

Structural and magnetic properties of the layered compound $\text{Ca}_{2.375}\text{La}_{0.125}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$

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Abstract. The brownmillerite-type layered compound $\text{Ca}_{2.375}\text{La}_{0.125}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$ has been synthesized. The crystal and magnetic structures have been refined by the Rietveld analysis of the neutron powder diffraction patterns at 300 and 20 K. This compound crystallizes in the orthorhombic symmetry under the space group $\text{Pcm}2_1$ ($a = 5.447(2)$, $b = 11.359(4)$ and $c = 5.322(2)$ Å). The compound is found to be antiferromagnetic at 20 K. The ordered Mn magnetic moment, aligned along the crystallographic b -direction, is derived to be $2.53(5) \mu_B$ per Mn ion at 20 K.

Keywords. Neutron diffraction; low-dimensional magnetism; antiferromagnetic.

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1. Introduction

Low dimensional magnetic materials are of particular interest in condensed matter physics due to the interesting physical properties revealed by them. Among the low dimensional magnetic materials, two-dimensional compounds of the type $A_3B'B_2\text{O}_8$ ($A = \text{La, Ca, Sr, Y}$ and $(B', B) = \text{alkali or transition metal ions}$) have recently attracted a lot of interest [1–5]. These compounds crystallize in the orthorhombic structure. The structure of these compounds consists of two layers of BO_6 octahedra separated by a layer of $B'\text{O}_4$ tetrahedra along the $[010]$ crystallographic direction. The cations A occupy the position between these layers in a disordered manner [2]. The magnetic properties of $\text{Ca}_{2.5}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$ show a crossover from a 2D short-range to a 2D long-range and then to a 3D long-range magnetic ordering with decreasing temperature [1]. A short-range antiferromagnetic ordering above 170 K, a 2D long-range antiferromagnetic ordering over 160–170 K, and a 3D long-range antiferromagnetic ordering below ~ 150 K [1] with an ordered magnetic moment of $3.09(1) \mu_B$ per Mn cation at 5 K (aligned along $[010]$) [2] have been reported for this system.

Since the electronic and magnetic properties of the oxides with this type of crystal structure strongly depend on the spin and charge states of the transition metal ions on the octahedral site, a change in the magnetic properties is expected if La^{3+} is doped at the Ca^{2+} site in the parent compound $\text{Ca}_{2.5}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$. In

this paper, we report the structural and the magnetic properties of the compound $\text{Ca}_{2.375}\text{La}_{0.125}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$. The La^{3+} doping is expected to buckle the MnO_6 octahedra due to the higher ionic radius of La^{3+} (1.18 Å) than that of Ca^{2+} (1.12 Å) and to increase the ratio between Mn^{3+} and Mn^{4+} (1 : 1 for the parent system).

2. Experimental

Polycrystalline sample of $\text{Ca}_{2.375}\text{La}_{0.125}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$ was synthesized by the conventional solid state reaction method. The stoichiometric amount of high purity (>99.9%) CaCO_3 , SrCO_3 , La_2O_3 , Ga_2O_3 and MnO_2 were initially mixed and decarbonated at 1000°C for 24 h and then pressed into a pellet form. The palletized mixture was heated for 195 h at 1100°C in air with intermediate grinding at regular intervals.

The neutron powder diffraction patterns for this sample were recorded in the scattering angular range of 5–138° at 300 and 20 K by using the five linear position sensitive detectors based neutron powder diffractometer ($\lambda = 1.249$ Å) at Dhruva reactor, Trombay, India.

3. Results and discussion

The neutron powder diffraction (NPD) pattern at 300 K is shown in figure 1. The Rietveld refinement of the NPD patterns using the FULLPROF program [6] confirms the single phase formation of the compound in the orthorhombic crystal structure (space group $\text{Pcm}2_1$). The compound shows the brownmillerite crystal structure with the lattice constants $a = 5.447(2)$, $b = 11.359(4)$, and $c = 5.322(2)$ Å $\sim (\sqrt{2}a_p \times 3a_p \times \sqrt{2}a_p$ (where a_p is the unit cell parameter of the primitive perovskite structure)) (figure 2). These values of lattice constants are similar to those for the other compounds in this series [2–4]. In the present compound, the octahedral sites are fully occupied by Mn ions, whereas, the tetrahedral sites are fully occupied by Ga ions alone. The entire La/Sr and 15.8% of Ca are found between the two layers of MnO_6 octahedra (2b site), and the remaining 84.2% Ca is located between the MnO_6 and GaO_4 layers (4c site). In a given layer, the Mn octahedra share corners. The refined unit cell parameters and other structural parameters are given in table 1.

To understand the microscopic magnetic structure for this compound we have carried out the neutron diffraction experiment at 20 K (figure 1). The appearance of the extra Bragg peaks at lower scattering angles confirms the presence of a 3D long-range antiferromagnetic ordering at this temperature. The Rietveld refinement of the NPD pattern confirms that the size of the magnetic unit cell is the same as that of the chemical unit cell. The site-averaged ordered Mn magnetic moment at 20 K is derived to be 2.53(5) μ_B per Mn ion. The absence of the temperature-dependent intensity of the (0 *k* 0) nuclear (fundamental) Bragg peaks, such as (0 1 0) and (0 2 0) confirms that the Mn magnetic moments are aligned along the [0 1 0] crystallographic direction. The Mn spin in a given *ac*-plane (single layer of MnO_6), separated by $c/2$ distance, is aligned antiparallel to its four nearest-neighbour Mn

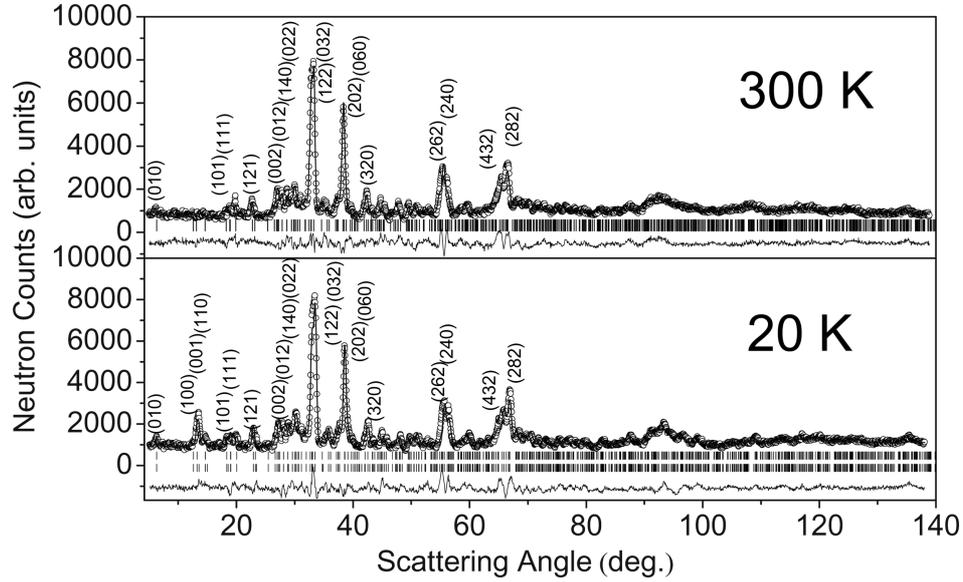


Figure 1. The observed (open circle) and calculated (solid line) NPD patterns for $\text{Ca}_{2.375}\text{La}_{0.125}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$ at 300 K and 20 K. Solid line at the bottom shows the difference between observed and calculated patterns. Vertical lines show the position of the nuclear (for both 300 and 20 K) and magnetic (20 K only) Bragg peaks. The (hkl) values corresponding to the intense nuclear and magnetic Bragg peaks are listed.

Table 1. Refined lattice constants, atomic positions, thermal parameters and the site occupancies for $\text{Ca}_{2.375}\text{La}_{0.125}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$ at 300 K. $a = 5.448(4)$, $b = 11.377(9)$, $c = 5.335(4)$ Å; space group = $\text{Pcm}2_1$.

Atom	Site	x/a	y/b	z/c	B (\AA^2)	Occ.
Ca	4c	0.230(4)	0.187(1)	0.516(1)	0.41(3)	1.03(9)
Ca/La/Sr	2b	0.254(4)	0.5	0.493(3)	0.41(8)/0.2(6)/ 0.29(9)	0.17(9)/0.08(9)/ 0.23(9)
Ga	2a	0.350(4)	0	0.066(1)	0.27(2)	0.46(9)
Mn	4c	0.277(8)	0.339(4)	0	0.31(3)	0.97(9)
O1	2a	0.355(1)	0	0.400(1)	1.14(8)	0.48(3)
O2	2b	0.265(3)	0.5	-0.013(15)	1.02(5)	0.53(9)
O3	4c	0.205(2)	0.162(9)	-0.022(12)	1.01(2)	1.01(9)
O4	4c	-0.001(4)	0.340(9)	0.229(14)	0.85(7)	1.06(9)
O5	4c	0.512(4)	0.310(1)	0.248(14)	1.03(4)	0.99(9)

spins. Along the b -axis, the Mn spin is found to be ferromagnetically coupled to the nearest-neighbour Mn spin in the other MnO_6 layer within a bilayer. The bilayers are coupled ferromagnetically.

A change in the Mn–O₄ bond lengths from 1.920(10) and 1.948(10) Å (for the parent system [2]) to 1.95(6) and 2.08(7) Å (for the present system) has been

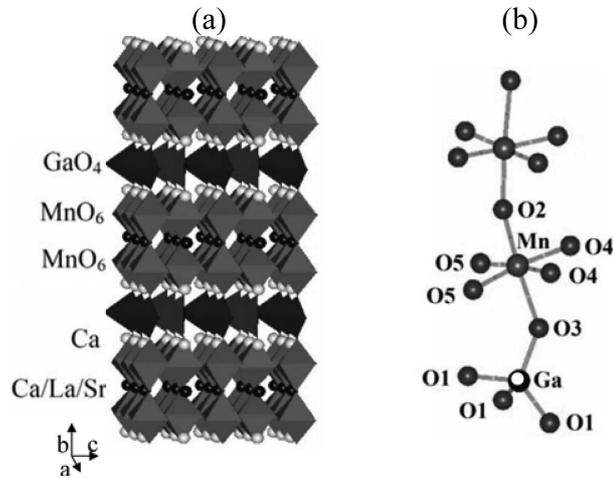


Figure 2. (a) The crystal structure of the compound $\text{Ca}_{2.375}\text{La}_{0.125}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$ at 300 K. (b) The local coordination around the Mn and Ga ionic sites.

observed. The Mn–O4–Mn bond angles change from $170.7(3)^\circ$ (for the parent system [2]) to $175(4)^\circ$ (for the present system). Since the strength of the superexchange interaction is more sensitive to the bond angle than to the bond length, an increase of the magnetic ordering temperature for the present system is expected (~ 150 K for the parent system) on the basis of the increase of the Mn–O4–Mn bond angle. With La doping, the (Mn–O2) bond length and (Mn–O2–Mn) bond angle along the *b*-axis change from $1.9504(4)$ Å and $165.7(5)^\circ$, respectively (for the parent system) to $1.83(5)$ Å and $174(4)^\circ$, respectively (for the present system). The larger Mn–O2–Mn bond angle along the crystallographic *b*-direction should lead to an enhancement of the strength of the ferromagnetic superexchange interaction between the Mn layers. In order to have a complete understanding of magnetic ordering for this compound further neutron diffraction study would be necessary.

4. Summary and conclusions

We have synthesized the polycrystalline bilayered compound $\text{Ca}_{2.375}\text{La}_{0.125}\text{Sr}_{0.5}\text{GaMn}_2\text{O}_8$. The present compound crystallizes in the orthorhombic crystal symmetry under the space group $\text{Pcm}2_1$. All La ions are located between the Mn octahedral layers within a given bilayer. A buckling in the crystal structure has been observed due to the La doping. Neutron diffraction study at 20 K confirms that the Mn ionic moments are aligned along the crystallographic *b*-direction. The moments are coupled antiferromagnetically in a single layer (perpendicular to the *b*-axis) and the layers are ferromagnetically coupled along the crystallographic *b*-direction. The observed antiferromagnetic ordered magnetic moment for this compound at 20 K is $2.53(5) \mu_B$ per Mn ion.

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