Compositionally induced phase transition in the Ca$_2$MnGa$_{1-x}$Al$_x$O$_5$ solid solutions: Ordering of tetrahedral chains in brownmillerite structure

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Abstract

The Ca$_2$MnGa$_{1-x}$Al$_x$O$_5$ solid solutions (0.2 $\leq x \leq$ 1.0) with brownmillerite-type structure were synthesized by solid state reaction at 1250°C for 40 h in Ar flow. The structures of the solid solutions were studied using X-ray powder diffraction, transmission electron microscopy and high resolution electron microscopy. Replacing Ga by Al introduces a phase transformation from the brownmillerite structure with the $Pnma$ space symmetry ($x \leq 0.5$) to a structure with $I2mb$ space symmetry ($x > 0.5$). The structures differ by the ordering pattern of the mirror-related tetrahedral chains (L and R): in the primitive structure the L and R chains form alternating layers whereas in the body-centered phase all chains are of the same type. The crystal structure of Ca$_2$MnGa$_{0.5}$Al$_{0.5}$O$_5$ was refined from X-ray powder diffraction data (space group $Pnma$, $a$ = 5.25175(5) Å, $b$ = 15.1426(2) Å, $c$ = 5.46029(6) Å, $R_I$ = 0.042, $R_P$ = 0.017). A specific feature of this structure is disorder in the Ga layer with intermixing of the L and R chains in a $\approx 2:1$ ratio. The disorder is related to the formation of numerous antiphase boundaries (APBs) with $R = 1/2[111]$ as a displacement vector, which produces two adjacent tetrahedral layers with the same type of chains in the initial –L–R–L–R–L– layer sequence of the $Pnma$ phase. The density of APBs increases with increasing $x$ resulting in the formation of slabs of the $I2mb$ phase up to a complete phase transformation. Dipole–dipole interactions between the tetrahedral chains are discussed as a possible driving force causing various patterns of tetrahedral chain ordering.

Keywords: Brownmillerite; Manganites; Anion ordering; Phase transition; Electron microscopy

1. Introduction

The brownmillerite structure is common among anion-deficient $A_2BB'O_5$ perovskites where the $B'$ cations are able to adopt a tetrahedral oxygen coordination. Generally this structure can be described as a –BO$_2$–AO–B'O$_4$– sequence of layers being viewed along the fourfold axis of the perovskite subcell. Anion vacancies are concentrated at the tetrahedral (B'O$_4$) layers. These layers consist of infinite chains of vertex sharing B'O$_4$ tetrahedra, which can be derived from the perovskite (BO$_2$) layers by an ordered elimination of half of the oxygen atoms. Vacant anion positions are arranged as rows running along [110]$_{\text{per}}$ (per stands for perovskite subcell) and alternating with rows of filled positions along [110]$_{\text{per}}$ (Fig. 1). The tetrahedra in the chains are subject to a cooperative rotation around [001]$_{\text{per}}$, which can occur either clockwise (CW) or counter-clockwise (CCW). Tetrahedra with a different sense of rotation alternate along the tetrahedral (B'O$_4$) layers. The layers consist of infinite chains of vertex sharing B'O$_4$ tetrahedra, which can be

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and vice versa, two neighbouring chains are of a different sign (L and R) [1,2]. The actual space symmetry of the brownmillerite structure depends on a mutual arrangement of the L and R chains. Within the $a \approx a_{\text{per}} \sqrt{2}$, $b \approx 4a_{\text{per}}$, $c \approx a_{\text{per}} \sqrt{2}$ orthorhombic unit cell random distribution of L and R chains results in the Imma space group. The $I\text{2}mb$ and $Pnma$ space groups respectively describe a structure where either only one type of chains (L or R) is present or layers of L chains alternate with layers of R chains along the b axis (Fig. 2). The ordering patterns can also be more complex related to a different ordered alternation of L and R chains within the same layer. In many cases this requires a formalism of $(3+1)$-dimensional crystallography to be applied for adequate structure description [3].

In spite of numerous structural data available on brownmillerite compounds, it is not yet clear what is the driving force causing tetrahedral chain ordering. Indeed, symmetry operations of the transformation of the L chain into the R one and vice versa are also symmetry operations of the perovskite structure that leads to the same configurational energy for the sets of L or R chains [1,2]. The L $\leftrightarrow$ R transformation does not change the first coordination spheres of the A, B and B’ cations and does not noticeably alter the interatomic distances. Nevertheless, for different combinations of A, B and B’ cations different ordering possibilities are experimentally found. Among Mn-based brownmillerites a variation of the A and B’ cations causes changes in the tetrahedral chain ordering type. $Ca_{2}MnGaO_{5}$ consists of two closely intermixed phases with the $I\text{2}mb$ and $Pnma$ space symmetry, forming separate crystallites together with narrow $I\text{2}mb$ domains in the $Pnma$ matrix [4]. For the Sr$_{2}$MnGaO$_{5}$ structure two possible variants corresponding to either the Imma or $I\text{2}mb$ space group were proposed [5–9]. However, a detailed electron microscopy investigation of this compound revealed a commensurate superstructure with $q = 1/2c$ [10]. The superstructure arises due to ordering of the L and R chains according to a –L–R–L–R– sequence, where L and R chains alternate along the c axis within the same (GaO) layer. Sr$_{2}$CaMnGaO$_{5}$ and $Ca_{2}MnAlO_{5}$ adopt a fully ordered $I\text{2}mb$ structure [11,5]. Tracking a correlation between the ordering of tetrahedral chains and the chemical composition is additionally complicated due to the influence of the preparation conditions. For example, in Sr$_{2}$MnGaO$_{5}$ the long range order of R and L chains is destroyed at a temperature lower than the preparation temperature of this compound. This indicates that the ordering of the tetrahedral chains does not occur during the solid state reaction, but appears upon cooling, and one can therefore expect the ordering pattern to depend strongly on cooling conditions [10].

The $Ca_{2}MnGaO_{5}$ and $Ca_{2}MnAlO_{5}$ compounds provide an excellent opportunity to investigate the transformation between two distinct ordering patterns of tetrahedral chains on going from the $Pnma$ structure ($Ca_{2}MnGaO_{5}$) towards the $I\text{2}mb$ structure ($Ca_{2}MnAlO_{5}$) due to the changing average size of the tetrahedrally coordinated cation upon replacement of Ga$^{3+}$ by Al$^{3+}$. In this contribution we report the preparation of the $Ca_{2}MnGa_{1-x}Al_{x}O_{5}$ solid solutions and investigation of the changes in the crystal and defect structure for the compositionally induced phase transition between the $Pnma$ and $I\text{2}mb$ structures. We will propose possible structural reasons of this transformation.
2. Experimental

The samples of the Ca$_2$MnGa$_{1-x}$Al$_x$O$_5$ (0.2 $\leq x \leq$ 1.0) solid solutions were prepared using CaCO$_3$, Mn$_2$O$_3$, Ga$_2$O$_3$ and Al$_2$O$_3$ (Reakhim, “chemically pure” purity grade, AlfaAesar, 99.99%) as initial reagents. The appropriate amounts of the initial compounds were mixed in an agate mortar under acetone and pressed into pellets. The pellets were annealed at 1000°C for 50 h and at 1250°C for 40 h with intermediate regrinding. The an-
ealing was performed in flowing Ar gas. The samples
were finally furnace cooled. The oxygen content in the as-
prepared samples was checked by iodometric titration. It
coincides with the nominal composition O$_{5.0}$ with the ac-
curacy of ±0.015.

Phase analysis and cell parameter determination were
performed using X-ray powder diffraction (XRPD) with a
focusing Guinier-camera FR-552 (CuK$_{\alpha_1}$-radiation, Ge was
used as an internal standard) and Huber G670 Guinier dif-
fractometer (CuK$_{\alpha_1}$-radiation, image plate detector). X-ray
powder diffraction data for crystal structure determination
were collected on a STADI-P diffractometer (CuK$_{\alpha_1}$-
radiation, curved Ge monochromator, transmission mode,
linear PSD). The JANA2000 program package was used for
the Rietveld refinement of the crystal structures from XRPD
data.

Samples for electron microscopy were made by grinding
the powder sample in ethanol and depositing it on a holey
carbon grid. Electron diffraction (ED) patterns and dark field
(DF) images were obtained using a Philips CM20 electron
microscope. High resolution electron microscopy (HREM)
observations were made on a JEOL 3000FX instrument. Im-
age simulation was carried out by means of the MacTempas
software.
3. Results

3.1. X-ray powder diffraction investigation

Samples of the Ca$_2$MnGa$_{1-x}$Al$_x$O$_5$ solid solution were obtained as single phase materials over the entire $0.2 \leq x \leq 1.0$ composition range. The XRPD patterns were indexed on an orthorhombic lattice with cell parameters listed in Table 1. The cell parameters of the orthorhombic unit cell are related to the perovskite subcell as $a \approx c \approx a_{\text{per}} \sqrt{2}$, $b \approx 4a_{\text{per}}$, typical for brownmillerite structure. The unit cell volume decreases monotonically with increasing amount of Al, in agreement with the smaller size of the Al$^{3+}$ cations in comparison with the Ga$^{3+}$ ones ($r$(Ga$^{3+}$) = 0.61 Å, CN = 4 [12]). The variation of the lattice parameters is not so straightforward. Both $a$ and $b$ parameters decrease with increasing $x$, but the $c$ parameter increases. Besides a variation of the lattice parameters, replacing Ga by Al is also accompanied by a systematic decrease of the intensity of the $hkl$, $h + k + l \neq 2n$ reflections. As it can be seen from Fig. 3, the 111 and particularly the 131 reflection is clearly present on the XRPD pattern of the Ca$_2$MnGa$_{0.8}$Al$_{0.2}$O$_5$ compound, but it weakens on going to the Ca$_2$MnGa$_{0.5}$Al$_{0.5}$O$_5$ phase, and only a weak diffuse intensity, displaced towards the low angle side, is left on the XRPD pattern of the Ca$_2$MnGa$_{0.4}$Al$_{0.6}$O$_5$ compound. Complete disappearance of the $hkl$, $h + k + l \neq 2n$ reflections is achieved at $x = 0.8$. The $hkl$, $h + k + l \neq 2n$ reflections on the XRPD patterns of the compounds with $x \leq 0.5$ can be attributed to the presence of the brownmillerite phase with the $Pnma$ structure. The evolution of the intensities and broadening of these reflections can be attributed to gradual changes in the defect structure of the solid solution, which finally results in a transformation of the $Pnma$ brownmillerite phase to the phase with body-centered unit cell, where $hkl$, $h + k + l \neq 2n$ reflections are forbidden. Among the two possibilities—a disordered centrosymmetric $Imma$ structure and an ordered acentric $I2mb$ one—the second has to be chosen according to the neutron powder refinement of the Ca$_2$MnAlO$_5$ structure, which showed undoubtedly the $I2mb$ symmetry for this compound [5].

The crystal structure of the Ca$_2$MnGa$_{0.5}$Al$_{0.5}$O$_5$ compound, which is intermediate between the Ca$_2$MnGaO$_5$ and Ca$_2$MnAlO$_5$ phases, was refined from XRPD data. Since the $hkl$, $h + k + l \neq 2n$ reflections are still visible on the XRPD pattern of Ca$_2$MnGa$_{0.5}$Al$_{0.5}$O$_5$, the $Pnma$ structure was taken as a first approximation to start the Rietveld refinement. The occupancy factor for the tetrahedrally coordinated cation position was set to be equal to $g$(GaAl) = 0.5Ga + 0.5Al. The refinement gave reasonable values of the reliability factors ($R_I = 0.051$, $R_P = 0.017$), but overestimation of the intensities of the $hkl$, $h + k + l \neq 2n$ reflections was obvious from the comparison of the experimental and calculated XRPD patterns. The atomic displacement parameters (ADP) for the atoms at the GaAl and O(3) (oxygen atoms in the (GaO) layers) positions were found to be substantially higher in comparison with those for other atoms in the structure (0.025–0.026 Å$^2$ for GaAl and O(3) in comparison with 0.007–0.016 Å$^2$ for other positions). This indicates

![Fig. 3. Part of the X-ray diffraction patterns of the Ca$_2$MnGa$_{1-x}$Al$_x$O$_5$ samples with $x = 0.2, 0.5, 0.6$ and 0.8.](image)

Table 1
Sample compositions and unit cell parameters of the Ca$_2$MnGa$_{1-x}$Al$_x$O$_5$ solid solutions

<table>
<thead>
<tr>
<th>$x$</th>
<th>$a$, Å</th>
<th>$b$, Å</th>
<th>$c$, Å</th>
<th>$V$, Å$^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.2</td>
<td>5.2672(4)</td>
<td>15.278(1)</td>
<td>5.4655(4)</td>
<td>439.83(4)</td>
</tr>
<tr>
<td>0.4</td>
<td>5.2612(4)</td>
<td>15.223(2)</td>
<td>5.4664(5)</td>
<td>437.80(5)</td>
</tr>
<tr>
<td>0.5</td>
<td>5.2595(4)</td>
<td>15.161(2)</td>
<td>5.4691(5)</td>
<td>436.10(5)</td>
</tr>
<tr>
<td>0.6</td>
<td>5.2572(5)</td>
<td>15.125(2)</td>
<td>5.4715(4)</td>
<td>435.05(5)</td>
</tr>
<tr>
<td>0.8</td>
<td>5.2521(4)</td>
<td>15.066(1)</td>
<td>5.4726(4)</td>
<td>433.02(4)</td>
</tr>
<tr>
<td>1.0</td>
<td>5.2431(4)</td>
<td>14.974(2)</td>
<td>5.4737(5)</td>
<td>429.73(5)</td>
</tr>
</tbody>
</table>
that the perfect \textit{Pnma} ordering pattern of the tetrahedral chains is violated, but that the long range \textit{12mb} structure is not formed yet. According to the TEM observations described below, the \textit{−L−R−L−R−} stacking of the tetrahedral layers along the \textit{b} axis in the \textit{Pnma} structure is randomly violated by appearance of \textit{−L−L−} or \textit{−R−R−} fragments of a \textit{12mb} structure. This random distribution of \textit{L} and \textit{R} chains can be approximated by splitting the GaAl and O(3) positions with occupancy factors related by \textit{g(GaAl(2)) = 1 − g(GaAl(1))}, \textit{g(O(3)) = g(GaAl(1))} and \textit{g(O(4)) = 1 − g(GaAl(1))}, where the refined \textit{g(GaAl(1))} value is equal to 0.65. The atomic coordinates of the GaAl(2) and O(4) atoms were fixed to those of the GaAl(1) and O(3) as shown in Table 3, so that if the GaAl(1) and O(3) atoms belong to \textit{L}-type chain, the GaAl(2) and O(4) pair forms \textit{R} chain and vice versa. The ADPs were fixed to be identical for the GaAl(1)−GaAl(2) and O(3)−O(4) pairs. The splitting resulted in a decrease of ADPs for the GaAl(1), GaAl(2), O(3) and O(4) positions and an improvement of the reliability factors (\textit{R}1 = 0.042, \textit{R}p = 0.017). The crystallographic parameters, atomic coordinates and the most relevant interatomic distances for \textit{Ca\textsubscript{2}MnGa\textsubscript{0.5}Al\textsubscript{0.5}O\textsubscript{5}} are listed in Tables 2–4. The observed, calculated, and difference X-ray diffraction patterns are shown in Fig. 4.

The crystal structure of \textit{Ca\textsubscript{2}MnAlO\textsubscript{5}} was also refined from XRPD data despite the good quality neutron powder data. The agreement between the experimental and calculated data agrees well with the results of the refinement of this structure from NPD data [5]. The replacement of Ga\textsuperscript{3+} by Al\textsuperscript{3+} is accompanied by a decreasing average metal-oxygen distance for the cations in the tetrahedrally coordinated position \textit{(d(B′−O)) = 1.860 Å for B′ = Ga [4], 1.783 Å for B′ = GaAl to 1.736 Å for B′ = Al}. A significant contraction occurs along the B′−O(2) bonds directed almost parallel to the \textit{b} axis, which causes a substantial compression of the structure along this direction. Elongation of the B′−O bonds along the direction of the tetrahedral chain propagation is to some degree compensated by a partial suppression of the rotation of the B′O\textsubscript{4} tetrahedra that results in straightening of the chains on going from \textit{Ca\textsubscript{2}MnGa\textsubscript{5}O\textsubscript{5}} to \textit{Ca\textsubscript{2}MnAl\textsubscript{5}O\textsubscript{5}}. The value of the B′−O(3)−B′ bond angle can be taken as a measure for the deformation of the tetrahedral chains. This angle increases from 120.7(2)\degree for B′ = Ga [4], 132.4(5)\degree for B′ = GaAl to 141.7(7)\degree for B′ = Al. In contrast to the \textit{a} and \textit{b} parameters which decrease with increasing amount of Al, the \textit{c} parameter slightly increases. One can assume that this allows the Ca atoms to keep an appropriate coordination when the structure compresses along the \textit{a} and \textit{b} direction. Indeed, the bond valence sum for the Ca cations stays very close to +2 in all three structures (BVS = +1.96 for B′ = Ga, +1.97 for B′ = GaAl and +1.93 for B′ = Al).

3.2. Electron microscopy investigation

The electron diffraction patterns of the \textit{Ca\textsubscript{2}MnGa\textsubscript{1−x}Al\textsubscript{x}O\textsubscript{5}} compounds exhibit systematic changes with compo-

<table>
<thead>
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<th>Table 2</th>
<th>Selected parameters from Rietveld refinement of X-ray powder data for \textit{Ca\textsubscript{2}MnGa\textsubscript{0.5}Al\textsubscript{0.5}O\textsubscript{5}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>\textit{Pnma}</td>
</tr>
<tr>
<td>\textit{a}, Å</td>
<td>5.2517(5)</td>
</tr>
<tr>
<td>\textit{b}, Å</td>
<td>15.1426(2)</td>
</tr>
<tr>
<td>\textit{c}, Å</td>
<td>5.46029(6)</td>
</tr>
<tr>
<td>\textit{Z}</td>
<td>4</td>
</tr>
<tr>
<td>Cell volume, Å\textsuperscript{3}</td>
<td>434.231(7)</td>
</tr>
<tr>
<td>Calculated density, g/cm\textsuperscript{3}</td>
<td>4.046</td>
</tr>
<tr>
<td>2\theta range, deg.</td>
<td>10 ≤ 2\theta ≤ 105; 0.01</td>
</tr>
<tr>
<td>Number of reflections</td>
<td>10123</td>
</tr>
<tr>
<td>Refinable parameters</td>
<td>23</td>
</tr>
<tr>
<td>Preferred orientation along the {010} axis</td>
<td>1.086(2)</td>
</tr>
<tr>
<td>\textit{R}1, \textit{R}p, \textit{R}wp</td>
<td>0.042, 0.017, 0.023</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Table 3</th>
<th>Positional and atomic displacement parameters of atoms for \textit{Ca\textsubscript{2}MnGa\textsubscript{0.5}Al\textsubscript{0.5}O\textsubscript{5}}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atom</td>
<td>Position</td>
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<tr>
<td>Ca(1)</td>
<td>8\textit{d}</td>
</tr>
<tr>
<td>Mn(1)</td>
<td>4\textit{a}</td>
</tr>
<tr>
<td>GaAl(1) &amp;</td>
<td>4\textit{c}</td>
</tr>
<tr>
<td>GaAl(2) &amp;</td>
<td>4\textit{c}</td>
</tr>
<tr>
<td>O(1)</td>
<td>8\textit{d}</td>
</tr>
<tr>
<td>O(2)</td>
<td>8\textit{d}</td>
</tr>
<tr>
<td>O(3)</td>
<td>4\textit{c}</td>
</tr>
<tr>
<td>O(4)</td>
<td>4\textit{c}</td>
</tr>
</tbody>
</table>

\textsuperscript{a} GaAl = 0.5Ga + 0.5Al.
sition, which agree with the features observed on the XRPD patterns. The ED patterns of the Ca$_2$MnGa$_{0.5}$Al$_{0.5}$O$_5$ sample (Fig. 5, left column) can be completely indexed on an orthorhombic unit cell with the lattice parameters determined from X-ray diffraction (Table 1). The reflections $h00$, $h, l \neq 2n$ on the [010]$^*$ ED pattern and $0k0$, $k \neq 2n$ on the [001]$^*$ and [101]$^*$ ED patterns are forbidden by Pnma symmetry and their presence is caused by multiple diffraction. The intensity of these forbidden reflections decreases drastically when the crystal is tilted around the corresponding reciprocal lattice axes. Moreover, the $h00$, $h \neq 2n$, reflections are absent on the [001]$^*$ ED pattern, and $0k0, 0l0, k, l \neq 2n$ reflections do not show up on the [100]$^*$ ED pattern (not shown in Fig. 5), confirming the Pnma symmetry.

Increasing the Al content causes the $hkl, h+k+l = 2n$ reflections to become weaker, as it can be seen on the ED patterns of the Ca$_2$MnGa$_{0.4}$Al$_{0.6}$O$_5$ compound (Fig. 5, central column). Rows of diffuse intensity also appear on the [001]$^*$ and [101]$^*$ ED patterns passing through the reflection rows parallel to the $b^*$ axis. The same features are also present on the [001]$^*$ and [101]$^*$ ED patterns of Ca$_2$MnGa$_{0.4}$Al$_{0.6}$O$_5$. A complete transformation from primitive to body-centered structure is achieved at $x = 0.8$, where only $hkl, h+k+l = 2n$ spots are observed (Fig. 5, right column).

The defects causing the appearance of diffuse intensity lines on the ED patterns of the compounds intermediate between the Pnma and I2mb structures were studied using dark field imaging. Fig. 6 shows DF images of the $x = 0.2$, 0.5 and 0.6 compounds taken from crystallites oriented approximately along the [101] zone. The images were obtained with the 2.15.2 reflection strongly excited (i.e., with the reflection forbidden for the I2mb structure). The DF images show dark stripes strictly perpendicular to the $b$ axis. These stripes are not observed when the DF image is taken with one of the $hkl, h+k+l = 2n$ basic spots. The fact that there is no shade difference across the stripes and that they are only visible in superlattice reflections allows to identify them as translational interfaces (antiphase boundaries (APBs)). In the $x = 0.2$ sample the APBs are separated by relatively
large domains of the \textit{Pnma} structure, producing regular \textit{hkl}, \textit{h} + \textit{k} + \textit{l} \neq 2\textit{n} spots. At $x=0.5$ the array of APBs becomes denser and the decreasing separation between the parallel but irregularly spaced APBs causes vanishing the \textit{hkl}, \textit{h} + \textit{k} + \textit{l} \neq 2\textit{n} reflections and the appearance of diffuse streaks parallel to $b^*$ on ED patterns. The density of the APBs increases with increasing $x$, as it can be seen from the DF image of the $x=0.6$ sample, and one may assume that the transition from the \textit{Pnma} to the \textit{I2mb} structure is completed when the displacement vector $\mathbf{R}$ of the translational domain interfaces becomes a new lattice translation. Then the $\mathbf{R}$ vector can be identified as $\mathbf{R} = 1/2[111]$, i.e.,

In the acentric \textit{I2mb} structure (point group 2\textit{mm}) a formation of mirror twins is possible due to the absence of the mirror plane perpendicular to the $a$ axis, which is present in the centrosymmetric \textit{Pnma} structure (point group mmm). An absent mirror plane becomes a plane of domain interfaces, so that one can expect twin boundaries to be perpendicular to the $a$ axis. The observation of mirror twins in Ca$_2$MnAlO$_5$ was performed using DF imaging on a crystal oriented along the [014] zone axis (i.e., along the zone axis which does not produce centro-symmetry in projection) with the excited 400 spot under multiple beam conditions [13]. The twin domains on Fig. 7 can be revealed by fringe contrast where the domain boundaries are imaged as fringes perpendicular to the $a$ axis.

Fig. 8 two parts of the [101] HREM image are shown along with the Fourier transforms. The presence of the \textit{hkl}, \textit{h} + \textit{k} + \textit{l} \neq 2\textit{n} spots on the Fourier transform taken from the top image on Fig. 8 and the absence of these spots

The vector of the body-centering translation. This conclusion will be further confirmed by HREM observation of the structure of the APB. However, a possibility of two (or larger even amount) of APBs next to each other also cannot be excluded. Even number of the adjacent APBs produce a shift over [111] vector so that no displacement of the structure occurs on going across the interface. This results in a thin slab of the \textit{I2mb} structure inside the \textit{Pnma} matrix, which is undistinguishable from a single APB at the chosen imaging conditions.

In the acentric \textit{I2mb} structure (point group 2\textit{mm}) a formation of mirror twins is possible due to the absence of the mirror plane perpendicular to the $a$ axis, which is present in the centrosymmetric \textit{Pnma} structure (point group mmm). An absent mirror plane becomes a plane of domain interfaces, so that one can expect twin boundaries to be perpendicular to the $a$ axis. The observation of mirror twins in Ca$_2$MnAlO$_5$ was performed using DF imaging on a crystal oriented along the [014] zone axis (i.e., along the zone axis which does not produce centro-symmetry in projection) with the excited 400 spot under multiple beam conditions [13].

The twin domains on Fig. 7 can be revealed by fringe contrast where the domain boundaries are imaged as fringes perpendicular to the $a$ axis.

The [101] HREM images of the Ca$_2$MnGa$_{0.5}$Al$_{0.5}$O$_5$ sample reveal a complicated microstructure with the presence of numerous APBs (consistent with the DF observations). Coalescence of the APBs leads to the formation of domains of the \textit{I2mb} structure embedded into the \textit{Pnma} matrix. On Fig. 8 two parts of the [101] HREM image are shown along with the Fourier transforms. The presence of the \textit{hkl}, \textit{h} + \textit{k} + \textit{l} \neq 2\textit{n} spots on the Fourier transform taken from the top image on Fig. 8 and the absence of these spots
interfaces are imaged as fringes perpendicular to the oriented approximately vertical) on going across the domain boundaries. The periodicity of 15.2 Å along the \([010]\) axis at this particular imaging condition can be seen by a sequence of dark stripes, better visible in the thicker part of the crystal (right part of Fig. 9). The APB appears as a band where a relative shift of periodicity of the dark stripes by 1/2 unit cell occurs. This displacement is marked by brackets for clarity. The displacement of the structure along the APB can not be observed on the [101] image because the 1/2[010] component of the displacement vector is at the same time a visible repeat period of the \(Pnma\) structure for this projection.

The structure model for the APBs can be proposed based on the experimental observations and the relationship between the \(Pnma\) and \(I2mb\) structure. The \(Pnma\) structure for this projection is in good agreement with the experimental one.

Fig. 9 shows a [101] HREM image of \(\text{Ca}_2\text{MnGa}_{0.5}\text{Al}_{0.5}\text{O}_5\) where a single APB (marked by an arrowhead) is present. The periodicity of 15.2 Å along the \(b\) axis at this particular imaging condition can be seen by a sequence of dark stripes, better visible in the thicker part of the crystal (right part of Fig. 9). The APB appears as a band where a relative shift of periodicity of the dark stripes by 1/2 unit cell occurs. This displacement is marked by brackets for clarity. The displacement of the structure along the APB can not be observed on the [101] image because the 1/2[101] component of the displacement vector is at the same time a visible repeat period of the \(Pnma\) structure for this projection.

The structure model for the APBs can be proposed based on the experimental observations and the relationship between the \(Pnma\) and \(I2mb\) structure. Shifting the \(Pnma\) structure by \(R = 1/2[011]\) results in the appearance of two adjacent tetrahedral layers with the same types of tetrahedral chains, so that the sequence of tetrahedral layers on going across the APB can be expressed as \(-L-R-L-L-R-L-\) (Fig. 10). The APB reproduces a fragment of the body-centered structure with the \(I2mb\) space symmetry. This model implies that the shift by \(R = 1/2[111]\) only affects the tetrahedral layers and does not change the octahedral layers nor the Ca sublattice, in agreement with the environmental equivalence of the tetrahedral chains of different types.

4. Discussion

The structural investigation of \(\text{Ca}_2\text{MnGa}_{1-x}\text{Al}_x\text{O}_5\) solid solutions clearly shows that changing the average size of the \(B'\) cation affects the pattern of tetrahedral chain ordering in the brownmillerite structure. The transformation from the \(Pnma\) structure with alternating layers of \(L\) and \(R\) chains towards the \(I2mb\) structure with all chains of the same type occurs as a gradual evolution of the defect structure of these materials. The driving force of this transformation should be related to the mutual interaction of the chains with different configurations. The two possibilities of rotation of the \(B'O_4\) tetrahedra, which determine the chain configuration, are associated with cooperative displacements of the \(B'\) and \(O(3)\) atoms, as it is shown in Fig. 11 by arrows. According to [1,2], such cooperative displacements in the \((B'O)\) layers result in a net shift of the chains along the \(a\) direction with respect to the surrounding structure matrix. Since the \((B'O)\) \((B' = \text{Ga}^{3+}, \text{Al}^{3+})\) layer is positively charged, a dipole can be associated with each chain so that for \(L\) and \(R\) chains the dipoles are anti-parallel. One can assume that the tetrahedral chain ordering is driven by the minimization of free energy due to the interaction between these anti-parallel dipoles. The most effective mutual compensation of the dipoles is achieved in the structures where the \(L\) and \(R\) tetrahedral chains alternate within the same layer thus minimizing the distance between the dipoles (Fig. 11). However, structures with such ordering pattern are rather rare among the brownmillerite family. Among such structures are \(\text{Sr}_2\text{MnGaO}_5\) [10], \(\text{Sr}_2\text{CuGaO}_5\) [14], \(\text{Ba}_2\text{In}_2\text{O}_5\) [15], \(\text{Ca}_2\text{Co}_{2-x}\text{Al}_x\text{O}_3\) [3] and \(\text{LnSr}_2\text{GaCu}_2\text{O}_7\) (\(Ln\)—rare-earth element) [1,2], which does not belong to the brownmillerite family, but has similar tetrahedral layers. A factor competing with the structure stabilization due to dipole–dipole interaction can be found from analyzing the displacements of the \(O(2)\) atoms composing two vertices of the \(B'O_4\) tetrahedra and located at the \((AO)\) layers above and below the tetrahedral layers with the same or alternating types of chains. When all chains in the layer are of the same type, the \(a\)-axis component of the displacement vector of the \(O(2)\) atoms from the ideal position in the perovskite sublattice is the same for all \(O(2)\) positions that reflects the displacement of the \((B'O)\) and \((AO)\) layers with respect to each other. The \(c\)-axis displacement component is out-of-phase for the \(O(2)\) atoms.
related by a translation over \(a_{\text{per}}\) that results in a cooperative tilt of the BO\(_6\) octahedra around the \(a\)-axis as shown in Fig. 11 (bottom left). When alternating L and R chains are present in the same layer, this tilt component remains unchanged. However, the \(a\)-axis displacement component for the O(2) atoms is now out-of-phase for the chains of different signs. It should introduce an additional tilt around the \(c\) axis for the BO\(_6\) octahedra, as shown in Fig. 11 (bottom right), but the direction of the tilts dictated by such displacements of the O(2) atoms is not compatible with the geometry of the perovskite octahedral layer. This means that an alternation of R and L chains in one layer should result either in a distortion of the BO\(_6\) octahedra or in a distortion in the (AO) layers. Both cases are likely to perturb the elastic equilibrium causing a structure destabilization. Thus layers with different chains are realized in the brownmillerite structure when either the dipole–dipole interaction prevails this destabilization effect or when the compensation of the dipoles by the placement of anti-parallel dipoles in neighboring layers is unfavorable due to an increasing sep-
Fig. 9. [101] HREM image of Ca$_2$MnGa$_{0.5}$Al$_{0.5}$O$_5$ showing single antiphase boundary (marked by an arrowhead). The APB appears as a band where the relative shift of periodicity of the dark stripes by $1/2b$ occurs (marked by brackets).

Fig. 10. The proposed structure of antiphase boundaries in Ca$_2$MnGa$_{1-x}$-Al$_x$O$_5$ viewed along the [100] direction.

aration between the layers, for example as a consequence of the large size of the A-cations (Sr, Ba). The value of the dipole moment associated with each tetrahedral chain is directly related to the degree of distortion of the chain, which can be measured by the value of the $B'$–O(3)–$B'$ bond angle. In the Ca$_2$MnGaO$_5$ structure the large deviation of this angle from 180° reflects a strong distortion, and the dipoles tend to compensate each other forming an alternating arrangement of layers of either L or R chains. On going from Ca$_2$MnGaO$_5$ to Ca$_2$MnAlO$_5$ the value of the $B'$–O(3)–$B'$ bond angle increases from 120.7(2)° for $B'$ = Ga to 141.7(7)° for $B'$ = Al. The larger impact of the dipole–dipole interaction into the free energy of the Ca$_2$MnGaO$_5$ structure leads to the stabilization of the Pnma structure where layers of anti-parallel dipoles are placed next to each other. For Ca$_2$MnAlO$_5$ this factor becomes less sufficient and one could expect a formation of the Imma structure with a disordered placement of the chains. However, instead of a disordered Imma structure the $I2mb$ structure is formed, where all chains are of the same sign. The compensation of the dipoles also takes place in this compound and occurs as the appearance of mirror twins. The mirror reflection operation with a mirror plane perpendicular to the $a$ axis transforms L chains to R chains and vice versa. Thus ferroelectric domains are formed with anti-parallel directions of the polarization vectors. The structure model of the L ↔ R transformation between the chains was recently described [10].

Apparently the gain in free energy due to a dipole–dipole interaction between tetrahedral chains is rather small and the resulting ordered pattern of tetrahedral chains depends significantly on a competition with other interactions in the structure. Besides structural reasons, synthesis conditions play an important role since increasing temperature can cause a transformation to a structure with disordered tetrahedral chains, as it was shown for Sr$_2$MnGaO$_5$ [10]. This makes the exact prediction of the ordering pattern of tetrahedral chains difficult for certain chemical compositions of the brownmillerite compound. Nevertheless, taking into account the mutual interaction between the tetrahedral chains is certainly an important factor for explanation of the ordering phenomena in compounds with the brownmillerite type structure.

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Fig. 11. Schematic representation of atomic arrangements in (B'O) layer and adjacent (AO) layers for two configurations of the tetrahedral chains (top). Arrows attached to atoms show the displacement direction with respect to the positions in the cubic perovskite structure. Thick arrows below each chain mark direction of a dipole associated with this chain. Tilting pattern of the BO₆ octahedra (bottom left) in the layer next to the tetrahedral layer with the same type of chains. Arrows mark a rotation direction around the a axis. Tilting pattern of the BO₆ octahedra (bottom right) in the layer next to the tetrahedral layer with alternating L and R chains. Second component of tilt around the c axis is marked by arrows placed next to each octahedron at the left side.

References