-Co^{2+}, Mn^{4+}-Mn^{4+}). Arrott plots combined with the thermal hysteresis confirm that the transition from ferromagnetic to antiferromagnetic state with negative slope is the first-order magnetic phase transition. Moreover, the positive slope closely to T_C indicates that the transition from paramagnetic to ferromagnetic state is the second-order transition. Magnetocaloric effect associated with Maxwell's relation is studied and the maximal value of $|\Delta S_M|$ is 1.4 and 3.5 J kg^{-1} K^{-1} at 6 T near T_C for Sm_2CoMnO_6 and Dy_2CoMnO_6. The large value of $|\Delta S_M|$ for Dy_2CoMnO_6 is obtained which is 9.1 J kg^{-1} K^{-1} at 20 K. The relatively smaller magneto entropy change for Sm_2CoMnO_6 may be attributed to the higher coercive field and the weaker magnetism.

1. Introduction

Rare-earth double perovskites ($A_2BB'O_6$) have recently attracted much attention due to the rich physical properties and numerous potential applications, such as giant magnetocaloric effect (MCE) [1], the magnetic field induced metamagnetic effect and multiferroic behavior [2]. Firstly, MCE effect has aroused great interest since the giant magnetocaloric effect in $Gd_5(Si_2Ge_2)$ was found [3]. It is deemed to be a clean and energy efficient technology to produce cooling effect in refrigeration cycle. At the same time, as multiferroic materials, the strong magnetic-electrical coupling property has been discovered in La_2CoMnO_6 and La_2NiMnO_6 which indicates these materials have extensive applications in magnetoelectric properties [4,5]. The origin of multiferroic in Lu_2CoMnO_6 and Y_2CoMnO_6 is attributed to the special magnetic structure and the exchange-striction mechanism is considered to induce the ferroelectricity [6,7]. Moreover, due to the possible commercial applications, the large magnetocapacitance and electrocaloric effect in these compounds are also interesting phenomena [8,9].

In Co/Mn double perovskite, the structure is ferromagnetic (FM) or antiferromagnetic (AFM) order in ground, which is related to the radius of earth ions and bond angle between B-sites transition elements. La_2CoMnO_6 shows the linear FM ordering along c-axis while Lu_2CoMnO_6 has an ↑↑↓↓ AFM configuration [10,11]. For most of rare-earth double perovskites, there are two phases coexisted in the system. FM super-exchange interaction dominates the magnetic properties when the ground state is ordered with $P2_1/n$ space group [2]. The ordered B-sites mean that transition metal ions

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occupy the Wyckoff position *2c* or *2d* in the monoclinic structure. However, Co^{3+} and Mn^{3+} randomly occupy B-sites causing the decease of T_C for the disordered phase with *Pbnm* space group [12]. In fact, the perfect double perovskite is difficult to obtain due to the easy formation of anti-site disorder. Researches show that the distribution of CoO_6 and MnO_6 octahedra is influenced by the annealing process and atmosphere [13,14]. The monoclinic structure is easier to form by slowed-cooled method while orthorhombic structure will appear under quenched annealing process [10,15].

Double perovskites Sm_2CoMnO_6 (SCMO) and Dy_2CoMnO_6 (DCMO) are prepared by a solid-state reaction method. This article aims to investigate the magnetic interaction between *3d-3d* under the influence of magnetic field. The metamagnetic effect is studied in details. Through the comparative study, we noticed that the magnetism is closely related to the A-site's ions. The effect of magnetic field driven metamagnetism has strong dependence on the radii of rare-earth ions which would result in the change of spin configuration.

2. Experimental

Polycrystalline samples of SCMO and DCMO were synthesized by a conventional solid-state reaction method. As starting materials, Sm_2O_3, Dy_2O_3, Co_2O_3 and MnO_2 are used with high purity. Stoichiometric mixture of precursor materials was thoroughly mixed and then sintered in air at 1373 K for 12 h. After that, the obtained calcined powders were carefully ground and pressed into pellets. Finally, the samples were annealed at 1623 K for another 12 h. Here, in order to obtain the ordered staking of B-site's ions, the cooling speed from 1623 K to 773 K is at 1 K/min and then natural cooling is used from 773 K to the room temperature. The crystal structures of the samples were characterized by X-ray diffractometer (XRD, Philips X'pert pro) with Cu-$K\alpha$ radiation. Magnetic measurements were performed using a vibrating sample magnetometer (VSM) on the Physical Property Measurement System (PPMS, Quantum Design).

3. Result and discussion

X-ray diffraction patterns of SCMO and DCMO at room temperature are depicted in Fig. 1. The crystal structure adopts the monoclinic structure with the space group $P2_1/n$ which is consistent with the previous reports [2,16]. The calculated lattice parameters are $a = 5.207$ Å, $b = 5.532$ Å, $c = 7.601$ Å and $\beta = 91.081°$ for SCMO, and $a = 5.241$ Å, $b = 5.577$ Å, $c = 7.466$ Å and $\beta = 90.163°$ for DCMO. The average lattice parameters of SCMO are larger than DCMO, which is due to the larger radii of Sm^{3+} ions at A-site. In Co/Mn double perovskites, both angel and lengh of Co-*O*-Mn bond decrease with decreasing the radii of A-site ions. Cationic ordering on B-sites is one of the distorted structures for double peroviskite. The structure with tilted CoO_6 and MnO_6 octahedral are corner-sharing and stacking up orderly along *c* direction in monoclinic lattice. Fig. 2 shows an obvious polyhedral linkage of the monoclinic double pervoskite structure. Rare earth ions of Sm^{3+} and Dy^{3+} are located between two consecutive layers. This structure is the typical rock salt arrangement for the octahedral sites. The cooperating tilting of the CoO_6 and MnO_6 octahedra with apparent distorted crystal structure can be seen in this perovskite.

Temperature dependence of the magnetization (*M-T*) in field cooled cooling (FCC) and field cooling warming process (FCW) under different magnetic fields are shown in Fig. 3(a) and (b). For SCMO, *M-T* curves with external magnetic field in the range of 0.01–0.4 T show magnetic phase transition from paramagnetic to ferromagnetic state. The almost same results of FCC and FCW can be

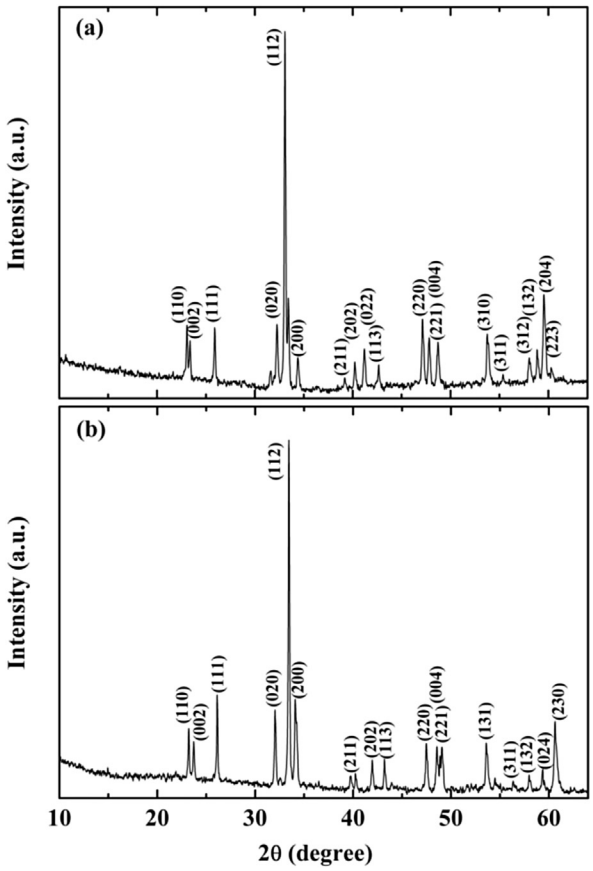

Fig. 1. Room temperature X-ray diffraction patterns of (a) SCMO and (b) DCMO.

seen from the overlapping lines. However, an obviously peak appears below T_C when the magnetic field increases to 0.7 T. This suggests another magnetic transition emerges in the system which can also be confirmed from the observed thermal hysteresis effect. Apparently, the transition temperature for the FCW process is higher than that for the FCC process for both of samples. The same phenomenon has also been observed in DCMO. The peak seems to be appeared more easily when the magnetic field reaches to 0.05 T. The result indicates that the interaction of *3d-3d* is closely related to the A-site's ions. It's evident that the larger radius of Sm^{3+} with smaller octahedral distortion of SCMO causes the higher magnetic transition temperature [5]. At low magnetic field region, it is harder to destroy the stability of the magnetic exchange interaction in the ordered monoclinic crystal [2]. Therefore, just one magnetic transition can be observed at low external magnetic field as the results presented in Fig. 3(a) and (b). It is important to note that just the middle range of magnetic field can induce the metamagnetic effect. Consequently, it is predictable that when the magnetic field is large enough all of the AFM state will transform into FM state. The rapid increase of magnetism at low temperature is due to the positive exchange interaction between *3d* and *4f* ions, especially for DCMO. The large effective moment of Dy^{3+} ($10.63\mu_B$) can explain this. The insets show the derivative of DC magnetism as a function of temperature. The minimum of differential curve represents the magnetic transition temperature of T_C, which is 123 K and 88 K for SCMO and DCMO, respectively. The metamagnetic phase transition temperature (T_s) could be obtained from the $dM/dT - T$ curve, which is constituted from *M-T* data. The T_s of SCMO are 120 K, 116 K, 103 K and 97 K under the cooling field of 0.4 T, 0.7 T, 1.5 T and 2 T, respectively. As for DCMO, the T_s are 84.5 K, 82 K, 79 K and 77 K,