Oxygen and fluorine doping in Sr$_2$MnGaO$_5$ brownmillerite

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Systematic study on crystal chemistry of Sr$_2$MnGaO$_{5+\delta}$ layered perovskites upon variation of anion stoichiometry and the Mn oxidation state ($V_{Mn}$) was performed. Starting from fully oxygenated Sr$_2$MnGaO$_{5.5}$ compound, the samples with $+3 \leq V_{Mn} \leq +4$ were prepared either by a reduction of oxygen content at controlled partial oxygen pressure or by a partial replacement of oxygen by fluorine. Varying $\delta$ is accompanied by structural transformations from $Imma$ ($0.03 \leq \delta \leq 0.13$, $a \approx c \approx \sqrt{2}a_0$, $b \approx 4a_0$) to $Bnmn$ ($0.41 \leq \delta \leq 0.46$, $a \approx c \approx \sqrt{2}a_0$, $b \approx 2a_0$) and to tetragonal $P4/mmm$ ($\delta = 0.505$, $a \approx a_0$, $c \approx 2a_0$). The tetragonal Sr$_2$MnGaO$_{5.8}$F$_{1.2}$ oxyfluorides ($a \approx a_0$, $c \approx 2a_0$) were prepared by treatment of Sr$_2$MnGaO$_{5.5}$ with XeF$_2$. In the Sr$_2$MnGaO$_{5.78}$F$_{1.22}$ structure the MnO$_6$ octahedra are characterized by two short apical Mn-O distances and four long equatorial ones. This is interpreted as an “apically compressed” Jahn–Teller distortion, in contrast to the “apically elongated” one in Sr$_2$MnGaO$_{5+\delta}$.

1 Introduction

The brownmillerites A$_2$MnGaO$_{5+\delta}$ (A = Ca, Sr) [1–6] are an attractive structural matrix for new CMR materials. Sr$_2$MnGaO$_5$ can be oxidized at elevated oxygen pressure [2] up to Sr$_2$MnGaO$_{4.47}$ composition transforming from the orthorhombic brownmillerite structure with $a \approx c \approx \sqrt{2}a_0$, $b \approx 4a_0$ into a tetragonal perovskite with $a \approx a_0$, $c \approx 2a_0$. The structure of the oxidized compound is compressed along the direction of Mn-O apical bonds due to decreasing Jahn–Teller deformation of the MnO$_6$ octahedra. An appearance of extra oxygen atoms in the (GaO$_{1+\delta}$) layers alters the magnetic structure from antiferromagnetic (AFM) G-type with Mn magnetic moments aligned normal to the (MnO$_2$) planes ($\delta \approx 0$) to the AFM C-type where Mn magnetic moments are ordered antiferromagnetically within (MnO$_2$) planes but the planes are ferromagnetically coupled ($\delta \approx 0.5$) [7]. Thus the amount of anions in the Ga-layers are important for the magnetic interactions in this material. An alternative way to vary the oxidation state of the Mn cations is an insertion of fluorine atoms into the Ga-layers. Different amounts of oxygen and fluorine are required to create the same Mn oxidation state that can alter the structure and properties of the oxyfluorides in comparison with the oxygen-doped compounds. In this contribution we describe the preparation and structures of the Sr$_2$MnGaO$_{5+\delta}$ compounds with different oxygen content and the Sr$_2$MnGaO$_{5-\delta}$F$_{1+\delta}$ oxyfluorides.

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2 Experimental

The initial Sr$_2$MnGaO$_{5+\delta}$ oxide with $\delta \approx 0$ was prepared by a solid state reaction as described in [2]. Then the sample was treated in flowing oxygen at 415 °C to reach $\delta \approx 0.5$. The batch was separated into several samples for further reduction in a closed circle filled with Ar/O$_2$ mixture at fixed partial oxygen pressure. The partial oxygen pressure inside the circle was controlled by a cell with a unipolar oxygen conductivity. After annealing the sample was quenched. The compounds with $\delta \approx 0, 0.5$ were also treated with XeF$_2$. The operations with XeF$_2$ were carried out in a glove box filled with dried N$_2$. 0.4 g of Sr$_2$MnGaO$_{5+\delta}$ was mixed with XeF$_2$, ground, placed in a Ni crucible and sealed into a N$_2$-filled copper tube. The samples were annealed at 500–600 °C for 10–20 h and then furnace cooled to room temperature. The Mn oxidation state ($V_{\text{Mn}}$) was determined by an iodometric titration. Powder XRD study was performed with a focusing Guinier-camera FR-552 and a STADI-P diffractometer (CuK$_{\alpha 1}$ radiation). The WINCSD program package and RIETAN-2000 program were used for the structure determination from X-ray powder data. The electron diffraction (ED) study was performed using JEOL 400EX and Philips CM20 transmission electron microscopes.

3 Results

The data on some representative oxygenated and fluorinated samples are given in Table 1. A difference between cell dimensions and $V_{\text{Mn}}$ of the as-prepared samples I and II illustrates the influence of subtle changes in synthesis procedure on the final oxygen content. Both samples were prepared using the same

<table>
<thead>
<tr>
<th>#</th>
<th>treatment conditions, P(O$_2$) in atm.</th>
<th>space group</th>
<th>cell parameters, Å</th>
<th>$V$, Å$^3$</th>
<th>$(c - a)/(c + a)$</th>
<th>$\delta$, $x$</th>
<th>$V_{\text{Mn}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>as-prepared I</td>
<td>Imma</td>
<td>$a = 5.4023(5)$</td>
<td>$b = 16.130(2)$</td>
<td>$c = 5.5645(7)$</td>
<td>484.9</td>
<td>0.0148</td>
</tr>
<tr>
<td>2</td>
<td>as-prepared II</td>
<td>Imma</td>
<td>$a = 5.3894(4)$</td>
<td>$b = 16.193(1)$</td>
<td>$c = 5.5348(4)$</td>
<td>483.0</td>
<td>0.0133</td>
</tr>
<tr>
<td>3</td>
<td>415 °C, lg(P(O$_2$)) = -5.19</td>
<td>Imma</td>
<td>$a = 5.3700(5)$</td>
<td>$b = 16.240(2)$</td>
<td>$c = 5.4976(4)$</td>
<td>479.5</td>
<td>0.0117</td>
</tr>
<tr>
<td>4</td>
<td>415 °C, lg(P(O$_2$)) = -4.04</td>
<td>Bnmm</td>
<td>$a = 5.3628(3)$</td>
<td>$b = 8.0193(8)$</td>
<td>$c = 5.4066(3)$</td>
<td>232.5</td>
<td>0.0041</td>
</tr>
<tr>
<td>5</td>
<td>415 °C, lg(P(O$_2$)) = -1.12</td>
<td>Bnmm</td>
<td>$a = 5.3666(6)$</td>
<td>$b = 7.959(2)$</td>
<td>$c = 5.3861(5)$</td>
<td>230.1</td>
<td>0.0018</td>
</tr>
<tr>
<td>6</td>
<td>415 °C, lg(P(O$_2$)) = 0</td>
<td>P4/mmm</td>
<td>$a = 3.7995(1)$</td>
<td>$b = 7.9209(3)$</td>
<td>$c = 5.457(4)$</td>
<td>114.3</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>1:1 XeF$_2$, 500 °C, 10 h</td>
<td>P4/mmm</td>
<td>$a = 3.8557(3)$</td>
<td>$b = 7.7843(8)$</td>
<td>$c = 462.9$</td>
<td>115.7</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>1:1 XeF$_2$, 600 °C, 20 h</td>
<td>P4/mmm</td>
<td>$a = 3.865(1)$</td>
<td>$b = 7.779(3)$</td>
<td>$c = 464.8$</td>
<td>116.2</td>
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</tr>
<tr>
<td>9</td>
<td>1:3 XeF$_2$, 600 °C, 20 h</td>
<td>P4/mmm</td>
<td>$a = 3.8794(3)$</td>
<td>$b = 7.7328(6)$</td>
<td>$c = 465.5$</td>
<td>116.4</td>
<td>0</td>
</tr>
</tbody>
</table>
Fig. 1 The dependencies of cell parameters of Sr$_{2}$MnGaO$_{5+\delta}$ from $\delta$. The cell parameters for all compounds are given in orthorhombic Imma setting.

XRD powder patterns of the samples from the low-oxidized region (samples #1–3) were indexed in an orthorhombic brownmillerite-type unit cell ($a \approx c \approx a_p \sqrt{2}$, $b \approx 4a_p$, S.G Imma). The XRD patterns of the samples #4 and #5 from a high-oxidized region were indexed in a B-centered orthorhombic unit cell with $a \approx c \approx a_p \sqrt{2}$, $b \approx 2a_p$. The XRD pattern of the sample #6 can be indexed with a tetragonal primitive unit cell ($a \approx a_p$, $c \approx 2a_p$). For the oxygenated samples cell volume and degree of orthorhombic distortion decrease concomitantly with increasing oxygen content (Fig. 1). The behavior of the cell parameters vs oxygen content is not so straightforward. The $c$ parameter decreases almost linearly with increasing oxygen content. In the low-oxidized region the $a$ parameter decreases whilst the $b$ parameter increases; this behavior changes to the opposite in the high-oxidized region (Fig. 1). It was found that the treatment of the reduced ($\delta \approx 0$) Sr$_2$MnGaO$_5$ phase with XeF$_2$ does not allow the preparation of single phase samples with a wide range of fluorine contents. Hence, the interaction of the oxidized Sr$_{2}$MnGaO$_{5+\delta}$ ($\delta \approx 0.5$) sample with XeF$_2$ was investigated. The XRD patterns of the fluorinated samples were indexed using a tetragonally distorted perovskite unit cell ($a \approx a_p$, $c \approx 2a_p$). Badly crystallised SrF$_2$ impurity was found in the samples in an amount growing with increasing amount of XeF$_2$ and with the temperature of fluorination. An increase of the fluorination temperature and a molar XeF$_2$/Sr$_2$MnGaO$_{5+\delta}$ ratio cause an increase of the $a$ lattice parameter and a decrease of the $c$ lattice parameter of the tetragonal phase. These changes occur simultaneously with a decrease of $V_{Mn}$. We should note that iodometric titration provides an estimate of $V_{Mn}$ for the fluorinated phases in samples #8 and #9 because of the presence of impurity phases.
3.1 Crystal structure of Sr$_2$MnGaO$_{5.46}$

The initial model for the refinement of the Sr$_2$MnGaO$_{5.46}$ crystal structure was calculated from the structure of tetragonal perovskite by transforming the atomic coordinates into an orthorhombic unit cell with $a \approx c \approx \sqrt{2}a_p$, $b \approx 2a_p$ and Bnmm space symmetry. The refinement with Ga in $(1/2, 0, 1/2)$ positions and O3 in $(1/4, 0, 1/4)$ results in abnormally high atomic displacement parameters (ADP) for these atoms. The Bm$_{22}$m, Bmm$_2$ and B222 models were also tested, but no significant improvement was achieved. For subsequent refinement the Ga position was split into 8-fold $(1/2, y, z)$ with occupancy factor $g = 0.25$ and the O3 position – into $(x, 0, y)$ with $g = 0.365$ that corresponds to $\delta = 0.46$ found by iodometric titration. This led to reasonable values of isotropic ADPs for Ga and O3 atoms and to a decrease of the reliability factor from $R_I = 0.033$ to $R_I = 0.026$. The Sr$_2$MnGaO$_{5.46}$ structure is characterized by strong disorder in the (GaO$_{1+\delta}$) layers since the significant amount of extra oxygen in these layers changes the coordination environment of the Ga atoms (Fig. 2). Formally Ga atoms are surrounded by an octahedron built of O3 and O2 atoms. However, due to the displacement of Ga and O3 atoms from their special positions, there are two equatorial squares of O3 atoms around Ga, each with the probability of 1/2. One equatorial square of oxygen atoms is displaced with respect to the other along the $c$ axis, as it is shown in Fig. 2. Ga atoms are not situated exactly within the equatorial plane since they are statistically displaced towards one of the apical oxygen atoms O2. Thus five short (1.809–1.941 Å) and one long (2.206 Å) Ga–O separations were found. If one takes into account that the probability to find the O3 atom in each equatorial vertex of one of equatorial square is close to 3/4, the average coordination number of Ga should be close to 5, comprising three O3 atoms at the distances of 1.912–1.941 Å, one O2 atom at 1.809 Å and one O2 atom at 2.206 Å. These five oxygen atoms form distorted trigonal bipyramid around the Ga cations. The BVS calculation for this coordination environment gave +2.88 which is close to the formal charge of the Ga cation. The CN = 5 is not unusual for Ga$^{3+}$ cations and the structures are known where Ga is situated in a trigonal bipyramid.

3.2 The crystal structure of Sr$_2$MnGaO$_{4.78}$F$_{1.22}$

The structure investigation was performed for the most pure sample #7, whose XRD pattern shows only traces of SrF$_2$. The reciprocal lattice of this compound was studied by electron diffraction. All reflections on the observed reciprocal lattice sections can be indexed on a tetragonal lattice with cell parameters as determined from XRD data. Since no extinctions were observed on the XRD and ED patterns, the $P4/mmm$ space group was chosen for the Rietveld refinement. The atomic coordinates were transformed from a perovskite structure and full occupancy was assigned to all anion positions giving the...
Sr$_2$MnGa(O,F)$_6$ composition. SrF$_2$ was introduced as a second phase into the refinement. The occupancy factors of the O(1), O(2) and O(3) positions were refined, which gives \( g_{O(1)} = 1.07(1) \), \( g_{O(2)} = 0.99(1) \), \( g_{O(3)} = 0.993(7) \) and shows that all anion positions are fully occupied. The reliability factors \( R_I = 0.012 \), \( R_P = 0.019 \) indicate a good agreement between experimental and calculated profiles. The main difference between the oxygen-doped Sr$_2$MnGaO$_{5.46}$ phase and the fluorinated Sr$_2$MnGaO$_{4.78}$F$_{1.22}$ phase is the full occupation of the anion positions in the latter structure. The Mn formal valence \( V_{Mn} = +3.78 \) known from iodometric titration allows to propose the Sr$_2$MnGaO$_{4.78}$F$_{1.22}$ formula for the fluorinated phase in the sample #7. In the Sr$_2$MnGaO$_{4.78}$F$_{1.22}$ structure the Mn and Ga atoms are situated in slightly distorted octahedra (Fig. 3). The bond valence sum calculations and evaluations of lattice energies support the location of fluorine in the \((1/2, 0, 1/2)\) position, i.e. in the equatorial environment of the Ga atoms. The octahedral environment around the Mn atoms can be described as "apically compressed" with two short apical Mn–O distances of 1.876(8) Å and four long equatorial ones of 1.9278(1) Å. The octahedron around the Ga atoms is characterized by two apical Ga–O distances of 2.016(8) Å, which are longer than four equatorial Ga–(O, F) ones. The average interatomic distances are \( \langle d(Mn–O) \rangle = 1.911 \) Å and \( \langle d(Ga–(O, F)) \rangle = 1.957 \) Å.

### 3.3 Electron diffraction study of anion ordering in Sr$_2$MnGaO$_{5.41}$

The reciprocal lattice for Sr$_2$MnGaO$_{5.41}$ was reconstructed using a large number of ED patterns (Fig. 4). All bright reflections on these patterns belong to the \( Bmnm \) sublattice, weaker reflections correspond to a superstructure indexed in monoclinic unit cell with parameters \( a = 10.813 \) Å, \( b = 8.019 \) Å, \( c = 8.486 \) Å, \( \beta = 108.57^\circ \), S.G. \( P21/m \). Ordering of oxygen atoms and vacancies can be assumed as possible reason for

**Fig. 3** The crystal structure of Sr$_2$MnGaO$_{4.78}$F$_{1.22}$. MnO$_6$ octahedra are darker shaded.

**Fig. 4** Electron diffraction patterns of the Sr$_2$MnGaO$_{5.41}$ sample.
the monoclinic superstructure. Since the average coordination number of Ga atoms in Sr$_2$MnGaO$_{5.41}$ is close to 5, we can propose an arrangement of GaO$_5$ pyramids for the (GaO$_{1+\delta}$) layer which is compatible with the monoclinic supercell and the P2/m space group. However, tetragonal pyramid is not a typical coordination environment for the Ga$^{3+}$ cation. In seldom cases of CN = 5 the Ga$^{3+}$ cations are located in trigonal bipyramids rather than at tetragonal pyramids. Appropriate displacements of O and Ga atoms can be introduced to transform the coordination environment of Ga into trigonal bipyramids (Fig. 5). This model corresponds to the Sr$_2$MnGaO$_{5.5}$ composition, but the experimentally determined oxygen content implies a smaller oxygen amount, that leads to a partial occupation of at least one anion position in the Ga layer by oxygen and vacancies, so that part of the Ga atoms have a tetrahedral coordination.

4 Conclusions

An increase of oxygen content in the Sr$_2$GaMnO$_{5+\delta}$ brownmillerite occurs as an oxidative process resulting in several trends which can be summarised as follows:
- decrease of the average size of Mn cations on going from a formal oxidation state +3 to +4. The ionic radii of Mn$^{3+}$ and Mn$^{4+}$ in octahedral environment are equal to 0.65 Å and 0.54 Å, respectively;
- suppression of Jahn–Teller distortion of MnO$_6$ octahedra due to a transition from $t_{2g}^3 e_g^1$ to $t_{2g}^3 e_g^0$ electronic configuration;
- decrease of tilting distortion of the (MnO$_2$) layers;
- increase of the average Ga–O distance due to appearance of extra oxygen atoms in the (GaO$_{1+\delta}$) layers.

In contrast to the oxygen insertion, at our particular experimental conditions the fluorination is a reductive reaction of partial replacement of oxygen by fluorine. The overall scheme of the fluorination process can be expressed by the equation:

$$\text{Sr}_2\text{MnGaO}_{5.5} + (1 + x)/2 \text{XeF}_2 \rightarrow \text{Sr}_2\text{MnGaO}_{5-x}\text{F}_{x} + (0.5 + x) [\text{O}] + (1 + x)/2 \text{Xe}$$

Oxygen atoms released in this reaction are absorbed at the inner walls of the copper tube. Increasing the temperature of the fluorination and the amount of XeF$_2$ increases the degree of the anion replacement resulting in a gradual decrease of the formal Mn valence in the samples #7–9.

It is interesting to compare the behavior of oxygen-doped Sr$_2$MnGaO$_{5+\delta}$ and fluorine doped Sr$_2$MnGaO$_{5-x}\text{F}_{x}$ compounds upon variation of the Mn oxidation state. In both cases the equatorial Mn–O distances in the MnO$_6$ octahedra increases simultaneously with decreasing V$_{\text{Mn}}$ (decreasing $\delta$ or increasing F content): from 1.9001 Å for V$_{\text{Mn}} = +4$ to 1.9222 Å (V$_{\text{Mn}} = +3.26$, $\delta = 0.13$) and 1.9411 Å (V$_{\text{Mn}} = +3.39$, $x_F = 1.61$, estimation). These changes follow an increase of the Mn cation size upon reduction. However, the apical Mn–O distance varies differently in the Sr$_2$MnGaO$_{5-x}\text{F}_{x}$ solid solutions in comparison to that in the Sr$_2$MnGaO$_{5+\delta}$ ones. Elongation of the Mn–O$_{ap}$ distance occurs together with a decrease of $\delta$ for the Sr$_2$MnGaO$_{5-x}\text{F}_{x}$ compounds due to an increase of the degree of Jahn–Teller distortion: 1.956(3) Å ($\delta = 0.5$), 1.983(6) Å ($\delta = 0.46$), 2.225(5) Å ($\delta = 0.13$), 2.372(5) Å ($\delta = 0.025$) and 2.411(4) Å ($\delta = -0.03$). For the Sr$_2$MnGaO$_{5-x}\text{F}_{x}$ solid solutions the c lattice parameter decreases to-
gether with decreasing $V_{Mn}$ which may indicate a progressive apical compression of the MnO$_6$ octahedra. Indeed, $d$(Mn–O$_{ap}$) = 1.876(8) Å in Sr$_2$MnGaO$_{4.78}$F$_{1.22}$ is clearly shorter than $d$(Mn–O$_{ap}$) = 1.956(3) Å in Sr$_2$MnGaO$_{5.5}$ [7]. At the same time, the apical Ga–O distance stays the same for these structures within the range of standard deviations: 2.024(3) Å for Sr$_2$MnGaO$_{5.5}$ [7] and 2.016(8) Å for Sr$_2$MnGaO$_{4.78}$F$_{1.22}$. It confirms that the compression of the unit cell of the Sr$_2$MnGaO$_{5.5}$, F$_{1.22}$ solid solutions along the $c$ axis occurs due to a shortening of the Mn–O$_{ap}$ bonds. Thus we can propose that the reduction of $V_{Mn}$ by fluorination reverses the type of Jahn–Teller distortion of the MnO$_6$ octahedra from “apically elongated” to “apically compressed”. We assume that the reversed Jahn–Teller effect in the fluorinated samples arises from an interplay between the decrease of the free energy from a stabilization due to a Jahn–Teller distortion and a simultaneous variation of the electrostatic lattice energy due to changes in the bond distances. In the oxygen doped Sr$_2$MnGaO$_{5.5+\delta}$ compounds the increase of the apical elongation of the MnO$_6$ octahedra is to some degree compensated by the decrease of the Ga–O$_{ap}$ distance due to a decrease of the coordination of Ga down to 4. For the Sr$_2$MnGaO$_{5.5}$, F$_{1.22}$ solid solutions the Ga–O$_{ap}$ distance does not alter since no changes in the coordination number occur and the average ionic radius of the apical anions does not change. Thus, if the reduction of the Mn cations will be accompanied by an elongation of the Mn–O$_{ap}$ distances, it will result in abnormally long Sr–O separations and in a decrease of the lattice energy. From the crystal field theory, for a high-spin d$^4$ electronic configuration “apically elongated” and “apically compressed” octahedra are energetically equivalent, but the latter in the Sr$_2$MnGaO$_{5.5}$, F$_{1.22}$ structure provides an additional stabilization due to the gain in the electrostatic energy.

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