Crystal and magnetic structures of new layered oxides A_2GaMnO_{5+y} ($A=Ca, Sr$)

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Abstract. Crystal and magnetic structures of new complex manganese oxides A_2GaMnO_{5+y} ($A = Ca, Sr$) were studied by neutron diffraction. Being perovskite-type derivatives, their crystal structures belong to a brownmillerite type and consist of alternating (CaO), (MnO₂), (CaO) and (GaO) or (GaO_{1+x}) layers. At temperatures between $\approx (100 - 200)$ K, these compounds undergo transitions into antiferromagnetic states. The magnetic ordering type depends on the compositions. The Mn magnetic moments are aligned in opposite directions within the MnO₂ layer, and the coupling between magnetic moments lying in the adjacent MnO₂ layers is, for example, antiferromagnetic for the reduced, and ferromagnetic for the oxidized Sr-containing compound Sr₂GaMnO₅ and Sr₂GaMnO_{5.52} compositions, respectively.

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The investigations of complex manganese oxides during recent years were strongly stimulated by the discovery of the effect of colossal magnetoresistance (CMR) (see e.g. [1]). The studies were mainly confined to a group of the three-dimensional perovskites, $AMnO_{3-y}$, in which the optimum (for the CMR effect) oxidation state of Mn ions was achieved by heterovalent substitutions in the A sublattice. Complex manganese oxides with reduced dimensionality of the crystal structure (like, for example, the members of the Ruddlesden–Popper series with general formula $A_{n+1}Mn_nO_{3n+1}$), also exhibit CMR at appropriate doping levels.

Recently, a new class of complex manganese oxides with two-dimensional chemical structures has attracted much attention. Their perovskite-related crystal structures are the result of an ordered distribution of the two types of cations with clearly different coordination environments over the B positions. The simplest of these anion-deficient double perovskites would have a brownmillerite-type chemical structure, which can be represented as a sequence of layers: $-(BO_2) - (AO) - (B'O) - (AO) - (BO_2) -$.

The first attempts to obtain such oxides having Mn as B and Ga or Zn as B' cations have already succeeded in synthesizing various new layered manganese oxide phases [2–4]. The variation of the formal oxidation state of the Mn ions in such compounds can be done through the filling of the vacancies in the incomplete oxygen anion sublattice. In this paper we briefly present the first results of recent neutron-diffraction studies of crystal and magnetic structures in this new family of complex manganese oxides A_2GaMnO_{5+y} ($A = Ca, Sr$).

1 Experimental results

The samples of Ca- and Sr-containing oxides were prepared by solid-state reactions, the synthetic routes being described in [2, 3]. The details of the crystal structure determination of the reduced Ca-containing composition $Ca_2GaMnO_{5.045}$ were also given in [2]. The structural model proposed in [2] has been confirmed in neutron-diffraction experiments carried out with the high-resolution powder diffractometer GPPD at the IPNS pulsed neutron source of Argonne National Laboratory. The major part of the sample volume was found to be single-phase, nearly stoichiometric material with an orthorhombic unit cell of *Pnma* symmetry. However, from the Fourier maps of scattering density in GaO layers, a small amount of the *Ima2*-ordered material (with the same unit-cell dimensions) was clearly observed and, later on, reliably fixed in the refinement. The only tiny difference in these two types of structures is in the mutual arrangement of the GaO chains in neighbouring GaO layers.

The crystal structure model of the oxidized composition $Ca_2GaMnO_{5.4}$ was proposed on the basis of high resolution electron microscopy data [2]. The oxidation only affects a half of the (GaO) layers, and the idealised structure of the oxidized compound can be represented as the following sequence of layers: $-(MnO_2) - (CaO) - (GaO) - (CaO) - (MnO_2) - (CaO) - (GaO_2) - (CaO) -$. However, up to now, no successful refinement of the crystal structure of the oxidized composition $Ca_2GaMnO_{5.4}$ has been achieved based on

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our neutron-diffraction data. Thus this model of crystal structure still needs to be refined further.

The crystal structure of Sr-containing compositions was studied with the use of the high-resolution diffractometer HRPT at the SINQ spallation neutron source of Paul Scherrer Institute. The reduced composition has an orthorhombic crystal structure with $Ima2$ symmetry. The main crystal structure parameters of this phase are given in Table 1.

The crystal structure of the oxidized composition $Sr_2GaMnO_{5.52}$, refined from the neutron powder diffraction data (taken on HRPT), has a tetragonal unit cell with $P4/mmm$ symmetry. In contrast to the Ca-containing oxidized phase, in which the ordering of oxygen vacancies upon oxidation leads to the ordering of GaO and GaO₂ layers, in the Sr-containing oxidized phase this ordering does not take place. Instead, the extra oxygen anions are distributed over the GaO_{~1.52} layers. All Ga cations in the $Sr_2GaMnO_{5.52}$ oxide are formally in the octahedral coordination. However, the in-plane oxygen sites are only partially filled. Besides that, the difference Fourier maps of the scattering density in this layer strongly suggest the disorder of the type $(x, 0, 0.5)$ for Ga cations and $(0.5, y, 0.5)$ for O anions. The refined crystal structure parameters are given in Table 2.

Finally, the drawings of the crystal structures of the studied novel complex oxides are given in Figs. 1 and 2.

Magnetic structures of these new complex oxides were studied with the DMC diffractometer at the SINQ spallation neutron source of Paul Scherrer Institute. Except for

Table 1. Structural parameters of $Sr_2GaMnO_{5.0}$ composition from HRPT data refinement. Space group $Ima2$. $Sr(x, y, 0.5)$, $Mn(0, 0, 0)$, $Ga(0.25, y, z)$, $O1(x, y, z)$, $O2(x, y, 0)$, $O3(0.25, y, z)$

	$T = 300\text{ K}$	$T = 11\text{ K}$
$a, \text{\AA}$	16.1979 (6)	16.1898 (6)
$b, \text{\AA}$	5.5257 (2)	5.5126 (2)
$c, \text{\AA}$	5.3863 (2)	5.3713 (2)
x (Sr)	0.1111 (1)	0.1109 (1)
y (Sr)	0.0106 (5)	0.0107 (5)
y (Ga)	0.9335 (5)	0.9333 (5)
z (Ga)	0.0382 (10)	0.0385 (10)
x (O1)	0.9965 (2)	0.9964 (2)
y (O1)	0.2527 (14)	0.2522 (14)
z (O1)	0.2514 (14)	0.2498 (14)
x (O2)	0.1442 (2)	0.1439 (2)
y (O2)	0.0401 (4)	0.0401 (4)
y (O3)	0.6265 (8)	0.6269 (8)
z (O3)	0.1174 (13)	0.1142 (12)

Table 2. Structural parameters of $Sr_2GaMnO_{5.52}$ composition from HRPT neutron powder data refinement. Space group $P4/mmm$. $Sr(0.5, 0.5, z)$, $Mn(0, 0, 0)$, $Ga(x, 0, 0.5)$, $O1(0.5, y, 0.5)$, $O2(0.5, 0, 0)$, $O3(0, 0, z)$

	$T = 301\text{ K}$	$T = 9\text{ K}$
$a, \text{\AA}$	3.80035 (16)	3.79250 (13)
$c, \text{\AA}$	7.9600 (5)	7.9288 (4)
z (Sr)	0.2357 (4)	0.2353 (3)
x (Ga)	0.035 (9)	0.056 (4)
y (O1)	0.082 (2)	0.0941 (14)
n (O1)	0.76 (1)	0.76 (1)
z (O3)	0.2456 (5)	0.2460 (3)

Fig. 1. Crystal structures of reduced phases: $Ca_2GaMnO_{5.045}$ (on the left) and $Sr_2GaMnO_{5.0}$ (on the right). They only differ by the mutual arrangements of the GaO chains in the neighbouring GaO layers

Fig. 2. Crystal structures of oxidized phases: $Ca_2GaMnO_{5.4}$ (on the left) and $Sr_2GaMnO_{5.52}$ (on the right). Note that the structure of the $Ca_2GaMnO_{5.4}$ composition (shown on the left) has not been refined completely; it is rather a model representation based on X-ray powder diffraction data

the oxidized $Ca_2GaMnO_{5.4}$ phase, whose crystal and magnetic structures are not yet finally solved, the magnetic ordering in all the other compositions was characterized completely. It turns out that both the Ca- and Sr-containing reduced oxides exhibit the same type of magnetic structure at low temperature. At $T_N \approx 160\text{ K}$ for $Ca_2GaMnO_{5.045}$, and $T_N \approx 180\text{ K}$ for $Sr_2GaMnO_{5.0}$, respectively, the magnetic moments of Mn ions are ordered into an antiferromagnetic structure. Its unit cell coincides with that of the crystal structure. The closest Mn magnetic moments are coupled antiferromagnetically within the MnO_2 layers and, besides that, the coupling between the Mn spins in the adjacent MnO_2 layers is also antiferromagnetic. Such a type of ordering seems to be unusual since the distance between the Mn ions in neighbouring MnO_2 layers is about twice as long as the in-plane separation. The values of the saturated magnetic moments at the lowest temperatures are $\approx 3.6\mu_B$ for the

$\text{Ca}_2\text{GaMnO}_{5.045}$, and $\approx 3.2 \mu_B$ for the $\text{Sr}_2\text{GaMnO}_{5.0}$ compounds, respectively.

A slightly different magnetic structure was found in the oxidized Sr-containing material $\text{Sr}_2\text{GaMnO}_{5.52}$. Below $T_N \approx 100$ K, Mn magnetic moments are also antiferromagnetically ordered. The in-plane coupling is antiferromagnetic, but the interplane coupling becomes ferromagnetic. The schematic representation of the magnetic structures of reduced and oxidized Sr-containing compositions is given in Fig. 3. In the case of the reduced compound $\text{Sr}_2\text{GaMnO}_{5.0}$, the magnetic unit cell coincides with that of the chemical structure. In the oxidized compound $\text{Sr}_2\text{GaMnO}_{5.52}$, the magnetic unit cell parameters a_m , c_m are connected with those of the crystal structure (a_c , c_c) as follows: $a_m = \sqrt{2}a_c$, $c_m = c_c$. The dependences of the refined Mn magnetic moment value on temperature for the reduced and oxidized Sr-containing compounds are given in Fig. 4.

Finally, the crystal and magnetic structures of new complex manganese oxides with a brownmillerite type of crystal structure have been studied by the neutron-diffraction technique. In these anion-deficient compounds,

Fig. 3. Schematic drawing of the magnetic structure unit cells of $\text{Sr}_2\text{GaMnO}_{5.0}$ (on the left) and $\text{Sr}_2\text{GaMnO}_{5.52}$ (on the right) compounds

Fig. 4. Dependences of the refined Mn magnetic moment value on temperature for the reduced $\text{Sr}_2\text{GaMnO}_{5.0}$ and oxidized $\text{Sr}_2\text{GaMnO}_{5.52}$ compounds

one has a freedom of varying the formal oxidation state of Mn ions due to the incomplete oxygen sublattice. The magnetic ordering type (and magnetic transition temperatures) in these compounds strongly depends on the formal oxidation state of Mn ions, which provides the principal possibility of searching for exotic magnetic and electronic properties in this new family of complex manganese oxides.

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