Disorder induced hexagonal-orthorhombic transition in $Y_{1-x}Gd_x^3MnO_3$

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We show that the transition in AMnO$_3$ from the orthorhombic perovskite phase to the hexagonal phase is promoted by inducing disorder on the A-site. The gap between the orthorhombic and the hexagonal phase is widened for disordered, mixed yttrium-gadolinium manganite samples. At the cost of the orthorhombic phase a two phase region emerges. The phase separation exhibits very unusual thermodynamical behaviour. We also show that high pressure synthesis favours the orthorhombic phase. YMnO$_3$ is formed in the orthorhombic phase at 15 kbar.

I. INTRODUCTION

In the search for new composition-properties relations ABO$_3$ compounds have attracted a lot of attention. The perovskite materials, ABO$_3$, have been researched extensively because this structure forms the basis for interesting physical properties such as high $T_c$ superconductivity [1] and colossal magnetoresistance [2]. Non-perovskite AMnO$_3$, with A = Y, Ho,...,Lu, attracted renewed interest, due to their ferroelectric properties [3]. These hexagonal AMnO$_3$ [4] have a basically different structure than most ABO$_3$ compounds, that are distorted perovskites. These properties arise due to the strong correlation of the 3d electrons with the O 2p orbitals.

In this paper, we report the transition from the orthorhombic perovskite (o) to the hexagonal (h) phase by changing the ionic radius of the A ion and by high pressure synthesis. The effect of the ionic radius on the transition is studied by partially replacing Y by Gd ions in YMnO$_3$. The resulting phase diagram leads us to discuss the effect of disorder, in terms of the ionic radius variance, on the stability of the hexagonal and orthorhombic phases.

The basic building block of the perovskite is an oxygen octahedron with a transition metal, B, in its centre. The A ions, usually lanthanides or alkaline earth metal ions, occupy the holes between the octahedra, that form a 3D corner shared network. In this picture B is sixfold and A is 12-fold coordinated. Most perovskites have a distorted structure, derived from this building block. The distortions have various origins, including a ferroelectric transition for B a $d^0$ transition metal ion like Ti$^{3+}$ [5]. The most common distortion originates from the relative small radius of the A ions compared with the holes between the octahedra. This results in a cooperative rotation of the octahedra known as the GdFeO$_3$ distortion [6]. While the structure is interesting in its own right, it has also large effects on the physical properties. It is well documented that the physical properties depend strongly on the magnitude of the structural distortions. An overview for the manganites is given in Ref.’s [7,8].

The magnitude of the GdFeO$_3$ distortion depends strongly on the tolerance factor, $t$:

$$t = \frac{r_{A^{3+}} + r_{O^{2-}}}{\sqrt{2(r_{B^{3+}} + r_{O^{2-}})}}.$$  (1)

where $r_X$ is the radius of the X ion. The tolerance factor gives the relation between the radii of ions A, B and O in an ideal cubic perovskite. For $t=1$ the size of the lanthanide is exactly right to compose the cubic perovskite system. For Mn$^{3+}$, $r_{Mn^{3+}} = 0.645$ Å and $r_{O^{2-}} = 1.42$ Å this yields an ionic radius $r_{A^{3+}} = 1.50$ Å, where the largest lanthanide, La, has a radius of 1.22 Å. The corresponding tolerance factor $t = 0.90$ indicates a large distortion for LaMnO$_3$. With increasing atomic number, the lanthanide radius decreases and thereby the distortion increases. For the manganites, the tolerance factor is conventionally regarded as the factor controlling the boundary between the hexagonal and orthorhombic structures. The orthorhombic perovskite phase is stable for $t > 0.855$, corresponding to $r_A > r_{Dy}$ [9]. For $t < 0.855$, $r_A < r_{Ho}$, the hexagonal phase prevails [10]. Yttrium, although not in the lanthanide series, behaves chemically identical and its radius falls between dysprosium and holmium. An overview on the ionic radii and tolerance factors of some relevant compounds is given in Table [11].

| Compound     | tolerance factor | ionic radius (Å) |
|--------------|-----------------|-----------------|
| LaMnO$_3$    | 0.902           | 1.215           |
| GdMnO$_3$    | 0.866           | 1.109           |
| DyMnO$_3$    | 0.857           | 1.083           |
| YMnO$_3$     | 0.854           | 1.075           |
| LuMnO$_3$    | 0.840           | 1.032           |
The high temperature phase of the hexagonal AMnO$_3$ consists of 8-fold coordinated A ions in bicapped antiprisms. Trigonal bipyramidal holes are formed between two layers of face-sharing antiprisms by the edges of the capping oxygens with the antiprisms. The capping oxygens of two adjacent layers are located on the same $ab$ plane. Half of the bipyramidal holes are occupied by Mn. The apical oxygens of the MnO$_5$ bipyramid are also the oxygens that make up the antiprism. The two polyhedra are sketched in Fig. 1, where the shared edge is shown. The Mn-O$_{ap}$ distance is thus equal to the distance between the antiprism oxygen layer and the capping oxygen layer. The steric hindrance of the Mn restricts this layer separation and therefore increases the A-O$_{ap}$ bond length. Thus, the eightfold co-ordination is not uniform. The two apical oxygens have slightly larger bond lengths. Furthermore, the structure is unstable against a ferroelectric distortion at lower temperatures. The apical oxygens move in such a way that one bond becomes ‘normally’ short, while the other becomes about 1 Å larger. The asymmetric A environment is the main reason for the ferroelectric behaviour. As we have two lanthanide positions in $P6_3cm$, we have two non-equivalent, although similar, dipole moments. Four out of the six moments per unit cell point upwards, the other two downwards.

Although the hexagonal phase of YMnO$_3$ at ambient conditions is the thermodynamically stable phase, there are several ways to obtain orthorhombic YMnO$_3$. Using thin film growth, an appropriate substrate will force the coherent growth of the orthorhombic phase [10]. Synthesis routes via organic precursors and low reaction temperatures yield the orthorhombic phase [11]. And last, high pressure synthesis favours the orthorhombic phase, because it has a higher density [12].

![FIG. 1. Sketch view of the local environment, showing AO$_7$, left side, and MnO$_5$, right side. The arrow indicates the distance between two oxygen planes. The dashed line indicates the Mn-O$_{ap}$ distance. Atoms marked with "*" and with "@" are identical, the double line indicates the shared edge.](image)

TABLE II. Ionic radii, tolerance factors and variance of the studied Y$_{1-x}$Gd$_x$MnO$_3$ samples.

| $x$ | $r_A$ (Å) | $t$ | $\sigma^2$ ($10^{-4}$Å$^2$) |
|-----|----------|-----|----------------------|
| 0   | 1.075    | 0.854 | 0                    |
| 0.06 | 1.077    | 0.855 | 68                   |
| 0.19 | 1.081    | 0.857 | 176                  |
| 0.25 | 1.084    | 0.857 | 217                  |
| 0.31 | 1.086    | 0.858 | 248                  |
| 0.38 | 1.088    | 0.859 | 271                  |
| 0.5  | 1.092    | 0.860 | 289                  |
| 1    | 1.109    | 0.866 | 0                    |
III. RESULTS AND DISCUSSION

In Fig. 3 we present a phase diagram of Y$_{1-x}$Gd$_x$MnO$_3$ as a function of $r_A$ and its variance $\sigma^2$ of samples given in Table II. The variance $\sigma^2$ is given by,

$$\sigma^2 = \sum_{i=1}^{n} x_i (r_i - \langle r_A \rangle)^2$$

(2)

The phase diagram can be divided in three regions. Low $r_A$ compounds, $\langle r_A \rangle < 1.078$, are hexagonal. Large $r_A$ and small $\sigma^2$ compounds are orthorhombic. The intermediate region shows both phases. The data for HoMnO$_3$ and DyMnO$_3$ have been taken from the literature [4].

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By changing the value of $x$ we substitute Y by Gd, whereby $r_A$ increases linearly. The tolerance factor of orthorhombic DyMnO$_3$ is equal to that of Y$_{1-x}$Gd$_x$MnO$_3$, with $x = 0.23$. Thus for $x \geq 0.23$ we expect to see the orthorhombic phase. For smaller $x$ and $t$ the hexagonal phase is expected. For $x = 0$ and $x = 0.06$ we indeed found the hexagonal structure. However, for $0.19 \leq x \leq 0.38$ we do not observe a sharp transition to the orthorhombic structure, but a mixture of the hexagonal and orthorhombic phases. Only for $x = 0.5$ an (almost) pure orthorhombic compound is found. The anomalous behaviour of the mixed Y,Gd samples is best illustrated by focussing on the sample with $x = 0.25$, which has an almost identical tolerance factor as DyMnO$_3$. Where the latter sample is orthorhombic, the former segregates in both phases. The only difference between the two compounds is that one is undoped and the other has a mixed lanthanide composition.

![Phase diagram of Y$_{1-x}$Gd$_x$MnO$_3$ as a function of $r_A$ and its variance $\sigma^2$](image)

**FIG. 2.** Phase diagram of Y$_{1-x}$Gd$_x$MnO$_3$ as a function of $r_A$, or $t$, and the variance, $\sigma^2$. Diamonds indicate hexagonal phase, triangles mixed phase and squares orthorhombic phase. The drawn lines are estimates of the phase boundaries as explained in the text. The end member GdMnO$_3$ has $r_A = 1.109$ Å.

The relative amounts of orthorhombic and hexagonal fractions are determined by Rietveld refinement of the powder diffraction data, see Fig. 4. We can rule out element segregation of Y and Gd, since the continuous increase in the lattice parameter $a$ of the hexagonal phase with increasing Gd concentration indicates perfect mixing of the A ions. A linear increase in $a$ with $r_A$ is also observed for the single A cation h-AMnO$_3$ series [4].

![Phase parameter a of the hexagonal phase as a function of the Gd content x](image)

**FIG. 3.** Lattice parameter $a$ of the hexagonal phase as a function of the Gd content $x$.

We construct a preliminary phase diagram by assuming that the h-o transition at $\sigma^2 = 0$ occurs halfway between hexagonal YMnO$_3$ and orthorhombic DyMnO$_3$. The phase boundaries are drawn in Fig. 2 as straight lines through the two calculated boundary values and the assumed $\sigma^2 = 0$ midpoint. This phase diagram can be described as follows. The phase line associated with the upper $t$ limit of the hexagonal phase does not depend on the variance. Slightly increasing $\sigma^2$ and $t$ results in the appearance of a two phase region, consisting of both the hexagonal and the orthorhombic phase. With increasing tolerance factor, the fraction of the orthorhombic phase increases until the lower boundary limit for the orthorhombic phase is crossed. This limit strongly depends on $\sigma^2$. The lower limit for the orthorhombic phase increases from $r_A = 1.078$ Å at $\sigma^2 = 0$ to $r_A = 1.093$ Å at $\sigma^2 = \sigma^2_{max}$. Note that $r_A = 1.093$ Å corresponds with the ionic radius of terbium, the second smallest lanthanide to form the perovskite structure.
We have shown the dependence of the h-o transition on the average radius $r_A$ and $\sigma^2$. In the next section, the effect of high pressure experiments on the h-o transition will be discussed.

We applied high pressure and high temperature to convert or synthesise some of the conventionally hexagonal samples in the orthorhombic state. Pressure generally stabilise the most dense phase, in this case the orthorhombic structure. First, we consider samples with $\sigma^2 = 0$. YMnO$_3$ is still hexagonal at 5 kbar, but the orthorhombic phase is found using a pressure of 15 kbar. The data is shown in Fig. 4. The necessary pressure for the h-o transition, less than 15 kbar, is much less than reported previously in the literature [12]. The h-o transition yields a critical pressure of \(\lesssim 27\) kbar for HoMnO$_3$. The error bar on this value, \(\sim 10\) kbar, is large because of the sparse data points.

![FIG. 4. Relative amounts of hexagonal, triangles, and orthorhombic, squares, fractions as a function of the Gd content $x$. An open square is plotted for DyMnO$_3$ at the corresponding value of the tolerance factor.](image)

These observations lead to the following conclusions. For $\sigma^2 = 0$ compounds either the hexagonal or the orthorhombic structure is stable. Whereas low temperature synthesis may yield mixed phase samples, a high temperature anneal will convert the unstable phase. The hexagonal or orthorhombic phase will be stable depending on the tolerance factor. However for $\sigma^2 \neq 0$ mixed phase samples can be obtained for a broad range of tolerance factors. Even a high temperature anneal retains the phase segregated state. Surprisingly, the phase segregation is not accompanied by two limiting compositions, e.g. Y$_{1-x}$Gd$_x$MnO$_3$ with $x = 0.1$ and $x = 0.5$. The continuous increase of the lattice parameters of both the hexagonal and the orthorhombic phase throughout the two phase region indicates that the composition of the hexagonal and the orthorhombic state are the same in the mixed state. We have no explanation for this unconventional form of phase segregation.

**IV. CONCLUSIONS**

We have constructed phase diagrams for the h-o phases of AMnO$_3$, including the effects of average ionic radius, hydrostatic pressure and variance. For compounds with $\sigma^2 \neq 0$ a phase separation in the orthorhombic and the
hexagonal phase is found. The mixed region exists only at low pressures. We have shown that at ambient pressure, this region expands towards higher values of the average radius with increasing variance. The upper limit for the hexagonal phase is not affected by an increase in the variance. We speculate that disorder, introduced by a large variance or soft chemical synthesis routes, allows the occurrence of the phase separation in the absence of other driving forces. Suppressing the disorder by applying external pressure or annealing at high temperatures prevents the existence of the phase separation. Pressure favours the denser, orthorhombic phase, whereas thermal annealing promotes the hexagonal phase.

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